Third Row Transition Metal Compounds as Electrocatalysts for Water Oxidation in Basic Buffers

Dissertation

Submitted in partial fulfilment of

The degree of M.Sc. (Physical Chemistry)

By

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To

School of Chemical Sciences

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Goa 403206

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STATEMENT

I hearby declare that the matter presented in this dissertation entitled, **“Third Row Transition Metal Compounds as Electrocatalysts for Water Oxidation in Basic Buffers ”** is based on the result of investigations carried out by me at the School of Chemical Science, Goa University under the supervision of **Dr.S.N.Dhuri** and the same has not been submitted elsewhere for the award of a degree or diploma.

Ms. Asmita Dileep Gaonkar
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CERTIFICATE

This is to certify that the dissertation entitled **“Third Row Transition Metal Compounds as Electrocatalysts for Water Oxidation in Basic Buffers”** is bonafide work carried out by **Ms. Asmita Dileep Gaonkar** under my supervision in partial fulfilment of the requirements for the award of the degree of Master of Science in Physical Chemistry at the school of Chemical Science, Goa University.

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CERTIFICATE

This is to certify that the dissertation entitled **“Third Row Transition Metal Compounds as Electrocatalysts for Water Oxidation in Basic Buffers”** is bonafide work by Ms. Asmita Dileep Gaonkar under the supervision of Dr. S. N. Dhuri for the award of the degree of Master of Science in Physical Chemistry at the school of Chemical Science, Goa University.

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It gives me a great pleasure to place this dissertation entitled "Electrocatalytic water oxidation of coordination complexes by using different voltammetry techinques: of first transition metal series" to Goa university as a part of second year Master of Science curriculum.

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INDEX

ABBREVATIONS

CV: Cyclic voltammetry

OER: oxygen evolution reaction

PS: Photosystem

Ep: Peak potential

SPE: Solid polymer electrolyte

SHE:Standard hydrogen electrode

RHE: Reversible hydrogen electrode

LSV: Linear sweep voltammetry

Compound 1: $[Co(NH_3)_6]Cl_3$

Compound 2: $[CoBQCN(H_2O)_2](ClO_4)_2$

Compound 3: $[CoBQEN(H_2O)_2](ClO_4)_2$

CHAPTER 1

1.1 INTRODUCTION

With the uncontrolled use of non-renewable energy sources, it is more important to utilize renewable energy more efficiently in the near future. Climatic changes and the scarcity of fossils fuels require our society to pursue clean and renewable energy sources. As the water is the most common substance on the earth hydrogen production by water oxidation and hydrogen evolution has become the focus area of renewable clean energy research which is related to environment protection and energy development.

The first recorded experiment on water electrolysis was carried out by Adriaan Paets van Troostwijk and Jan Rudolph Deiman in Haarlem, The Netherlands, in 1789 Paets van Troostwijk and Deiman used an electrostatic machine invented by Martinus van Marum to discharge an electric potential difference between two gold electrode, and oxygen evolved on the other gold electrode.The best and most stable inorganic catalysts for water splitting are oxides. The most common oxides which are used as electrocatalyst are IrO_2 and RuO_2.[1]

The generation of oxygen through the water oxidation reaction is an energetic reaction; E_o is 1.23V. In natural photosystem –II(PS-II),manganese (Mn) based metalloenzymes are consider to be as a good catalyst for oxygen evolution reactions, where Mn_4CaO_5 cluster is an active centre for OER and is more efficient in terms of physiological conditions.OER in PS-II is an attracting area of research from last few decades and also their implementation in electrochemical power sources.Despite of many heterogeneous and homogenous catalyst for electrochemical OER the major focus is on the homogenous catalyst system due to their easily synthesis with better reproductivity and predictable mechanistic probes. In addition under potential operating condition the homogenous catalyst precipitates and forms the metaoxides which further leads to confusion of active reaction.[2] The development of electrocatalysts such as metal oxides and non-metal oxide materials has been reviewed by several groups.On the basis of their abundance and cheapness, first-row transition metals, such as Cu, Fe, Co, and Ni, have been emerged as water oxidation catalysts for practical applications.[3] Co-based oxygen evolution reaction catalysts Metallic Co is a promising catalyst selection for Oxygen evolution reaction. In order to exploit high efficient alternative oxygen evolution reaction electrocatalysts, numerous Co based catalysts such as metal oxides, hydro(oxy)oxides, perovskites, sulfides, nitride and phosphates have been studied.[4]

A mononuclear cobalt (II) complex as homogenous molecular catalyst for electrochemically induced oxygen evolution is presented.

1.1.1 Water oxidation reaction

Decomposition of pure water into hydrogen and oxygen at standard temperature and pressure (25^0C 1 atm) is not favourable in thermodynamic terms, as described by the following equations:

Anode: $2H_2O\ (l) \rightarrow O_2\ (g) + 4H^+\ (aq) + 4e^-$ $E_o ox = -1.23$ V

Cathode: $2H^+\ (aq) + 2e^- \rightarrow H_2\ (g)$ $E_o red = 0.00$ V

The standard oxidization potential of the oxygen evolution reaction is defined as 1.23 V related to relative hydrogen electrode (RHE) and the standard reduction potential of hydrogen evolution reaction is 0V (vs RHE) at 25°C, 1 atm. However, in a practical water electrolysis process, larger applied potential is always required because it involves complex electron and ions transfer processes, which leads to sluggish kinetics and poor energy efficiency. Specifically, during the water electrolysis, some disadvantageous factors of electrode materials, such as activation energy, ion and gas diffusion, and some factors related to device such as solution concentration, wire and electrodes resistances, electrolyte diffusion blockage, bubble formation, and heat release should be considered. These factors result in additional potential over the standard one, which is called overpotential (η).[4]

1.1.2 Structures of Cobalt(II) compounds

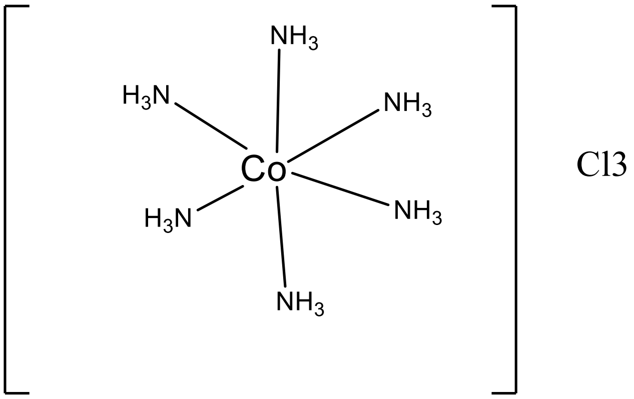

Figure 1. The structure of $[Co(NH_3)_6]Cl_3$ **1**

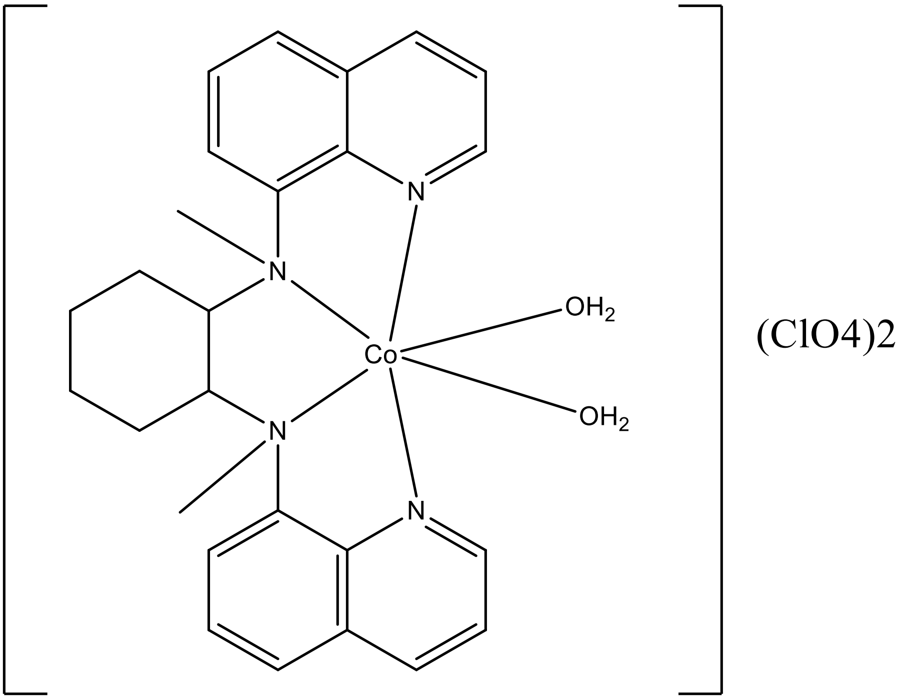

Figure 2. The structure of $[CoBQCN(H_2O)_2](ClO_4)_2$

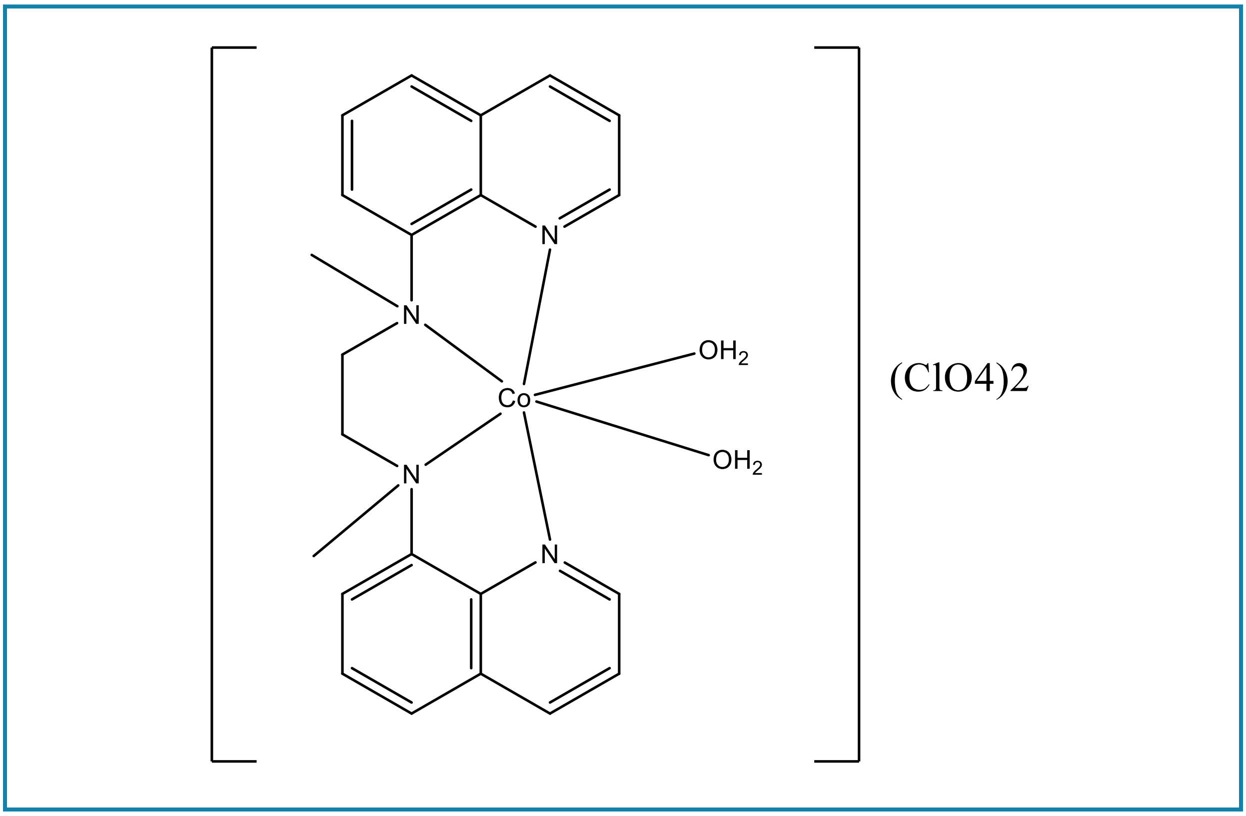

Figure 3. The structure of $[CoBQEN(H_2O)_2](ClO_4)_2$ **3**

1.2.1 Instrumentation

A system consists of an electrolysis cell, a potentiostat, a current to-voltage converter, and a data acquisition system. The electrolysis cell consists of a working electrode, counter electrode, reference electrode, and electrolytic solution. The working electrode’s potential is varied linearly with time, while the reference electrode maintains a constant potential. The counter electrode conducts electricity from the signal source to the working electrode. The purpose of the electrolytic solution is to provide ions to the electrodes during oxidation and reduction. A potentiostat is an electronic device which uses a dc power source to produce a potential which can be maintained and accurately determined, while allowing small currents to be drawn into the system without changing the voltage. The current-to-voltage converter measures the resulting current, and the data acquisition system produces the resulting voltammogram.

Three electrode used are

i) Reference Electrode

A reference electrode has a well-defined and stable equilibrium potential. It is used as a reference point against which the potential of other electrodes can be measured in an electrochemical cell. The applied potential is thus typically reported as a specific reference. Some common reference electrodes used are saturated calomel electrode (SCE), standard hydrogen electrode (SHE) and the AgCl/Ag electrode.These reference electrodes are generally separated from the solution by a porous frit. It is best to minimize junction potential by matching the solvent and electrolyte in the reference compartment to the one used in the experiment.Most commonly employed reference electrode is Ag^+/Ag which consist of silver wire in a small tube fitted with frit and fill the tube with electrolytic solution.

ii) Working Electrode

The working electrolyte carries out the electrochemical event of interest. A potentiostat is used to control the applied potential of the working electrode as a function of the reference electrode potential. It is composed of the redox inert material in the potential range of interest. The type of working electrode can be varied from experiment to experiment. As the electrochemical event of interest occurs at working electrode, the surface should be extremely clean. Sometimes pretreating procedure is referred. The most common working electrode used are platinum and glassy carbon.

iii) Counter Elcetrode

When a potential is applied to the working electrode such that reduction (or oxidation) of the analyte can occur, current begins to flow. The purpose of the counter electrode is to complete the electrical circuit .Current is recorded as electrons flow between the working electrode and counter electrode. To ensure that the kinetics counter electrodes of the reaction occurring at the counter electrode do not inhibit those occurring at the working electrode, the surface area of the counter electrode is greater than the surface area of the working electrode. A platinum electrode or disk is commonly used as counter electrode. When studying a reduction at the working electrode, an oxidation occurs at the counter electrode. As such, the counter electrode should be chosen to be as inert as possible. Counter electrodes can generate by products depending on the experiment therefore these electrodes may sometimes be isolated from the rest of the system by a fritted compartment.

1.2.2. INSTRUMENTATIONAL VIEW

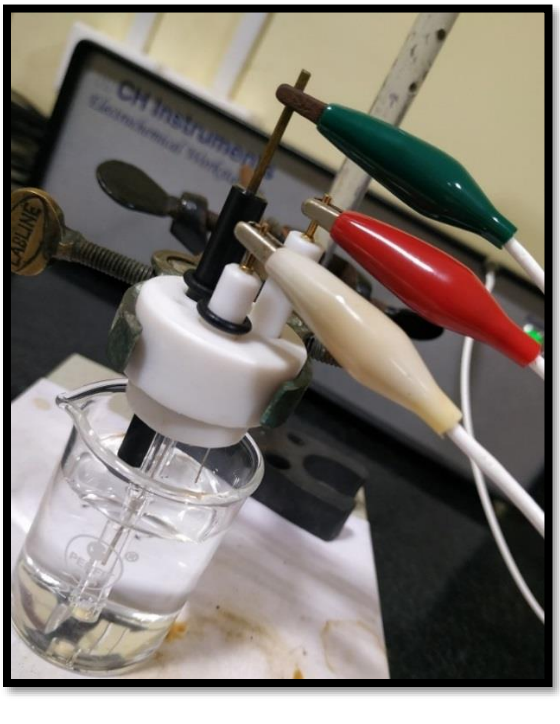

Figure 4: A Three electrode electrochemical cell used in electrocatalytic water oxidation

1.2.3. Preparation of Electrolyte

As the transfer occurs during a cyclic experiment, electrical neutrality is maintained via migration of ions in solution. As electron transfer from the electrode to the analyte,ions move in solution to compensate the charge and close the electrical circuit. A salt called a supporting electrolyte is dissolved in the solvent to help to decrease the solution resistance. The mixture of the solvent and supporting electrolyte is commonly termed as “electrolyte solution’’. The electrolyte, solvent and nature of the working electrode all influence the potential for the experiment.

A good solvent has these characteristics:

- It is liquid at experiment temperatures.
- It dissolves the analyte and high concentration of the supporting electrolyte completely.
- It is stable toward oxidation and reduction in the potential range of the experiment.
- It does not lead to deleterious reactions with the analyte or supporting electrolyte.
- It can be purified.[5]

a) Supporting electrolyte

A good supporting electrolyte has these characteristics:

- It is highly soluble in the solvent chosen.
- It is chemically and electrochemically inert in the condition of the experiment.
- It can be purified.

Large supporting electrolyte concentrations are necessary to increase solution conductivity. As electron transfers occur at the electrodes, the supporting electrolyte will migrate to balance the charge and complete the electrical circuit. Ammonium salts have become the electrolyte of choice for inorganic experiments performed in organic solvents as they fulfil the three condition of electrolyte choice. For dichloromethane or acetonitrile, tetrabutylammoium salts are most commonly used. The conductivity of the solution is dependent on the concentrations of the dissolved salt. Without the electrolyte available to achieve charge balance, the solution will be resistive to charge transfer. To avoid interference from dissolved O_2, all electrolyte solutions should be sparged with an inert gas before measurements are taken.

1.2.4 Importance of Scan rate

The scan rate of the experiment controls how fast the applied potential is scanned. Faster scan rates lead to a decrease in the size of the diffusion layer; as a consequence, higher currents are observed. For electrochemically reversible electron transfer processes involving freely diffusing redox species, the Randles−Sevcik equation describes how the peak current ip (A) increases linearly with the square root of the scan rate υ (V s^{-1}) where n is the number of electrons transferred in the redox event, $A(cm^2)$ is the electrode surface area (usually treated as the geometric surface area), Do (cm^2 s^{-1}) is the diffusion coefficient of the oxidized analyte, and C^0 (molcm−3)is the bulk concentration of the analyte.

$$\boxed{Ip= 0.446nFAC^0 (nf_v D_O/RT)^{1/2}}$$

The Randles−Sevcik equation can give indications as to whether an analyte is freely diffusing in solution. As analyte scan sometimes adsorb to the electrode surface, it is essential to assess whether an analyte are mains homogeneous in solution prior to analysing its reactivity.[5]

1.3 Characterization Techniques

1.3.1 Cyclic Voltammetry

It is a specific type of voltammetry, that is an electrochemical potentiodynamic measurement that allows study of redox properties of compounds and interfacial structures. It is a powerful and popular electrochemical technique commonly employed to investigate the reduction and oxidation process of molecular species. In cyclic voltammetry, the electrode potential ramps linearly versus time in cyclic phases. The potential is measured between the working electrode and the reference electrode, while the current is measured between working electrode and the counter electrode.The utility of cyclic voltammetry is highly dependent on the analyte being studied. Often the analyte displays a reversible cyclic voltammogram wave which is observed when all of the initial analyte can be recovered after a forward and reverse scan cycle.Although such reversible couples are simpler to analyse they contain less information than more complex waveforms. The waveform of even reversible couples is complex owing to the combined effects of polarization and diffusion.The difference between the two peak potential(Ep), Ep, is of particular interest

$$Ep = Epa - Epc > 0$$

This difference mainly results from the effects of analyte diffusion rates. In the ideal case of a reversible $1e^-$ couple, Ep is 57mV and the full-width half–max of the forward scan peak is 59mV.Focusing on current reversible couples are characterized by $i_{pa}/i_{pc} = 1$.When a reversible peak is observed thermodynamic information in the form of a half cell potential $E^0_{1/2}$ can be determined. When waves are semi-reversible it may be possible to determine even more specific information. Many redox process observed by cyclic voltammetry are non-reversible. In such cases the thermodynamic potential $E^o_{1/2}$ is often deduced by stimulation .The reversibility is indicated by i_{pa}/i_{pc} is not equal to 1. Deviation from unity are attributed to a subsequent chemical reaction that is triggered by electron transfer. Such electrochemical process can be complex, involving isomerization,dissociation,association.[6]

1.3.2. LINEAR SWEEP VOLTAMMETRY

Linear sweep voltammetry is a voltametric method where the current at a working electrode is measured while the potential between the working electrode and a reference electrode is swept linearly in tie. The oxidation or reduction is a peak in the current signal at which the species begins to be oxidized or reduced. The experiment set up for the linear sweep voltammetry is the same as the cyclic voltammetry. The slope of the potential v/s time graph is called the scan rate and can range vary from mV/s to 1,000,000 v/s. The working electrode is one of the electrode at which the oxidation/reduction reactions occurs–the process that occur at this electrode are the ones being monitored.

Es is the reduction potential of **A** (if the electrolyte and the electrode are in their standard conditions, then this potential is a standard and reduction potential). As E approaches Es is the current on the surface increases and when E=Es then the concentration of $[A]=[A^-]$ at the surface. As the molecules on the surface of the working electrode are oxidized/ reduced they move away from the surface and new molecules come into contact with the surface of the working electrode. The flow of electron causes the current. The current is a direct measure of the rate at which electrons are being exchanged through the electrode-electroyte interface. When this rate becomes higher than the rate at which the oxidizing or reducing species can diffuse from the bulk of the electrolyte to the surface of the electrode, the current exhibits a peak. Linear sweep voltammetry can identify unknown species and determine the concentration of solution.$E_{1/2}$ can be used to identify the unknown species while the height of the limiting current can determine the concentration. The sensitivity of current changes v/s voltage can be increased by increasing the scan rate. Higher potential per second result in more oxidation/reduction of a species at the surface of the working electrode.[14]

1.3.3. Tafel Plot

A Tafel equation is an equation in electrochemical kinetics relating the rate of an electrochemical reaction to over potential. A Tafel plot can be drawn representing the relationship between over potential and logarithmic current density. It can be utilize to find the values of the Tafel slope, the slope depend on alpha which is the transfer coefficient. This is a measure of the symmetry of the energy barrier in a standard free energy and reaction coordinate diagram indicating the reaction mechanism. Hence the change in slope basically indicates a change in reaction mechanism.

The Tafel slope shows how efficiently an electrode can produce current in response to change in applied potential. So if the slope (mV/decade) is lower means less over potential is required to get high current. So for oxygen evolution reaction a catalyst that gives higher current densities for these reactions a low over potential that is lower Tafel slope. It also tells how much you have to increase the over potential to increase the reaction rate by factor ten.This will be determined by the magnitude of the change in the activation energy for a given increase in potential. In a reaction involving only one step with one electron transfer, Tafel slope will be determined by symmetry factor, which is usually 0.5 (corresponding to a Tafel slope of 120 mV). In more complex reaction involving several steps and several electron transfer the Tafel slope will be determined by the rate determining step and by the number and of the preceding steps.On single electrode the Tafel equation can be stated as

$$\text{Overpotential} = A \times \log_{10} (i/i_o)$$

Where, A: Tafel slope "V" i: current density, A/m^2;

i_o: " exchange current density" , A/m^2

The exchange current is the current at equilibrium, i.e. the rate at which oxidized and reduced species transfer electron with the electrode. In other words the exchange current density is the rate of reaction at the reversible potential. At the reversible potential the reaction is in equilibrium meaning that the forward and reverse reactions progress at the same rates. This rate is the exchange current density. When electrochemical reaction occurs in two half reactions on separate electrodes, the Tafel equation is applied to each electrodes separately. The Tafel equation assumes that the reverse reaction rate is negligible compared to the forward reaction rate.[7]

1.3.4. pH meter

A pH meter is an instrument used to measure acidity or alkalinity of a solution. pH is the unit of measure that describes the degree of acidity or alkalinity. It is measured on a scale of 0 to 14. The quantitative information provided by the pH measurement expresses the degree of the activity of an acid or base in terms of hydrogen ion activity. The pH value of a substance is directly related to the ratio of hydrogen ion $[H^+]$ and the hydroxyl ion $[OH^-]$ concentration.

The most often used pH electrodes are glass electrodes. Typical model is made of glass tube ended with small glass bubble. Inside of the electrode is usually filled with buffered solution of chlorides in which silver chloride is immersed. The pH of internal solution varies. Active part of the electrode is the glass bubble. While tube has strong and thick walls, bubble is made to be as thin as possible. Surface of the glass is protonated by both internal and external solution till equilibrium is achieved. Both sides of the glass are charged by the adsorbed protons, this charge is responsible for potential difference. This potential in turn is described by the Nernst equation and is directly proportional to the pH difference between solutions on both sides of the glass. The majority of pH electrodes available commercially are combination electrodes that have both glass H^+ ion sensitive electrode and additional reference electrode.

1.4. Literature Survey

1. To mimic the strategy used by natural photosynthesis photosystem(II), a biological cubane-like tetranuclear cluster $[Cu_4(pdmH)_4(OAc)_2](NO_3)_2.3H_2O$ is synthesised. The heart of the

oxygen-evolving complex (OEC) is a tetranuclear manganese cluster (Mn_4CaO_5-cluster) with cubane-like structure connected by mono-u-oxo, di-u-oxo and hydrogen bridges acting as an electrical accumulator. A Cyclic voltammograms of 0.5mM complex in 0.1M sodium acetate buffer with a glassy carbon electrode and a scan rate of $100mVs^{-1}$ at different pH values is studied.[8]

2. Phosphate buffer solutions at various pH values are obtained by adjusting the pH of 0.2M Na_2HPO_4 aqueous solution with solid NaOH.Cyclic voltammetry was recorded with a glassy carbon,Ag/AgCl and Pt wire electode as the working,reference and auxillary electrodes respectively in 0.2M phosphate buffer solution at various pH values. Electrochemical measurements were further carried in phosphate buffer at various basic pH values (from pH 10-12)[12]

3. Another way of performing electrolysis is by using solid polymer electrolyte (SPE). The main feature of SPE water electrolysis technology lies in replacing the traditional caustic solution electrolytes with SPE. Solid polymer is perfluorosulfonic acid proton exchange membrane (Nafion). Sulfonic acid groups can deliver hydronium ions and become a good conductor. The standard electrode potential for OER is 1.23V v/s RHE but most of the metal electrodes dissolve before reaching this potential only few metals and their oxides present adequate stability. It can be seen that the oxygen evolution current values of different material surfaces can differ by several orders of magnitude at a certain over potential. Ru and RuO_2 electrodes are the best electro-catalyst for oxygen generation in acidic solution. It shows the relationship between the metal oxide over potential and the enthalpy of oxidation of different valence oxides at a current density of 1 mA cm^{-2}. RuO_2 and IrO_2 are promising oxygen anode

catalysts which are at the top of the curve. Both have the most suitable metal-oxygen bond strength and are the most conductive to the oxidation reaction with smallest overpotential.[11]

4. The electrochemical cell with one compartment and three electrodes, a gold wire as counter electrode, reversible hydrogen electrode as reference electrode and roughened gold surface as working electrode are used. The working electrode was mechanically polished to mirror finish using alumina. Next the gold electrode was electrochemically roughened by 25 oxidation–reduction cycles in a 0.1M solution of KCl. The ORC were performed between -0.30 and 1.20V v/s SCE, during which the potential was held for 30 seconds the negative limit and for 1.3 seconds at the positive limit. Online electrochemical mass spectrometry experiments were performed using an Evolution Mass spectrometer system result from the cyclic voltammogram of the gold electrode recorded between 0 and 1.8V v/s RHE. These results show that the formation of gold surface oxides starts at 1.3V and that the onset of continuous anodic current is at 1.9V v/s RHE.[13]

5. A) By using catalyst as a working electrode, an indium tin oxide were used as both the working and counter electrode, with Ag/AgCl as the reference electrode. Dissolved 0.02g of dry cobalt complex in (NaH_2PO_4/$NaHPO_4$ buffer solution at pH 7.0).A potential of 1.2V was applied to the system for seven hours.

B) The catalytic film used as a working electrode a platinium mesh as counter electrode and Ag/AgCl electrode as reference. The electrolyte used for all the tests was 25mL of a 0.1M neutral phosphate buffer solution (pH 7) to stimulate natural water. Potential ranges for all the CV tests were between -0.2V to1.4V at a scan rate of 10mV/s.[15]

6. Biuret–modified teraamidomacrocyclic cobalt complex is shown to catalyse electrochemical water oxidation at basic pH leading to formation of O_2. Cyclic voltammetry in phosphate buffer is represented and and in duetarated phosphate buffer. CVs of different catalyst concentration is studied at pH 9. Inset shows that variation of catalytic current with catalytic concentration.[9]

Some reported complexes which can be used as water oxidation active catalyst are

a) Iron complexes

For iron based water oxidation electrocatalyst, Collins and Bernhard first reported their precedent in which iron (III) was coordinated with a teraamido macrocyclic ligand (TAMLs). However the catalytic activity of Fe-TAML vanishes after a few seconds. The Meyer's group is the first to report single-site Fe complexes $[Fe^{III}(dpag)(H_2O)](ClO_4)_{2,}$ (dpag=2[bis(pyridine-2-ylmethyl)]amino-N-quinolin-8-yl-acetamido).[8]

b) **Copper complexes**

The copper based electrocatalyst named Copper-bipyridinehydroxo complex.The electrocatalyst generated by simply mixing a copper salt and bipyridine shows overpotential of 0.75V with a turnover frequency of $100s^{-1}$ for water oxidation .Another copper-based electrocatalyst with 6,6'-dihydroxy-2,2'-bipyridine as the ligand.Because of the hydrogen bonding interaction between the hydroxyl substituent and the bound hydroxo/aquo ligands this complex exhibits a lower overpotential for water oxidation than that of Copper-bipyridinehydroxo complex.A single site copper complex with N,N-bis(2-(2-pyridyl)ethyl)pyridine-2,6-dicarboxamidate, denoted as Py_3P).In contrast to other two copper complexes this electrocatalyst can work at low pH (8.0) with $HPO4^{-2}$ as a proton acceptor.Liao and Zhang reported a 1,8-naphthyridine based dinuclear copper complex with 2,7[bis(2-pyridylmethyl)aminomethyl]-1,8-naphthyridine.Beside binding to pyridine derivatives copper can be coordinated with other nitrogen ligands such as peptide and imidazole derivatives.Also copper complexes formed with triglycylglycine shows good electrocatalytic ability towards water oxidation at 1.23 V (v/s.SHE) with a turnover frequency of $33s^{-1}$.[8]

c) **Cobalt complexes**

From the standard potential of the $M3^+/M2^+$ redox couple in the first –row transition metal system cobalt provides the most oxidization system(E0=1.84V vs NHE) which is higher than that of manganese and iron. Verpoort and co-workers reported a photo and electrochemical cobalt water oxidation catalyst,$[Co^{II}(TCA)_2(H_2O)]$(TCA=1-mesityl-1,2,3-1H-trizole-4-carboxylate).[8]

d) Nickel complexes

Ke and Lu found that the nickel complex, $[Ni(meso\text{-}L)](ClO_4)_2$,(L=5,5,7,12,12,14 hexamethyl-1,4,8,11-tetrazacylotetradecane) that can electro-catalyse H_2 production from water can also catalyse water oxidation at neutral pH 7. The other water–soluble cationic nickel complex with meso-tetrakis(4-N-methylpyridyl)porphyrin can electro-catalyse water oxidation for oxygen evolution at neutral pH.9 Ni-Fe-CNTs and $Co_xNi_yS_Z$ octahedral nanocage showed the over potential of 247Mv and 362Mv at 10mA cm^{-2}.Among them NiO is easily available and possesses a high specific capacitance that is suitable in electrochemical reaction. It was reported that a NiO/Ni heterojunction showed highlighted performance, with the over potential reaching 1.5V (RHE) at 20 mA cm^{-2}.[10]

CHAPTER 2

2.1 Experimental Details

The water oxidation evolution reaction is studied by using instrument, C-H electrochemical workstation. Here using three electrode cell the oxygen evolution peak was investigated at different pH. The three electrochemical analysis which were used are cyclic voltammetry, linear sweep voltammetry and Tafel plot. Cyclic voltammetry gives information about whether given metal is undergoing any oxidise or reduces process or not. From linear sweep voltammetry over potential is calculated. And from Tafel plot slope is being calculated, which states that lower the slope, better is the OER activity.

The three electrodes were selected on the basic of availability of them in laboratory are:

i) Working electrode: Platinum

ii) Counter electrode: Platinum

iii) Reference electrode: AgCl/Ag

Electrolyte solution: KCl

Solvent: 0.1M sodium acetate buffer

Taken 0.5mM complex and dissolved in 0.1M sodium acetate. Before starting with the electrochemical analyses the reference electrode should be prepared. The reference electrode which is used (silver-silver chloride) is stored in saturated KCL, as the electrolytic solution used as KCl. The mobility difference of K^+ and Cl^- is the least among which creates smaller liquid junction potential. The surface of working electrode should be clean properly as the reaction of interest occurring there. The pH of the solvent is maintained by further addition of 2-3 drops of NaOH for basis medium and acetic acid for acidic medium.

The reaction occurring in the experiment are:

Cathode: $Ag + Cl \rightarrow AgCl$ $E^o = 0.222\ V$

Anode: $2H_2O \rightarrow O_2 + 4H + 4e^-$ $E^o = -1.23\ V$

From electrode potential it is calculated that:

$$E_0 = E_{0\ \text{Cathode}} - E_{0\ \text{anode}}$$

$$= 0.222 - (-1.23)$$

$$= 1.452\ \text{V}$$

Therefore oxygen evolution reaction should found at the potential of approximately at 1.452 V. The experiment was performed under inert condition that is passing of nitrogen for few minutes through the solution which was prepared for the analysis. The connection is made in such a way that all three electrodes should not touch each other and among four wires, one wire is attached to instrument. Then initializing of instrument had done and experiment was performed. The first coordination Compound **1** which was tried is $[Co(NH_3)_6]Cl_3$ and it showed good solubility in the solvent.

Compounds **2** $[CoBQCN(H_2O)_2](ClO_4)_2$ and **3** $[CoBQEN(H_2O)_2](ClO_4)_2$ also showed good solubility.

The same procedure was applied to this complexes;

1) $[MnBQEN(H_2O)_2](ClO_4)_2$
2) $[Ni(BQCN)]H_2$
3) $[Cu(BQCN)]H_2$

But the problem here was solubility; all of them were partially soluble in the sodium acetate buffer as well as in phosphate buffer. Therefore another solvent had been prepared. Another solvent prepared is tetrabutylammonium(NBu_4) salts in acetonitrile solutions. In this solvent among three complexes only $[MnBQEN(H_2O)_2](ClO_4)_2$ dissolved and further experiment was performed in inert condition.

The pH of the solution is measured using pH meter. Firstly, calibration of the pH meter is done by using pH tablet.

2.2 Preparation of solution for calibration of pH meter

The one tablet of pH 4 has been taken and dissolved in minimum quantity of distilled water and then made it into 100ml standard measuring flask. Same procedure is applied for the preparation of pH 7 tablet. Both the solutions are used to calibrate the pH meter.

2.3. The Proposed Mechanism for water oxidation reaction

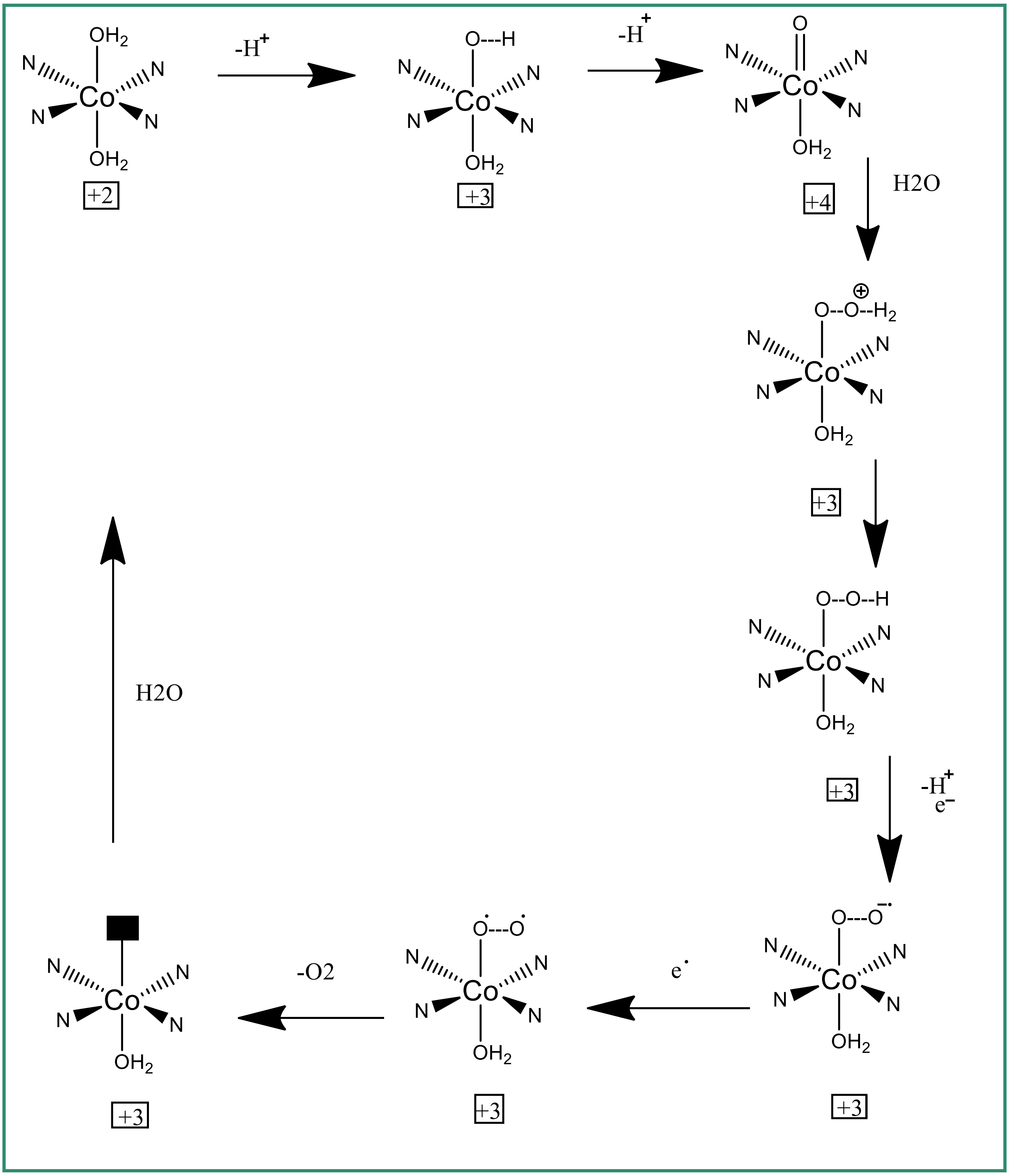

Figure 5: Proposed water oxidation mechanism for Co(III) compound

CHAPTER 3

3.3 Electrochemical Analysis

3.3.1. Cyclic Voltammetry

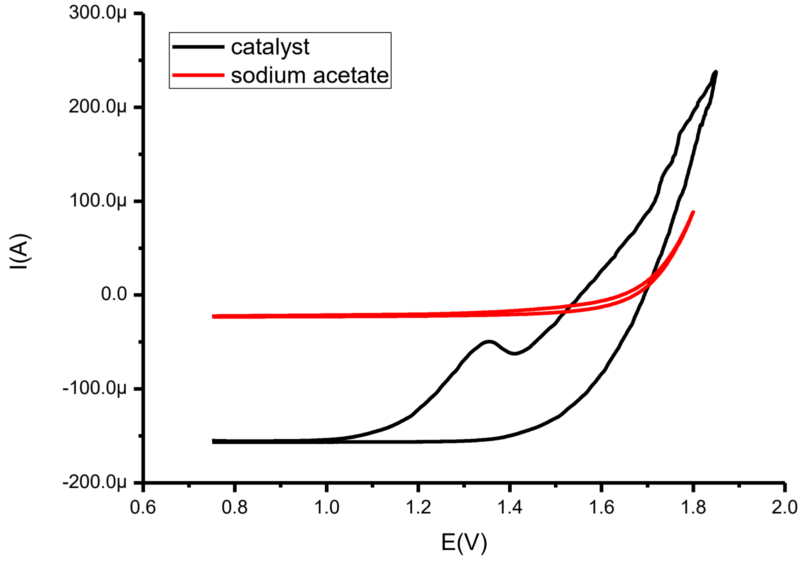

Figure 6a: Comparison of Catalyst (black) with sodium acetate (red) CV plots

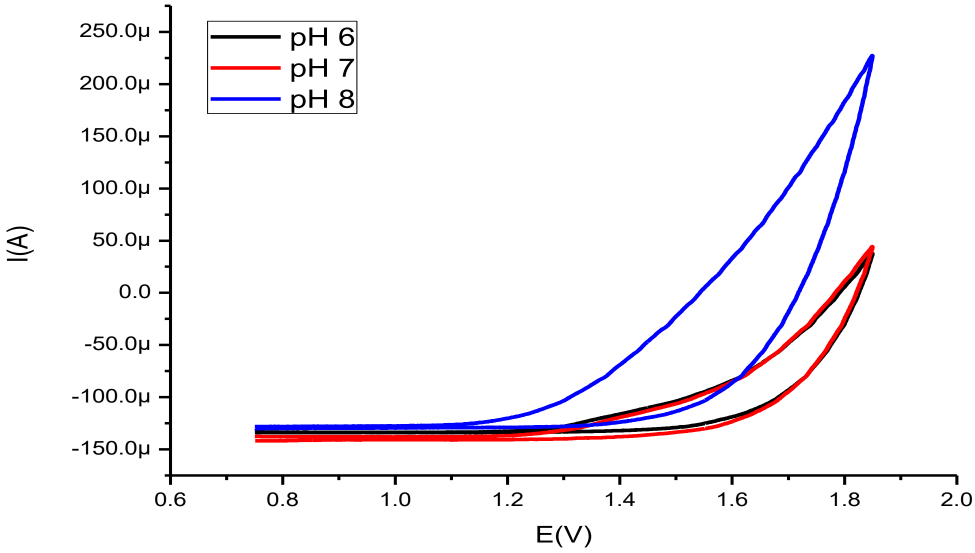

Figure 6b. The CV plots of $[Co(NH_3)_6]Cl_3$ in N_2 inert atmosphere : No peak

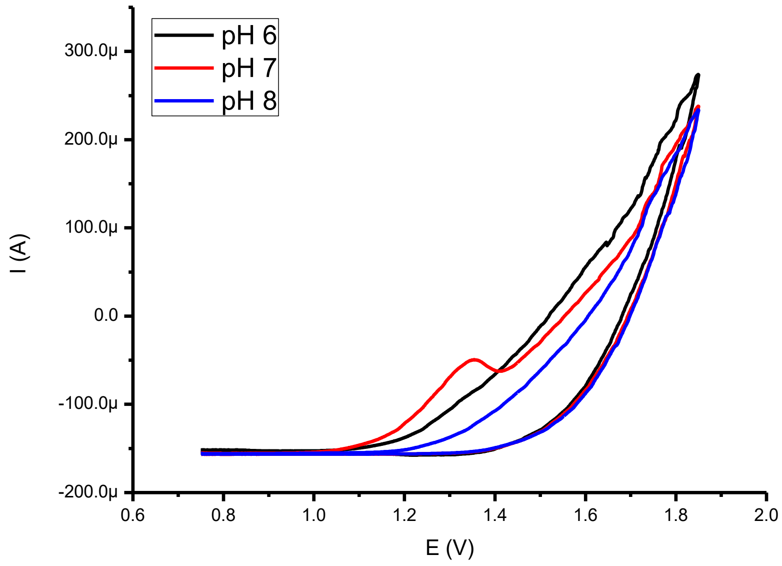

Figure 6c: The CV plots of [CoBQCN(H_2O)$_2$](ClO_4)$_2$ in N_2 atmosphere at pH = 7

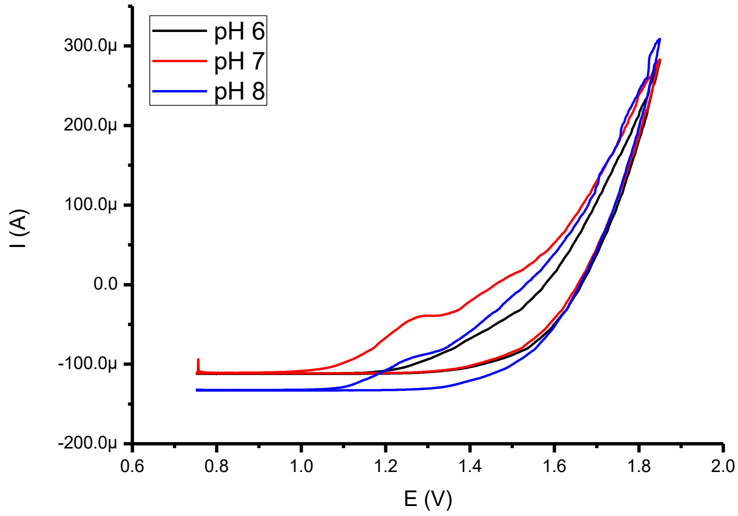

Figure 6c: The CV plots of [CoBQEN(H_2O)$_2$](ClO_4)$_2$ in N_2 atmosphere at pH = 7

From the cyclic voltammetry technique one can state that whether the complex which has taken is undergoing oxidation-reduction process or not.

All the graph of cyclic voltammetry is obtained. In the figure 6.a the comparison between the sodium acetate and catalyst has been clearly indicate that the sodium acetate is the suitable solvent for that particular catalyst. As the marked a difference can be seen in both the graphs. In the Figure 6b the voltammogram of $[Co(NH_3)_6]Cl_3$ is obtained, where it does not show any oxidation peak at any pH. Therefore the compound **1** is not suitable for the water oxidation reaction. The cobalt is in already +3 oxidation states in this complex.

In the Figure 6c the voltammogram of compound **2** $[CoBQCN(H_2O)_2](ClO_4)_2$ is obtained. The oxygen evolution reaction at pH = 6, pH = 7, and pH = 8 are been studied. It shows that the Co(II) oxidation peak is observed in the potential range of 1.1 - 1.4 V, which corresponds to the oxidation of centre metal ion to higher oxidation states. The peak is obtained only at pH 7, which states that water oxidation activity observed at this pH only.

In the Figure 6d. another catalyst has been studied, the catalyst $[CoBQEN(H_2O)_2](ClO_4)_2$, the oxidation peak is observed at the same potential that is 1.1 - 1.4V. The oxidation peak is obtained at pH 7 and pH 8 which show the indication of water oxidation. With comparison to both the peak, pH 7 shows better water activity compare to pH = 8 in case of **3**. Theoretically the water oxidation peak is observed at 1.23V when standard hydrogen electrode is used as reference electrode but due to the silver-silver chloride electrode is used as reference electrode there is little shift in potential that is approximately at 1.42V. Therefore the complex2 and complex3 is stable and undergoing water oxidation process only at pH=7 which is the original nature of catalyst.

3.2. Linear Sweep Voltammetry

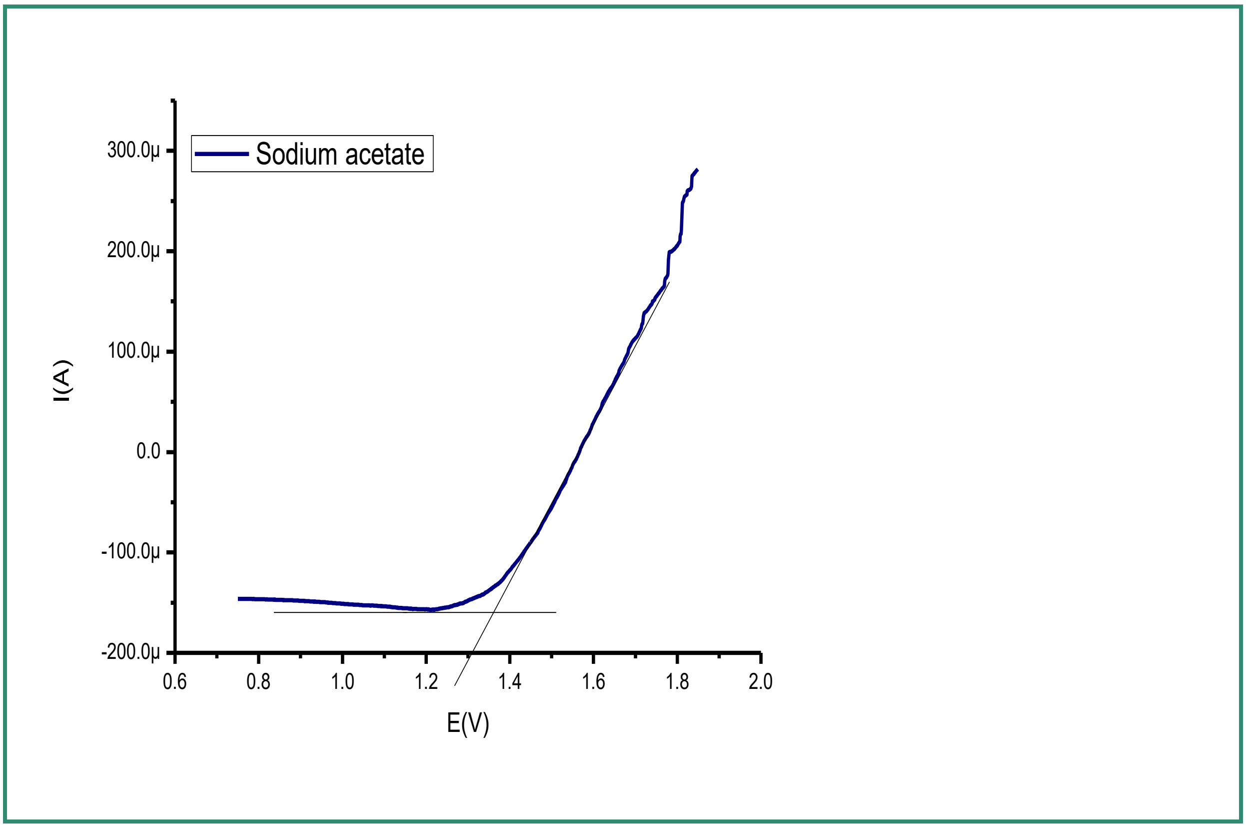

Figure 7a. Linear sweep voltammogram of sodium acetate

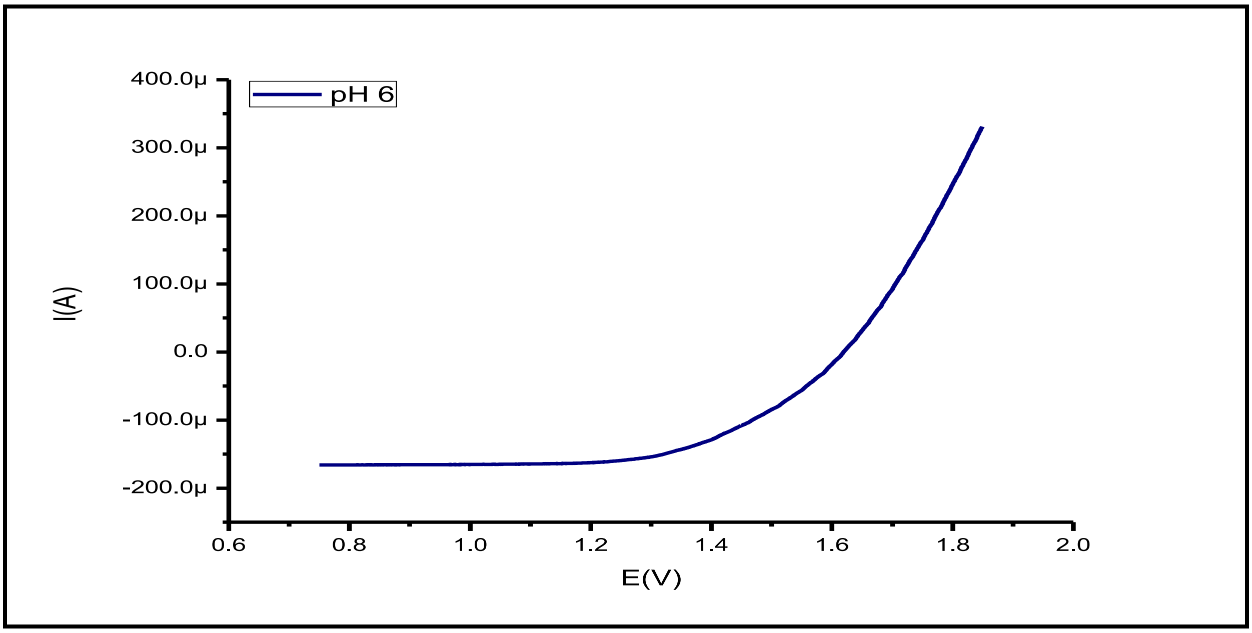

Figure 7b. Linear sweep voltammogram of $[CoBQCN(H_2O)_2](ClO_4)_2$ at pH= 6

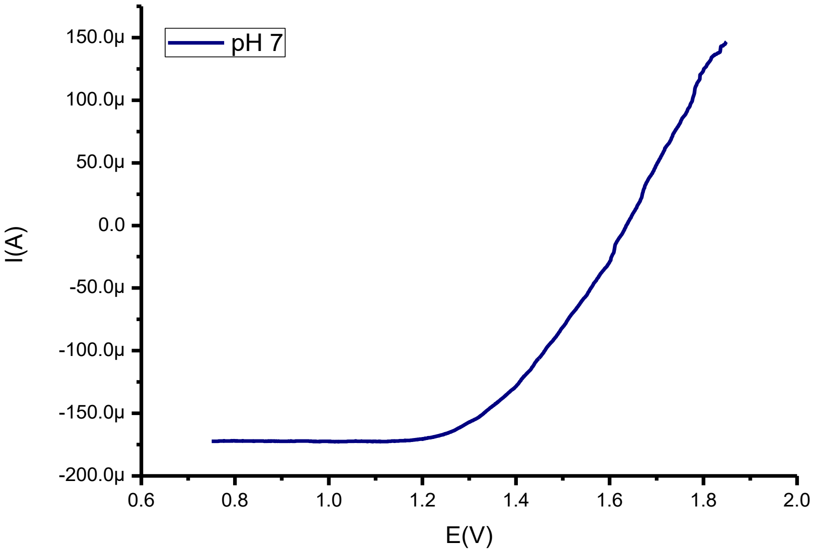

Figure 7c. Linear sweep voltammogram of [CoBQCN(H_2O)$_2$]($ClO4$)$_2$ at pH=7

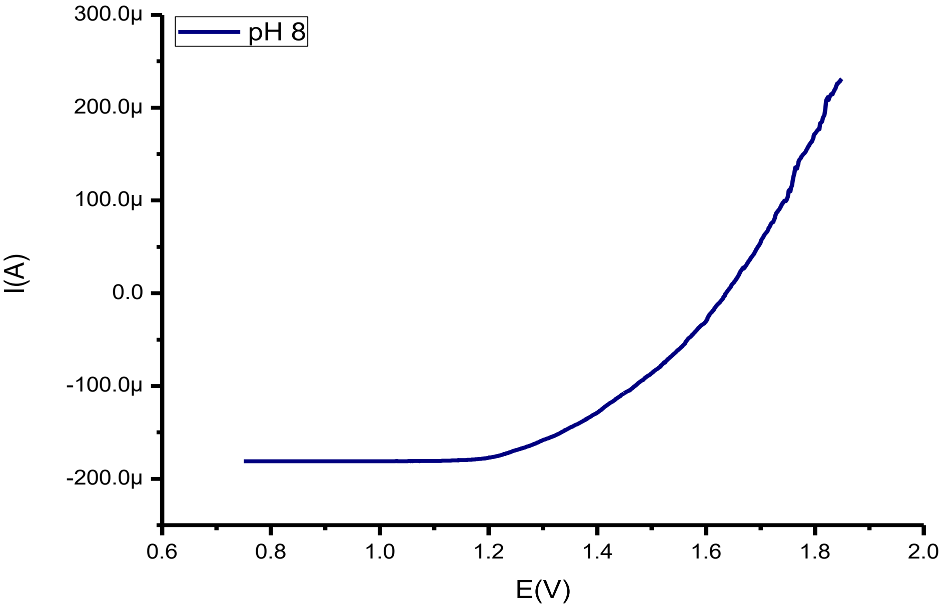

Figure 7d. Linear sweep voltammogram of [CoBQCN(H_2O)$_2$](ClO_4)$_2$ at pH = 8.

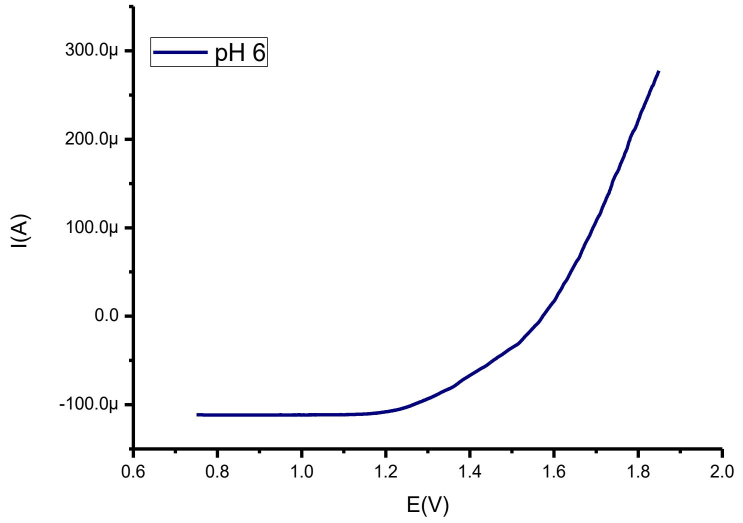

Figure 7e. Linear sweep voltammogram of [COBQEN(H_2O)$_2$](ClO_4)$_2$ at pH = 6

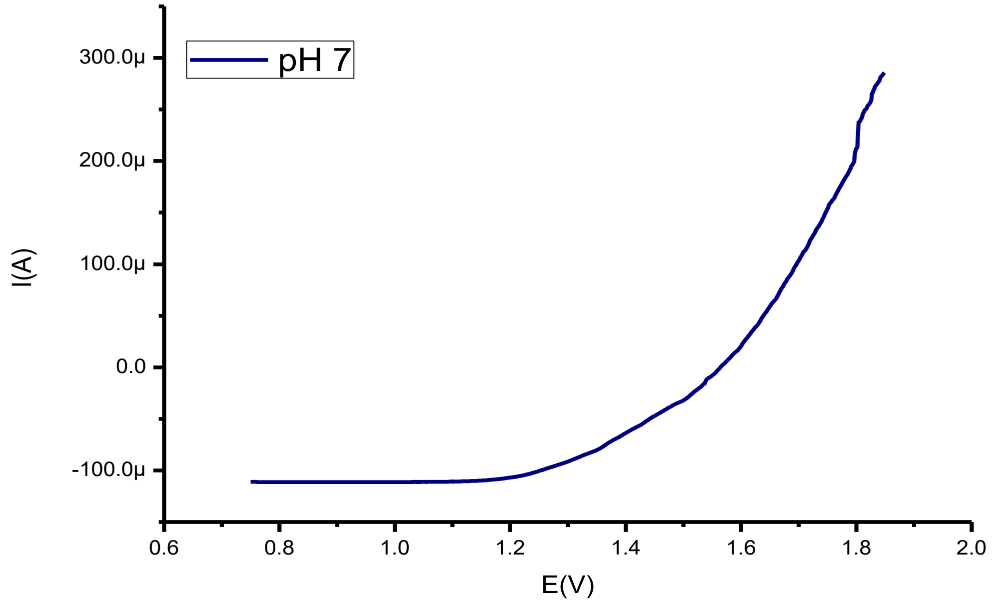

Figure 7f. Linear sweep voltammogram of [CoBQEN(H_2O)$_2$](ClO_4)$_2$ at pH = 7

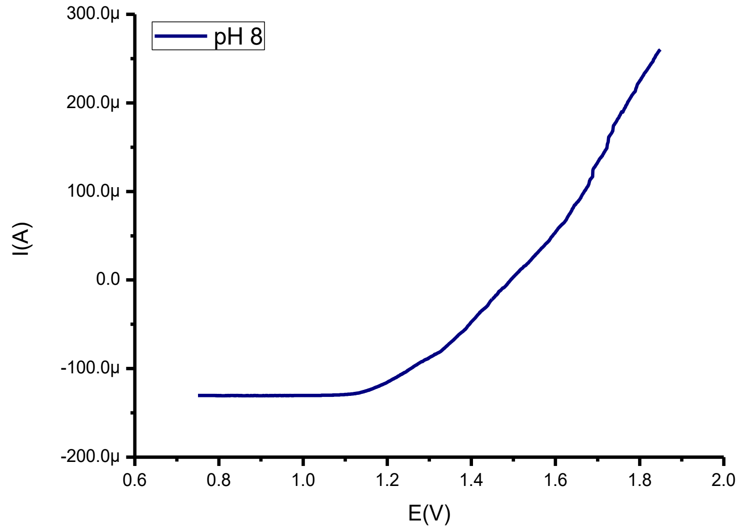

Figure 7g. Linear sweep voltammogram of $[CoBQEN(H_2O)_2](ClO_4)_2$ AT pH 8

Linear sweep voltammogram at different pH is obtained. As the complex1 is not showing any result in cyclic voltammetry further studies of this is not done .It can be seen from the Linear sweep voltammogram that the better oxygen evolution reaction activity is in a neutral comparison to acidic and basic for both the complexes2 and complex3.The onset potential of compound **2** that is $[CoBQCN(H_2O)_2](ClO4)_2$ is found to be 1.50V,1.30V and 1.42V at pH6, pH = 7 and pH = 8 respectively. The onset potential is obtained directly from the voltammogram.

The onset potential of complex **3** that is $[CoBQEN(H_2O)_2](ClO_4)_2$ is 1.50V, 1.45V and 1.52V at pH = 6, pH = 7 and pH = 8 respectively. The calculated over potential is found out by using standard potential of the reference electrode which is shown below

[Electrode – experimental (onset potential)]

From this equation it got to know that calculated over potential for pH = 7 for both the compounds **2** and **3** are lower compared to basic and neutral medium. Linear sweep voltammogram of the solvent is obtained. The onset potential of sodium acetate is 1.38 V. The compound that showed lowest calculated over potential is the better water oxidising catalyst. To make this understand, we plotted Tafel graph.

3.3. Tafel Plot

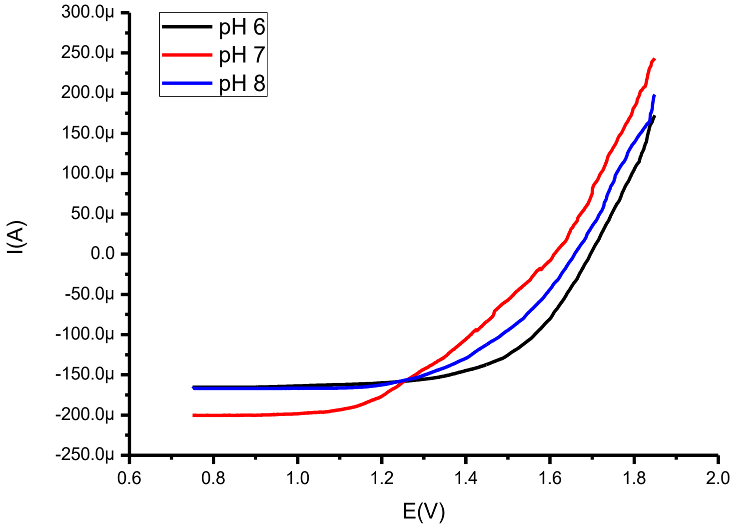

Figure 8a. Tafel Plot of [CoBQCN(H_2O)$_2$](ClO_4)$_2$

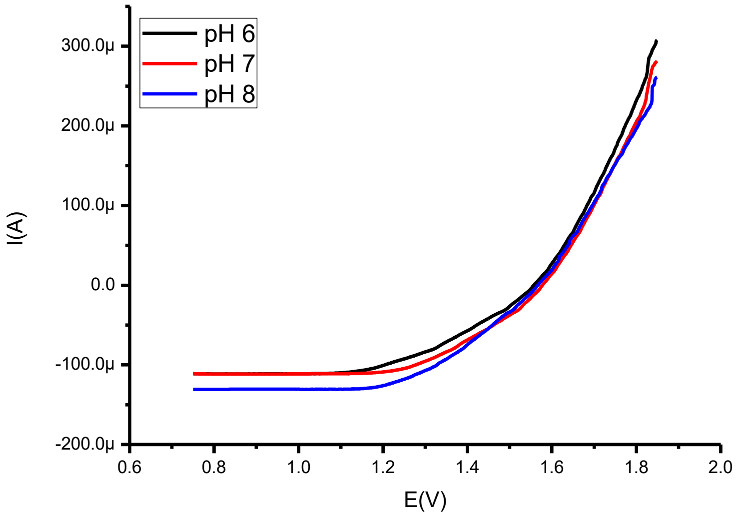

Figure 8a. Tafel Plot of [CoBQEN(H_2O)$_2$](ClO_4)$_2$

From the Tafel plot we gets the slope. It states that, lower the slope better is the oxygen evolution activity. For compound **2** the anodic slope is observed directly from the instrumentation for pH = 6, pH = 7 and pH = 9 is 6.446 V, 5.676 V and 6.347 V. In the same way slope for compound **3** has been observed that is 5.931 V, 5.734 V and 5. 732 V for pH = 6, pH = 7 and pH = 8 respectively which confirms oxygen evolution activity is better for pH = 7. It is confirmed from all the obtained data that the both the complexes 2and 3 shows better water oxidation activity at neutral medium. This could be all the reason like better stability of that complex in that solvent, viability of the catalyst in that solvent, solvent-catalyst system is inert in their condition.

4. Results

COMPLEX	**pH = 6**	**pH = 7**	**pH = 8**
$[Co(NH_3)_6]Cl_3$ (1)	No OER activity	No OER activity	No OER activity
$[CoBQCN(H_2O)_2](ClO_4)_2$ (2)	No OER activity	OER activity observed	No OER activity
$[CoBQEN(H_2O)_2](ClO_4)_2$ (3)	No OER activity	OER activity observed	Slight OER activity is observed

5. Conclusions

- All the three complexes dissolved in the selected solvent that is in sodium acetate. Also the catalyst-solvent system was in stable condition.
- The reference electrode used as silver-silver chloride, therefore the calculated potential should be approximately 1.452V.
- The comparison of both catalyst and solvent in figure 6.a shows that the selected solvent is suitable for all three complexes.
- The compound **1** cannot be used as electro-catalytic water oxidation catalyst, as can been seen from the Figure 6b that there is no peak observed at any pH.
- The compound **2** shows the water oxidation peak is in the range of 1.1-1.4 V at pH = 7 which can be used as an electro-catalytic catalyst. The LSV of compound **2** at pH = 7 has lower over potential compared to acidic and basic condition. Even the Tafel slope of compound **2** at pH = 7 is lower.
- The compound **3** also shows the water oxidation peak is in the range 1.1-1.4 V at pH = 7 and also at pH = 8 slightly. The LSV plot of compound **3** at pH = 7 has lower over potential compared to acidic and basic medium. The Tafel slope of compound **3** at pH = 7 was lower compared to pH = 8 and pH = 9.
- From LSV one could find out the overpotential, the complex which shows the lowest overpotential is the better water oxidising catalyst.
- From the tafel plot we can calculated the anodic slope, lower the slope better is the water catalytic activity.
- Comparing compound **2** with complex 3, complex 2 shows better water oxidation activity. This can be seen from the data of LSV, where the calculated over potential of complex 2 is less than complex 3.

- To support this even Tafel slope shows the anodic slope for compound **2** is lower than compound **3**.
- From all the data obtained from electrochemical analyses it is concluded that compound **2** and compound **3** shows better water activity at neutral pH which is its original pH, this could be due to the better viability of the catalyst in higher oxidation states and which gives the driving force for the OER activity.
- It is concluded that both the complexes shows water oxidation activity at pH= 7 and when to compare among these compounds, **2** shows better water activity than **3**.

6. References

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