Evaluation of Schiff-base Nickel complex towards electrochemical hydrogen production

A Dissertation submitted in partial fulfillment

of the requirements for the degree

of

Master of Science in Chemistry

THAPAR INSTITUTE
OF ENGINEERING & TECHNOLOGY
(Deemed to be University)

Submitted by

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July 2019

CERTIFICATE

This is to certify that the dissertation entitled "**Evaluation of Schiff-base Nickel complex towards electrochemical hydrogen production**" being submitted by Ms. Mandeep Kaur in partial fulfillment of the requirements for the award of degree of Masters of Science in Chemistry to School of Chemistry and Biochemistry, Thapar Institute of Engineering and Technology, Patiala is a bonafide work carried out by her under my attendance . To our knowledge, the work has reached the requisite standard required for the submission of this thesis.

This work in the present form or in part has not submitted anywhere for any other degree or diploma.

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DECLARATION

I hereby declare that the project work entitled, **"Evaluation of Schiff-base Nickel complex towards electrochemical hydrogen production"** embodied in this dissertation has been carried out by me at School of Chemistry and Biochemistry, Thapar Institute of Engineering and Technology, Patiala under the guidance and supervision of **Dr. Davinder Kumar.** Further, I declare that the content embodied in the thesis are original and have been written by me. Referred contents have been cited maintaining standard procedures.

Mandeep

(Mandeep Kaur)

ACKNOWLEDGMENT

During this project, I have been supported by many persons. It is the time now to express my hearty gratitude to all of them personally at the end of my Dissertation. First I would like to thank my supervisor **Dr. Davinder Kumar,** Assistant Professor, School of Chemistry and Biochemistry, Patiala for his guidance, suggestions and constant motivation. His enthusiasm and view on research have left a deep impact on my mind.

I take this opportunity to thank **Dr. Amjad Ali**, Head of Chemistry Department, for giving us such a chance to test ourselves in the research field and his consent to use all the facilities in the department.

I would like to thank all my teachers for their encouragement during the period of my work. I would like to thank the Ph.D. Scholar Miss. Aman, Mr. Santosh,Mr. Sanjeev,Miss. Sonia, Miss. Shivali for sharing their experiences which helped me a lot to understand and carry out my work during my thesis. I also want to thank our MSc lab attendant Mr. Hemant for his kind and constant support throughout.

I am really grateful to my loving parents for their unconditional love and support. Last but not least, I would like to thank all my friends Jemini, Chandana, Anisha for their help and constant support.

DEDICATION

This thesis work is dedicated to my parents who have always loved me unconditionally and whose example taught me to work honestly for the things that I aspire to achieve and to the most important person **Dr.Davinder Kumar,** my guide or my inspiration who taught me that everything is possible with patience and hard work.

Mandeep

Mandeep Kaur

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ABSTRACT

Today with the advancement of technology and population, global energy demands has increased many folds. 90% of worldwide vitality request is satisfied by the carbon-based non-renewable energy sources which resulted in the emission of greenhouse gases like CO_2 in the atmosphere. Thus the furthermost challenge for the scientist is to find a clean energy source. Among the various candidates, hydrogen is the potential substitute as its byproduct is only water so it can be used efficiently in the fuel cell. Hydrogen is also called the “energy currency”.

Among three primary pathway for hydrogen creation like coal gasification, steam reformation of methane and water electrolysis the third one gives us plan to manageable hydrogen generation as its feedstock is water which is renewable and present in abundant amount. The issue with its essentialness is its discontinuity and unpredictable nature as it is dependent on sun and wind energy. Until this point, for evolution of hydrogen Pt and hydrogenase enzyme are amazing electrocatalyst. However, Pt high cost and constrained accessibility have motivated the quest for financially feasible, earth inexhaustible catalysts and at the same time, the large scale utilization of hydrogenase is restricted by its chemical sensitivity which in turn prompted the quest for feasible and reasonable homogeneous and heterogeneous materials numerous which utilize transitions metals from the first row which are earth-abundant as well as less costly and effective at the same time.

Electrocatalyst that are based on the first-row transition series like nickel, iron, cobalt has gained much attraction from researchers all over the world owing to their fairly catalytic activities. In this work, nickel complex was synthesized by the binding of $NiCl_2$ with Schiff's base ligand which was developed using salicylaldehyde and aniline. The Ni-based electrocatalyst developed was characterized with the help of spectroscopic strategy cyclic voltammetry and UV-VIS Spectroscopy. The outcomes obtained with characterization techniques depicts that the prepared electrocatalyst is active in nature towards hydrogen evolution as suggested by increase in current with increase in acid concentration. The overpotential for the electrocatalyst is determined to be 390mV with the TOF value of $6.39s^{-1}$.

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LIST OF SYMBOLS AND ABBREVIATIONS

SYMBOLS

F = Faradaic Constant

N = No. of moles

V = Volt

A = Ampere

ABBREVIATIONS

$NiCl_2$ = Nickel Chloride

KOH = Pottasium Hydroxide

Fe = Iron

S = Sulphur

Pt = Platinum

Re = Rhenium

Rb = Rubedenium

CH_3COOH = Acetic acid

CF_3COOH = Trifluoro acetic acid

CO = Carbon Monoxide

CO_2 = Carbon Dioxide

ACN = Acetonitrile

DMF = Dimethyl formamide

FI = Fluoroscein

Ps = Photosensitizer

TEOA = Triethanolamine

TBAHFP = Tetrabutylammonium Hexafluorophosphate

SHE = Standard hydrogen electrode

HER = Hydrogen evolution reaction

Uv – Vis = Uv – Visible

i_p = Cathodic current

i_{cat} = Catalytic current

TON = Turnover number

TOF = Turnover Frequency

FOWA = Foot of Wave analysis

HOMO = Highest Occupied molecular orbital

LUMO = Lowest unoccupied molecular catalyst

GREEK LETTERS

ε = Molar Absorptivity

η = Overpotential

CHAPTER 1

INTRODUCTION

The major issue today is to meet the growing energy demand which will be increasing from 15 TW in 2011 to 50 TW in 2050 with the increase of 2 billion people. Till now the biggest source of the energy are the fossil fuels like coal, petroleum etc. Society's strong dependence on the fossil fuels particularly oil and gas has resulted our economy susceptible to many major issues like price spikes, etc. Overuse of our fossil fuels with increasing demand resulted major issues including decreasing finite natural resources, global warming, air pollution, the production of environment friendly by-products etc. which has become the burning issue today. Thus the need of the hour is to develop a clean and renewable source of energy that can replace fossil fuels and this next generation energy source must overcome the stringent criteria of environment friendly byproducts and abundance. Among various alternative energy strategies constructing energy infrastructure hydrogen is renewable and clean fuel and is considered as a potential energy carrier for future energy infrastructure. It enables us secure and clean energy future [1].

Therefore the need of great importance is to build up a perfect and inexhaustible energy source that must be environment friendly [2]. Among different elective techniques building vitality foundation, hydrogen is inexhaustible and clean fuel and is considered as a potential transporter of energy for future energy framework [3] due to its properties like it stores exceptionally high density of energy by weight , it has gravimetric energy density of 120 KJ/g, which is seven times higher than the conventional fossil fuels and 2.5 times the energy density of hydrocarbons also it does not remove any greenhouse gas in the atmosphere like fossil fuels as its byproduct is pure water [4].

1.1 HYDROGEN EVOLUTION METHODS

1.1.1 Hydrogen evolution by steam reforming of methane (CH_4)

It is the least expensive wellspring of large scale hydrogen evolution [5]. Procedure of it comprises of the decomposition of Methane to CO and H_2 by the endothermic process which results on heating of gas at 700 to 1100°C inside seeing the steam and the nickel catalyst.

$$CH_4 + H_2O \longrightarrow CO + 3H_2$$

In the subsequent stage extra hydrogen is produced through the exothermic, lower – temperature, water gas shift reaction, at around 360 °C.

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

Basically, for CO to CO_2 oxidation, the additional water (steam) provides us the (O) atom. This oxidation similarly offers essentialness to keep up the reaction. Additional requirement of energy is given with CH_4. The disadvantage to this methodology is that its genuine outcomes are CO_2, CO and also other harmful gases [6]. Contingent upon the idea of the feedstock (combustible gas, Naptha, etc.), 9 to 12 tons of CO_2 will be moreover made from just 1 ton H_2 delivered [7].

1.1.2 Hydrogen evolution from water

Hydrogen evolution in eco- friendly way is by splitting of a water molecule using the electricity generated from renewable resources like solar energy, wind energy, etc. [6]. In the electrolyzer, we have an electrolyte, for example, water or alkaline electrolysis for example KOH. The cathode and anode made up of nickel and are coated with the catalyst that speeds up the hydrogen and oxygen evolution respectively for example electrodes are coated with the platinum and manganese oxide. Now on the application of externally applied voltage the water is decomposed into hydrogen and oxygen according to the reaction given below:

Overall reaction

$$H_2O \longrightarrow H_2 + 1/2O_2$$

In acidic solution

Cathode $2H^+ + 2e^- \longrightarrow H_2$

Anode $H_2O \longrightarrow 2H^+ + 1/2O_2 + 2e^-$

In neutral and alkaline solutions

Cathode $2H_2O + 2e^- \longrightarrow H_2 + 2OH$

Anode $2OH \longrightarrow H_2O + 1/2O_2 + 2e^-$

Now although this reaction is environment-friendly it has certain limitations like for electrode coating the catalyst that is used is platinum that creates problem in their commercial making due to its high cost and limiting earth resources. So the potential substitute for platinum would be

something that is of low cost and high abundance in the earth these both conditions are fulfilled by the transition metals like iron, cobalt, nickel, etc. [7].

1.1.3 Hydrogen evolution from coal

One of the most seasoned and most inexhaustible non-renewable energy source assets on the earth is coal. We have 892 million tons of coal with us as reported by world coal association and these will degrade after 110 year [8].

Hydrogen is delivered from coal by gasification in which fuel of solid nature is changed over to gas so as to get the more value of energy density, another reason is to save the environment from the harmful rays emitted (CO_2 major greenhouse gas) when coal is burnt [9], so gasified coal is preferred over burnt coal. In the gasification process at elevated temperature and pressure, we oxidize the coal with steam and O_2. The product obtained is syngas that is H_2, CO, in steam and CO_2 [10]. The syngas obtained is directly used as an energy source for various reactions. It can also be used to produce electricity through turbines, after processing the syngas [11].

This technique can't be used as it releases sulfur in the atmosphere which leads to issues like acid rain in industrial sites, sulfurous fog, etc. Also, its techniques are not well defined as hydrogen production from other fossil fuels like natural gas, etc. Only 18 % of hydrogen is obtained using this method.

1.1.4 Thermochemical method

Another method which is barely used for the hydrogen production includes water heated to 800-1000 °C causing water to break into its constituents that is hydrogen and oxygen called thermochemical cycle as it includes the thermal energy. It is very uncommon as it is highly costly, production here depends upon the uranium salts and also as it makes use of the nuclear power to heat the water.

1.1.5 Biological evolution of hydrogen with hydrogenase

Biological methods used for hydrogen evolution are the future of dream society that will be environmentally sustainable and nearly infinite. Hydrogenase is enzymes present in various microorganisms and catalyzes the oxidation of the molecular hydrogen molecule [12].

$$H_2 \longrightarrow 2H^+ + 2e^-$$

$H_2 \longrightarrow H^+ + H^-$

Apart from their diverse nature in the form of size, shape, etc. These are of mainly of three types the [Ni-Fe], [Fe-Fe] and [Fe]-hydrogenase [13].

[Ni-Fe] hydrogenase

It is present in bacteria and also in archaea and is used in hydrogen evolution oxidation. It is reversibly non activated by O_2 For the impediment of CO and O_2 it less tactful than the Fe-Fe hydrogenase.4- Cysteine residues having in total 8 atoms are coordinated to the Ni-Fe bimetallic center.2 CN and 1 CO which are the nonprotein ligands are also coordinated to the Fe center [14]. The active structure is shown in (figure 1.1) [15].

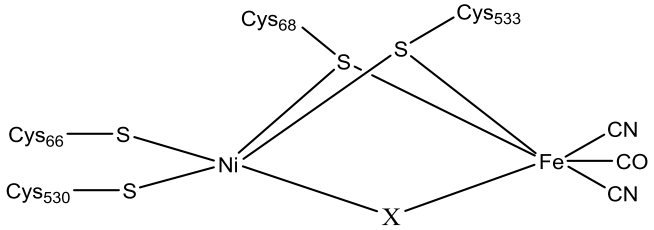


Figure 1.1: [Ni-Fe] hydrogenase active site structure

[Fe-Fe] hydrogenase

These are used for the H_2 production and are found in a few kinds of prokaryotes and also in green algae, it is reversibly inactivated with O_2 and show sensitivity towards oxygen these have only 1 catalytic subunit that may differ in the size unlike the [Ni- Fe] which must have 2 subunits at the least. Here active site is in the domain of Ca 350 [16]. Also in the different domain than the active site we have our Fe-S cluster. Active site structure is shown in (figure 1.2) [15]. The only hydrogenase present in eukaryotes [17], also present in the anaerobic prokaryotes for eg. Clostridiene. It allows algae to survive under anaerobic condition by providing an electron valve.

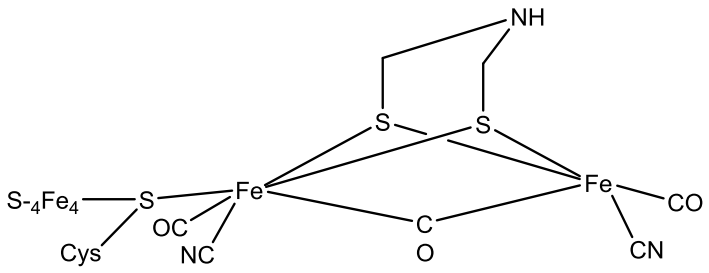


Figure 1.2: [Fe-Fe] hydrogenase active site structure

[Fe] hydrogenase

These are earlier thought to be metal free as these does not contain the Ni and the Fe – S cluster but as these have the Fe as the active center so these are termed as the "Fe- hydrogenase". The Fe here is redox inactive as proved it does not catalyze this reaction in the reverse order. It is oxygen tolerant [18].

$2H^+ + 2e^- \longrightarrow H_2$

It also differentiates itself from the other two in the form of its primary and the tertiary structures. Active site structure is shown in (Figure 1.3) [19].

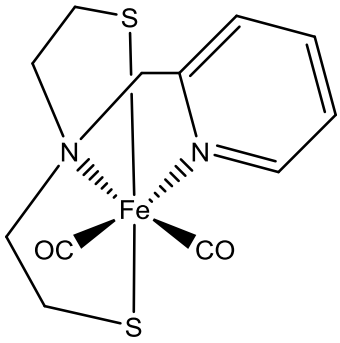


Figure 1.3: [Fe] hydrogenase active site structure

Biological hydrogen production using hydrogenase is considered as an important process for hydrogen production because it requires low overpotential. Among the three the most active for hydrogen production is [Fe-Fe] with the turnover frequency of the order $9000s^{-1}$ [20]. The three differ in their sensitivity towards oxygen. It splits hydrogen into an electron and two protons and

also facilitates the reverse reaction. Whereas there exist various serious issues regarding their use in the industries like the hydrogenase tolerance to the oxygen, another important thing is the sustainability of the activity of enzymes, and the third one which creates hinderance is the high cost that is required for the synthesis of enzymes [21].

1.2 Electrochemical hydrogen evolution

The electrochemical hydrogen advancement response is a well-examined electrochemical response which includes e^- protons reduction for hydrogen creation. It requires an exceptionally effective and strong catalyst to bring down the overpotential and vitality utilization. Transition metals of the first row are considered very efficient in energy conversions. The best catalyst for hydrogen development is unquestionably platinum, which works for H^+/H_2 transformation at the thermodynamic potential of (0V versus SHE, pH 0) [22]. Pt is very dynamic for hydrogen development however its shortage and cost confine its broad application. Consequently, the molecular catalyst that should use low cost and make use of transition metals that are abundant on earth is the core and heart of the technology used for hydrogen evolution [23]. Although various metal catalyst is present for HER then it is very difficult to design and develop a complex of metal to act as a catalyst for HER in solution over large pH range with good efficiency. This needs to take care as there may be the low affinity of metal ion to bind with the ligand in highly acidic or basic conditions [4].

Propelled by the efficiency of the proteins of natural occurring, that is, hydrogenase, that catalyze both the HER and HOR with a movement similar to platinum, inorganic scientific experts have extensive exertion as of late into the advancement of coordination molecular catalyst that are molecularly like the active locales of [Fe-Fe] and [Fe-Ni] hydrogenases and into the investigation of these mixes synergist movement in the HER, for the most part in non-aqueous medium [24]. Dubois and Bullock group reported a catalyst of nickel which initiated the idea of synthesis of the molecular catalyst of small size for HER [25]. Molecular complexes of iron, nickel, cobalt are gaining importance for the efficient H_2 production as reported by researchers [26] so taking inspiration from the work done before on the electrocatalyst we have developed an electrocatalyst of Ni where Ni is coordinated with the ligand synthesized using salicylaldehyde and aniline.

1.3 Electrocatalyst

A catalyst is a substance which being available in little extents expands the rate of response of substance harmony without itself undergoing any physical and chemical change. Something very similar is finished by electrocatalyst however with electron transfer. It quickens the variety in the rate of response and contributes in electron transfer response at the anode. In electrochemistry, as in catalysis, rate of response depends just on given parameters however if there should arise an occurrence of electrocatalyst it relies upon the cathode potential moreover. In electrochemical responses, catalyst surface is in contact with different species (electrolyte particles and dissolvable atoms) additionally other than the responding species which makes the electrocatalyst action fascinating. There is a scattering of catalyst particles in mass if there should arise an occurrence of homogeneous catalyst while on the anode surface the catalyst particles are covered in case of the heterogeneous catalyst which creates a difference between the two.

1.3.1 Homogeneous catalyst

Homogeneous catalysis by dissolvable complexes of transition metals offers numerous favorable circumstances over heterogeneous catalysis, for example, milder response conditions, higher exercises and selectivities, and better control of working conditions. Such unrivaled execution emerges from the capacity of progress metals to complex with different types of ligands in various geometries and to effortlessly change starting with one oxidation state then onto the next. Despite the fact that heterogeneous catalysts rule the mechanical scene today (85% of all current synergist forms), the significance and piece of the overall industry of homogeneous impetuses are developing. Its coordination with progress metals is an ideal method to initiate it for hydrogen development. Because of this coordination, actuation vitality brings down required for further responses and furthermore upgrades rate of response. Numerous reports of homogeneous electrocatalysts for electrochemical HER have shown up in writing in past years. It delivered a reduction of 2 electrons. Proficiency reaches up to 80%. In this way, the homogeneous electrocatalysts considered as useful for the development of Hydrogen.

CHAPTER 2

LITERATURE REVIEW

In recent years many researchers have contributed their work towards the synthesis of appropriate electrocatalyst which is of paramount importance. Many different kinds of electrocatalyst are used for example metal complexes, metals, electrocatalyst supported by metal, metal oxides, etc. To know the developments made in this field in the past few years Literature review is important which is explained in detail in this chapter. This part directs the already done work with the electrocatalysts for the evolution of hydrogen electrochemically.

Grapperhaus group reported a electrocatalyst using the mononuclear metal thiolate which is coordinatively saturated ReL_3 (diphenylphosphinobenzenethiolate) [27]. H_2 production solely depends upon the applied potential and the acid and base presence. At the potential less than -1.60V it catalysis the hydrogen evolution from the acid catalyst gives hydrogen production at an overpotential of 380mv with any of the acetic acid or sulphuric acid and at the TOF of $32\pm3s^{-1}$ The rate law unveils that it is dependence on the acid conc. by second order and on the catalyst conc. by the first order. The overall rate constant is found third order with $K=184 \pm 2M^{-2}\ s^{-1}$.The ligand centered nature of catalyst is suggested from the isoelectronic nature of species with the derivatives made from the redox active addition of ReL_3 with ethylene.

Grapperhaus group reported NiL_1, which is a neutral and monomeric complex of Ni(II) with diacetyl-bis(N-4-methyl-3-thiosemicarbazonato) for the hydrogen production in the DMF and ACN by the metal-centered ligand assisted process which is supported by computational studies [28]. For CH_3COOH and CF_3COOH, TOF is 48 and 24 in ACN and 13 and 3 in DMF. In DMF, the overpotential is 0.85V for CH_3COOH in DMF and 0.53V in ACN. First-order reliance as for the catalyst is built up. NiL_1 shows 87% faradaic efficiency using FOWA catalyst display TOF at 4200 and $1200s^{-1}$ for COOH in DMF.

Wesley Sattler et al. reported one of the most versatile catalyst is [Tris(2-pyridylthio)methyl]zinc hydride, [κ_3-Tptm]ZnH which can perform various functions such as evolution of hydrogen with the help of protolytic cleavage by either methanol or water, hydrosilylation of carbon dioxide, aldehydes and ketones, catalyzing hydrosilylation reaction of triethoxysilane and carbon dioxide to form triethoxy-silylformate which can be converted into N,N-dimethylformamide and ethyl formate and also catalyzes the methanolysis of phenylsilane for the release of hydrogen gas (3 equivalents) with a TOF of more than106 h^{-1} for first 2 equivalents and turnover number as 105.18 [29].

Grapperhaus group reported the metal-assisted ligand-centered electrocatalyst of Cu (II) with diacetyl-bis(N-4-methyl-3-thiosemicarbazonato) exhibiting overpotential of 0.76 V and 0.80V with TOF of 5100s^{-1} and 1000s^{-1} in DMF and acetonitrile respectively [30]. Hydrogen evolution was confirmed with the help of GC using electrolysis that was potential controlled. Complex posses FE as high as 83% with TOF 73s^{-1} and is stable upto time period of 23 h.

Lu Gan et al. reported complex, [Ni (bdt)(dppf)] (bdt = 1,2-benzenedithiolate, dppf = 1,1′-bis(diphenylphosphino)ferrocene).The process is taking place in the presence of any feeble acid and it is enduring for 4 h in acidia media [31]. TOF of 1240s^{-1} with the overpotential value of 265mV was found depicting the quickness of catalyst.

Ryan J. Dirisio et al. reported complexes of cobalt (III) [Co(L-(NO_2)$_2$)$_2$)]BF_4 and [Co(L-NO_2)$_2$)PF_6 using low cost precursor and one-pot synthetic method having cost-effective Schiff base ligand and are active in hydrogen production a low value of overpotential is found of just 120mV and 280mV due to the presence of electron withdrawing dinitro and tetranitro groups [32].TOF value obtained was 4100s^{-1} using FOWA. The relation between TOF and overpotential was developed using Tafel plot as TOF 1.07 s^{-1} shown at the 0 overpotential with the catalyst which is most effective.

Arnab Dutta group discussed that the protein platform assumes a key job in the metalloenzyme catalysis by enzymes [33]. Here we have sanely structured a chemical roused external coordination circle in the of protic functionalities, for example, characteristic phenolic −OH

gatherings inferred by amino acids and a carboxylic acid, at edge of the cobalt-salen like species. This fuse has engaged electrocatalytic H_2 advancement for idle cobalt-salen like centre complex that has a carboxylic acid group at the periphery shows a hydrogen evolution that is pH-switchable and is joined with the carboxylic acid having the *p*ka value of approx. 4. indicating the role of the carboxylate group in the activity of the catalyst.

Ejaz Ahmad et al. synthesized a nickel-based atomic impetus $[Ni(QCl\text{-}tpy)_2]Cl_2.7H_2O$ (where QCl-tpy = 2-choloro-3-(2,6-di (pyridine-2yl)pyridine-4-yl) quinoline) has been combined, portrayed by single gem XRD and other spectroscopic methods [34]. The complex $[Ni(II)(QCl\text{-}tpy)_2]^{2+}$ has too been utilized for the electrocatalytic proton decrease in DMF/H_2O (95:5 v/v) utilizing trifluoro acidic acid (TFA) as the proton source. The catalyst showed its optimal performance in organic media. The complex $[Ni(II)(QCl\text{-}tpy)_2]$ shows better catalytic performance like the high value of the catalytic current and overpotential value as low as 180mV than the parent complex that is $[Ni(II)(tpy)_2]$ 2p in the electrolysis process. It is normal because of the nearness of 2-chloroquinoline moiety in the terpyridine system. Electrocatalyst exhibits TOF $3.68s^{-1}$ at 1.0mM done at a scan rate of $100mVs^{-1}$. In view of the spectroscopic proof and electrochemical examinations, a conceivable instrument is developed for H_2 evolution.

Zhen Xin Chen team progression of Ni catalyst joining non-innocent ligands displaying hydrogen evolution at low overpotential with TOF of 2572 s^{-1} also with small volume of acid [35]. As electronic impact can differ the energy of the formation of hydride of metal so just by adjusting the substituents present in imide they increased the rate constant of the reaction by the order of 2.

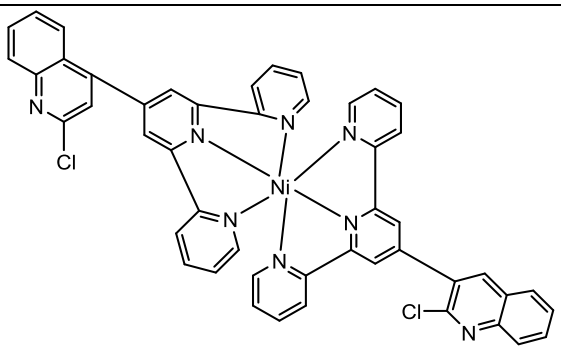
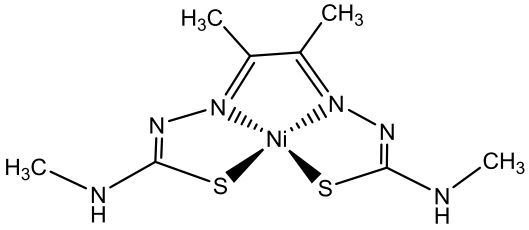
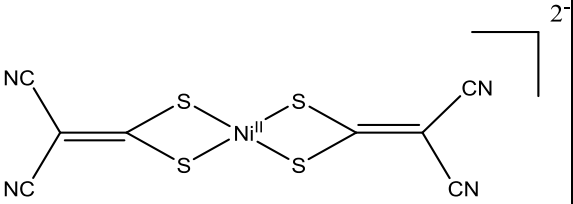
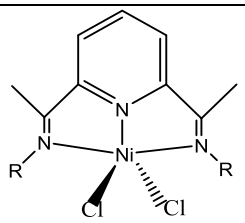
Fukuzumi group reported that in Ni(II) complex, higher activity is exhibited by 5-membered SC_2S-Ni chelated ring than that of 6-membered SC_3S-Ni chelated ring in both photocatalytic and electrocatalytic H_2 evolution [36]. A stepwise reduction from Ni(II) to Ni(0) of Ni centre takes place in electrochemical process. Also, it was clarified that in electocatalytic system Ni (II) complexes act as homogeneous catalysts. . The difference in action between the two catalysts was gotten from the activation barrier of the responses between the Ni (II) − H intermediates and

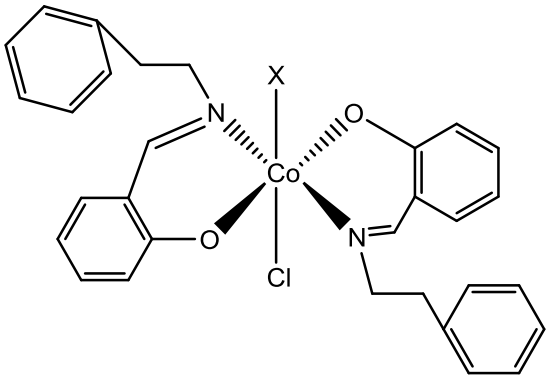
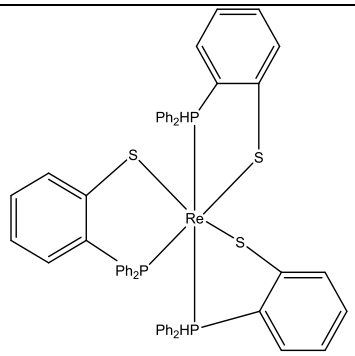
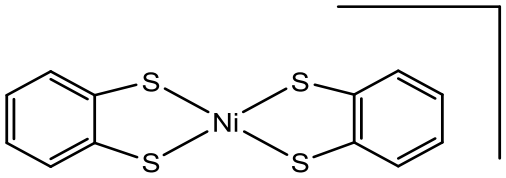
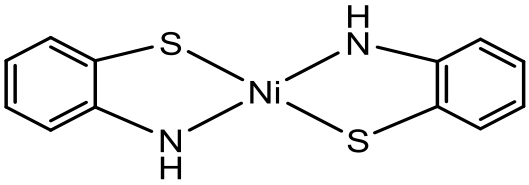
proton, which is steady with the way that expansion of concentration of proton quickens the H_2 development.

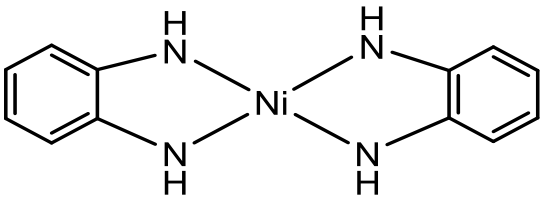
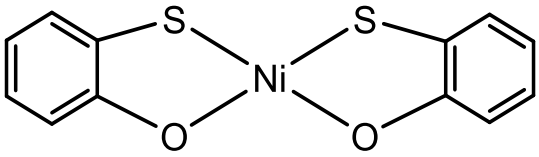
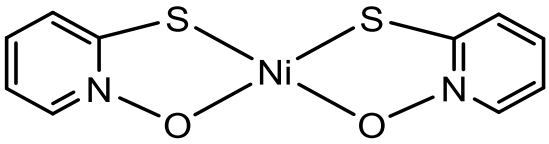
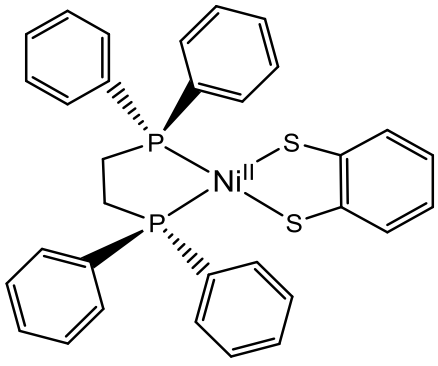
Tatiana Straistari group reported a dinuclear bis(thiosemicarbazone) complex of cobalt $[Co_2L_2(NCS)_2]$.Complex shows acatalytic activity when (Et_3NHBF_4) is a proton source in DMF [37]. The determination that the procedure is catalytic and the generation of dihydrogen were affirmed by gas examination during controlled potential electrolysis tests. Catalyst is ligand – assisted metal- centered as demonstrated. Evolution of hydrogen was confirmed by Gas chromatograpgy.

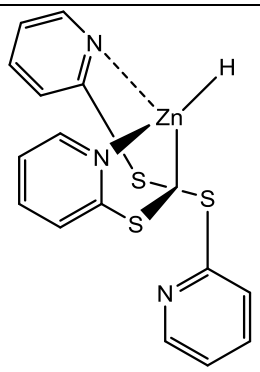
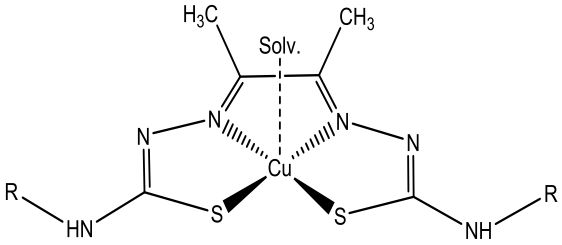
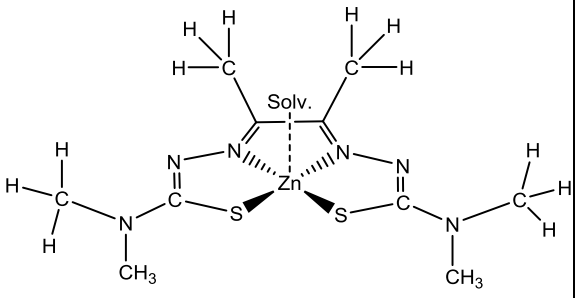
Grapperhaus and group directed us to all new method for the synthesis of electrocatalyst independent of the intermediates like metal – hydrides like so far [38] . They reported 2 complexes Diacetyl-bis(N-4-methyl-3-thisemicarbazone) and zinc diacetyl-bis(N-4methyl-3-thiosemicarbazide) displaying TOF 1320 s^{-1} and 1170 s^{-1} respectively. These values are highest of all other homogeneous electrocatalyst reported so far .All these results are determined on the basis of the density functional theory and the electrochemical studies.

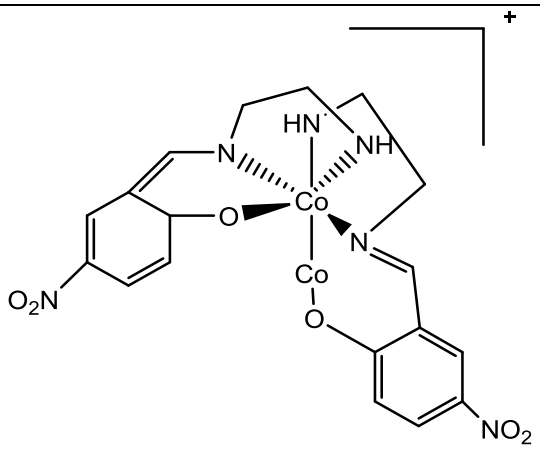
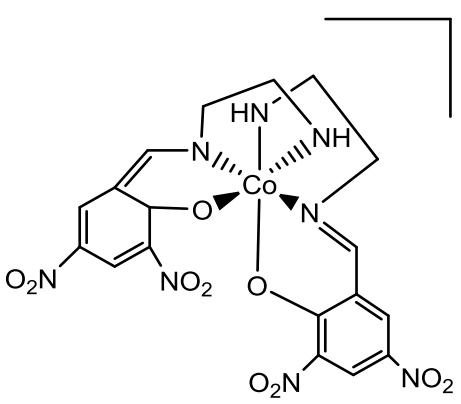
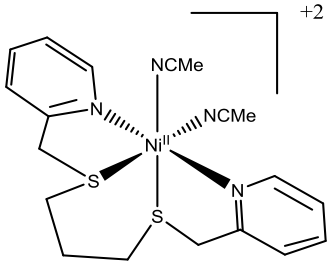
Table showing electrocatalyst for HER

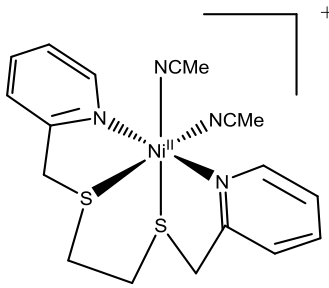
Sr.No	Catalyst structure	Year of publishing	Faradaic efficiency	Over-potential	TOF	TON
1	 Ejaz Ahmad and Co-workers	2019	86±4%	650-950mV	3.68s^{-1}	--
2	 Craig A. Grapperhaus and co-workers	2018	87%	0.53mV	4200s^{-1}	--
3	 Jia-Mei-Lei and co-workers	2018	91%	837.6mV	--	55340 mol
4	 Zhixin Chen and Co-workers	2018	>99%	--	2572 s^{-1}	-- 12

5	 Arnab Dutta and co-workers	2019	--	670mV	255±11 .01s^{-1}	--
6	 Craig A. Grapperhaus and co-workers	2015	--	380mV	32±3s^{-1}	--
7	 Amit Das, Richard Eisenberg and group	2015	--	--	0h^{-1}	0
8	 Amit Das, Richard Eisenberg and group	2015	--	--	75h^{-1}	6190

9	 Amit Das, Richard Eisenberg and group	2015	--	--	$16h^{-1}$	900
10	 Amit Das, Richard Eisenberg and group	2015	--	--	$60h^{-1}$	5600
11	 Amit Das, Richard Eisenberg and group	2015	--	--	$74h^{-1}$	5900
12	 Lu Gan and Co-workers	2015	--	265mV	$1240s^{-1}$	--

13	 $[K_3\text{-Tptm}]ZnH$ Wesley sattler and Gerard Parkin	2012	--	--	$10^6 h^{-1}$	10^5
14	 L=R=p-$CH_3O(C_6H_4)$ Grraperhaus Copper Ligand	2017	81%	0.80V	10,000 s^{-1}	73
15	 Grapperhaus Zinc Ligand	2016	75%	0.756V	$1170S^{-1}$	37

16	 Ryan J. Dirisio and group	2017	85%	120mV	$7s^{-1}$	--
17	 Ryan J. Dirisio and group	2017		280mV	$3s^{-1}$	4100
18	 Ni^{II} – bppt(2) Fukuzumi and co-workers	2018	80%	--	$3.6\ h^{-1}$	19

19	 Ni^{II} – bpet(1) Fukuzumi and co-workers	2018	95%	--	2.3 x $10^2 h^{-1}$	1.1x1 0^3

CHAPTER 3

MATERIALS AND METHODS

It includes the various things which have been utilized during research work. The methodology of synthesis and the characterization techniques used like UV-Visible spectroscopy and Electrochemistry are also discussed.

3.1 MATERIALS

3.1.1 Apparatus

Magnetic Stirrer, Condenser, Rubber tubing, thermometer, guard tube, Round bottom flask(100ml), beakers(100ml), magnetic bead, micropippete , measuring cylinder, spatula, dropper, appendoff ,glass vial, water bath, filter paper, Buchner funnel , rubber funnel adaptor, watch glass, tongs ,tips, cotton, Erlenmeyer flask.

3.1.2 Chemicals and instrumentation

All the chemicals used for the synthesis of the target compounds that is Aniline (≥99.5%), Salicylaldehyde (98%), Triethylamine (≥99.5%), $NiCl_2$, were of reagent grade. These all have been purchased from Loba Chemicals and were used as received. Distilled water and other solvents like Ethanol, Methanol, Diethyl ether, acetonitrile, hexane, DCM purchased from Sigma Aldrich and used without any further purification as these were of analytical grade.

Perkin Elmer Lambda 35 UV/VIS Spectrometer was used to measure UV – VIS studies. Potentiostat has been acquired from auto lab/ DY-2300 Potentiostat outfitted with a cell of three electrodes, including e a glassy carbon (area = 0.071 cm^2) acting as working electrode, Platinum electrode as counter and the reference electrode is Ag/AgCl in 3M KCl solution.

3.3 Synthesis of the nickel complex

Chemicals used: Aniline, Salicaldehyde, Triethylamine, $NiCl_2$

Reaction Condition: 50 - 60°C

Solvent Used: Ethanol

Aniline (372.52mg, 4mM) was dissolved in ethanol (5ml). The ethanolic solution of salicylaldehyde (488.88mg, 4mM) was added dropwise to solution of aniline. The reaction mixture was refluxed and stirred for 1 hour at 55°C to yield the ligand. To this added dropwise Triethylammine with constant stirring and stirred the solution for another 15 minutes. Now taken the complex of $NiCl_2$ (259.19mg, 2mM) and dissolved it in a minimum amount of ethanol(5ml). Then the ethanolic solution of $NiCl_2$ was added dropwise to the ligand formed taking time of 15-20 minutes with constant stirring and heated this solution for 1 hour at 60 °C and the product got is dried using rota-evaporator, filtered using vacuum filtration with given washings from diethyl ether then with distilled water and then again with diethyl ether and air dried.

Yield: 82%

Color of Ligand: Yellow

Color of compound:Green

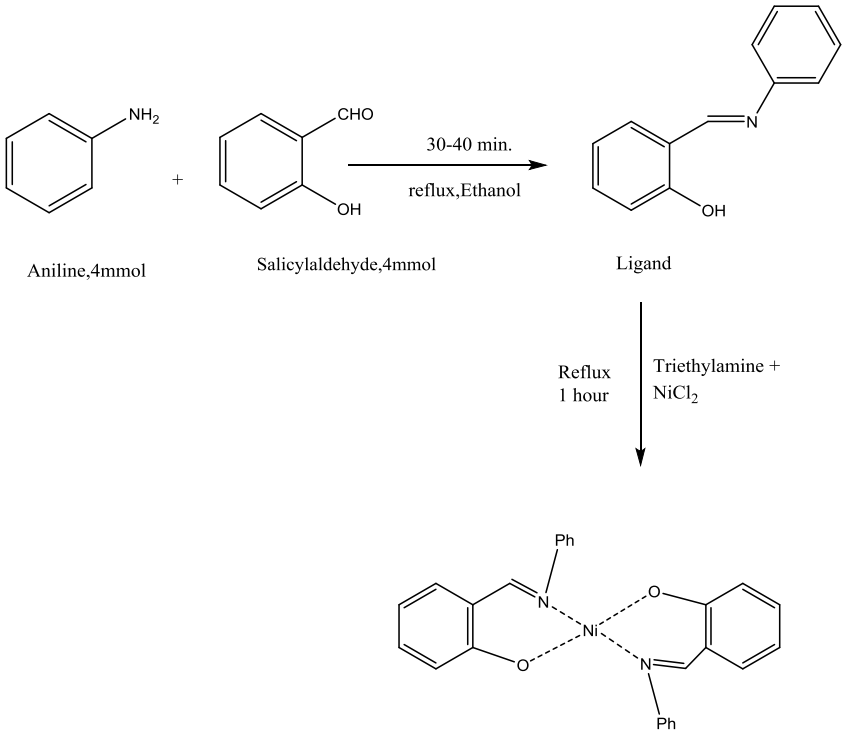


Figure 3.1: Reaction for the Synthesis of Schiff's base Nickel complex

Triethylamine + $NiCl_2$

1 hour

Figure 3.2: Reaction set- up for the ligand Synthesis

Figure 3.3: Reaction set up for the Ni complex synthesis

Figure 3.4: Nickel Schiff base complex

3.4 UV-VISIBLE Spectroscopy

UV-Visible spectroscopy(Figure 3.5) is the absorption of the electromagnetic radiation in the UV-Visible region (210-900nm). When light from the light source that is deuterium lamp passes through our cuvette from the side at which cuvette is transparent we get the absorption spectra. Transitions occur between the various energy levels from the ground state (bonding energy orbitals) to the excited state (antibonding energy orbitals) as also shown in (Figure 3.6) and the most common transition is from HOMO (Highest Occupied molecular orbital) to LUMO (Lowest Unoccupied molecular orbital).

Principle

The principle that lies in the UV-Visible Spectroscopy is the Beer-Lambert's Law, which states the absorbance of solution is proportional to concentration and the thickness of absorbing solution.

Expression for the law is given below

$$\mathbf{A = \varepsilon cl = \log (I_0 \backslash I)}$$

Where

A = solution's absorbance

c = concenteration of solution in mol dm^{-3}

l = solution's path length in cm

ε = molar absorptivity in $dm^3mol^{-1}cm^{-1}$

I_0 = Incident's light intensity for the reference cell

I = Intensity of the light coming out of the sample cell.

Figure 3.5: Set up for the UV – Visible Spectroscopy

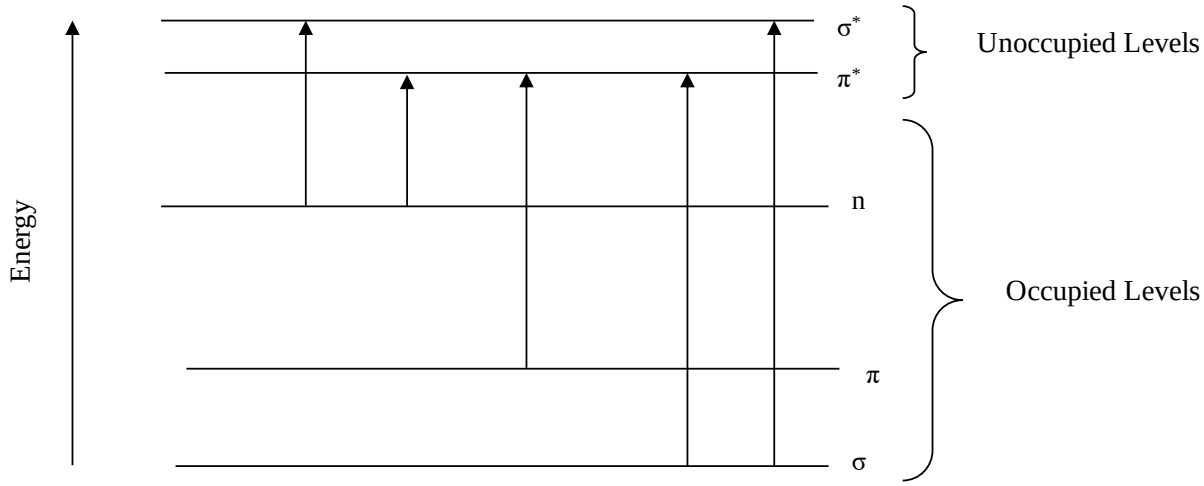


Figure 3.6: Possible electronic transitions

Working

The light from the light source emits light in the UV range and the subsequent light source which is a tungsten light discharges light in the range visible to human eye and enters the monochromator having altering cuts which spotlight on the wavelength of test cell, usually made up of glass or plastic with a straightforward side from where the light enters. The light at that point goes through the example cell and achieves the detector whose function is to record the

transmitted light's intensity. Some important transitions in different types of compounds are shown in (Figure 3.7).

$\sigma \rightarrow \sigma^*$	Present in alkanes
$\sigma \rightarrow \pi^*$	Present in Carbonyl Compounds
$\pi \rightarrow \pi^*$	Present in alkynes, azo compounds, alkenes, carbonyl compounds, etc.
$n \rightarrow \sigma^*$	Present in Sulphur, halogen, nitrogen and oxygen compounds
$n \rightarrow \pi^*$	Present in carbonyl compounds

Figure 3.7: Table showing some important transitions

3.5 Cyclic Voltammetry

It is a well-known and most significantly used strategy for electrochemical examinations. It recites us the chemical changes occurring from the electron flow. Set up shown in (Figure .3.8)

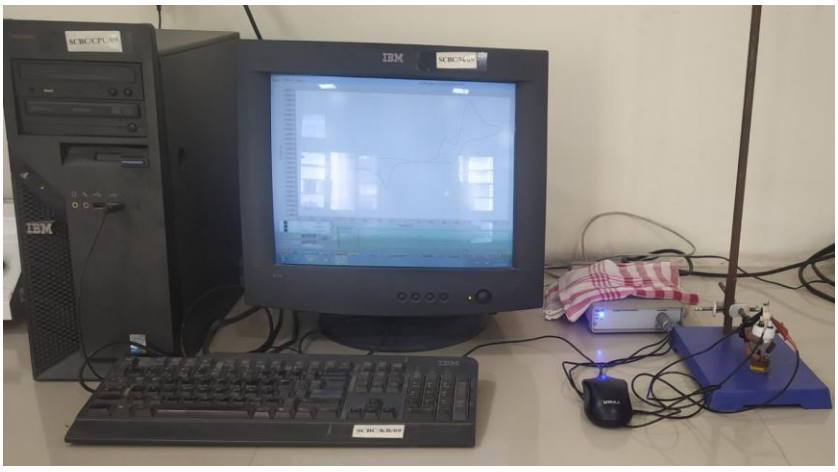


Figure3.8: Experimental set up for the Cyclic Voltammetry

Cyclic voltammetry estimations were performed with a Digi-IVY DY-2300 model potentiostat electrochemical framework at the room temperature in a cell which is washed and dried overnight before use fitted by three electrodes. The glassy carbon is a working electrode having 3mm diameter, the reference electrode here is Ag/AgCl. And the Pt electrode plays the role of the counter electrode. Working electrode was cleaned utilizing aluminium polish before chronicling the information and the reference and counter electrode was washed with distilled water and then with ACN . Then the Pt electrode and glassy carbon electrode was sonicated for 10 seconds.

In the cyclic voltammetry experiment, 2 mM arrangement of the catalyst was set up in the working dissolvable (ACN) containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAHFP) acts as a supporting electrolyte. Information is gathered at different sweep rates 0.1, 0.2, 0.5, and 1.0 V/s. Increases in acid concenteration have proceeded till the current saturates. Under acid immersing conditions, the sweep rate was shifted until output rate independent conditions were set up.

Working

Here, potential is connected to working terminal which is typically a triangular waveform has appeared in the (Figure 3.9**).** Current developing from the processes like electrochemical or chemical processes on the working electrode is plotted against the scanned anodic or cathodic that is working electrode's potential. For the most part, the arrangement is left static while gathering the information. Under these conditions, the deliberate redox current is dictated by the reactant concentration, the dispersion coefficient of product and reactant, and output rate.

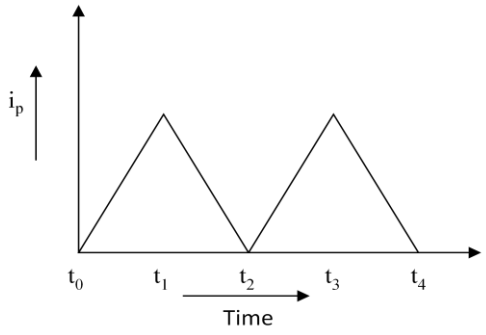


Figure 3.9: Cyclic Voltammetry Waveform

Randel – Sevcik equation gives us the value of peak current that is i_p

$\boldsymbol{i_p = 2.69 \times 10^5\ n^{3/2} A D_0^{1/2} v^{1/2} C}$

$i_p = 0.4463FA[cat](FvD/RT)^{1/2}$ related to diffusion equation

n = no. of e^- involves in the chemical or redox reaction

v = sweep rate expressed in the units mV/s

D_0 = it represents the redox species diffusion coefficient and is expressed in cm^2/sec

C = Concentration of the species expressed in units mol/L

A = Area of the electrode in cm^2

Diffusion constant obtained using slope from Cotrell equation and Randel-Sevcik equation[39]

Slope = $0.4463FA[Cat][FD_0/RT]^{1/2}$

For TOF determination [40] from 1 and 2, we get

$i_{cat}/i_p = n/0.4463\ (RTk_{obs}/Fv)^{1/2}$

When n=2, we get

$(i_{cat}/i_p)^2 \times 1.94 = k_{obs} = TOF$

Determination of overpotential having Ag/AgCl as reference on addition of 0.2 M AcOH

$\eta = E_{ref} - E_{cat/2}$

Chapter 4

RESULTS AND DISCUSSIONS

This chapter discusses the results of various techniques that have been used to examine the prepared electrocatalyst. Analyzation of UV – VIS study and Cyclic Voltammetry techniques are explained in the following discussion.

4.1 Electronic spectroscopy

The electronic Spectroscopy of [NiL_1] complex in acetonitrile gives us MLCT peak at 410nm as shown in (Figure 4.1) which shows metal is being coordinated with ligand here and thus showing absorption for Metal to Ligand Charge transfer. The absorption band falls in the visible region corresponds to d-d transitions.

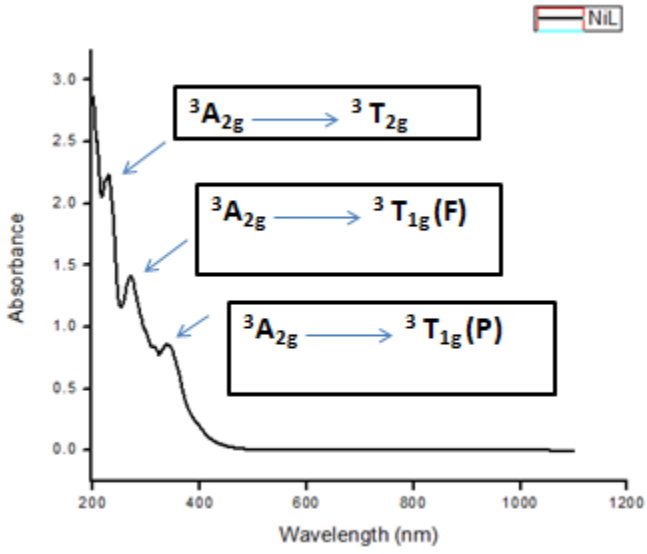


Figure 4.1: UV – Visible Spectrum of 0.1mM solution of [L_1Ni] in acetonitrile

4.2 Electrochemical characterization

When performed CV of [NiL_1] having TBAHFP 0.1M present as a supporting electrolyte in the presence of acetonitrile (ACN) shows a $Ni^{II/I}$ occasion at -1.45V which is reversible in nature vs Ag/AgCl. Extra CV information gathered at different sweep rates from 0.1 V to 1V/s in ACN (Figure 4.2) was utilized to plot Cottrell plots (Figure 4.3), setting up that $Ni^{II/I}$ reduction is diffusion restricted, in this manner showing the capability of NiL_1 as a homogeneous electrocatalyst. 3.96×10^{-6} cm^2/s is the value of diffusion constant in ACN as obtained from the slope of the plot.

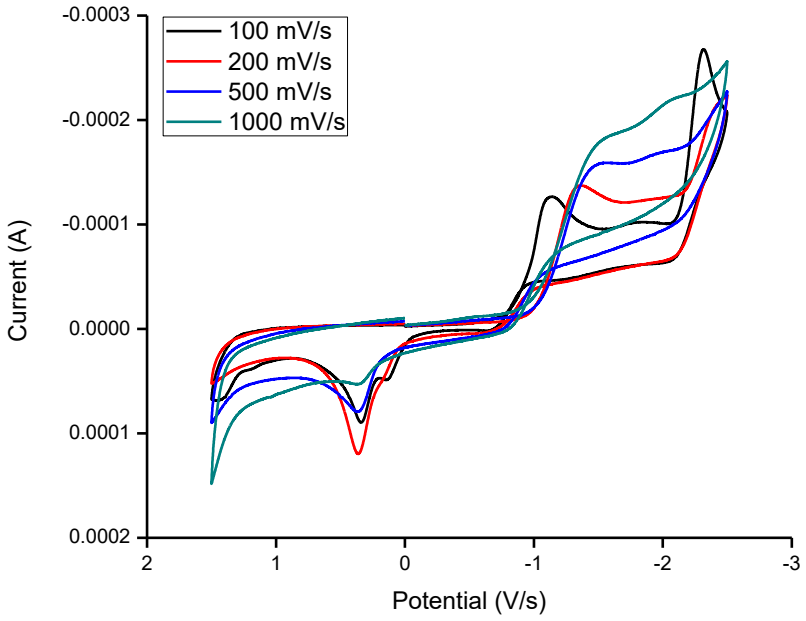


Figure 4.2: CV of [L_1Ni] at various sweep rates ranging 100 mVs^{-1} to 1000 mVs^{-1}

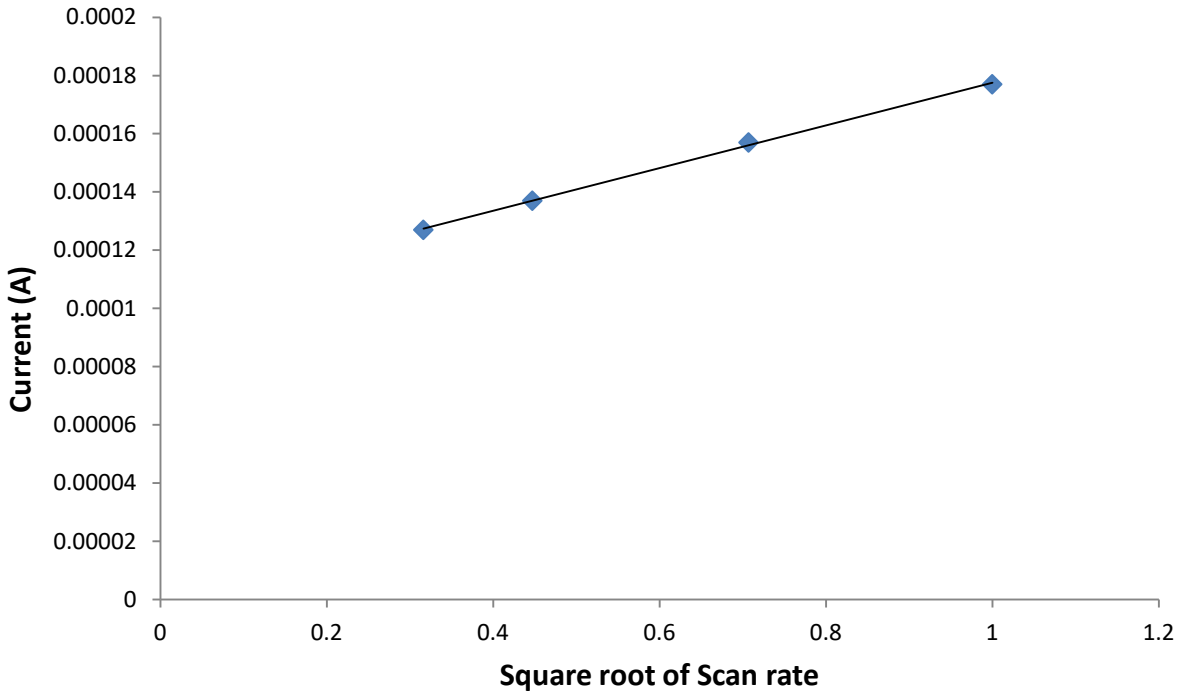


Figure 4.3: Plot of i_p vs square root of sweep rate

Calculations:

Diffusion constant obtained using slope from Cotrell equation and Randel-Sevcik equation [43]

Slope = $0.4463FA[Cat][FD_0/RT]^{1/2}$

Slope = 7.6×10^{-6}

$D_0 = 3.966 \times 10^{-6}$ m^2/s

4.4 Electrochemical studies of electrocatalyst by varying acid conc.

When performed CV of solution having TBAHFP 0.1M present as a supporting electrolyte in the presence of acetonitrile (ACN) against the solution having [NiL_1] containing TBAHFP (0.1 M) as electrolyte in ACN(Figure 4.4) the value of current gets almost double than it is in the absence of electrocatalyst indicating that the Nickel based electrocatalyst synthesized is active , appropriate and giving positive result with our proton source glacial acetic acid for HER giving us a direction direction that it can be used in HER.

The reduction potential for $Ni^{II/I}$ shifts from -0.669V to 0.76V vs Ag/AgCl in ACN solution of [NiL_1] on the expansion of conc. of acetic acid from 5 mM to 57 mM (Figure 4.5). This 1.42

move is predictable with protonation before the initial electrochemical reduction. Here 86.2 uA is the value of ip for the reduction of $Ni^{II/I}$, and 496V is the value of i_{cat} obtained from the region that is independent of the acid concent

ration at the overpotential value of 0.3V. The i_{cat}/i_p estimation comes out to be 5.74, which is providing a TOF of 6.9 s^{-1}.

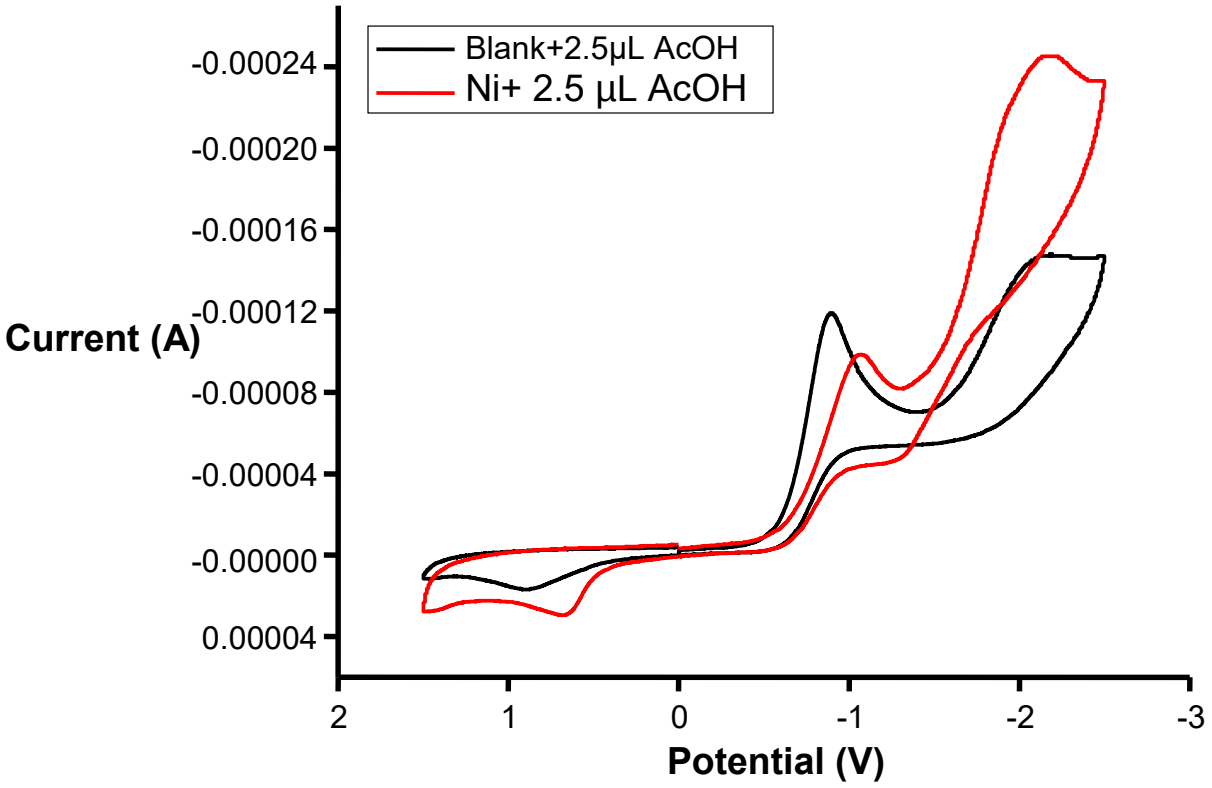


Figure 4.4: Plot representing Peak Current vs Potential for the for 2.5 µl acetic acid for Blank and nickel complex

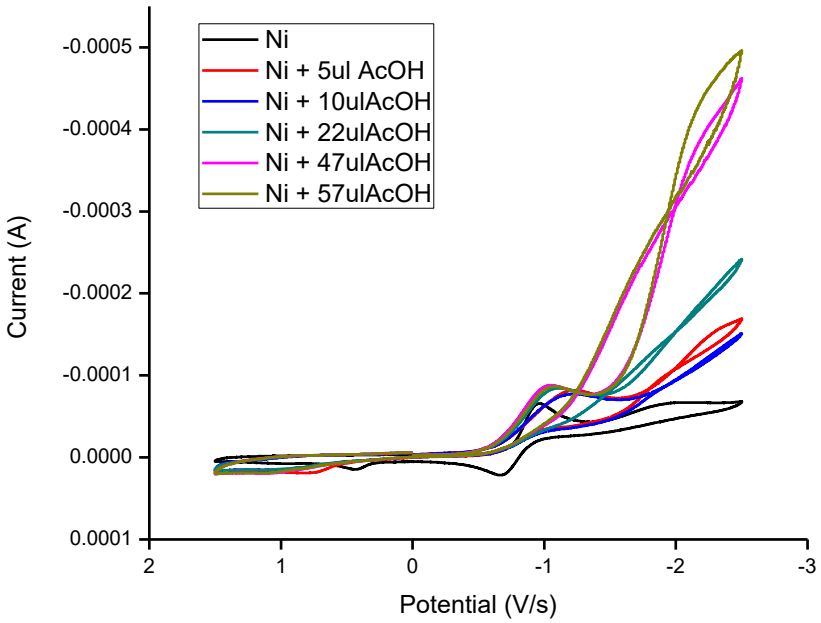


Figure 4.5: Plot of 0.1 M TBAHFP ACN solution, showing blank with different conc. of AcOH

Parameters determined

For TOF determination [43] from 1 and 2, we get

$i_{cat}/i_p = n/0.4463\ (RTk_{obs}/Fv)^{1/2}$

When n=2, we get

$(i_{cat}/i_p)^2 \times 1.94 = k_{obs} = TOF$

$i_{cat} = 4.95 \times 10^{-4}$ A

$i_p = 8.62 \times 10^{-5}$ A

TOF = 6.39 s^{-1}

Determination of overpotential having Ag/AgCl as reference on addition of 0.2 M AcOH [44]

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

E_{H^+} *vs* Fc^+/Fc = -0.028 – (0.0591 × 23.5) = -1.41 V

Here 23.51 is *pk*a of acetic acid[46]

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

Overpotential (η) = E_{H^+} - $E_{cat/2}$ = 1.41 – (1.80) = 0.39 V

CHAPTER 5

CONCLUSION AND FUTURE DIRECTIONS

5.1 Conclusion

In this report we have synthesized the Ni based homogeneous electrocatalyst from the reaction between $NiCl_2$ with the Schiff's base ligand which was developed with aniline and salicylaldehyde .The nickel complex so formed was further examined with the techniques UV – VIS spectroscopy and cyclic voltammetry. When the electrocatalyst was utilized for the proton reduction electrochemically in ACN using the proton source as glacial acetic acid and TBAHFP as supporting electrolyte a shift in reduction potential is seen towards the less positive value and also there is rise in the catalytic current. These experimental observations suggests that the hydrogen is being produced at the working electrode surface. However, gas chromatography needs to be done to confirm the product of reaction. The electrocatalyst displays TOF of $6.39s^{-1}$ with an overpotential value of 390mV.

5.2 Future Directions

The synthesized electrocatalyst has proved to be suitable for hydrogen evolution with the increase in catalytic current. The future scope to the research work is that we can do electrochemical studies by varying the metal concentration, we can confirm and get the hydrogen with the help of Gas chromatography followed by CPC (Controlled potential coulometry) .Once the hydrogen is evoloved the determination of two more factors that is faradaic efficiency and TON can be done so as to have more clear knowledge about the electrocatalyst. By using various precursors in place aniline and salicylaldehyde or by alteration of the substituents at the ligands synthesized lead to the formation of absolutely new complex with all new activity and properties. With this electrocatalyst photocatalytic hydrogen production is also possible in both homogeneous and heterogeneous way. Homogeneous hydrogen production can be done by simply using photosensitizer like $[Ru(bpy)_3]^{2+}$ and for heterogeneous we have to load it on nanorods like CdS, CdSe, and ZnS and perform the photocatalytic studies accordingly.

REFERENCES

1. Hosseini, S.; Wahid, M. Hydrogen production from renewable and sustainable energy resources: Promising green energy carrier for clean development *Renew. Sustain. Energy Rev.* **2016**, *57*, 850-866
2. Imahori, H.; Umeyama, T.; Ito, S. Large π -aromatic molecules as potential Sensitizers for Highly Efficient Dye-Sensitized *Acc. Chem. Res.* **2009**, *42*, 1809–1818
3. Dubois, M. R.; Dubois, D. L. Development of Molecular Electrocatalysts for CO_2 Reduction and H_2 Production / Oxidation *Acc. Chem. Res.* **2009**, 42, 1974-1982.
4. Kapdan, I. K.; Kargi, F. Bio-hydrogen production from waste materials *Enzyme Microbial Technol.* **2006**, *38*, 569–582
5. Yang, J.; Sudik, A.; Siegel, D. J. High capacity hydrogen storage materials : attributes for automotive applications and techniques for materials discovery *Chem. Soc. Rev.* **2010**, *39*, 656–675
6. Wang, M.; Chen, L.; Sun, L. Recent progress in electrochemical hydrogen production with earth-abundant metal complexes as catalysts *Energy Environ. Sci.* **2012**, *5*, 6763
7. Gan, L.; Groy, T.; Tarakeshwar, P.A. Nickel Phosphine Complex as a Fast and Efficient Hydrogen Production Catalyst *ACS Catal*. **2015, 137, 1109-1110**
8. Collodi, G. & Wheeler, F. Hydrogen Production via Steam Reforming with CO_2 Capture *Neueophysiology* **1987**, 19, 490-494
9. Ehsan, S.; Wahid, M. A. Hydrogen production from renewable and sustainable energy resources : Promising green energy carrier for clean development *Renew. Sustain. Energy Rev.* **2016**, 57, 850–866
10. Lei, X.; Lei, H.; Guo, X.; Zhao, X.; Ding, S.; Gao, S.; Zhang, W.; Cao, Rao. Graphene-Supported Pyrene-Modified Cobalt Corrole with Axial Triphenylphosphine for Enhanced Hydrogen Evolution in pH 0 – 14 Aqueous Solutions *ChemSusChem* **2017**, *10*, 4632–4641
11. Seyitoglu, S. S.; Dincer, I.; Kilicarslan, A. ScienceDirect Energy and exergy analyses of hydrogen production by coal gasification *Int. J. Hydrogen Energy* **2016**, *42*, 2592–2600
12. Guangul, F. M.; Sulaiman, S. A.; Ramli, A. Bioresource Technology Gasifier selection, design and gasification of oil palm fronds with preheated and unheated gasifying air *Bioresour. Technol* **2012**, 126, 224–232

13. Dincer, I.; Acar, C. ScienceDirect Review and evaluation of hydrogen production methods for better sustainability *Int. J. Hydrogen Energy* **2015**, 40, 11094–11111
14. Acar, C.; Dincer, I. ScienceDirect Comparative assessment of hydrogen production methods from renewable and non-renewable sources *Int. J. Hydrogen Energy* **2013**, 39, 1–12
15. Jugder, B.-E.; Welch, J.; Aguey-Zinsou, K.-F.; Marquis, C. P. Fundamentals and electrochemical applications of [Ni–Fe]-uptake hydrogenases *RSC Adv.* **3**, **2013**, 8142
16 Vignais, P. M.; Billoud, B.; Meyer, J. Classification and phylogeny of hydrogenases *FEMS Microbiol. Rev.* **2001**, 25, 455-501
17. Cammack, R., Frey, M. & Robson, R. *Hydrogen as a fuel : learning from nature Taylor & Francis* **2001**, 178, 188-189
18. Turker, L., Gumus, S. & Tapan, A. Biohydrogen production: molecular aspects. *Journal of Scientific & Industrial Research* **2008**, 67, 994-1016
19. Adams, M. W. W. The structure and mechanism of iron-hydrogenases *Biochem. Biophys. Acta - Bioenerg* **1990**, 1020, 115–145
20. Vignais, P. M.; Vignais, P. M.; Colbeau, A. Lipases and phospholipase A in rat lver cells View project Molecular Biology of Microbial Hydrogenases.*Mol. Biol.* **2004**, 6, 159-188
21. Fontecilla-Camps, J. C.; Volbeda, A.; Cavazza, C.; Nicolet, Y. Structure/Function Relationships of [NiFe]-and [FeFe]-Hydrogenases.*Chem. Rev.* **2007**, 107(10), 4273-4303
22. Heinekey, D. M. Hydrogenase enzymes: Recent structural studies and active site models *J. Organomet. Chem.* **2009**, 694, 2671–2680
23. Greening, C.; Berney, M.; Hards, K.; Cook, G.;Conrad, R. A soil actinobacterium scavenges atmospheric H_2 using two membrane-associated, oxygen-dependent hydrogenases *Proc. Natl. Acad. Sci. U.S.A.* **2014**,111, 4257–61
24. Ding, C.; Yang, K.-L.; He, J. Biological and fermentative production of hydrogen *Handb. Biofuels Prod* **2016**,34303–333
25. Artero, V. Bioinspired Catalytic Materials for Energy-Relevant Conversions *Nat. Energy* **2017**,2, 17131
26. Koper, M. T. M.; Bouwman, E. Electrochemical Hydrogen Production: Bridging Homogeneous and Heterogeneous Catalysis *Angew. Chem. Int. Ed.* **2010**, 49, 3723–3725
27. Haddad, A. Z. Proposed Ligand-Centered Electrocatalytic Hydrogen Evolution and

Hydrogen Oxidation at a Noninnocent Mononuclear Metal − Thiolate *J. Am. Chem.Soc.* **2015**, 137, 9238-9241

28. Lei, J. M.; Luo, S. P.; Zhan, S. Z. A water soluble cocatalyst based on a cobalt(II) complex of S,S'-bis(2-pyridylmethyl)-1,2-thioethane for photochemical driven hydrogen evolution from water under visible light *J. Photochem. Photobiol. A Chem.* **2018**, 364, 650–656
29. Luo, G. G.Recent progress in ligand-centered homogeneous electrocatalysts for hydrogen evolution reaction *Inorg. Chem. Front.* **2019**, 6, 343–354
30. Jain, R.; Mamun, A. Al; Buchanan, R. M.; Kozlowski, P. M.; Grapperhaus, C. A. Ligand-Assisted Metal-Centered Electrocatalytic Hydrogen Evolution upon Reduction of a Bis(thiosemicarbazonato)Ni(II) Complex *Inorg. Chem.* **2018**, 57, 13486–13493
31. Sattler, W.; Parkin, G. Zinc Catalysts for On-Demand Hydrogen Generation and Carbon Dioxide Functionalization *J. Am. Chem.* **2012**, 134, 17462–17465
32. Haddad, A. Z.; Cronin, S. P.; Mashuta, M. S.; Buchanan, R. M.; Grapperhaus, C. A. Metal-Assisted Ligand-Centered Electrocatalytic Hydrogen Evolution upon Reduction of a Bis(thiosemicarbazonato)Cu(II) Complex *Inorg. Chem.* **2017**, 56, 11254–11265
33. Dirisio, R. J.; Armstrong, J. E.; Frank, M. A.; Lake, W. R.; Mcnamara, W. R. Cobalt Schiff Base Complexes for hydrogen generation *Dalton Trans.* **2017**, 46, 10418–10425
34. Khandelwal, S.; Zamader A.; Nagayach, V.; Dependu, D.; Mir, A.; Dutta, A. Inclusion of Peripheral Basic Groups Activates Dormant Cobalt-Based Molecular Complexes for Catalytic H_2 Evolution in Water *ACS Catal.* **2019**, 9, 2334–2344
35. Ahmad, E.; Rai, S.; Padhi, S. K. Proton reduction by a Ni (II) catalyst and foot-of-the wave analysis for H_2 evolution *Int. J. Hydrogen Energy* **2019**, 44, 16467–16477
36. Meng, Y.-S.; Rao, Y.; Wang, B.-W.; Zheng, J.; Gao, S.; Zhang, J.-L. Enhancing the reactivity of nickel(II) in hydrogen evolution reaction (HERs) by β-hydrogenation of porphyrinoid ligands *Chem. Sci.* **2017**, 8, 5953
37. Hong, D.; Tsukakoshi, Y.; Kotani, H.; Ishizuka, T.; Ohkubo, K.; Yoshihito, S.; Yoshizawa, K.; Fukuzumi S.; Kojima T. Mechanistic Insights into Homogeneous Electrocatalytic and Photocatalytic Hydrogen Evolution Catalyzed by High-Spin Ni(II) Complexes with S_2N_2-Type Tetradentate Ligands *Inorg. Chem.* **2018**, 57, 7180–7190
38. Straistari, T.; Hardre, R.; Fize, J.; Shova, S.; Giorgi, M.; Reglier, M.; Artero, V.; Orio, M.

Hydrogen Evolution Reactions Catalyzed by a Bis (thiosemicarbazone) Cobalt Complex : An Experimental and Theoretical Study *Eur. J.* **2018**, 24(35), 8779–8786

39. Bernhardt, P. V; Jones, L. A. Electrochemistry of Macrocyclic Cobalt (III/II) Hexaamines : Electrocatalytic Hydrogen Evolution in Aqueous Solution *Inorg. Chem* **1999**, 38, 5086–5090
40. Das, A.; Han, Z.; Brennessel, W. W.; Holland, P. L.; Eisenberg, R. Nickel Complexes for Robust Light-Driven and Electrocatalytic Hydrogen Production from Water *ACS Catal.* **2015**, 5, 1397-1406
41. 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 *J. Am. Chm.* **2016**, 138(25), 7844-7847
42. Skoog, D.A.; Holler F.J.; Nieman, T.A, Principles of Instrumental analysis **2007**, Philadelphia:Saunders College Pub.
43. Appel, A. M. & Helm, M. L. Determining the Overpotential for a Molecular Electrocatalyst *ACS Catal.* **2014**, 4, 630–633
44. Kutt, A.; Leito, I.; Kaljurand, I.; Soovali, L.; Vlasov, V.; Yagupolskii, L.; Koppel I. A comprehensive self-consistent spectrophotometric acidity scale of neutral Bronsted acids in acetonitrile *J. Org. Chem.* **2006**, **71**, 2829–2838

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