Electrochemical and Photo Electrochemical Studies for CO_2 Reduction and Dye Removal using Co_3O_4 as Anode

Thesis submitted in partial fulfillment of the requirements

for the degree of

DOCTOR OF PHILOSOPHY

by

V Shyam Kumar Yadav

Department of Chemical Engineering
Indian Institute of Technology Guwahati
Guwahati-781039, India
June, 2016

भारतीय प्रौद्योगिकी संस्थान गुवाहाटी
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Dedicated to my Parents for whom I have become what I am today

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CERTIFICATE

It is certified that the work contained in the thesis entitled "**Electrochemical and photo electrochemical studies for CO_2 reduction and dye removal using Co_3O_4 as anode**", submitted by **V Shyam Kumar Yadav**, has been carried out under my supervision. The work documented in this thesis has not been submitted to any other University or Institute for the award of any degree or diploma.

Dr. Mihir Kumar Purkait

Professor

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V shyam Kumar Yadav

Abstract

Global warming effect was caused by the combustion of fossil fuels which releases greenhouse gases during energy generation and causes great damage to the society. The different gases like methane, nitrous oxide, other halocarbons and CO_2 were evolved during the process. Out of these, CO_2 is the main contributor to global warming effect. There is a need to reduce these CO_2 before it cause damage to the environment. Several methods were in existence towards reduction of CO_2 to different products, the main focus went on electrochemical CO_2 reduction because of its several advantages. The studies reported that reduction depends on different conditions like electrocatalyst, electrolytes, and applied voltages. Moreover, the production of fuel from CO_2 is of special interest for the storage of renewable energy (solar, wind etc).

The studies discussed here were mainly focused on the electrocatalyst synthesis by electrodeposition method and their analysis using a 2-electrode glass reactor. The synthesized electrocatalysts Cobalt oxide (Co_3O_4) was used as the anode for water oxidation reaction in place of expensive platinum (Pt) electrocatalyst. The other synthesized electrocatalysts (Copper oxide (Cu_2O), Lead oxide (Pb_2O), Zinc (Zn) and Tin (Sn) were used a cathode for reduction of CO_2 to products electrochemically (RCPE). The synthesized electrocatalyst were characterized using X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, Particle size analyzer (Delsa Nano). The performance of characterized electrocatalyst was studied using a reactor for liquid product formation in different electrolyte ($KHCO_3$, $NaHCO_3$, K2CO_3 and Na_2CO_3) solutions. The electrodes for anode and cathodes were prepared by coating the electrocatalyst ink on the surface of graphite plate. The reacted sample was analyzed by using an Ultra-Fast Liquid Chromatography (UFLC) and different products like ethanol (C_2H_5OH), methanol (CH_3OH), formic acid (HCOOH), formaldehyde (HCHO), Acetic acid (CH_3COOH) and propanol

(C_3H_7OH) respectively. Cu_2O (cathode) and Co_3O_4 (anode) electrodes were used for electrochemical CO_2 reduction. Along with other liquid products, ethanol was produced as main reduced product from CO_2 with high Faradaic efficiencies at different applied voltages. At 1.5 V and 2 V, maximum Faradaic efficiencies of 76.31 % and 96.15 % for ethanol were obtained at 5 min of reaction in $KHCO_3$ solution. Similarly in K_2CO_3 solution, high Faradaic efficiencies of 40.62 and 54.5 % were observed at 1.5 V for ethanol at 20, 25 min reaction along with 36.6 % is observed at 2.5 V at 10 min. Maximum Faradaic efficiency of ethanol was 98.1 % at 2 V and for formic acid (36.6%) at 1.5 V was observed in $NaHCO_3$ solution. On the other hand, using Na_2CO_3 electrolyte solution maximum efficiency for ethanol was 55.21% at 1.5 V and formic acid was 25.1% at 2 V.

From the discussed results multiple products were formed during CO_2 reduction using Cu_2O as electrocatalyst and confirmed that the selected anode (Co_3O_4) electrocatalyst was the right choice in place of Pt. However, multiple products were formed from the reaction made the system complex. Further studies were conducted using a selected electrocatalysts (Pb_2O, Zn and Sn) which showed high selectivity for HCOOH from CO_2 reduction. The electrochemical studies were done using different electrocatalyst with common anode Co_3O_4. For all the studies HCOOH was the only product formed at all applied voltages and electrolytes using this electrocatalyst. For Pb_2O (cathode) and Co_3O_4 (anode) as electrocatalysts maximum Faradaic efficiencies of ~60 % and ~50 % for HCOOH at 2 V were obtained after 10 min of reaction in $KHCO_3$ and $NaHCO_3$ electrolyte solution, respectively. For Zn (cathode) and Co_3O_4 (anode) as electrocatalysts in $KHCO_3$ electrolyte solution at 1.5 V, maximum Faradaic efficiencies of 78.54 % and 78.46 % for HCOOH were obtained at 5 and 10 min reaction. Similarly, in $NaHCO_3$ solution efficiencies of 60.5 and 64.7 % for reaction 5 and 10 min were obtained at 2.5 V. High Faradaic efficiencies of

68.72% were observed at reaction time of 25 min at 1.5 V which is the most optimum condition for RCPE.

From electrochemical studies, the ability of selected electrocatalyst towards RCPE was studied. However, electrical energy was used as a source for reaction. Use of solar energy might be a better alternative as this energy is available in free of cost. From the results of electrochemical studies, bicarbonate electrolyte solutions showed higher efficiencies than carbonated solutions. The RCPE using solar energy as a source was studied in different concentrations of bicarbonate electrolytes. Using Cu_2O (cathode) and Co_3O_4 (anode) as electrodes in $KHCO_3$ solution the optimized condition towards C_2H_5OH was observed to be 1.277 mmol for 40 min reaction in 0.2M and HCOOH was 0.377 mmol for 10 min in 0.6M. Maximum formation for C_2H_5OH and HCOOH were observed to be 0.96 and 0.178 mmol for the reaction of 50 min in 0.2M $NaHCO_3$ electrolyte solution. When Pb_2O was used as cathode HCOOH formation on Pb_2O electrocatalyst was 0.242 mmol for 30 min reaction in 0.2M $NaHCO_3$ and 0.157 mmol of HCOOH formed for 10 min reaction in 0.2M $KHCO_3$. Similarly, RCPE using Sn as electrocatalyst maximum moles of product formed in 0.2M for 10 min reaction were 430.04 µmol ($KHCO_3$) and 494.60 µmol, respectively. With respect to Zn electrocatalyst in 0.2M electrolyte solution 400 µmol ($KHCO_3$) for 10 min and 254 µmol ($NaHCO_3$) for 40 min were obtained.

From both electrochemical and photo electrochemical studies, it was observed that Sn and Zn electrocatalysts showed better Faradaic efficiencies and selectivity towards HCOOH formation in bicarbonate based solutions. So, using these electrocatalysts, studies on the simultaneous CO_2 reduction and dye removal was done electrochemically. Mixture of Crystal

violet (CV) dye and electrolyte was used for CO_2 saturated solution. HCOOH was the only reduced products formed from RCPE along with dye removal. High Faradaic efficiency of 45.33% for HCOOH at Zn electrocatalyst in $KHCO_3$ solution was observed in reaction time of 5 min. Methylene blue (MB) dye plus electrolyte was used as CO_2 saturated electrolyte. Maximum Faradaic efficiency of 57.9 % ($KHCO_3$) was observed using Sn as electrocatalyst for reaction time of 15 min and 31.7 % ($KHCO_3$) in 5 min using Zn as electrocatalyst. Similarly, for the case of brilliant green dye electrolyte, maximum Faradaic efficiencies of HCOOH in $KHCO_3$ and $NaHCO_3$ were obtained as 40.6 % (5 min) and 76.3% (5 min) using Sn as cathode. When using Zn as cathode, Faradaic efficiencies were 69.9% (10 min) – 2 V and 50.7 % (5 min) – 2 V respectively. In case of Zn electrocatalyst, the removal was 95.1 % (5 min) and 94.6 % (20 min) at 2 V and 3.8 V, respectively.

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List of Symbols

mM	Milli molar
µl	Micro litre
nm	Nano meter
V	Applied voltage (V)
%	Percentage (%)
A	Ampere
M	Molar
h	Time (hour)
θ	Diffraction angle
D_v	Median size (nm)
min	Minute

List of abbreviations

BG	Brilliant green
CV	Crystal violet
FTIR	Fourier transform infra-red
IPA	ISO propyl alcohol
MB	Methylene blue
RCPE	Reduction of CO_2 to products electrochemically
UFLC	Ultra-fast liquid chromatography
UV	Ultra violet
XRD	X-Ray diffractometer

Chapter 1

Introduction

Chapter 1

Introduction

1.1 Challenges in 21st century

The main challenges of today's world faced by the scientists are to reduce the CO_2 concentrations and to generate alternate energy source for our future generations. Fossil fuels are used as a world's primary energy source, since the energy produced from the fossil fuel is cheap and most of the energy generating using present's technology is by using fossil fuels. Utilization of fossil fuel energy is drastically increasing due to rapid rise in population. However, the fossil fuels accounts for more than 85 % usage for energy generation.[1] The process of energy generation deals with the combustion of fossil fuels like coal, natural gas, petroleum, etc. The different gases like methane, nitrous oxide, other halocarbons and CO_2 were evolved during the combustion process that causes global warming effect. The evolution of these greenhouse gases causes great damage to the society. CO_2 is the main contributor to the global warming effect. The international community aims to reduce the global rise in temperature by 2^o C to reduce the problems regarding climate change and there is progress in reducing the emissions has been reported.[2] The CO_2 concentrations were drastically increasing for pre-industrial period marking present concentration of 397.64 ppm given by the Mauna Loa[3] Observatory and measurements. The main source of CO_2 emissions were humans, volcanoes and geysers. The first data regarding emissions worldwide were available in 1951 and reported to be 11 million tons of CO_2. Slowly the energy generation of industrial growth leads to increases in 1000 times more than the emissions that were reported in 1951 during the 1960s.[3] After this period the world depends on energy for their sustainable development in order to improve their standards. Due to which the drastic rise in emissions was observed to be 35 billion metric tons globally.[3] The contribution towards CO_2 emissions by different countries in 2014 is shown in Figure 1.1.

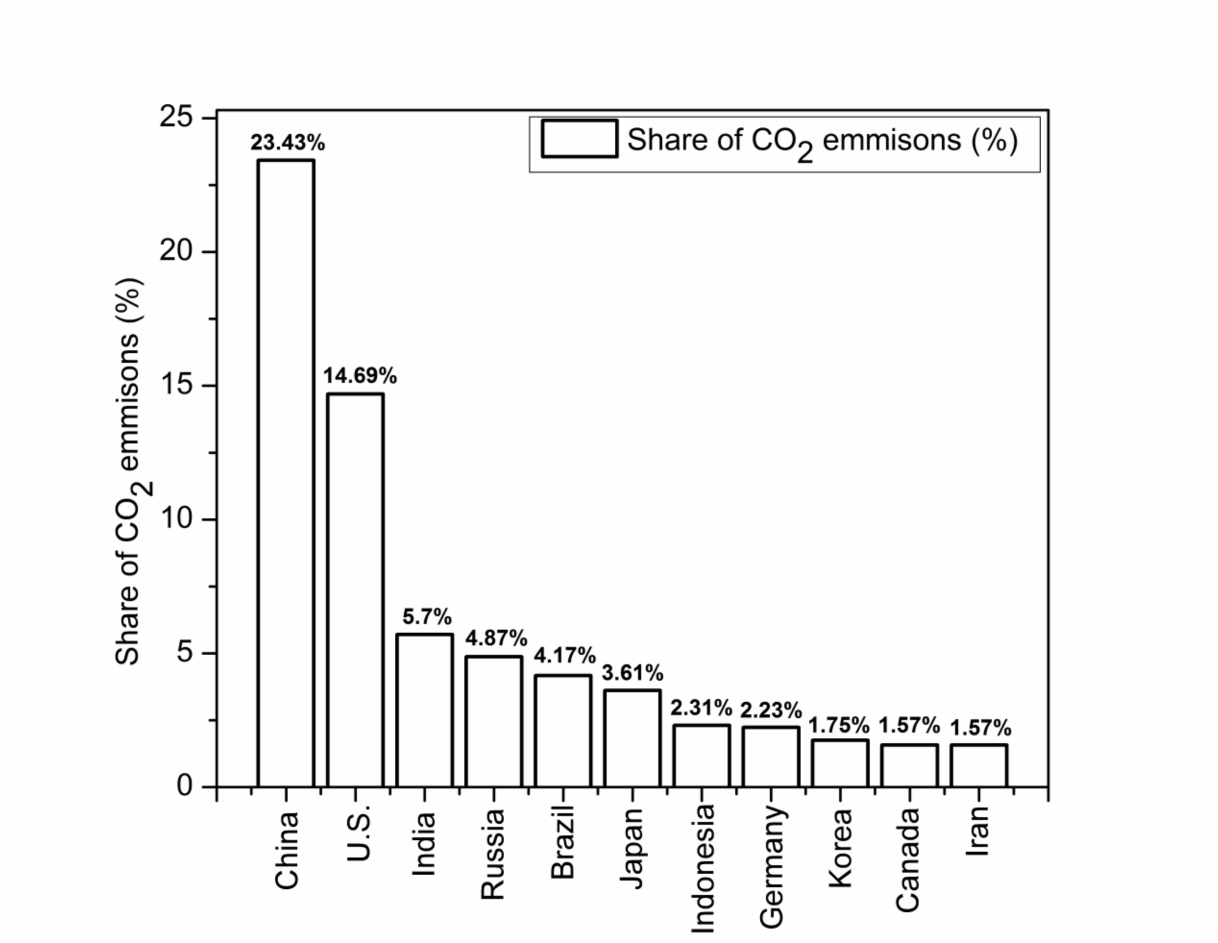

Figure 1.1. Share of CO_2 emissions by various countries in 2014[3]

The results shown in figure 1.1 depicted that china is the main contributor of CO_2 emissions with 23.43 % and US stood second position of 14.69 %. Maximum emissions globally were contributed by these countries for the year 2014. The energy consumption is directly proportional to combustion of fossil fuels that cause CO_2 emissions. Due to the large usage of fossil fuels, CO_2 emissions were gradually increased with time. The increase in these concentrations was the main cause for global warming. To reduce this effect the atmosphere CO_2

was to be captured and convert to into some useful energy. This might be a solution to decrease the global warming and an energy source replacing fossil fuel based energy for our future generation. The other renewable sources like solar, wind, photo voltaic, hydroelectric, nuclear energy and biomass etc. were the alternatives. The combination of all these alternative energy sources may contribute to the large fuel energy requirements globally. The present electrochemical devices were able to convert these CO_2 to different fuels using electrical energy as source which is generated from fossil fuel. If a CO_2 can be converted by the use of renewable energy that might be a better alternative to store the intermittent renewable energy in the form of fuel. Therefore, the reduction of CO_2 process is more attractive towards the formation of different products like methane, methanol, formic acid, alcohols, etc. These can be used as an energy source alternative to fossil fuels.

1.2. Reduction of CO_2 to products electrochemically (RCPE)

The reason for the reduction of CO_2 to products electrochemically (RCPE) becoming a significant process mainly due to two main reasons. As CO_2 is produced from almost all reactions involving carbon based compound oxidation that increases its concentration in the atmosphere. This may be used as a source to produce different chemicals which can be used in so many applications. In this process, energy that can be used to reduce CO_2 to various chemicals is derived from various renewable sources. Different methods were there for RCPE such as heterogeneous catalysis to hydrogenate CO_2 at high temperatures and pressures to different chemicals using different electrocatalysts like Zinc (Zn) and Copper (Cu). The other photosynthesis method can be used by using organism to store solar energy in the form of fuel. Similarly, the solar panel can be used directly in place of electrical source in order to save the electrical energy consumption.

The RCPE can be done by an applied voltage between the two electrodes in an electrochemical cell. Mainly two reactions are possible at the anode and cathode when enough potential difference is applied. The oxidation of water takes place at anode generates a proton which goes to cathode for reduction of CO_2 to different products and hydrogen generation. However, other reactions are also possible at cathode based on electrocatalyst used and applied conditions.[4] A typical electrochemical reactor setup for RCPE is shown in Figure 1.2.

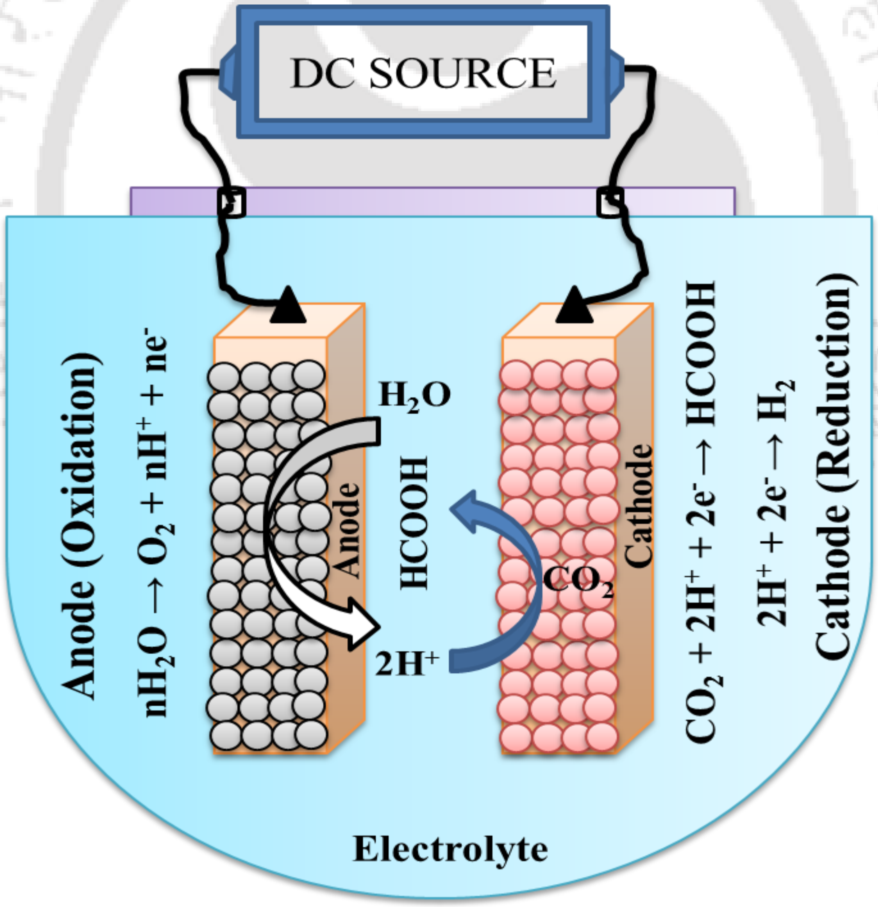

Figure 1.2: Schematic of electrochemical reactor for CO_2 reduction reaction

The attention towards the electrochemical reduction process has increased due to its several advantages. Few are listed below.

1) The atmospheric CO_2 concentrations can be reduced to decrease global warming effect.
2) By converting CO_2 to different chemicals which can be used for future energy applications.
3) Can replace electrical energy with free solar energy as a source for an electrochemical reactor to store solar energy in the form of fuel.
4) The reactions can be done at room temperatures and atmospheric pressures.
5) The waste water can be used for proton generation at anode in order to purify the water simultaneously with CO_2 reduction.
6) Scale up is easy.

In the same way, RCPE has several challenges that need to be improved for advancement. These are as follows.

1) Selecting best and cheap electrocatalyst suitable for CO_2 reduction.
2) Maximum CO_2 reduction should be achieved.
3) Reduce the hydrogen evolution at anode by transporting maximum CO_2 molecules to cathode.
4) Increase the catalyst activity by removing surface impurities on the catalyst surface.
5) Generation of single product selectivity with high Faradaic efficiency.

6) Analysis of products that formed during RCPE.
7) Simultaneous water purification (e.g. dye removal) at anode along with CO_2 reduction at the cathode.
8) Converting maximum energy that is to be supplied during the reaction to chemicals from CO_2 reduction.
9) Solar energy driven water purification and CO_2 reduction.

To solve these problems, a suitable cheap and effective electrocatalysts have to be selected for CO_2 reduction and water oxidation reaction. If anode catalyst can produce an equal number of protons with CO_2 molecules at the cathode, maximum supplied energy can be utilized for CO_2 reduction which also suppresses the hydrogen evolution. Conversion of CO_2 to single product with high efficiency by selecting a suitable cathode electrocatalyst is needed.

1.3. Electrochemical CO_2 reduction trends

Studies were going on from past decades on CO_2 reduction. However, significant studies on RCPE were reported using different electrocatalyst and their effect in reducing CO_2 in bicarbonate based solutions.[5] A review on RCPE for different products in aqueous and non-aqueous based electrolytes were reported with mechanism for different product formation during CO_2 reduction.[6] Maximum papers were concentrated on finding a better electrocatalyst material to get yield of various products. Different products like carbon monoxide, methane, methanol, formic acid and ethanol, etc. were reported using different electrocatalysts.[7-9] The studies were reported that not only type of electrode affecting the CO_2 reduction, but also electrolytes used plays a major role in different product formation. Since, the solubility of CO_2 in different electrolytes varies that effect the CO_2 reduction. Mainly electrolyte pH is affecting the reaction and maximum studies were done near to neutral conditions. High pH may cause catalyst deactivation and low pH is not suitable for maximum CO_2 solubility.[10-11] Near to neutral conditions was the best alternative for maximum CO_2 reduction. The effect of catalyst surface also changes the CO_2 reduction rate. The studies were reported on copper electrocatalysts as best to reduce CO_2 to different hydrocarbons. Various products were reported during CO_2 reduction on copper based electrocatalysts.[12] Different metallic electrodes used in aqueous based electrolytes towards CO_2 reduction have also been reported. The metals like the Tin (Sn), lead (Pb), mercury (Hg) and Zn were used towards formation of HCOOH using Pt anode.[13-17] Gold (Au) and silver (Ag) are responsible to produce mainly carbon monoxide as product from carbon dioxide.[18-21] When copper was used as electrocatalyst for cathode, hydrocarbons, aldehydes and alcohols were produced during RCPE using Pt as anode.[12,22] The effect of CO_2 reduction to ethanol and ethylene on copper oxide electrocatalyst in potassium based electrolyte were also reported.[23] Product selectivity was very poor due to formation of multiple products which makes a system complex. For a better electrochemical system high efficiencies need to be produced for commercialization. Therefore, various challenges regarding electrocatalyst, efficiency, stability and overall cost for an electrochemical system has to be developed.[24] However, water oxidation is more challenging as it generates electrons and the formation of oxygen bonds. For more potential has to be applied to system than the actual thermodynamic value required for reactions due to relative slow kinetic and resistance to generate fuel production at the cathode. This can be solved by improving the overall reaction rate by selecting a specific electrode that could the system requirements like low fabrication cost, high efficiency and high stability. The literature studies show that expensive Pt was used as the anode for water oxidation reaction in RCPE. The replacement of Co_3O_4 with Pt is a better alternative as it is used in several water oxidations for oxygen evolution reactions.[25] The preparation cost for electrocatalyst has to be reduced since maximum methods like sol gel and co-precipitation methods were used for synthesis. This problem can be solved by preparing electrocatalyst using electrodeposition method as it can be done at room temperature, low process time and cost effective. This method can be used in solar energy in place of electrical energy to apply voltage between the two electrodes. For electrochemical reduction of CO_2 to generate different products requires electrical energy. The process can be more efficient if a system used solar energy in place of electrical energy which indirectly stores solar energy in the form of fuel. Several studied were reported for solar driven CO_2 reduction to different value added products. Li et al., had given a review on fundamental aspects in developing a novel photocatalysts for CO_2 reduction along with recent advances in reactor design. This review mainly focuses mainly on photo catalyst (metal oxides) and its possibilities in increasing the catalyst activity for maximum CO_2 reduction.[26] The studies for simultaneous CO_2 reduction and water purification by removing a methyl orange dye was studied using copper based electrocatalysts using solar energy. The studies show that the photo electrochemical system was able to convert CO_2 to different products like formic acid (HCOOH), methanol (CH_3OH), formaldehyde (HCOH) and methane (CH_4) along with oxidation of hazardous dye material.[27] Generally CO_2 reduction is conducted using electrochemical reactor containing a proton exchange membrane, cathode and anode. From the studies high faradaic efficiencies were reported at low applied voltages without diaphragms. The possible reason for getting high Faradaic efficiencies may be due to eliminates system electrical resistance that was there when the diaphragm was used.[28] Most of the literatures used expensive Pt as anode for water oxidation reaction in an electrochemical reactor during RCPE using diaphragm. This work is focused on the use of low cost Co_3O_4 as anode without diaphragms during RCPE. The outlook of the thesis is explained in the subsequent section

1.4 Organization of the thesis

Chapter 1 is the introduction addressing various challenges and trends towards CO_2 reduction. Detail literature review and objective of the current research is reported in Chapter 2. Chapter 3 describes the synthesis of Co_3O_4 (anode) and Cu_2O (Cathode) electrocatalysts, their characterization and performance evaluation by RCPE in different electrolytes. Synthesis of Pb_2O, Zn and Sn electrocatalysts, their properties and performances of RCPE for HCOOH formation are explained in Chapters 4, 5 and 6, respectively. Electrical energy was replaced with solar energy (which is free of cost) and RCPE was performed in different electrolyte concentrations and elaborated details in Chapter 7. Chapters 8 and 9 dictate the simultaneous CO_2 reduction and dye removal electrochemically using Sn and Zn based electrocatalyst, respectively. Finally, various conclusions drawn from the research work and possible future work is summarized in Chapter 10.

Chapter 2

Literature Review


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Chapter 2

Literature Review

The overall view on electrochemical and photo electrochemical reduction of CO_2 and their effects were discussed in the previous chapter. The effect of various electrocatalysts and experimental conditions for CO_2 reduction is discussed in this chapter. The literature review on recent advancements in the development of suitable electrocatalyst is also discussed here.

2.1. Background

From the past literature studies, it is found that the biggest challenge in RCPE is low performance of electrocatalysts mainly due to catalyst activity and stability. Different products were formed from RCPE through the electron pathways in different electrolytes. Different products like CO, HCOOH, HCHO, CH_3OH, CH_4, C_2H_5OH and C_2H_4 were reported along with other products.[29-30] Though the electrocatalysts were used in RCPE but the reaction rates are slow such that current catalyst were not active enough to get the desired reaction to take place. Other cases showed that some catalyst was able to reduce CO_2 to multiple products and its formation was mainly electrocatalyst and applied voltage depended. Due to the formation of multiple products, the system becomes more complex.[31-32] This shows the electrocatalyst used is not sufficient in getting selectivity of particulate product. There is a need to develop a suitable electrocatalyst combination to get maximum efficiencies is the biggest challenge in RCPE.[33] Well-established studies were reported on RCPE which might give a better solution in developing and focusing on suitable electrocatalysts for a better electrochemical process.[34]

2.2. Different electrocatalysts used in RCPE

Different electrocatalyst were reported in reducing CO_2 to different products based on applied experimental conditions. Mainly transition metals are used as electrocatalyst in RCPE.

These metals can easily activate the bond between the metals and adsorbed carbon dioxide molecules due to vacant free orbits with active d electrons. The effect of different metal electrocatalysts on CO_2 reduction is discussed in subsequent sections.

2.2.1. Copper (Cu) electrocatalyst in RCPE

Copper was used as electrocatalyst and coated over electrodes for RCPE to produce various hydrocarbons at significant applied current densities and reported well in Table 2.1. Gatrell et al., given a good review on copper catalysts for the reduction of CO_2 in aqueous medium.[35] Hori et al. studied the effect of CO_2 reduction on different copper surfaces in 0.1M $KHCO_3$ solution. The results showed that crystal surfaces had an impact on the formation of various products like acetic acid (CH_3COOH), acetaldehyde (CH_3CHO), ethanol (C_2H_5OH) and other products.[36-37] The mechanism for the formation of different hydrocarbons from RCPE was reported with two reaction paths. The reaction paths were given for methane and ethylene.[38] The effect of CO_2 reduction on copper catalyst for the formation of methane and ethylene was reported in sodium based electrolytes and showed the effect of applied voltage on product formation.[39-40] Studies of methane and CO formation was reported on copper foil type electrodes and suggested that dissociation of carbon monoxide adsorbed due to transfer of electrons as a rate determining step.[41] A study of electrocatalyst (Cu/CuO) electrochemical behavior in potassium based solution was shown and suggested the ability of electrocatalyst for better CO_2 reduction. Further modification for electrocatalyst is required to decrease the hydrogen evolution, such that maximum protons will participate in the CO_2 reduction reaction.[42] Activity of electrode decreased gradually for the formation of hydrocarbons from CO_2 during the electrochemical studies at neutral solution using Cu foil electrode.

Table 2.1 Studies on RCPE using Copper based electrocatalyst

S. No.	Electrode (Cathode, Anode)	Electrolyte	Applied Voltage (V)	Only Main Products (Faradaic efficiency)	Ref.
1	Cu, Pt	CsOH in CH_3OH	3.5	C_2H_4 (32.3%)	[39]
2	Cu/Cu_2O, Pt	1M $KHCO_3$	1.78	CO (21%), HCOOH (20%)	[42]
3	Cu foil, Pt	3M KBr	1.8	C_2H_4 (63%), CH_4 (16.8%)	[43]
		2M KBr		C_2H_4 (40.5%), CH_4 (28.8%)	
4	Cu foil, Pt	0.1M $KHCO_3$	1.9	C_2H_4 (11%) , C_2H_6 , CH_4	[44]
5	Cu_2O, Pt	0.1M $KHCO_3$	0.99	C_2H_5OH (16%), C_2H_4 (39%)	[23]
6	Cu, Pt	0.1M $KHCO_3$	1.37	C_2H_5OH (14.4%), CH_3COOH (2.1%), HCOOH (3.2%), C_2H_4 (50.2%)	[36]
7	CuO, Pt	0.2M $KHCO_3$	1.7	C_2H_5OH (15.5%), C_3H_7OH (3.6 %)	[54]
		0.2M $NaHCO_3$		C_2H_5OH (18.4%), C_3H_7OH (2.9 %)	
8	Cu, Pt	Nafion	1.1	HCOOH (62.2%)	[45]
9	Cu, Pt	3.5M KCl	1	C_2H_6 (43%)	[46]
10	Cu, Pt	0.1M $KHCO_3$	1.55	C_2H_5OH (7.4%), CH_4 (49.5%), HCOOH (6.6%), C_2H_4 (15.1%)	[49]
11	Cu, Pt	0.1M $KHCO_3$	1.37	C_2H_5OH (19.3%), CH_4 (5.5%), HCOOH (10.3%), C_2H_4 (46.4%)	[53]

To solve this effect, a new system was proposed for reduction on a three (gas/liquid/solid) phase on the copper mesh electrode by modifying the electrode in an acid solution. The hydrogen evolution was suppressed by using this electrode for the maximum CO_2 reduction.[43]

Gonclaves et al., proposed a new method for converting CO_2 to hydrocarbons efficiently. The electrodeposition of copper was deposited on the surface of copper electrode such that the active surface area was increased with reaction depending on electrode surfaces. Ethane and ethylene hydrocarbons were formed when the honeycomb structure was used by suppressing methane formation.[44] A new method for preparing working electrode was proposed by synthesizing copper oxide electrocatalyst. The synthesized electrocatalyst was coated on the surface of carbon layer which acts as a gas diffusion layer. The electrocatalysts used were more active and stable for selectivity of product formation.[45] The change in product formation was observed by modifying the copper surface by electrodeposition.[46]

The shift in product distribution was shown when a copper electrocatalyst was coated with polypyrrole and reported the formation of different products at more negative applied volatges.[47] The investigation on RCPE for CH_4 and CH_3OH formation of copper based alloys was shown theoretically. Initial studies were done using Cu and Zn combination as cathodes for CO_2 reduction in different electrolyte solutions. Further the importance of bare copper was studied by Hori et al. for hydrocarbon generation. The effective studies were done therefore by changing the properties of copper electrocatalyst to improve the selectivity and reactivity towards RCPE.[48-50] Selective formation of CH_3OH and CO from RCPE was studied on synthesized copper based electrocatalysts. The catalyst was prepared by a two-step method for the synthesis of copper hydroxide and cupric oxide nano wires on copper foil which shows better electrocatalytic activity towards RCPE for CO formation.[51-52]

The studies for the formation of ethanol and ethylene on copper oxide electrocatalyst were reported in $KHCO_3$ solution. The effect of reactivity with respect to products was studied by changing the thickness of catalyst layer.[22-23] The studies were done by varying the particle size, morphology and thickness of electrocatalyst and reported for the formation of multiple products. Different morphologies showed different catalyst activities with respect to CO_2 reduction and with varying Faradaic efficiencies.[53] Kuhl et al., studied the RCPE on copper based electrocatalysts and reported the formation 16 products and given a scheme for possible ways for every products.[12] The electrochemical CO_2 reduction on copper electrocatalyst showed the formation of multiple products with higher efficiencies based on the conditions used during RCPE. [54]

2.2.2. Lead (Pb) electrocatalyst in RCPE

The reaction rate towards CO_2 reduction has to be increased for a better system condition. However, that can be achieved by increasing the solubility of CO_2. The formation of multiple products makes the system complex to solve this problem an electrocatalyst has to select which will give a maximum efficiency of single product. Works has been started using different electrocatalysts like Indium, lead, Tin and Zinc for the formation of high yield of HCOOH with maximum Faradaic efficiency. The effect of CO_2 reduction to form HCOOH on lead (Pb) is shown in Table 2.2**.** In 1995, Todoroki et al., studied the RCPE at high applied pressures In $KHCO_3$ electrolyte solution using different electrode silver (Ag), mercury (Hg) and lead (Pb) and reported that the effect of reduction depends on pressure, current density and applied voltage. The formation of CO suppresses the formation of HCOOH, and if pH at the electrode surface is larger than the bulk solution, then higher efficiency of HCOOH was observed as a product.[55] The production of formate using Sn and Pb was studied and their comparison was showed, that Sn is more favorable than Pb for HCOOH formation. The importance of using both electrocatalyst for the application of HCOOH formation with high efficiencies is reported clearly.[56-57]

Table 2.2 Studies on RCPE using Lead electrocatalyst

S. No.	Electrode (Cathode, Anode)	Electrolyte	Applied Voltage	Only Main Products (Faradaic efficiency)	Ref.
1	Pb, Pt	0.5M $KHCO_3$	200 mA/Cm^2	HCOOH (42.2%)	[55]
2	Pb, Pt	Nafion	22 mA/Cm^2	HCOOH (36.7%)	[57]
			12.2 mA/Cm^2	HCOOH (54.6%)	
			2.25 mA/Cm^2	HCOOH (60.8%)	
3	Pb, Pt	0.05 M $KHCO_3$	2.2 V	HCOOH (16.5%)	[61]
4	Pb, Pt	0.5M $KHCO_3$	1.8 V	HCOOH (16.7%)	[58]
5	Pb, Pt	1M $KHCO_3$	1.62 V	HCOOH (72.5%)	[5]
6	Pb, Pt	0.5M $KHCO_3$	1.8 V	HCOOH (65%)	[58]
			1.9 V	HCOOH (53%)	
			1.5 V	HCOOH (30%)	
7	Pb, Pt	0.5M NaOH	1.91 V	HCOOH (46%)	[59]
			1.67 V	HCOOH (69%)	
			1.8 V	HCOOH (58%)	
8	Pb, Pt	0.05M $KHCO_3$	1.15 V	HCOOH (7%)	[62]
	Pb/Cu, Pt			HCOOH (50%)	

Hori et al. (1985) studied the RCPE on different electrocatalyst and showed the importance of each electrocatalyst for RCPE. The studies reveal that Pb was able to generate more HCOOH than Sn with respect to particular electrolytes used for RCPE.[5] The studies on Pb and Sn electrocatalysts was performed in an undivided fixed bed reactor, which aims to increase the activity of electrocatalyst to get high selectivity and efficiency. Maximum Faradaic efficiencies towards HCOOH was reported for both electrocatalysts in Bicarbonate based solution.[58] Innocent et al., studied the RCPE for formate formation using lead cathode in aqueous medium and reported that reduction can be enhanced at 8.6 pH of the solution. The studies show the effect of operating temperature to convert CO_2 to HCOOH.[59]

2.2.3. Zinc (Zn) electrocatalyst in RCPE

The electrocatalyst Zn plays a major role in reducing carbon dioxide to formic acid. Zinc catalyst is capable of a force that makes an oxide formation which can be utilized for RCPE by using hydrogen. The oxide of catalyst forms by oxidation of Zn in water which has an autocatalytic role for an efficient CO_2 reduction. A highly efficient method that reduces CO_2 to HCOOH has been reported using a simple Zn powder.[60] The effect of CO_2 reduction on Zn electrocatalyst is shown in Table 2.3. Azuma et al., studied the effect of CO_2 reduction in $KHCO_3$ solution at low temperatures and studied the capability of electrocatalyst for applying voltage. The studies reported the formation of HCOOH as main product with slight CO from RCPE.[61]

The effects of RCPE on Zinc alloys (Zn-Cu) were studied and showed the performance of electrocatalyst in reducing CO_2 to different products like HCOOH and CO.[62] Comparing with normal Zn powder the activity of nanostructured dendrites shows high with stability.[63] Brown et al studied the effect of Zn and Cu complexes for methanol generation from CO_2 hydrogenation. The electrocatalyst was prepared by the reaction between carboxylate; Cu and Zn to get a precatalyst solution.[64]

Table 2.3 Studies on RCPE using Zinc electrocatalyst

S. No.	Electrode (Cathode, Anode)	Electrolyte	Applied Voltage (V)	Only Main Products (Faradaic efficiency)	Ref.
1	Zn, Pt	Selemion	1.54	HCOOH (6.1%), CO (79.4%)	[66]
2	Zn, Pt	0.1M $KHCO_3$	1.7	HCOOH (40.5%), CO (48.7%)	[67]
3	Zn, Pt	0.05 M $KHCO_3$	2.2	HCOOH (19.5%)	[61]
4	Zn, Pt	1M $KHCO_3$	1.56	HCOOH (85%)	[5]
5	Cu /Zn, Pt	0.05M $KHCO_3$	1.15	HCOOH (28%)	[62]
6	Cu/ZnO, Pt	0.5M KH_2PO_4	1.4	HCOOH (1.3%), C_2H_5OH (5.6%)	[65]
			1.25	HCOOH (1.5%), C_2H_5OH (16.2%)	

2.2.4. Tin (Sn) electrocatalyst in RCPE

The effect of CO_2 reduction on Sn electrocatalysts was studied and reported high Faradaic efficiencies towards HCOOH acid formation and shown in Table 2.4. The electrochemical studies were performed towards RCPE in oxides of tin with nitrogen doped nano carbon tubes in potassium based electrolytes solution. The composites have a better activity towards CO_2 reduction to get HCOOH.[68] The effect of Sn particle deposition on carbon support as electrode towards RCPE in reducing CO_2 to HCOOH was studied. The process has shown an initiation of a continuous process for CO_2 reduction in aqueous medium. The effect of different particle sizes on CO_2 reduction was studied at low electrocatalyst loading.[69]

Table 2.4 Studies on RCPE using Tin electrocatalyst

S. No.	Electrode (Cathode, Anode)	Electrolyte	Applied Voltage (V)	Only Main Products (Faradaic efficiency)	Ref.
1	Sn, Pt	0.1M $KHCO_3$	1.39	HCOOH (92.3%)	[67]
2	SnO_2, Pt	0.1M $KHCO_3$	1.3	HCOOH (46%)	[68]
3	Sn, Pt	Nafion	1.8	HCOOH (68.8%)	[69]
4	SnO_2, Pt	0.1M $KHCO_3$	1.7	HCOOH (84%)	[67]
5	Sn, Pt	Nafion	1.6	HCOOH (70%)	[72]
6	Sn, Pt	$KHCO_3$	1.8	HCOOH (91%)	[73]
7	Sn, Pt	0.5M $KHCO_3$	1.8	HCOOH (78.6%)	[74]
8	Sn, Pt	Nafion	1.6	HCOOH (3%)	[71]
			0.5	HCOOH (5%)	
			0.7	HCOOH (12%)	
9	SnO_2, Pt	$NaHCO_3$	1.8	HCOOH (93%)	[75]
10	Sn, Pt	0.5M $KHCO_3$	1.8	HCOOH (72.99%)	[76]
11	Sn, Pt	0.05M $KHCO_3$	2.2	HCOOH (28.5%)	[61]

Similarly, the effect of the oxide layer on tin electrocatalyst was studied in RCPE which generate formate as main product. The Sn electrodes were treated by using two different methods like annealing and itching and studied the activities of both the electrocatalyst towards RCPE. CO_2 saturated $KHCO_3$ solution was used as an electrolyte solution and it was observed that the oxide form of Sn shows better results than pure Sn electrocatalyst.[70] A electrocatalyst ink was prepared and sprayed on the surface of carbon plate which able to reduce CO_2 to HCOOH effectively.[71]

2.2.5. The other electrocatalysts in RCPE

Several other electrocatalysts were studied for the electrochemical CO_2 reduction and their applications for different product formation. [5,61] The effect of RCPE using different electrocatalysts was shown in Table 2.5. Ohmori et al., studied the effect of RCPE on a sputtered gold (Au) electrode in potassium based electrolytes. The studies reveal that CO is mainly formed when nanostructured Au is used as electrocatalyst.[77] As the layer of Au nanoparticles increased, the rate of reaction increased and become saturated after certain thickness which may be due to the agglomeration of particle creating disturbance in active surface area.[78] The effect of using an electrocatalyst made of palladium (Pd) deposited on Pt was studied which shoes two different reaction pathways. Firstly, the formation of HCOOH takes place from, either by bicarbonate reduction or from CO_2 reduction, which is formed from bicarbonate at the electrode surface at low applied voltages. Secondly, direct CO_2 reduction that generates HCOOH at the cathode surface. But the activity of catalyst towards RCPE was decreasing due to poisoning by adsorbing some impurities on the surface of elctrodes.[79]

Table 2.5 Studies on RCPE using different electrocatalysts

S. No.	Electrode (Cathode, Anode)	Electrolyte	Applied Voltage (V)	Only Main Products (Faradaic efficiency)	Ref.
1	In, Pt	1M $KHCO_3$	1.51	HCOOH (92.7%), CO (0.9%)	[5]
	Ag, Pt		1.45	HCOOH (1.6%), CO (61.4%)	
	Au, Pt		1.14	HCOOH (0.4%), CO (81.2%)	
	Ni, Pt		1.39	HCOOH (0.3%), CH_4 (1.2%)	
	Fe, Pt		1.42	HCOOH (2.1%), CH_4 (1.4%)	
2	Hg, Pt	0.05 M $KHCO_3$	2.2	CO (0.64%), HCOOH (87.6%), C_2H_4 (0.0002%)	[61]
	In, Pt			CO (14.7%), HCOOH (33.3%), C_2H_4 (0.0046%)	
	Al, Pt			CH_4 (0.012%), HCOOH (0.78%), C_2H_4 (0.0002%)	
	Ag, Pt			CO (30%), HCOOH (16%), C_2H_4 (0.009%)	
	Pd, Pt			CO (3.2%), HCOOH (8.6%), C_2H_4 (0.061%)	
3	Ti, Pt	0.1M $KHCO_3$	1.57	HCOOH (4.6%), C_2H_4 (0.08%), CH_4 (0.18%)	[67]
	Mo, Pt		1.34	HCOOH (6.5%), C_2H_4 (0.02%), CH_4 (0.4%)	
	Au, Pt		1.3	CO (64.7%), HCOOH (11.8%), CH_4 (0.21%)	

2.3. Photo electrochemical studies on CO_2 reduction

The electrochemical reduction process gained much importance in reducing the CO_2 to different products like methane, methanol, formic acid ethanol and formaldehyde.[29-32] However, the process requires electrical energy which is not of energy free. So, reduction process is mainly focused on using free solar energy for photo electrochemical CO_2 reduction to useful fuels. Several authors have studied the photo electrochemical process using different electrocatalysts and electrolytes and given the possibilities of reduction in detail.[80-81] Hallman studied for the first time in 1978 about the use of cathode photo catalyst towards reduction of CO_2 to products photo electrochemically.[82] Shown et al., showed a microwave synthesis process for different types of copper nano particles modified with graphene oxide as photo catalysts towards reduction of CO_2 to fuel using solar energy.[83] Boston et al., studied the effect of different Ruthenium complexes as Photocatalysts towards CO_2 reduction to different products like HCOOH, HCHO and CH_3OH.[84] Ganesh et al., given a brief review on the reduction of CO_2 to methanol and also the effect of different Photocatalysts materials to develop a well-designed photo electrochemical reactor for the reduction of different other products.[85] Similarly, the several studies were reported using copper and complexes as electro catalyst for the photo chemical reduction of CO_2.[86-87] The studies on using a low cost Nickel cyclam as photo electrocatalyst for CO_2 reduction was studied which is clear sign for developing an efficient photo electrodes.[88] Jin et al., studied the effect of CO_2 reduction with autocatalytic water dissociation to form HCOOH on Zinc electrocatalyst.[60] Peng et al., studied on simultaneous dye removal (for water purification) and CO_2 reduction using solar energy as source and copper as electrocatalyst in $KHCO_3$ based electrolyte. Different products like HCOOH, HCHO, CH_3OH and CH_4 were formed from photo electrochemical CO_2 reduction.[89,27]

2.4. Summary review of literature

Electrocatalysts plays a crucial role in the reduction of CO_2 to various products. However, the major challenges for RCPE were found to obtain low energy efficiencies, consumption of high energies, selectivity and high cost. Different electrocatalysts used in literature were able to reduce CO_2 to different products based on the applied voltages and experimental conditions. Selectivity of products mainly depends on electrocatalyst, applied voltage and electrolyte used for RCPE. Electrolyte concentration itself affects the rate of reaction on product formation based on conductivity of the solution. Copper is accepted as a better electrocatalyst in reducing CO_2 to hydrocarbons, but due to the formation of multiple products from RCPE the system becomes complex. A process capable of reducing CO_2 to single liquid product with high Faradaic efficiency would be a better sustainable approach for future industrial applications. However, all the work focused only on the use of expensive Platinum (Pt) electrocatalyst. There is a need to select a better alternate electrocatalyst such that the overall process cost can be decreased. Therefore, the current objective of the work is set based on the literature survey to show the alternate efficient and cheap electrocatalyst for CO_2 reduction.

2.4. Objectives of this work

The literature studies show that electrocatalyst plays a vital role in the effective CO_2 reduction. However, expensive platinum was used as anode for all electrochemical studies. Hence, the main objective of the present study is

1) To prepare a cheap anode electrocatalyst as alternate to Pt having excellent CO_2 reduction capabilities.

2) To synthesis various cathode electrocatalysts for CO_2 reductions

3) To observe the performance and selectivity of CO_2 reduction capabilities of synthesized electrocatalysts

To fulfill the objective**,** a simple reactor was selected for studies on CO_2 reduction both electrochemically and photo electrochemically. The single anode electrocatalyst and multiple cathode electrocatalysts were synthesized by using simple electrodeposition technique. The performance of these electrocatalysts was evaluated towards CO_2 reduction in bicarbonates and carbonates of potassium and sodium based electrolytes electrochemically. Finally, electrochemical studies were performed for simultaneous dye removal and CO_2 reduction. Work done for all the catalysts is reported separately in subsequent chapters.

Chapter 3

Electrochemical studies for CO_2 reduction using synthesized Co_3O_4 (anode) and Cu_2O (Cathode) in different electrolytes


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Chapter 3

Electrochemical studies for CO_2 reduction using synthesized Co_3O_4 (anode) and Cu_2O (Cathode) in different electrolytes

In this work, Co_3O_4 and Cu_2O were synthesized using electro-deposition method and used as electrocatalyst for RCPE. Two graphite plates coated with Cu_2O and Co_3O_4 were used as cathode and anode, respectively. Electrochemical characteristics of synthesized catalysts were studied for CO_2 reduction at different applied voltages. A homemade 2-electrode electrochemical cell was fabricated to study the effect of CO_2 reduction with high efficiencies. Experimental procedure and the results obtained are analyzed well and discussed in this chapter.

3.1. Experimental

3.1.1 Materials

Copper plates were procured from local vendor and graphite plates of active area (1.5×2.5) cm^2 were procured from Sunrise Enterprises, Mumbai. Copper nitrate trihydrate ($Cu(NO_3)_2.3H_2O$), Cobalt nitrate hexahydrate ($Co(NO_3)_2.6H_2O$), Acetone (CH_3COCH_3), Iso-propyl alcohol ($(CH_3)_2CHOH$) and Potassium bicarbonate ($KHCO_3$) were procured from Merck, India. Reagent grade chemicals were used in all the experiments without any further purification. Electrochemical experiments were performed using a DC source (Crown, India). All experiments were conducted using deionized water.

3.2. Electrochemical synthesis

3.2.1. *Electrochemical synthesis of Cu_2O powder*

Copper oxide powder was synthesized by electrodeposition method.[90] The schematic for the synthesis of copper oxide (Cu_2O) is shown in Figure. 3.1a. Copper oxide was prepared from the solution of 0.1 M Cu $(NO_3)_2.3H_2O$ by using electrolytic cell containing anode (copper plate), cathode (graphite plate) and a current source. Electrodeposition of copper takes place on the surface of cathode at constant current of 0.2 A for 3 min. Deposited catalyst was removed in acetone for complete dispersion. Further, catalyst solution was heated at 100 ^{o}C for 1h to obtain Cu_2O powder.

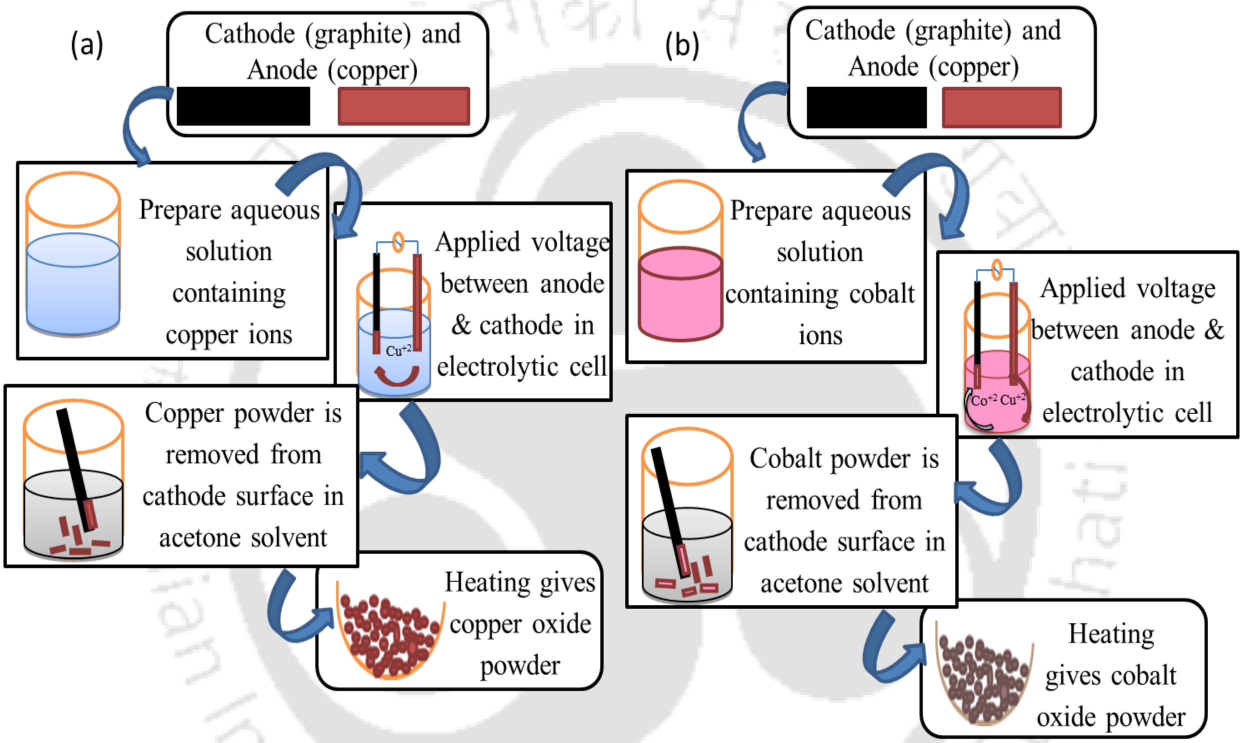

Figure 3.1 Schematic diagram for the synthesis of (a) copper oxide, and (b) cobalt oxide

3.2.2. Electrochemical synthesis of Co_3O_4 powder

Co_3O_4 powder was prepared by electrodeposition method and the schematic for the synthesis process is shown in Fig. 3.1b. The bath solution (0.1 M Co $(NO_3)_2.6H_2O$) was placed in single compartment of two electrode cell. Electrodeposition experiments were conducted using copper and graphite plates as anode and cathode, respectively. Current of 0.2 A was applied for 3 min time interval between electrodes. Removal of deposited cobalt (Co) from the surface of cathode was done using acetone. Catalyst solution was heated at 100^oC for 1h to get Co_3O_4 powder.

3.3. Characterization

Synthesized electrocatalysts were characterized by different techniques in order to find the properties of material. Cu_2O and Co_3O_4 electrocatalysts were characterized using FTIR (Fourier Transform Infrared Spectrophotometer) spectra recorded in the range of 500-4000 cm^{-1} (make: Shimadzu; model: IR Affinity-1) by crushing the sample with KBr (IR grade). XRD Analysis was done using XRD (x-ray diffractometer) by (make: Bruker; model: D8 advance) between (10^o to 80^o) 2θ. Particle size analysis of synthesized electrocatalysts was done using Delsa nano (make: Beckman coulter; model: Delsa nano C) particle size analyzer,

3.4. Electrodes preparation by coating method

Preparation of electrode starts with coating electrocatalyst on graphite plate surface using catalyst ink. The ink was prepared by adding 7.5 mg of catalyst (Cu_2O or Co_3O_4) in 200 µl nafion and mixture of iso-propyl alcohol (IPA) (1:5) and sonicated for 30 min to get complete dispersion. Dispersed solution was coated on graphite plate surface of active area 3.75 cm^2 to get loading rate of 2 mg cm^{-2} at 80^oC. Thereafter, the plate was kept for 2h in an oven at 100 ^oC to get electrode.

3.5. Reduction of CO_2 to products electrochemically (RCPE) experiments

Reduction experiments were performed at ambient temperature and pressures. Electrolyte solution was prepared using 0.5 M $KHCO_3$ (80 ml) and bubbled with CO_2 for 50 min to get saturated solution. Fig. 3.2 shows the schematic diagram of RCPE experimental setup. The immersed electrodes were connected with DC source for conducting RCPE experiments at different applied voltages to study CO_2 reduction rate on electrocatalyst. Reaction products were collected after every reaction time (0-5, 10, 15, 20 and 25 min) interval, which are analyzed using ultra-fast liquid chromatography (UFLC, shimadzu LC-20AD).

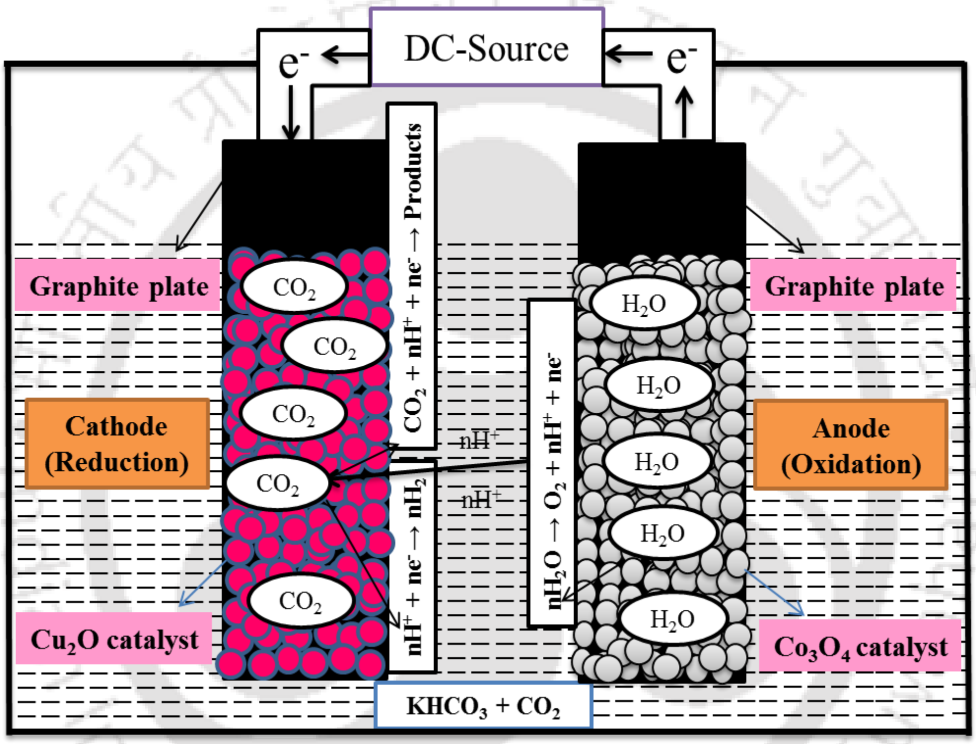

Figure 3.2 Schematic diagram of reduction of CO_2 to products electrochemically

3.6. Analysis of products from the RCPE

Ethanol was formed as major product from RCPE along with other products like methanol, formaldehyde, formic acid and acetic acid which were detected using UFLC with UV-detector of deuterium lamp (SPD-20A). A sample of 20 µl is injected through the C-18 Column (10×4 mm), mobile phase: 5 mM Tetrabutyl ammonium hydrogen sulphate, flow rate: 1 ml min^{-1}

and products are analyzed at 205 nm wavelength. Quantified products from RCPE at different time intervals and effect on time vs Faradaic efficiency of products was calculated based on charge utilized for overall reaction at different applied voltages.

3.7. Results and discussion

3.7.1. Characterization and mechanism of Cu_2O and Co_3O_4 electrocatalyst formation

FTIR spectra of synthesized electrocatalysts are shown in Figure. 3.3a. The peak around 3400 cm^{-1} corresponds to O-H stretching vibration and 1642.21 cm^{-1} coressponds to O-H bending mode which may be due to moisture content on surface of electrocatalyst.[91] Presence of band at 459 cm^{-1} and 754.16 cm^{-1} correspond to Co_3O_4[92-93] and bands at 519.12 cm^{-1} and 729 cm^{-1} represents structure of Cu_2O lattice.[94-95] XRD patterns of synthesized crystalline electrocatalysts are shown in Figure. 3.3b. The diffraction peaks at 36.21°, 41.5°, 52.1°, 63.4°, and 74.3° corresponds to Cu_2O planes (111), (200), (211), (220), (311) respectively. [94-95] Peak positions at 19.2°, 32.1°, 35.2°, 38°, 59.5°, and 65.7° with respect to (111), (220), (311), (222), (511), (531) planes are matching closely to standard crystalline Co_3O_4 structure.[96,92,97] Particle size distribution of synthesized catalysts is presented in Figure. 3.3c. The particle sizes of Co_3O_4 and Cu_2O were found in the range of 130 - 350 nm and 120 - 800 nm, respectively. The distribution median size (D_{v50}) of Co_3O_4 and Cu_2O electrocatalyst particles are found to be 201 nm and 206 nm, respectively. Mechanism of Cu_2O powder formation is shown in Figure. 3.4a. Deposition of copper (Cu) on cathode surface from electrolyte solution takes place by accepting electron generated at anode (oxidation). Deposition takes place due to driving force by the newly formed Cu^{++} at anode into solution. For every one Cu^{++} deposition on cathode surface there is a formation of new copper nitrate trihydrate molecule in the solution.

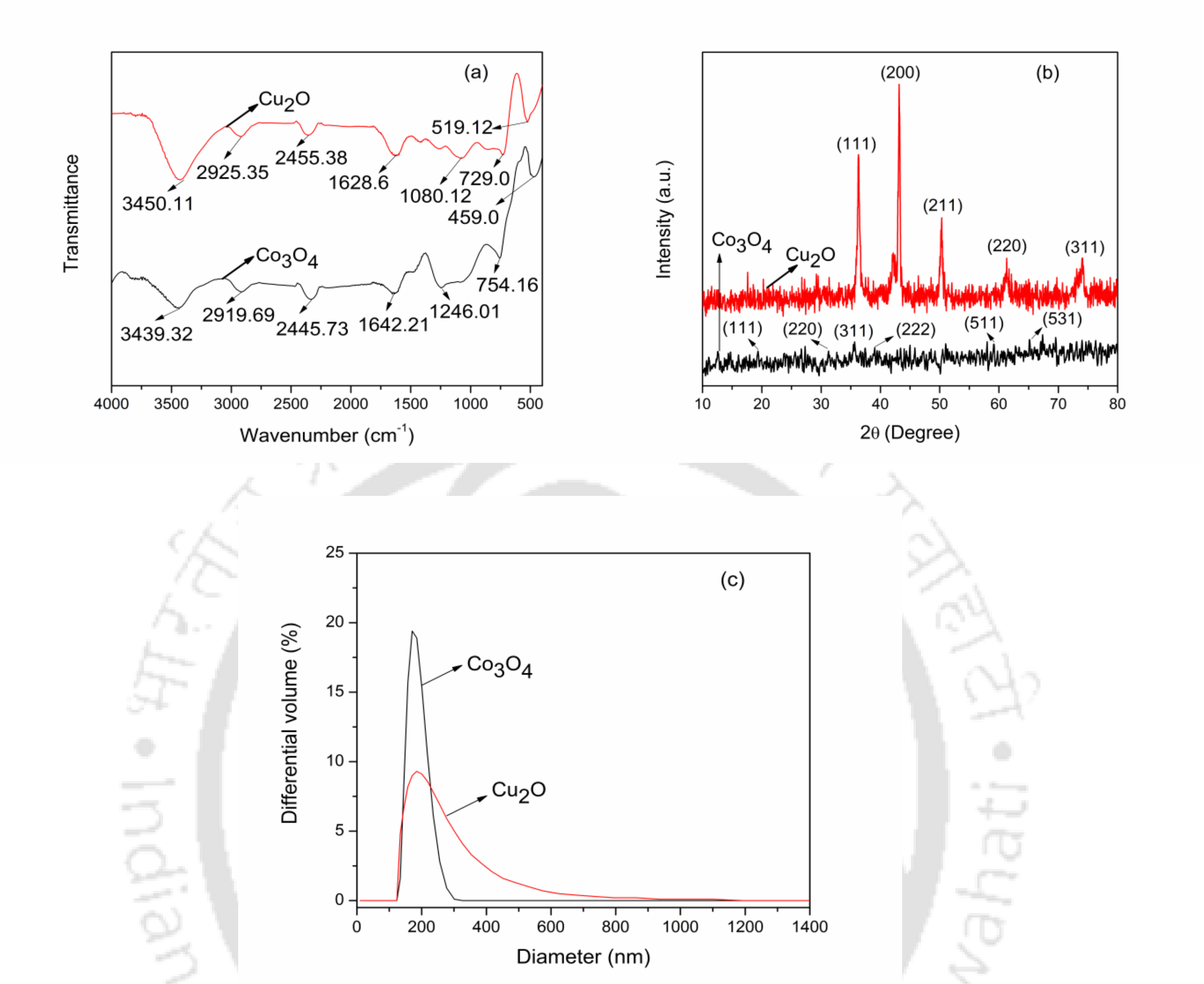

Figure 3.3 Characterization of Cu_2O and Co_3O_4 electrocatalysts, (a) FTIR, (b) XRD, and (c) particle size analysis

The deposited Cu produces Cu_2O in presence of oxygen upon heating. The formation mechanism for Co_3O_4 powder is given in Figure. 3.4b. Deposition of cobalt (Co) on cathode takes place due to the replacement of Cu^{++} that formed at anode in place of Co^{++} in solution to form new copper nitrate hexahydrate molecule. Co^{++} converts to Co (reduction) by taking electrons generated due to oxidation reaction at anode. The formed Co is heated in presence of oxygen to get Cobalt oxide (Co_3O_4) powder.

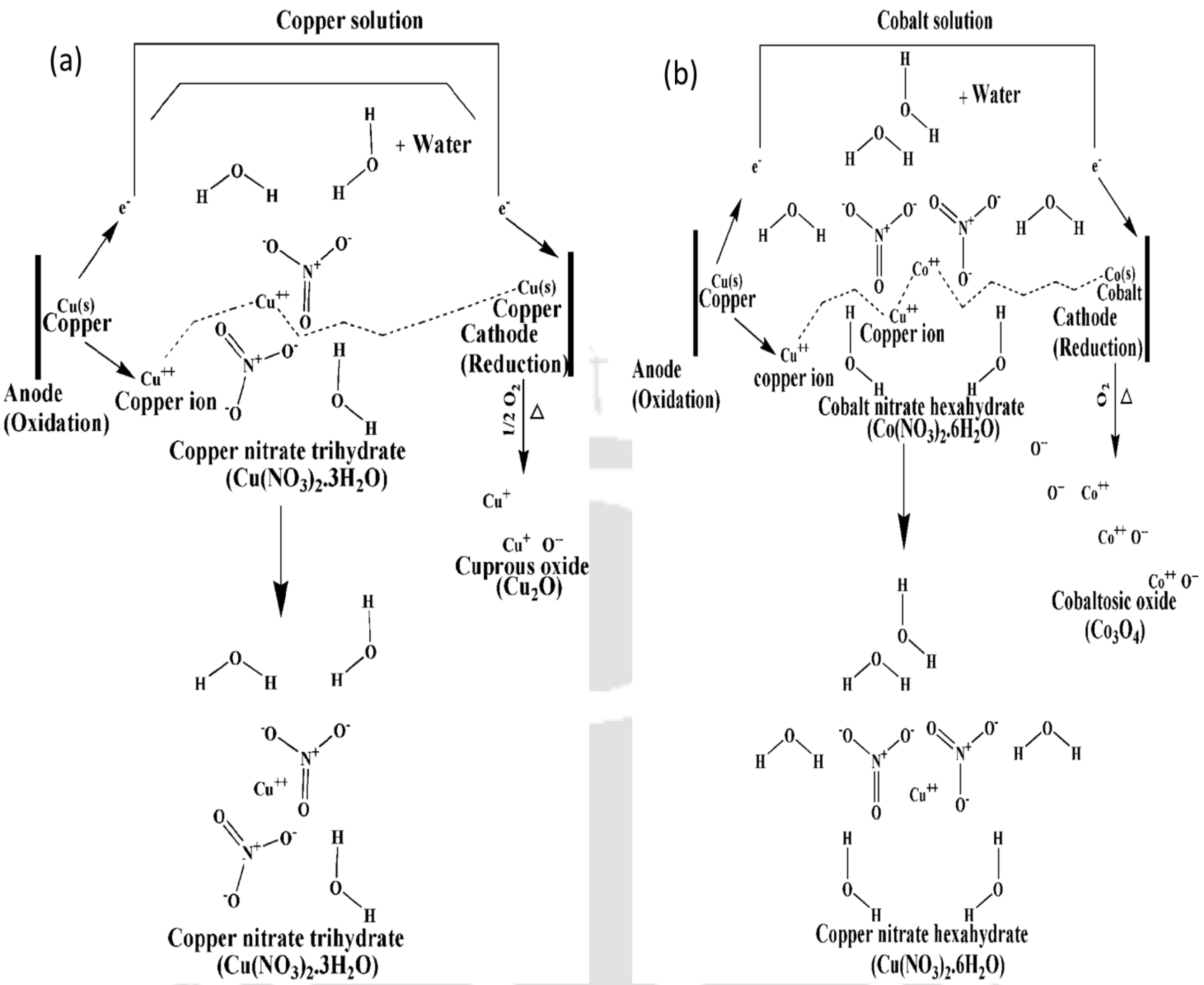

Figure 3.4 Mechanism for the formation of (a) Cu_2O and (b) Co_3O_4 electrocatalysts

3.7.2. Elementary mechanism for RCPE.

Formation of different products mainly ethanol from RCPE is given in Figure. 3.5. Mechanism illustrates the reduction of CO_2, starts with accepting electron from Cu_2O and adsorbs on it to form CO_2 free radical. Further, by accepting new electron from Cu_2O with some internal arrangements to form CO_{ads}/CO. CO so formed escapes from surface of cathode and CO_{ads} will further participate in reaction by getting electrons and protons from anode to form different products mainly ethanol.[38, 98, 99]

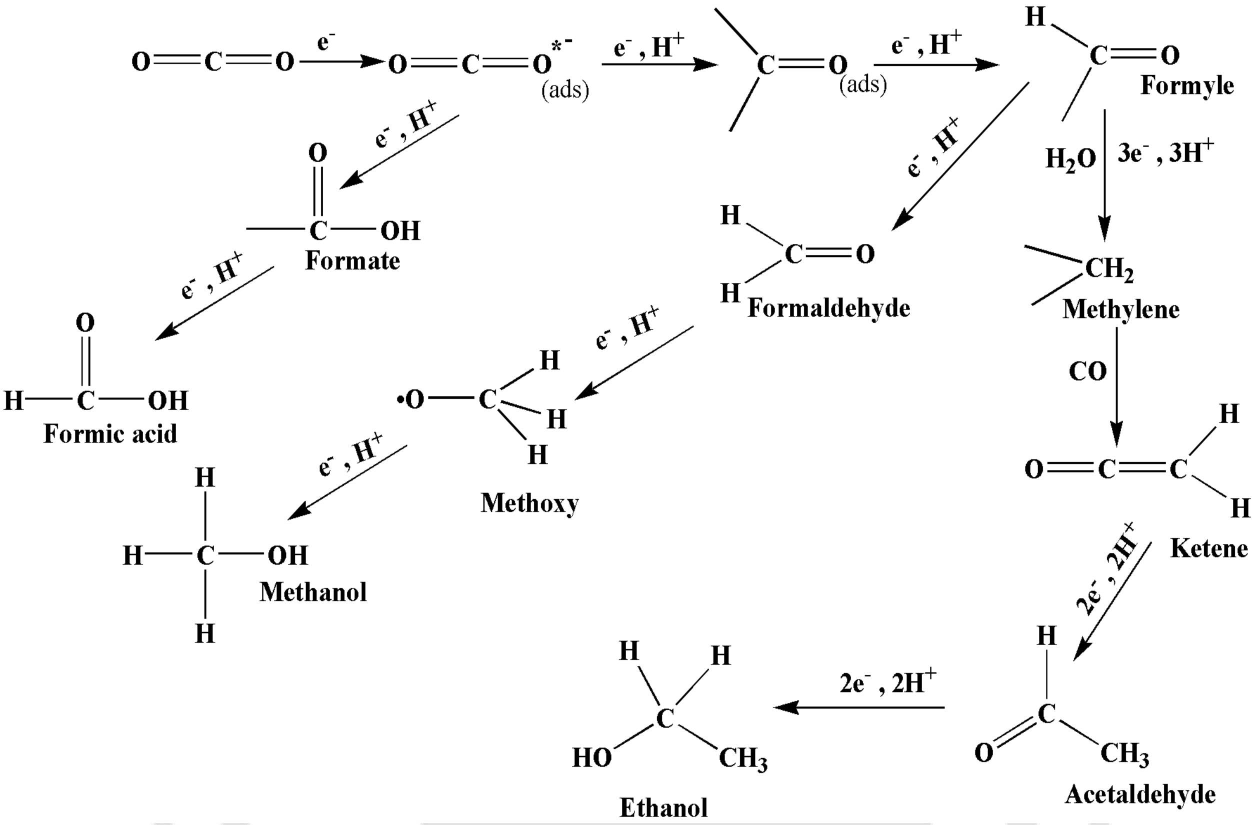

Figure 3.5 Proposed elementary mechanism for RCPE

3.8. Reduction of CO_2 to products electrochemically (RCPE).

3.8.1. Variation of Faradaic efficiency of product formed with time in $KHCO_3$ solution

Variation of current density on applied voltage is shown in Figure. 3.6a. It may be seen from the figure that current density increases gradually with increasing applied voltages. Increase in current density shows the effect of charge utilized towards CO_2 reduction or hydrogen generation at Cu_2O electrode. Current densities of 0.9, 4.5, 8.4, 9.7, and 39 mA cm^{-2} were obtained for applied voltages of 1.5, 2, 2.5, 3, 3.5 V, respectively. Sharp increase in current density at 3.5 V was observed due to hydrogen formation is competing with CO_2 reduction. However, Figure. 3.6 show that ethanol is obtained as main product in RCPE along with some low quantities of formic acid, methanol, formaldehyde, acetic acid and propanol.

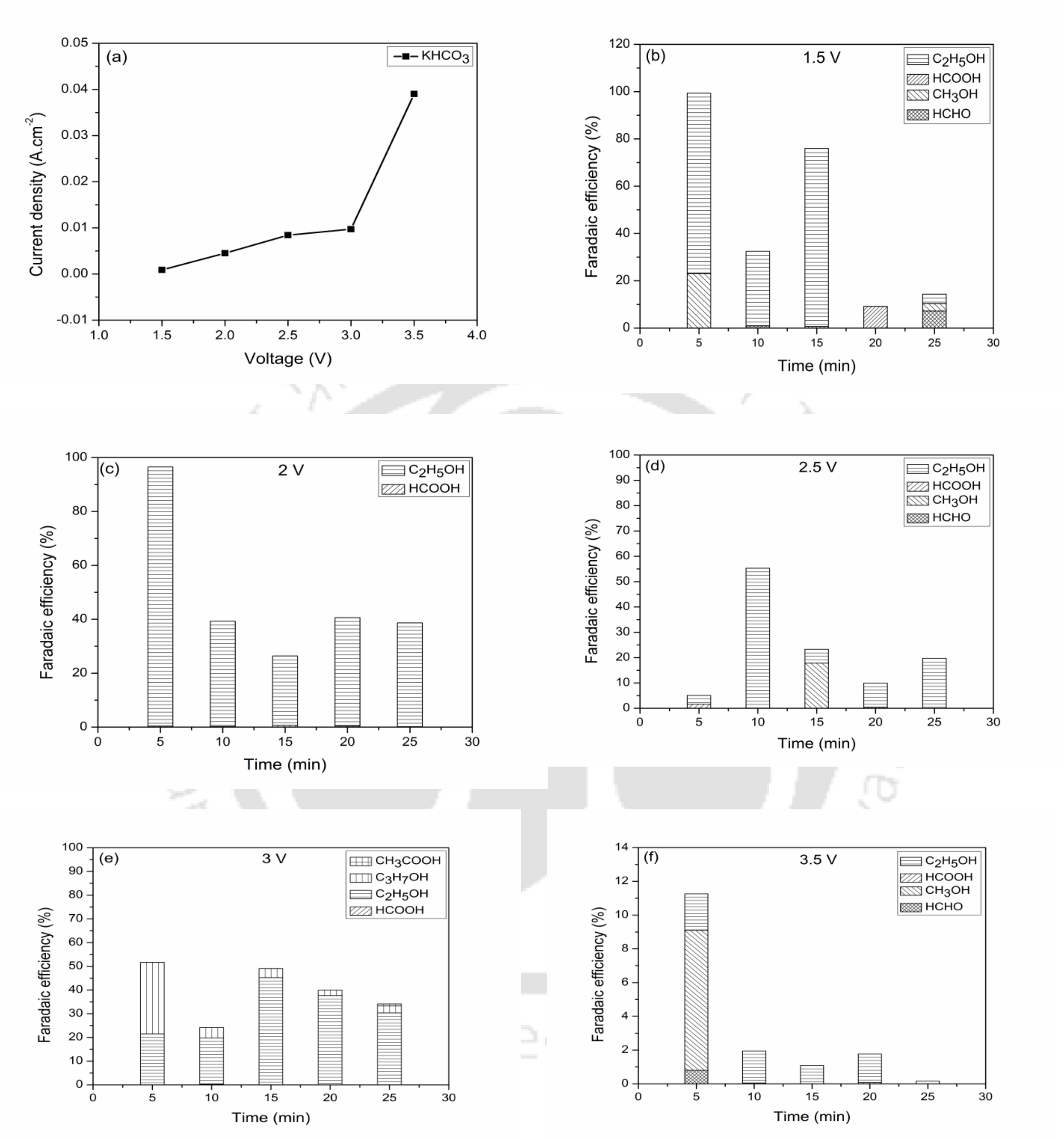

Figure 3.6 (a) Effect of voltage on the current density and (b - f) variation of Faradaic efficiencies of products formed with time at different applied voltages during of RCPE using KHCO$_3$.

It was observed that product formation and their concentrations were different at same working and experimental conditions for different applied voltages. However, Figure. 3.6 show that ethanol is obtained as main product in RCPE along with some low quantities of formic acid, methanol, formaldehyde, acetic acid and propanol. It was observed that product formation and their concentrations were different at same working and experimental conditions for different applied voltages.

Results in Figure.3.6 depict the fact that Faradaic efficiencies of products formed depend on applied voltages and reaction time. Formation of products takes place due water oxidation at anode (Co_3O_4). This gives proton which reaches Cu_2O (cathode) and react with already adsorbed CO_2 to give reduced products. Possible reactions that take place at cathode and anode are shown in Figure 3.2. Effect of Faradaic efficiency of product formation on applied potential with varying time is shown in Figure. 3.6(b-f). Higher Faradaic efficiencies denote that the maximum applied energy utilized for CO_2 conversion. At 1.5 V (Figure. 3.6b), Faradaic efficiencies of 76.31, 31.44, 75.3 and 3.93 % were observed at different reaction times of 5, 10, 15, 25 min with ethanol as product. Similar results were reported using copper catalyst in $KHCO_3$.[54,100] For formic acid at reaction times of 10, 15 and 20 min, Faradaic efficiencies were 0.08, 0.65 and 9.2 %. Interestingly, for 20 min reaction formic acid was observed as only product. Formaldehyde was observed at 10 and 25 min with efficiency of 0.92 and 7.2%, methanol was observed at 5 and 25 min reaction time with 23.1 and 3.2%. Overall, 1.5 V is most favorable voltage for the formation of ethanol. However, optimum condition to obtain ethanol at 1.5 V for 5 min reaction is 76.31% efficiency. For reaction at 2 V (Figure. 3.6c), at reaction time (5, 10, 15, 20 and 25 min) the Faradaic efficiencies for ethanol was observed as 96.15, 39.03, 2.7, 40.2 and 38.5%, respectively. Similarly, for formic acid with Faradaic efficiencies of 0.37, 0.26, 0.67, 0.4 and

0.16% were obtained. The result for ethanol Faradaic efficiency at 2 V on copper catalyst was reported as 0.1 %.[101] Overall, for the reaction at 2 V significant results were observed for ethanol with high Faradaic efficiency of 96.15% for 5 min reaction. At 2.5 V (Figure. 3.6d), Faradaic efficiencies for ethanol at reaction time (5, 10, 15, 20 and 25 min) were 3.48, 55.3, 5.48, 9.54 and 19.73%, respectively. For formic acid (5 min), methanol (15 min), formaldehyde (20 min), Faradaic efficiencies of 1.61, 17.83 and 0.42%, respectively were observed. Comparing with applied voltages of 1.5 V and 2 V, Faradaic efficiencies were less; however, ethanol was observed as product with 55.3% efficiency at reaction time of 10 min. Low efficiency of 0.1% for ethanol at 2.4 V is reported for the same experimental conditions and efficiency increased to 2.5 % in KCl solution.[101,43] At 3 V, main products were ethanol and propanol (Figure. 3.6e). Faradaic efficiencies at reaction time of 5, 10, 15, 20 and 25 min were observed as 21.4, 19.5, 45.2, 37.7 and 30.3% for ethanol and for 30.2, 4.4, 3.8, 2.3 and 2.9% for propanol, respectively. These products were reported using copper as catalyst in 0.1 M $KHCO_3$.[36] Whereas, higher Faradaic efficiencies for ethanol and propanol on copper oxide catalyst were reported.[54] Interestingly, acetic acid was formed after reaction time of 25 min with Faradaic efficiency of 0.85%. Formic acid was observed at reaction time of 10 min with 0.28% Faradaic efficiency. Higher Faradaic efficiencies of 45.2% and 30.2% were observed for ethanol and propanol at reaction time of 15 min and 5 min, respectively. At 3.5 V, for ethanol at reaction time (5, 10, 15, 20 and 25 min) with Faradaic efficiencies of 2.2, 1.9, 1.1, 1.7 and 0.16%, respectively were observed. Low efficiencies may be due to the evolution of hydrogen gas.[98] Formic acid is observed at reaction time of 10 min and 20 min with Faradaic efficiencies of 0.05% and 0.07%. Mechanism for the reduction of CO_2 to ethanol is given in Figure. 3.5. At 5 min, Faradaic efficiencies of 0.8 % and 8.3% were observed for formaldehyde and methanol (figure 3.6f).

Table 3.1 Faradaic efficiency of ethanol at different experimental conditions on Cu_2O electrocatalyst

Electrode		Electrolyte	Applied Voltage	Reaction Time	Faradaic efficiency (C_2H_5OH only)	References
Anode	Cathode		(V)	(min)	(%)	
Pt	CuO	0.2 M KI	1.5	-	34.1	[54]
		0.2 M $KHCO_3$	1.7	-	15.5	
		0.2 M $NaHCO_3$	1.7	-	18.4	
Pt	Cu	0.1 M $KHCO_3$	1.44	5	5.7	[100]
Pt	Cu	0.1 M $KHCO_3$	1.55	10	2.6	[36]
			1.37	10	14.4	
Pt	Cu	3 M KCl	2.4	30	2.6	[43]
	CuCl/Cu	3 M KCl	2.4	30	1.9	
Pt	Cu_2O	0.1 M $KHCO_3$	0.99	59	16	[23]
Co_3O_4	Cu_2O	0.5 M $KHCO_3$	1.5	5	76.3	**Present work**
			2	5	96.2	
			2.5	10	55.3	
			3	15	45.2	
			3.5	5	2.2	

A maximum Faradaic efficiency of 2.17 % for ethanol with reaction time (5 min) was obtained. The selective reduction of CO_2 to C_2H_5OH and C_2H_4 copper oxide electrocatalysts were reported in $KHCO_3$ electrolyte solution.[23] The variation in Faradaic efficiencies of product was changing with time due to oxidation of product concentration after certain time of reaction.[18] A comparison for the production of ethanol from RCPE using various electrocatalysts is shown in Table 3.1.

From the Table it may be concluded that ethanol formation is most favorable reaction with high Faradic efficiencies (>96%) for the synthesized electrocatalysts. Replacement of platinum with Co_3O_4 as anode towards RCPE resulted in significant influence towards reduction of CO_2 to ethanol as major product.

3.8.2. Variation of Faradaic efficiency of product formed with time in K_2CO_3 solution

The reduction of CO_2 is studied by using Co_3O_4, Cu_2O electrodes at different time intervals for the applied potentials in K_2CO_3 solution. Figure 3.7a shows that applied potentials are directly proportional to the current density obtained for the reaction. However, the rate of reaction depends on the current density obtained for the reaction. For 1.5, 2, 2.5, 3, 3.5 V potentials, the current densities 0.717, 5.73, 13.6, 26.5, 47.6, 89.0 mA cm^{-2} were obtained. Different products were observed based on the applied potentials and reaction time. At 1.5 V acetic acid formed at the Faradaic efficiencies in 0.89, 11.5, 25.3 and 1.2 % for the reaction time of 5, 10, 15 and 25 min. Ethanol is observed at the reaction times of 20, 25 min with efficiencies of the 40.6 and 54.5 %. Formic acid is observed in reaction times of 5, 20, 25 min with efficiencies of 24.5, 5.5, 4.6 % along with formaldehyde at 15min with 32.8 % (Figure 3.7b). The effect of CO_2 reduction using potassium based electrolyte on copper electro catalyst was reported for formation of different products.[54] However, the Faradaic efficiencies of ethanol are more observed at the reaction time 20, 25 min, along acetic acid (15 min), formaldehyde (15 min) respectively. At 2 V, mainly ethanol, formic acid and acetic acid were observed. However the Faradaic efficiencies of acetic acid for reaction time 5, 15, 20 and 25 min with efficiencies

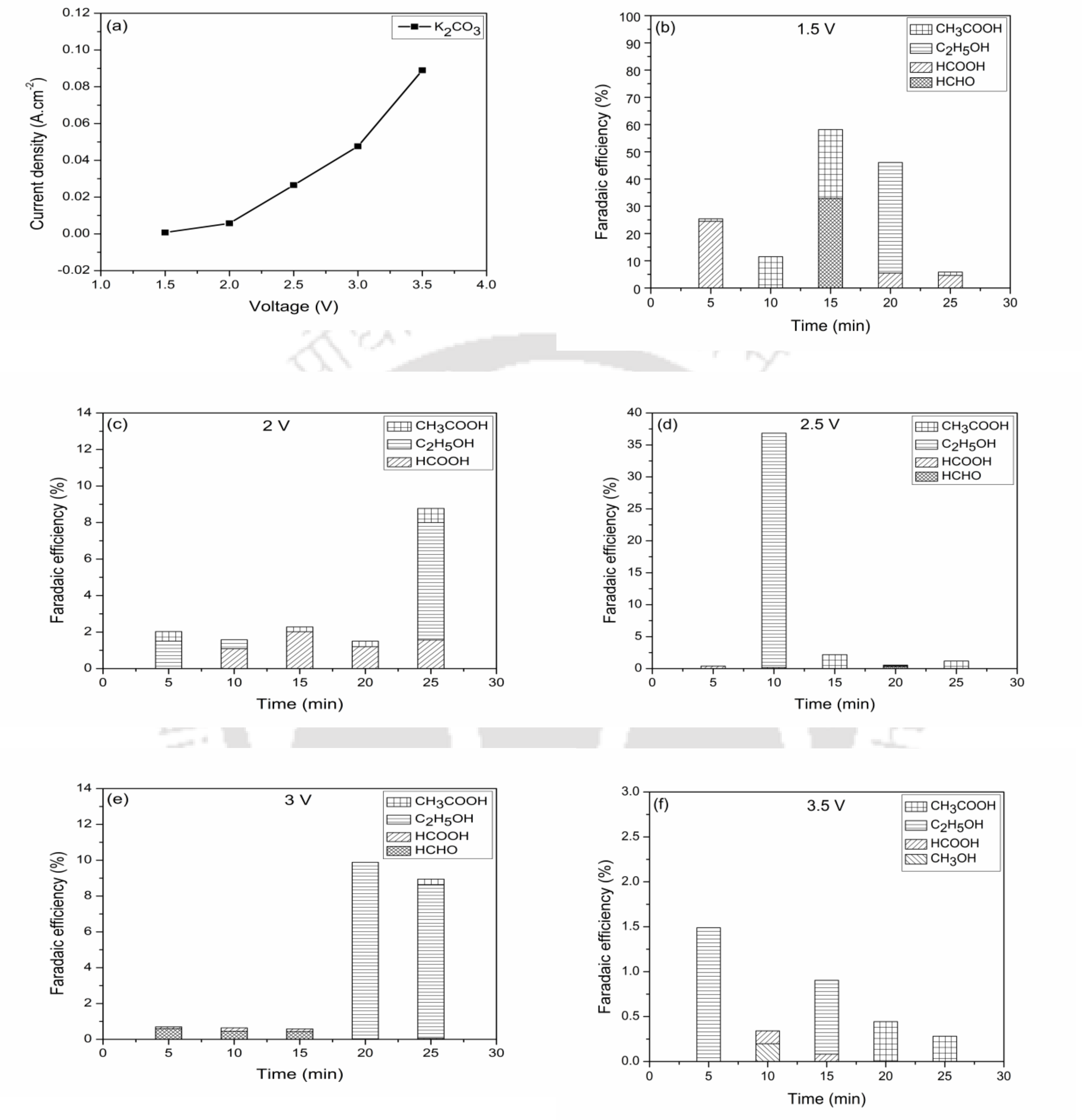

Figure 3.7 (a) Effect of voltage on the current density and (b - f) variation of Faradaic efficiencies of products formed with time at different applied voltages during of RCPE using K_2CO_3.

of 0.52, 0.26, 0.30 and 0.26 %, and formic acid, Faradaic efficiencies were 1.08, 2.01, 1.2, and 1.56 % of the reaction time of 10, 15, 20 and 25 min. Ethanol as product with efficiencies 1.5, 0.49, 6.4 % of reaction times of 5, 10, 25 min (Figure 3.7c). The Faradaic efficiency of ethanol has 6.42 % at reaction time of 25 min. mainly three products were observed here are ethanol, formic acid and acetic acid. The studies for the formation of ethanol at 2.4 V on Cu electrocatalyst was shown as 0.1% in bicarbonate based solution.[101]

The reaction at 2.5 V for RCPE shows that formic acid is formed with Faradaic efficiency in 0.39, 0.18 and 0.12 at the reaction time of 5, 10 and 20 min (Figure 3.7d). Acetic acid (15, 20, 25 min) with 2.18, 0.10 and 1.17 % along with formaldehyde as product at time 20 min with an efficiency of 0.31 %. Ethanol with high Faradaic efficiency of 36.6 % observed at the reaction time of 10 min. Low efficiencies was observed due to the oxidation of formed products at anode.[73] Comparatively low Faradaic efficiencies were observed except for ethanol with high faradaic efficiency in the reaction time of 10 min.

The RCPE observed at voltage of 3 V (Figure 3.7e), formic acid observed as product with Faradaic efficiencies of 0.09, 0.18, 0.14 and 0.05 % for reaction time 5, 10, 15, 25 min. Formaldehyde (5, 10, 15 min) give Faradaic efficiencies of 0.59, 0.45 and 0.43 % along with ethanol is observed after the reaction time of 20 and 25min with efficiencies of 9.85, 8.56 %. Slight quantity of acetic acid is observed at the efficiency of 0.32 % at reaction time of 25 %. Lower Faradaic efficiencies were observed for reaction at this voltage with ethanol is observed with high efficiencies in 9.85, 8.56 % at the reaction time of 20 and 25 min.

The reduction of CO_2 at 3.5 V (Figure 3.7f) is observed; very low Faradaic efficiencies were observed formic acid (10, 15, 20 min) with efficiencies of 0.14, 0.08, and 0.001 % were observed. Methanol is observed at reaction time 10min with faradaic efficiency of 0.19 %, ethanol (5, 15min) with 1.5, 0.82% efficiency, acetic acid (20, 25 min) with 0.44 and 0.28 % efficiency. The Low efficiencies observed at this applied voltage may be due to the formation of maximum protons at anode which converts into hydrogen gas at cathode.[98] The Faradaic efficiencies are very low when compared to other applied voltages, the formation of Products were formed based on the time of the reaction, as time proceeds new products were coming that may be due to the oxidation and reduction of formed products after certain time of the reaction.

3.8.3. Variation of Faradaic efficiency of product formed with time in $NaHCO_3$ solution

Figure 3.8 illustrates the effect of current density with applied voltages towards RCPE by electrocatalysts used. Figure 3.8a shows that current density increases with an increase in voltage which resembles rate of reaction. Various products were detected for applying voltages at different time intervals, however, ethanol was observed as main product for all applied voltages along with reasonable quantities of propanol, formic acid and methanol. Based on applied voltages (1.5, 2, 2.5, 3 and 3.5 V) respective current densities of 0.84, 3.5, 13.6, 26.5 and 56.9 mA cm^{-2} were obtained. At 1.5 V, Faradaic efficiencies of 14.8, 39.6 and 47.7 % were obtained for ethanol at reaction times 5, 15, 25 min, respectively. Formic acid (10, 15 min) 36.6 and 3.5 %, acetic acid (10, 20 min) 42.5, 32.9 %, methanol (5, 15 min) 5.3, 20.7 %, formaldehyde (20 min) 10.5 %, respectively, were obtained (Figure 3.8b). Faradaic efficiency of 47.7 % at reaction time 25 min was observed as an optimized condition for ethanol formation. Results for RCPE towards ethanol and formic acid formation were reported on copper electrocatalyst. In 0.5 M $KHCO_3$ is ethanol (2.6%) at 1.55 V (10 min) and formic acid (11.5%) was reported.[36] At 2 V, ethanol was observed as main product.

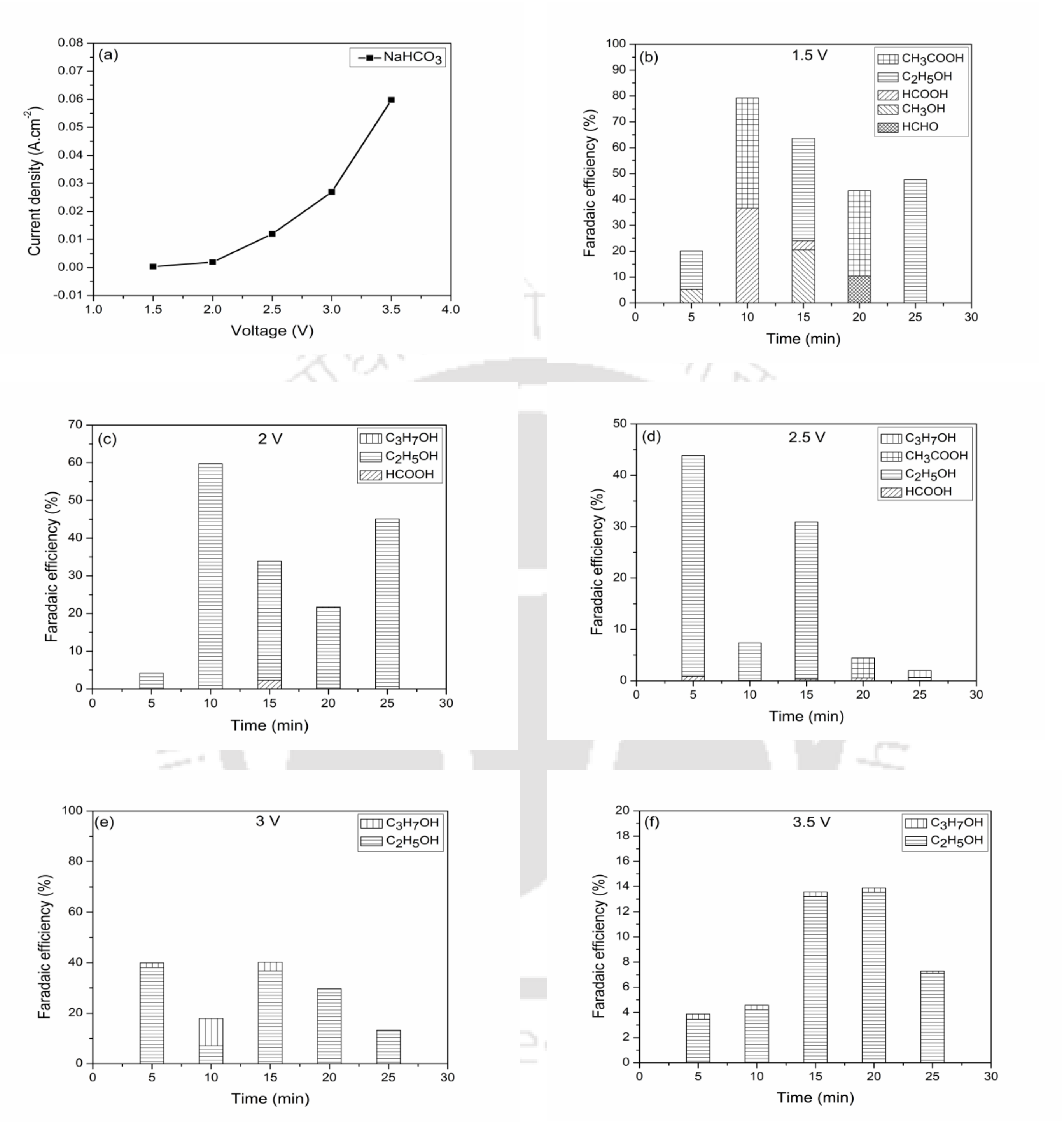

Figure 3.8 (a) Effect of voltage on the current density and (b - f) variation of Faradaic efficiencies of products formed with time at different applied voltages during of RCPE using NaHCO$_3$.

With reaction time of 5, 10, 15, 20, 25 min, Faradaic efficiencies of 4.2, 59.8, 31.6, 21.4 and 45.1 % respectively, were observed. Lower Faradaic efficiencies were observed for formic acid (15 min) 2.3%, propanol (20 min) 0.3 % of this voltage. Higher Faradaic efficiency for ethanol was obtained at reaction time of 10 min is 59.7 %, which were accepted to be an optimized condition towards reduction to CO_2 to ethanol. RCPE at 2.5 V illustrates the formation of ethanol with reaction time (5, 10, 15, 25 min) with Faradaic efficiencies of 43.1, 7.3, 30.5 and 0.59 % were observed respectively Figure 3.8d. However, lower Faradaic efficiencies of formic acid were observed at all reaction times by 0.8, 0.06, 0.34, 0.6 and 0.05 %. Other products like methanol (25 min), propanol (25 min), acetic acid (20 min) were formed with Faradaic efficiencies in 0.3, 1.3, and 3.9 %. This voltage gives the most feasible results towards ethanol formation with reasonably good efficiencies. The optimized condition for the ethanol formation was 5 min reaction time with Faradaic efficiency of 43.1 %. Chi et al., studied the reduction of CO_2 to ethanol and propanol at cuprous oxide at Pt electrocatalyst.[54] RCPE at 3 V (Figure 3.8e), ethanol and propanol, was observed as products at all reaction times with Faradaic efficiencies of ethanol (38.01, 7.1, 36.8, 29.6 and 13.1 %) and propanol (1.8, 10.9, 3.5, 0.14, 0.24 %), respectively. Ethanol formation with 38.01 % Faradaic efficiency for reaction time of 5 min, which accepted to be a most optimized condition towards ethanol formation reaction. RCPE at 3.5 V showed very low faradic efficiencies (Figure 3.8f). Ethanol and propanol were the main products observed in applying voltage. Faradaic efficiencies were observed to be 3.45, 4.2, 13.2, 13.5 and 7.1 % for ethanol, 0.2, 0.36, 0.34, 0.35, and 0.17 % for propanol. However, at these voltage maximum current densities towards RCPE was observed for low Faradaic efficiencies of product formed which may be due to high hydrogen evolution.[73]

Results of applied experimental conditions show the fact that electrocatalysts and electrolyte plays a major role in CO_2 reduction. Ethanol is observed as main product for all applied voltages along with propanol, formic acid, acetic acid and methanol. The effect of Co_3O_4 for water oxidation towards RCPE has been studied. The results clearly show the impact of electrocatalyst towards RCPE which can be used as a replacement for high cost platinum electrocatalyst with cobalt oxide. Quantities of product formed are not same with respective time interval may be due to oxidation or reduction of formed products in Figure 3.8.

3.8.4. Variation of Faradaic efficiency of product formed with time in Na_2CO_3 solution

RCPE depends on the observed current density for the applied different voltages. The effects of current density at different applied voltages in Na_2CO_3 are shown in Figure 3.9a. It may be seen from the figure that the current density increases with applied voltage. This depicted the high reaction rate. The current densities 0.456, 3.31, 18.9, 42.2 and 69.3 mA cm^{-2} were obtained for the applied voltages 1.5, 2, 2.5, 3 and 3.5 V. Different products were observed at various applied voltages and reaction time. The products observed at 1.5 V (figure 3.9b) are formic acid, ethanol and acetic acid. Ethanol is formed at reaction time of 15, 20 and 25 min with Faradaic efficiencies of 55.21, 32.1, 46.2 %, acetic acid (5, 10 min) 15.95, 53.51 %, formic acid (10, 15, 20 min) with efficiencies of 17.76, 14.13, 8.92 % were observed. At this voltage, high Faradaic efficiencies of 55.21 and 53.51 % of the reaction time of 15 and 10 min which are the optimum conditions for reduction of CO_2 with high efficiency. Hori et al., studied the CO_2 reduction to different products in aqueous phase on copper - Pt electrocatalyst.[98] The Faradaic efficiencies of the reduced CO_2 products with time at 2 V are shown in figure 3.9c. Mainly, formic acid is formed with Faradaic efficiencies of 8.44, 6.27, 5.03 and 21.14 % at 10, 15, 20,

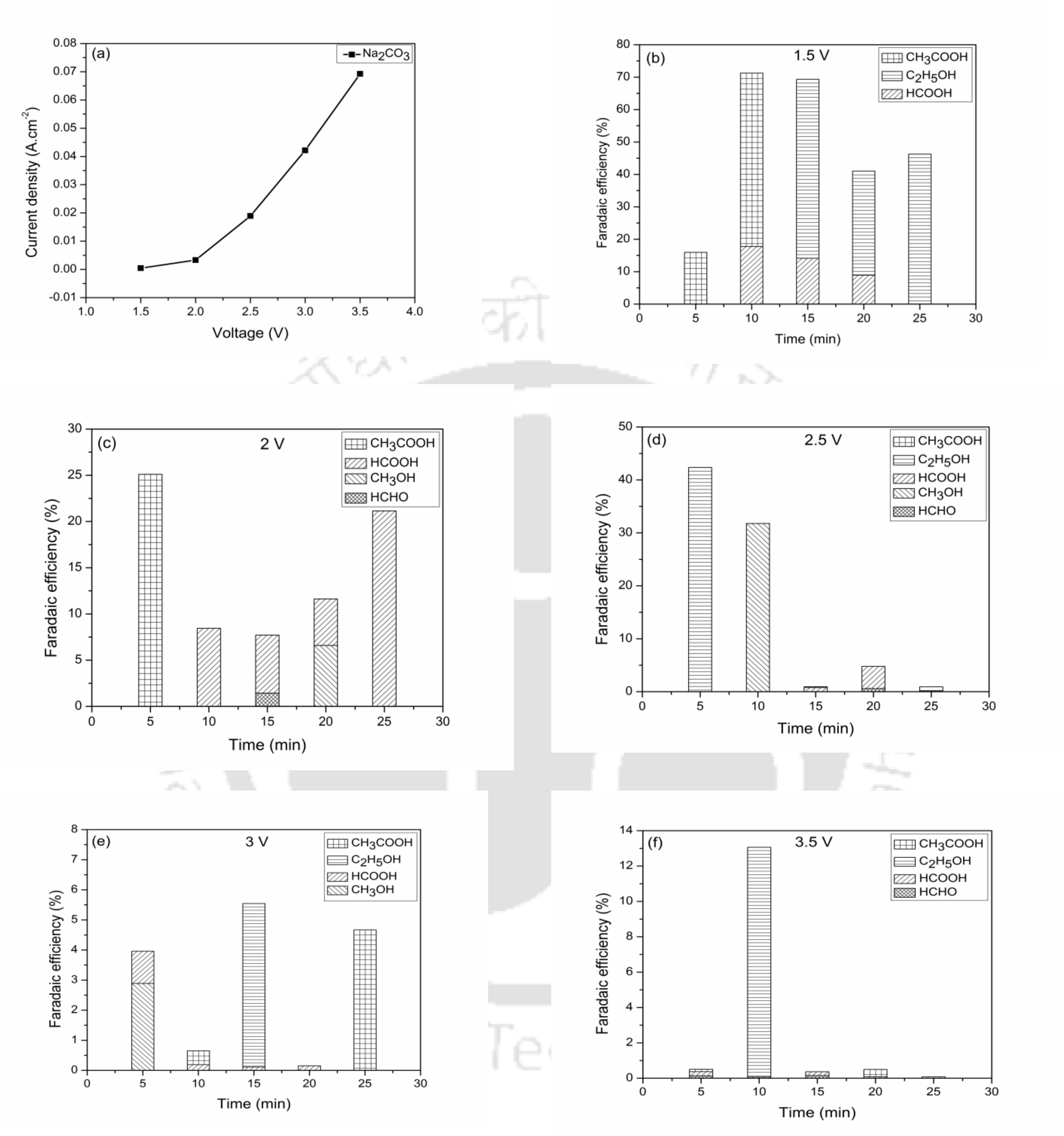

Figure 3.9 (a) Effect of voltage on the current density and (b - f) variation of Faradaic efficiencies of products formed with time at different applied voltages during of RCPE using Na_2CO_3.

25 min time of reaction, and the efficiencies of acetic acid (5 min), methanol (20 min) and formaldehyde (15 min) is 25.1, 6.59 and 1.436 %. At this applied voltage the maximum Faradaic efficiencies are observed by 21.14 % for ethanol at reaction time of 20 min and 25.1 % for formaldehyde at the reaction time of 15 min which is the optimized reaction for the reduction of CO_2. At 2.5V (figure 3.9d), different products like formaldehyde (20, 25 min) 0.59, 0.19 %, methanol (10 min) 31.76 %, formic acid (15, 20 min) 0.79, 4.18 %, ethanol (5, 25 min) 42.349, 0.736 % and acetic acid (15 min) 0.183 % Faradaic efficiencies were observed. Maximum Faradaic efficiency of 42.34 % for reaction time of 5min for ethanol and 31.76 % efficiency for methanol at reaction time of 10 min were found to be the best reaction condition. Yano et al., reported the CO_2 reduction to different products on copper-Pt electrocatalyst in acid solution and shown that the reaction at 2.4 V for ethanol to be 0.1% in 0.5 M $KHCO_3$ solution.[101] Formic acid is formed at the reaction time of 5, 10, 15 and 20 min with efficiencies of 1.07, 0.19, 0.11 and 0.15 %. For acetic acid at reaction time of 10, 25 min with 0.46, 4.66 %, ethanol (15 min) 5.43%, methanol (5 min) 2.88 % was observed. Low Faradaic efficiencies were obtained though the high current density is obtained due to the hydrogen formation favors than CO_2 reduction.[73] The effect of Faradaic efficiency with time of the reaction at 3.5 V is given in Figure 3.9f. Different products like formic acid with reaction time of 5, 10, 15, 20 min with Faradaic efficiencies of 1.07, 0.19, 0.11 and 0.15 %. Ethanol (20 min) 5.43 %, methanol (5min) 2.89 % and acetic acid (10, 25 min) with Faradaic efficiency of 0.46, 4.66 % were observed. However, the Faradaic efficiencies are very low with lower applied voltages. The results show that time of reaction also depends on the Faradaic efficiency.

The result shown in Figure 3.9 reveals the fact that formation of products depends on the applied voltage and time of reaction and respective Faradaic efficiencies with time in Figure 5.

All the products formed depends on the time of reaction, ethanol and formic acid are observed at low voltages of 1.5, 2 V. Though the reaction is happening at same voltage, the product formation is changing with time of reaction that may be due to the oxidation or reduction of forming products after the certain time of reaction due to the decrease in concentration of CO_2.

3.9. Summary

Electrocatalysts (Co_3O_4 and Cu_2O) were synthesized, characterized and used for RCPE experiments. The studies were done in potassium and sodium based electrolytes. Results depicted that ethanol as dominating product was formed at all applied voltages along with some other small quantities of products like; formic acid, formaldehyde, propanol, methanol and acetic acid. Maximum Faradaic efficiencies were obtained at low voltages compared to high voltages. However, RCPE is very much complex and its performance is dependent on catalyst selectivity, Faradaic efficiency and electrode stability. Finally, multiple product formation makes a system complex such that an alternate electrocatalyst has to be selected for reduction of CO_2 to a single product with high Faradaic efficiency and to study the effect of anode.

Chapter 4

Synthesis of Pb_2O electrocatalyst and its application towards the reduction of CO_2 electrochemically to HCOOH in various electrolytes

Chapter 4

Synthesis of Pb_2O electrocatalyst and its application towards the reduction of CO_2 electrochemically to HCOOH in various electrolytes

This chapter covers the performance of RCPE using synthesized Pb_2O as cathode and Co_3O_4 as anode towards the HCOOH formation in the presence of carbonates and bicarbonates of sodium and potassium salts. A 2-electrode system was designed to study the effect of synthesized electrocatalyst on the RCPE at different applied voltages with varying time. The influence of applied voltage and time on the performance of the process was examined and results are explained well in this chapter.

4.1. Experimental

4.1.1. Materials

Graphite plates (1.5 × 2.5 cm^2) were procured from Sunrise Enterprises, Mumbai. Sodium bicarbonate ($NaHCO_3$), potassium bicarbonate ($KHCO_3$), Sodium carbonate (Na_2CO_3), Potassium carbonate (K_2CO_3), Lead nitrate ($Pb(NO_3)_2$), Acetone (CH_3COCH_3) and Iso-propyl alcohol ($(CH_3)_2CHOH$) were procured from Merck, India. Nafion (5 wt %) solution was purchased from DuPont, USA. All the chemicals were used without any further purification and deionized water was used in all the experiments.

4.1.2. Synthesis of Pb_2O powder electrochemically

Lead oxide (Pb_2O) powder was synthesized by electrodeposition method.[102-104] The schematic for the synthesis of Pb_2O is shown in Figure 4.1. Catalyst powder was extracted from the solution of 0.1 M $Pb(NO_3)_2$ by using a current source in an electrolytic cell containing anode (lead metal plate) and cathode (graphite plate). The lead deposition takes place on the cathode surface on applying a constant current of 0.2 A for 3 min. The lead deposition takes place on the cathode surface on applying a constant current of 0.2 A for 3 min. Catalyst was removed from the graphite surface using acetone. Further, catalyst solution was heated at the 100 °C for 1h to obtain Pb_2O powder.

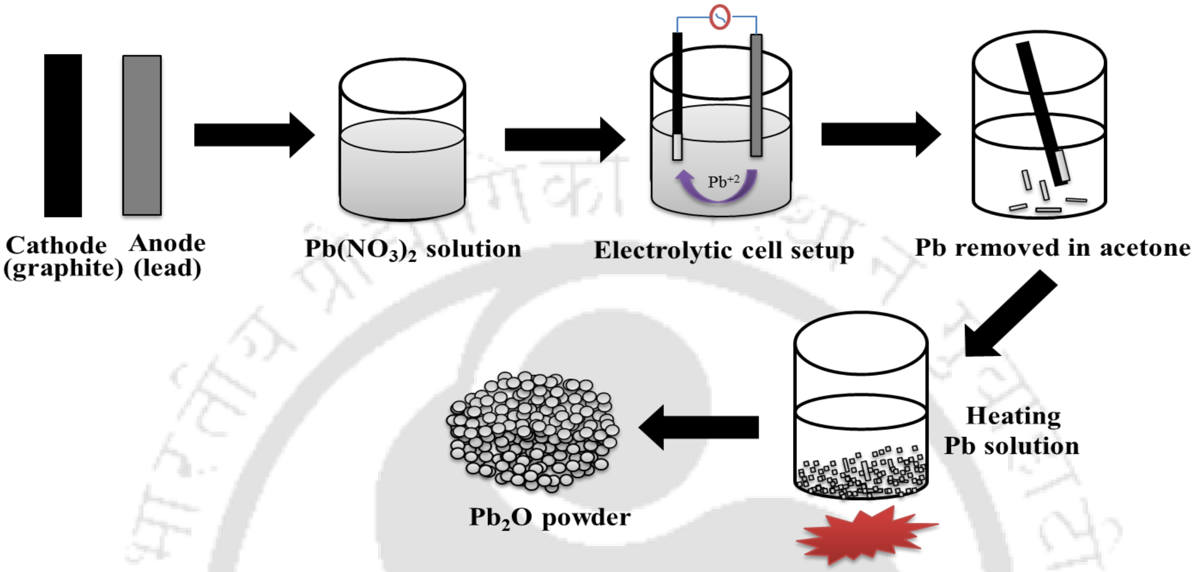

Figure 4.1. Schematic representation for the synthesis of Pb_2O powder

4.1.3. Characterization

Synthesized electrocatalyst was characterized using Fourier Transform Infrared Spectrophotometer (FTIR, make: Shimadzu; model: IR Affinity-1) recorded in the range of 500-4000 cm^{-1} by crushing the sample with KBr (IR grade). X-ray diffractometer (XRD; make: Bruker; model: D8 advance) analysis was done between 10^o to 80^o 2θ. Particle size analysis of synthesized electrocatalysts was done using Delsa nano (make: Beckman coulter; model: Delsa nano C) particle size analyzer.

4.1.4. Preparation of electrodes

Surface of graphite plates was coated with the synthesized electrocatalysts to fabricate anode (Co_3O_4) and cathode (Pb_2O) electrode. Catalyst inks was prepared by taking 200 µl of (nafion + iso propyl alcohol) solution at 1:5 ratio in which 7.5 mg of electrocatalyst was added and sonicated for 30 min. Ink was coated on graphite plates to get an active area of 2 mg cm^{-2} at 80 ^{o}C and dried for 2 h at 100 ^{o}C each to obtain fully prepared electrode.

4.1.5. Reduction of CO_2 to products electrochemically (RCPE)

Experiments in the RCPE process was performed by a two electrode system in the electrochemical glass cell. Schematic diagram of the entire process is shown in Figure 4.2.

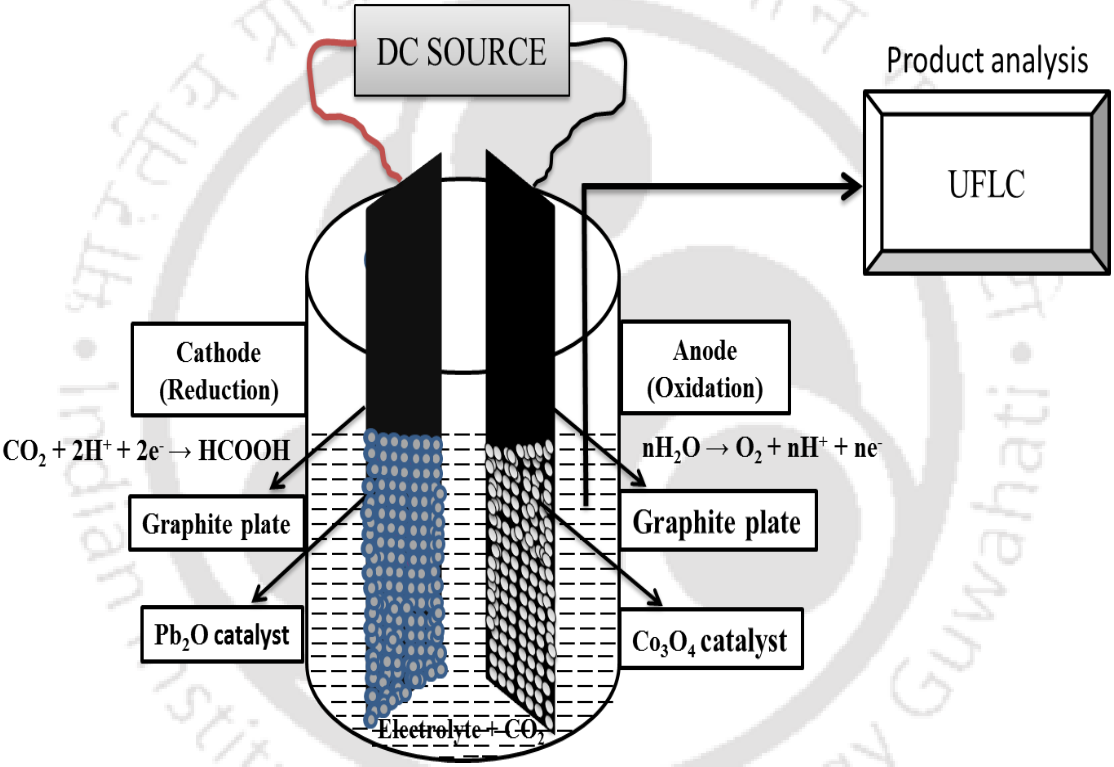

Figure 4.2. Schematic diagram of RCPE experimental setup using Pb_2O electrocatalyst

CO_2 gas was bubbled in 0.5 M electrolyte solutions ($KHCO_3$, $NaHCO_3$, K_2CO_3 and Na_2CO_3) separately, for 50 min to get CO_2 saturated solution. CO_2 was electrolytically reduced at cathode under voltage of 1.5 to 3.5 V and reaction samples were collected at fixed applied voltage for every time interval of 5, 10, 15, 20 and 25 min for analysis.

4.1.6. Products analysis from RCPE

Formic acid was observed as the only product in the present reaction for all the electrolytes considered herein. Products obtained were analyzed using ultra-fast liquid chromatography (UFLC, Shimadzu LC-20AD with UV-detector of deuterium lamp SPD-20A). Reacted solution of 20 µl was taken as source sample which was injected through C-18 Column (10 × 4 mm), mobile phase: 5 mM tetrabutyl ammonium hydrogen sulfate, flow rate: 1 ml min^{-1} at 205 nm wavelength. Faradaic efficiency was calculated using charge utilized for a particular product to the total charge utilized for the overall reaction. The formation of various products including HCOOH was confirmed by using ultrafast liquid chromatography (UFLC).

4.2. Results and discussion

4.2.1. Characterization and mechanism of Pb_2O electrocatalyst

FTIR spectrum of synthesized electrocatalyst was represented in Figure 4.3a. The broadband around 3000-3600 cm^{-1} and 1642 cm^{-1} corresponds to O-H stretching vibrations and O-H bending vibrations, respectively, which may be due to moisture content on electrocatalyst surface. Band at 1242 cm^{-1} confirms the presence of Pb_2O.[105] XRD patterns of synthesized electrocatalyst are shown in Figure 4.3b. Peak positions at 31.2^o, 36.3^o, 52.2^o, 62.1^o and 65.2^o are matched closely to Pb_2O structure.[106] Particle size distribution of synthesized catalyst is shown in Figure 4.3c. The particle size of Pb_2O was found in the range of 68 - 295 nm. The distribution median size (D_{v50}) of Pb_2O electrocatalyst particle was found to be 107 nm. A mechanism for the formation of Pb_2O electrocatalyst is shown in Figure 4.4. Lead ion from the electrolyte solution was deposited on the cathode surface by accepting electrons generated at anode (oxidation). However, driving force for the deposition was due to the newly formed Pb^{++} at anode into solution.

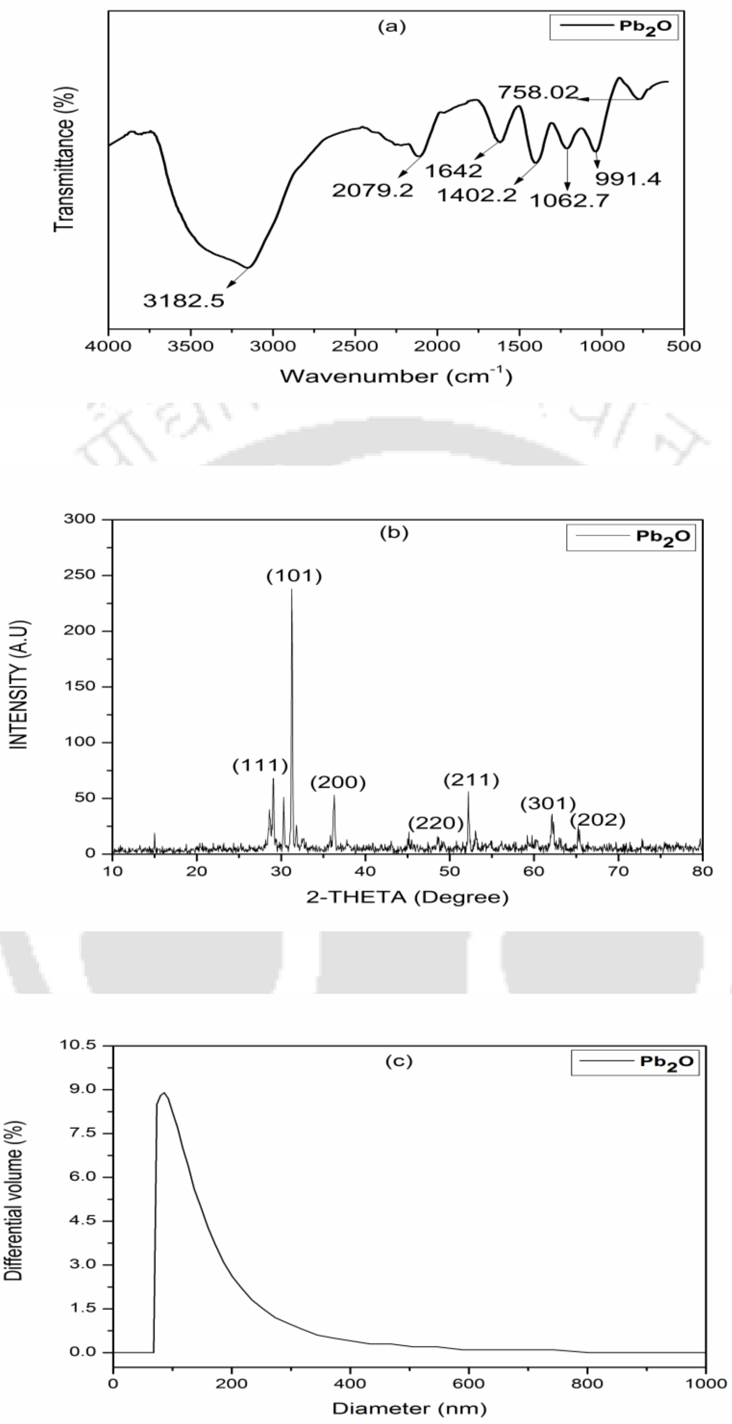

Figure 4.3. Characterization of synthesized Pb$_2$O electrocatalyst, (a) FTIR, (b) XRD, and (c) particle size analysis

Deposition is directly proportional to the formation of a new lead nitrate molecule in solution. Further, upon heating the deposited Pb in presence of oxygen gives Pb_2O electrocatalyst.

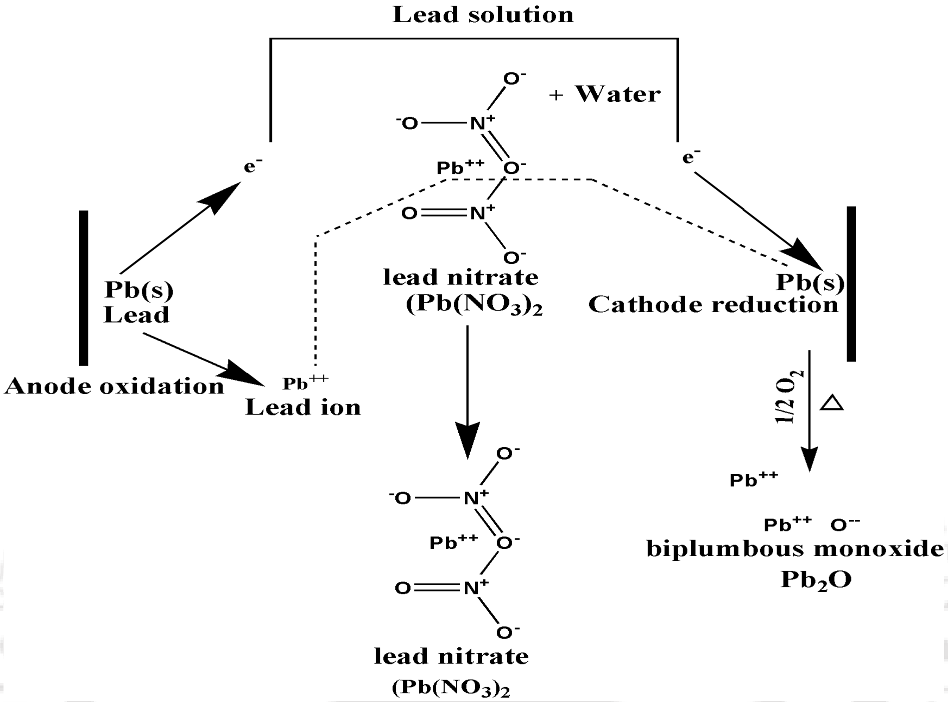

Figure 4.4. Mechanism for the formation of Pb_2O electrocatalyst

4.3. RCPE in different electrolytes solutions

4.3.1. Effect of current density on applied voltage for all the electrolytes

Experimental results for the synthesized electrocatalyst with respect to current density on applied voltage in different electrolytes were shown in Figure 4.5. It can be seen that the current density is directly proportional to applied voltages for all the cases. An increase in current density signifies high reaction rate with respect to RCPE along with hydrogen gas generation. However, Figure 4.5 shows that carbonate based electrolytes gives high current density compared with bicarbonates this confirms that the rate of reaction is more for carbonates of potassium and sodium. High current densities were observed for potassium electrolytes than sodium electrolytes. Overall, the rate of reaction towards RCPE in various experimental conditions with respect to current density depicted that reduction occurs at the surface of the cathode.

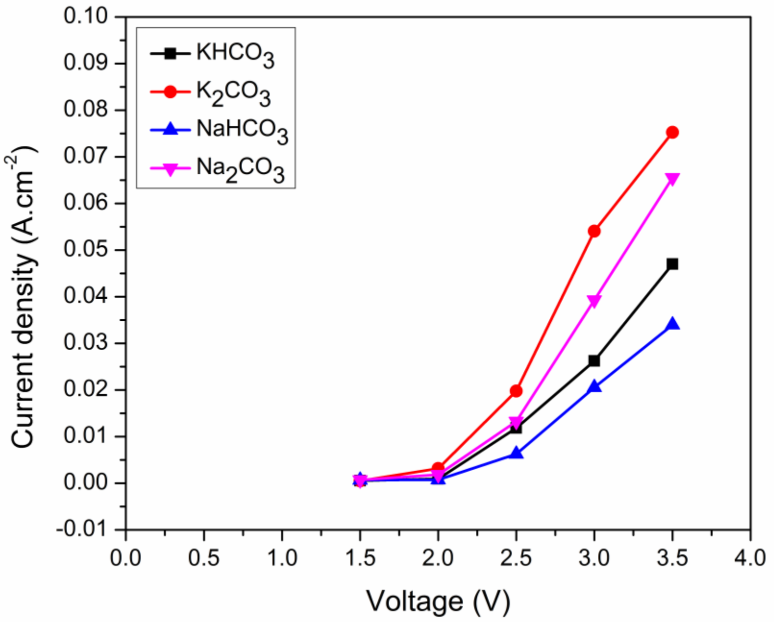

Figure 4.5. Variation of current density with applied voltage during RCPE using various electrolytes

4.3.2. Effect of time on Faradaic efficiency with respect to voltage in KHCO$_3$ solution

Hori et al., studied the effect of CO$_2$ reduction on Pb and Pt electrocatalysts as the anode and cathode in KHCO$_3$ electrolyte solution and reported formation of different products like; HCOOH, CO, CH$_4$ and H$_2$.[5] Faradaic efficiency of product was calculated with time for different applied voltages in 0.5 M KHCO$_3$ electrolyte solution and was shown in Figure 4.6. Koleli et al., studied the effect of RCPE in 0.5 M KHCO$_3$ electrolyte using Pb as anode and Pt as cathode. The only product was reported as HCOOH.[58] It may be seen from the figure that, the only product formed at all different applied voltages is HCOOH. High Faradaic efficiencies were obtained at low applied voltages of which maximum efficiencies were observed at 2 V than 1.5 V. At 1.5 V Faradaic efficiencies for HCOOH at reaction time of 5, 10, 15, 20 and 25 min were 6.54, 31.6, 37.2, 31.9 and 8.8 %, respectively.

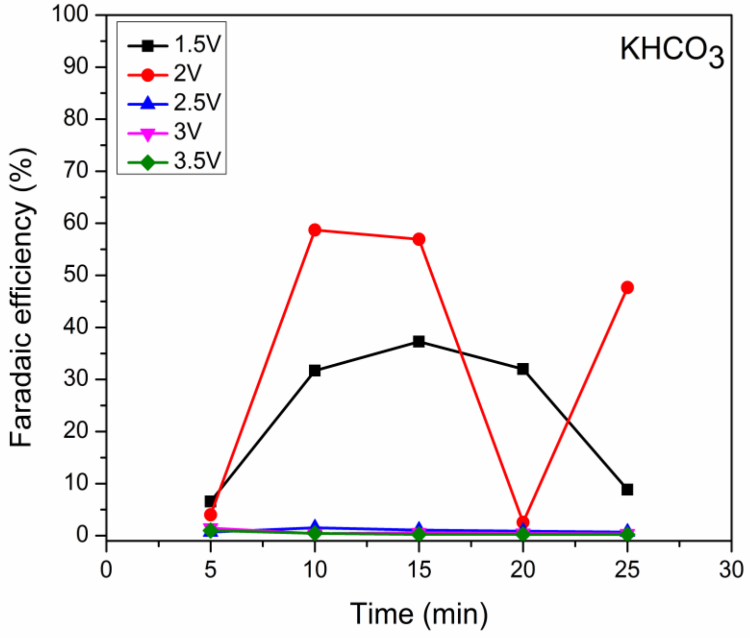

Figure 4.6. Effect of Faradaic efficiency Vs time for RCPE in $KHCO_3$ solution at different applied voltages

Overall, for reaction at 1.5 V, significant results were observed for HCOOH formation with high Faradaic efficiency of around 37 % for 15 min reaction. Reaction at 2 V, Faradaic efficiencies was obtained to be 4, 58.7, 56.9, 2.5 and 47.6 %, respectively (Figure 4.6). RCPE at 2 V shows significant results for HCOOH with high Faradaic efficiency of 58 % for 10 min reaction. Similar studies were done at 2 V using Pt, Pb as anode and cathode respectively and Faradaic efficiency of 47 % after 30 min was reported.[58] Low Faradaic efficiencies of 0.69, 1.53, 1.07, 0.87 and 0.69 % were obtained at 2.5 V compared with the above. That may be due to other side reactions especially hydrogen generation.[5] RCPE at 3 V and 3.5 V, obtained Faradaic efficiencies were 1.47, 0.39, 0.56, 0.44 and 0.34 % and 0.98, 0.46, 0.25, 0.23 and 0.21 % respectively, though current densities are high at this voltage (Figure 4.5). RCPE signifies that HCOOH is formed in all conditions, but high efficiencies were observed at 1.5 V (15 min) and 2 V (10 min) which are the most optimized applied voltages towards HCOOH formation. However, from the above results synthesized electrocatalyst (Pb_2O) was able to reduce CO_2 to HCOOH using Co_3O_4 as an anode.

4.3.3. Effect of time on Faradaic efficiency with respect to voltage in K_2CO_3 solution.

Koleli et al., reported the formation of formic acid using Pb as a cathode Pt as anode catalyst in 0.1 M K_2CO_3 solution and it was reported that HCOOH formation rates changes with respect to time.[58] Figure 4.7 shows the effect of Faradaic efficiency towards HCOOH formation with time for applied voltages in 0.5M K_2CO_3 electrolyte solution. Significant results were obtained towards RCPE at low applied voltages, particularly at 2 V than 1.5 V. Faradaic efficiencies for HCOOH at 1.5 V with reaction time of 5, 10, 15, 20 and 25 min were 2.04, 9.05, 14.8, 16 and 21.1%, respectively. Optimized reaction condition at this potential was 21% for 25 min reaction. HCOOH is the only product observed at 2 V and its Faradaic efficiencies were 12.56, 6.8, 5.1, 3.36 and 3.28 %. Faradaic efficiency of around 13 % for 5 min reaction was observed as an optimized reaction at this particular applied voltage. Faradaic efficiencies of 3.71, 1.23, 0.23, 0.66 and 0.54 % were observed at 2.5 V. However, low efficiencies were observed compared with above applied voltages though high current densities (Figure 4.5). At 3 V and 3.5 V, very low Faradaic efficiencies were obtained for 5, 10, 15, 20 and 25 min reaction are (1.03, 0.49, 0.33, 0.26 and 0.18 %) and (0.79, 0.39, 0.25, 0.18 and 0.14 %) respectively.

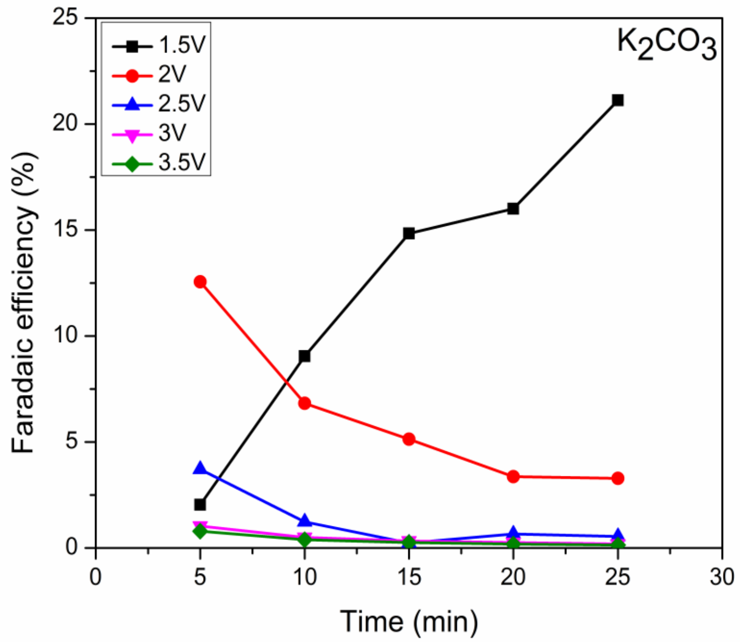

Figure 4.7. Effect of Faradaic efficiency Vs time for RCPE in K_2CO_3 solution at different applied voltages

RCPE studies show that HCOOH is formed in all experimental conditions, but low efficiencies were observed when compared to $KHCO_3$ electrolyte solution (Figure 4.6) though obtained current densities were high. This may be due to the fact that the hydrogen evolution is more competing with CO_2 reduction.[5] It is discussed in the preceding section (Figure. 4.2) that the reduction of CO_2 and hydrogen evolution is taking place simultaneously in cathode. In both the reaction protons (H+) are required that are generated at anode. Bicarbonates shows high Faradaic efficiencies (~60 %) at lower current density (5 mA/cm^2 in Figures. 4.5, 4.6) confirms that maximum H^+ were utilized for CO_2 reduction than that of carbonates. At high current density (9 mA/cm^2), lower Faradaic efficiency (~13 %) were observed (Figure. 4.5, 4.7). This was because of the fact that the H^+ were utilized towards hydrogen evolution reaction. Results depicted that the performance of reduction of CO_2 to HCOOH in carbonate based solutions is promising.

4.3.4. Effect of time on Faradaic efficiency with respect to voltage in $NaHCO_3$ solution.

Reduction of CO_2 using bicarbonate based electrolytes was reported using Pb and Pt as cathode and anode catalysts.[5,58] The variation of Faradaic efficiency in HCOOH formation with different applied voltages in 0.5 M $NaHCO_3$ electrolyte solution for the present case is shown in Figure 4.8. Competent results were obtained at low applied voltages. HCOOH is the only product at all applied voltages with 5, 10, 15, 20 and 25 min reaction. Faradaic efficiencies of around 17, 11, 13, 12 and 10 % at 1.5 V respectively, were obtained.

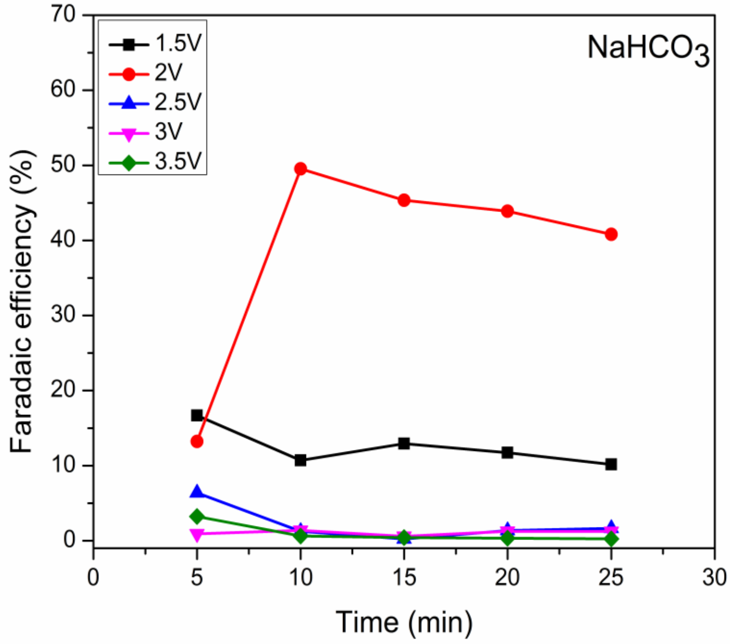

Figure 4.8. Effect of Faradaic efficiency Vs time for RCPE in $NaHCO_3$ solution at different applied voltages

However, maximum Faradaic efficiency of 17 % for 5 min reaction is observed as finest condition towards RCPE. Higher Faradaic efficiencies were obtained to be 13, 50, 46, 44 and 41 % for RCPE at 2 V. The reduction of CO_2 at 2.1 V in bicarbonate based solution using Pt, Pb as electrodes were reported with 45 % Faradaic efficiency.[58] This potential reduces CO_2 with high faradaic efficiency in these experimental conditions. For reaction at 2.5 V, low efficiencies were observed to be around 6, 1.2, 0.22, 1.34 and 1.6 % (Figure 4.8). Low efficiencies were observed, though high current density was obtained that may be due to hydrogen generation favors the reaction (Figure 4.5). RCPE at 3 V and 3.5 V towards HCOOH Faradaic efficiencies were observed as (0.91, 1.37, 0.58, 1.25 and 1.22 %) and (3.23, 0.61, 0.41, 0.33 and 0.25 %), respectively. Reduction of CO_2 to HCOOH was taking place at all the applied voltages considered herein and maximum efficiency was observed at 2 V. The Faradaic efficiencies were observed to be inversely proportional to applied voltage for a given experimental conditions. However, the reduction of CO_2 to HCOOH at lead, tin and indium electrocatalyst were studied in various aqueous, acid medium.[107] RCPE using electrocatalysts in sodium based salts shows good results towards HCOOH formation.

4.3.5. Effect of time on Faradaic efficiency with respect to voltage in Na_2CO_3 solution.

Reduction of CO_2 in 0.5 M Na_2CO_3 solution towards HCOOH formation is shown in Figure 4.9. The reduction of CO_2 to formic acid using Pb catalyst in carbonate based solution was reported.[58] Results show that HCOOH is formed at all applied conditions as above and respective Faradaic efficiencies in 5, 10, 15, 20 and 25 min reaction was clearly shown. Low Faradaic efficiencies with $NaHCO_3$ (Figure 4.8) were observed though high current densities were obtained, but Low applied voltages favors towards high Faradaic efficiency in RCPE. Faradaic efficiencies of around 15, 21, 18, 17 and 16 % were obtained at 1.5 V. However, the optimized condition for RCPE at this potential is 21 % for 10 min reaction. At 2 V, Faradaic efficiencies of around 19, 9, 7, 13 and 19 % were observed (Figure 4.9). RCPE at 2.1 V in carbonate based solution using Pt, Pb as electrodes were reported with 27.1 % efficiency for 30 min reaction.[58]

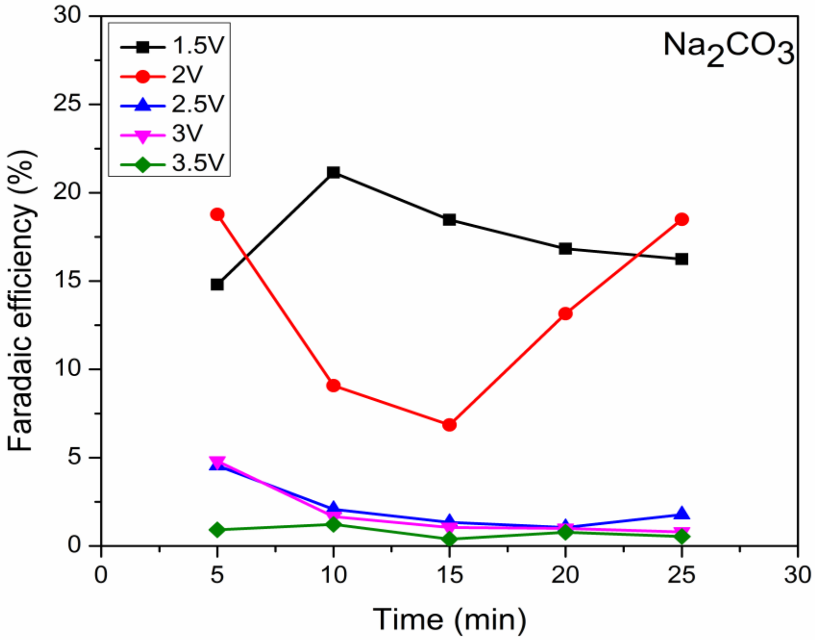

Figure 4.9. Effect of Faradaic efficiency Vs time for RCPE in Na_2CO_3 solution at different applied voltages

It was observed that at these two applied voltages efficiencies were less with reaction in $NaHCO_3$. Similar efficiencies were obtained at 2.5 V (4.54, 2.07, 1.33, 1.04 and 1.78 %) and 3 V (4.80, 1.66, 1.04, 0.99 and 0.78 %), respectively. Low Faradaic efficiencies of 0.91, 1.22, 0.38, 0.77 and 0.53 % were obtained at 3.5 V compared with above applied voltages which may be due to high hydrogen evolution at the cathode surface.[5] The reduction of CO_2 forms HCOOH as a single product at all applied voltages and maximum efficiencies were observed at 1.5 V and 2 V which are the most optimum applied voltage towards RCPE.

A comparison of the maximum Faradaic efficiency of HCOOH with time from RCPE using various electrolytes is shown in Table 1. From the Table it may be concluded that HCOOH formation is most favorable reaction for synthesized electrocatalyst. Optimized experimental conditions to get high HCOOH Faradaic efficiency in RCPE have shown with respect to the applied voltage. However, maximum Faradaic efficiencies were obtained for bicarbonates than carbonate electrolyte solutions.

A mechanism for the formation of HCOOH by CO_2 reduction on Pb_2O electrocatalyst is shown in Figure 4.10. It starts with accepting electron from Pb_2O and adsorbs on it to form CO_2 radical anion. Further, formation of formate starts with water molecule which may protonate the formed radical anion to form neutral radical. Thus neutral radical accepts new electron with some internal arrangements to form formate. The formate takes H^+ to form HCOOH.[106]

Table 4.1 Maximum Faradaic efficiency of HCOOH obtained at different experimental conditions

Applied Voltage	**Maximum Faradaic efficiency (Time)**							
	$KHCO_3$		**K_2CO_3**		**$NaHCO_3$**		**Na_2CO_3**	
(V)	**(%)**	**(min)**	**(%)**	**(min)**	**(%)**	**(min)**	**(%)**	**(min)**
1.5	37.27	15	21.11	25	16.68	5	21.13	10
2	58.71	10	12.56	5	49.52	10	18.79	5
2.5	1.53	10	3.71	5	6.37	5	4.54	5
3	1.47	5	1.03	5	1.37	5	4.8	5
3.5	0.98	5	0.79	5	3.23	5	1.22	10

Finally, this study describes the electrochemical reduction of CO_2 to get formic acid. The investigation is on experimental phase and environmental assessment studies of the impacts that the electrochemical conversion of CO_2 to formic acid produces is required. Although, RCPE is efficiently used to produce formic acid is an attractive process from the environmental point of view, but it is ambiguous that this makes up for the higher energy consumption.

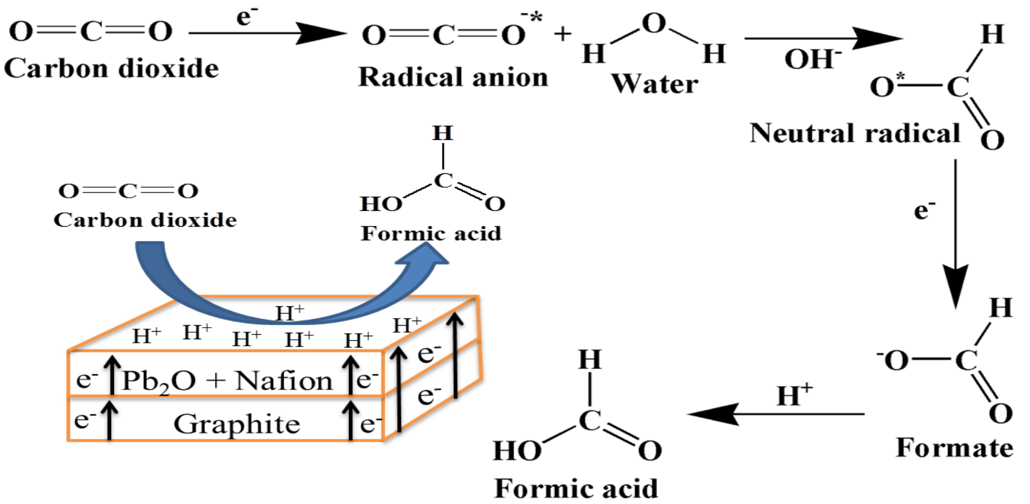

Figure 4.10. Proposed elementary mechanism for HCOOH formation from RCPE

4.4. Summary

Pb_2O and Co_3O_4 were synthesized to achieve enhanced RCPE performance. The effect of electrocatalyst towards CO_2 reduction was studied in presence of carbonates and bicarbonates of sodium and potassium electrolyte solutions. Results showed that only HCOOH was formed at all applied voltages. Maximum Faradaic efficiencies towards HCOOH were obtained for bicarbonate than carbonate solutions at low applied voltages. This preliminary investigation will be helpful to improve RCPE towards high Faradic efficiency and electrode stability for future applications.

Chapter 5

Electrochemical reduction of CO_2 to HCOOH using Zinc and Cobalt oxide as electrocatalysts

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Electrochemical reduction of CO_2 to HCOOH using Zinc and Cobalt oxide as electrocatalysts

This chapter covers the procedure for synthesis of Zinc (Zn) powder by electrodeposition method. Characterization and its applications in RCPE using various electrolyte solutions to produce single liquid product was investigated and described in details.

5.1. Experimental

5.1.1. Materials

Sodium bicarbonate ($NaHCO_3$), potassium bicarbonate ($KHCO_3$), sodium carbonate (Na_2CO_3), potassium carbonate (K_2CO_3), Zinc chloride dihydrate ($ZnCl_2.2H_2O$), Cobalt nitrate hexahydrate ($Co\ (NO_3)_2.6H_2O$), acetone (CH_3COCH_3) and iso-propyl alcohol ($(CH_3)_2CHOH$) were purchased from Merck, India. Graphite plates $(1.5 \times 2.5)\ cm^2$ were procured from (Sunrise enterprises, Mumbai). Nafion (5 wt.%) solution and DC (direct current) source were purchased from (DuPont, USA) & (Crown, India). All the chemicals were used without any further purification and deionized water was used for all the cases.

5.1.2. Synthesis of Zn powder

Zinc (Zn) powder was synthesized by electrodeposition method.[108] Synthesis for Zn powder in Figure 5.1 starts with deposition of Zn on surface of graphite plate from 0.1M $ZnCl_2.2H_2O$ solution when a constant current of 0.2 A for 3 mins was applied between the copper metal plate and graphite plate in an electrolytic cell. Further, the deposited Zn powder was removed in acetone solvent and heated at 100 ^oC for 1h to obtain Zn powder.

5.1.3. Characterization of synthesized Zn powder

Synthesized electrocatalyst was characterized by using Fourier Transform Infrared Spectrophotometer (FTIR) (make: Shimadzu; model: IR Affinity-1). The spectra were recorded in the range of 500 - 4000 cm^{-1} by crushing the electrocatalyst with KBr (IR grade). X-ray diffraction analysis was done using an X-ray diffractometer (XRD; make: Bruker; model: D8 advance) between 10^{o} to 80^{o} 2θ. Particle size analysis was done by Delsa nano (make: Beckman coulter; model: Delsa nano C) particle size analyzer.

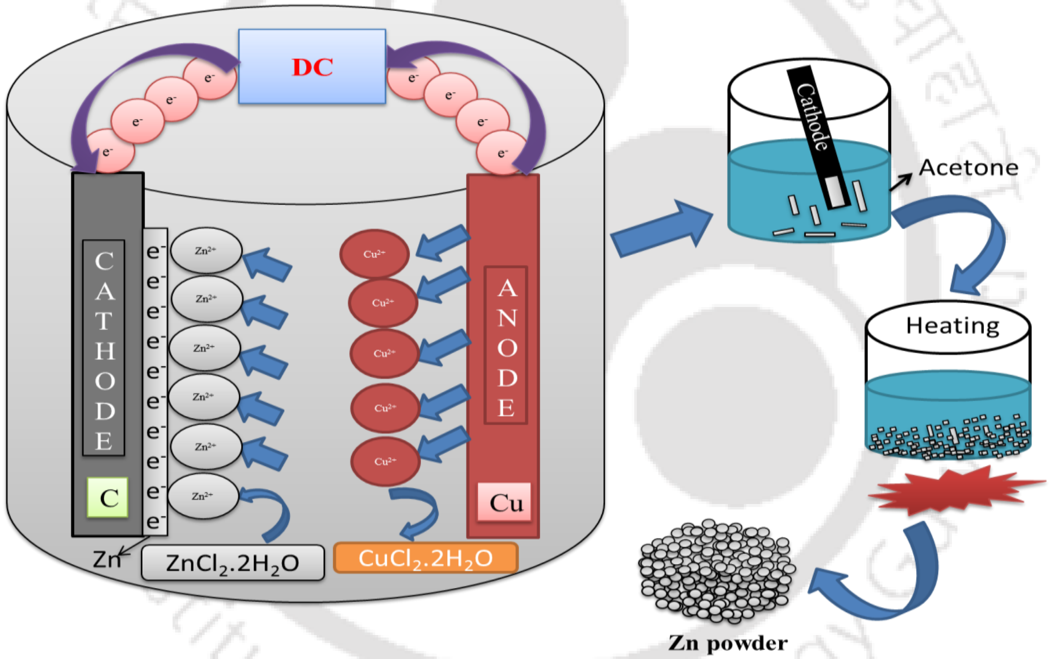

Figure 5.1. Schematic for the Zn powder synthesis by electrodeposition method

5.1.4. Preparation of anode and cathode electrodes

The cathode and anode were prepared by coating the Co_3O_4, Zn electrocatalysts on the surface of graphite plates. The binder is prepared by mixing the solutions of nafion + IPA (Iso propyl alcohol) at 1:5 ratios of 200 µl solution. To which 7.5 mg of electrocatalyst was mixed and sonicated for 30 min to form catalyst ink. Catalyst inks were coated on the active area of graphite plate at the 80 °C to get electrode of 2 mg/cm^2. Coated electrodes were dried at the 100 °C for 2h to form finished electrode.

5.1.5. Electrochemical reduction of CO_2

RCPE experiment was conducted in a two electrode glass cell. Co_3O_4 and Zn electrode was used as the anode and cathode in order to study the effect of CO_2 reduction. For all the experiments, 80 ml of 0.5M electrolyte solution was used as a base solution which was bubbled with CO_2 for 50 min to get CO_2 saturated electrolyte solution.

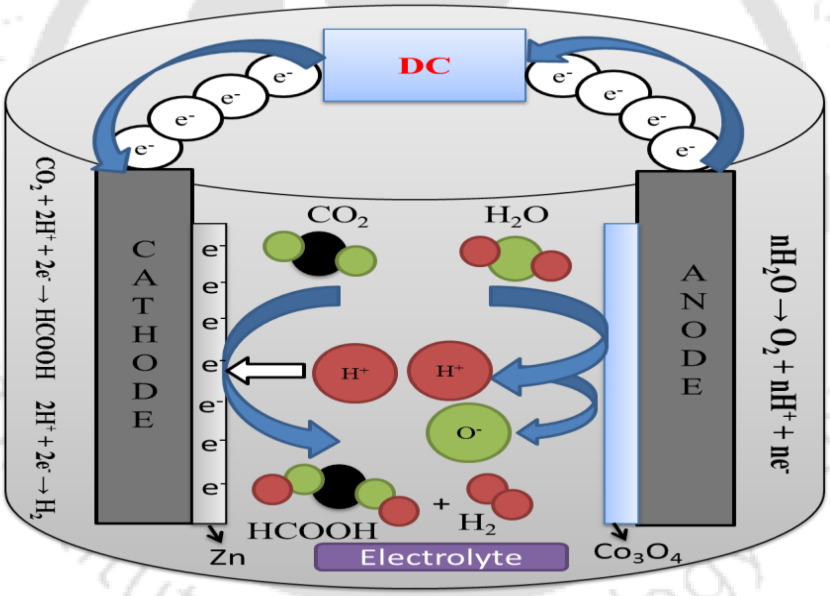

Figure 5.2. Schematic diagram for reduction of CO_2 to HCOOH on Zn electrocatalyst

Saturated solution was taken in a glass cell and experiments were conducted by connecting two electrodes to DC source as shown in figure 5.2. RCPE was done at different potentials (1.5, 2, 2.5, 3, 3.5 V) with varying reaction time (0-5, 10, 15, 20, and 25 min) using different electrolyte solutions.

5.1.6. Analysis of products

The products from CO_2 reduction were detected using ultra-fast liquid chromatography (UFLC), Shimadzu LC-20AD, UV-detector of deuterium lamp (SPD-20A) at 205 nm wave length. Solution of 20 µl was injected to the C-18 column of size (10 × 4 mm), 5 mM Tetrabutyl ammonium hydrogen sulfate was used as mobile phase at 1 ml min^{-1} flow rate. Formic acid was observed as the only product in the present reaction for all electrolytes considered herein. Faradaic efficiency was obtained by using charge utilized for the formation of a particular product to total charge utilized for the reaction.

5.2. Results and discussion

The Zn electrocatalysts were synthesized by using electrodeposition technique in order to study the effect of RCPE. Experimental results for Zn and Co_3O_4 electrocatalysts on RCPE were discussed in subsequent sections.

5.2.1. Characterization of Zn electrocatalyst and its formation mechanism

FTIR spectrum of Zn catalyst is shown in figure 5.3. The broadband around 3000 - 3500 cm^{-1} and 1616 cm^{-1} corresponds to O-H stretching vibrations and O-H bending vibrations which may be due to moisture content on electrocatalyst surface. Other peaks at 1390 and 1121 cm^{-1} correspond to C-OH in-off and out-off bending modes, respectively. Band at 624 cm^{-1} confirms the presence of Zn.[109] XRD pattern of Zn catalyst is shown in figure 5.3. Peak positions at 36.15°, 38.85°, 43.15°, 54.25°, 67.95, 70.5 and 76.9° are matching closely with Zn structure.[110] Particle size distribution of Zn is represented in figure 5.3. Particle size was found in the range of 178 - 454 nm, respectively. The distribution median size (D_{v50}) of Zn particles was found to be 241.1 nm.

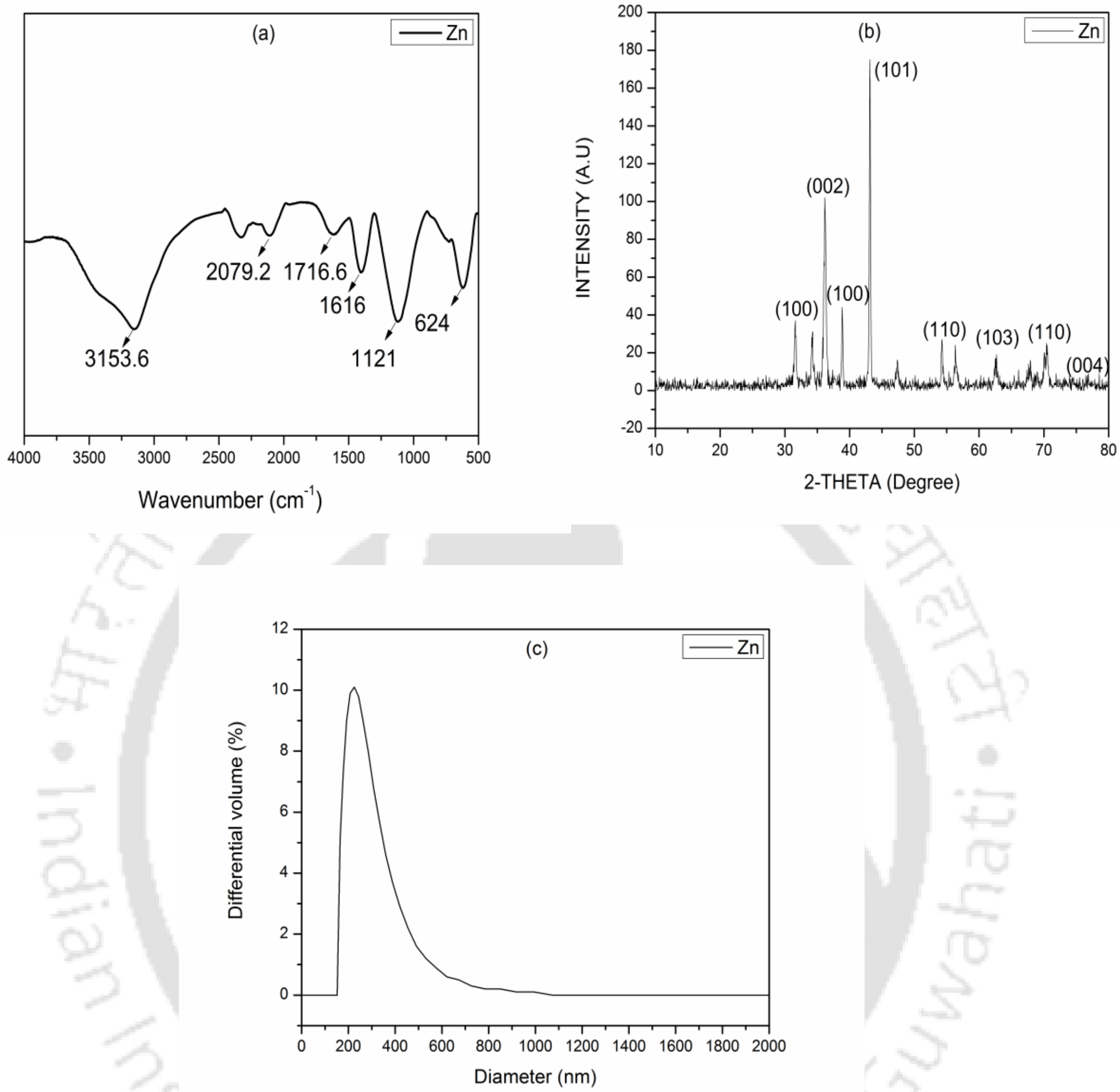

Figure 5.3. Characterization Zn electrocatalyst, (a) FTIR, (b) XRD, and (c) particle size analysis

Under the application of voltage between two electrodes as shown in figure 5.4, Zn ion from electrolyte solution was deposited on the cathode surface by accepting electrons generated at anode (oxidation). Cupric chloride molecule was formed in the solution corresponds to Zn deposition on the cathode surface. Further, upon heating the deposited electrocatalyst bestow Zn powder.

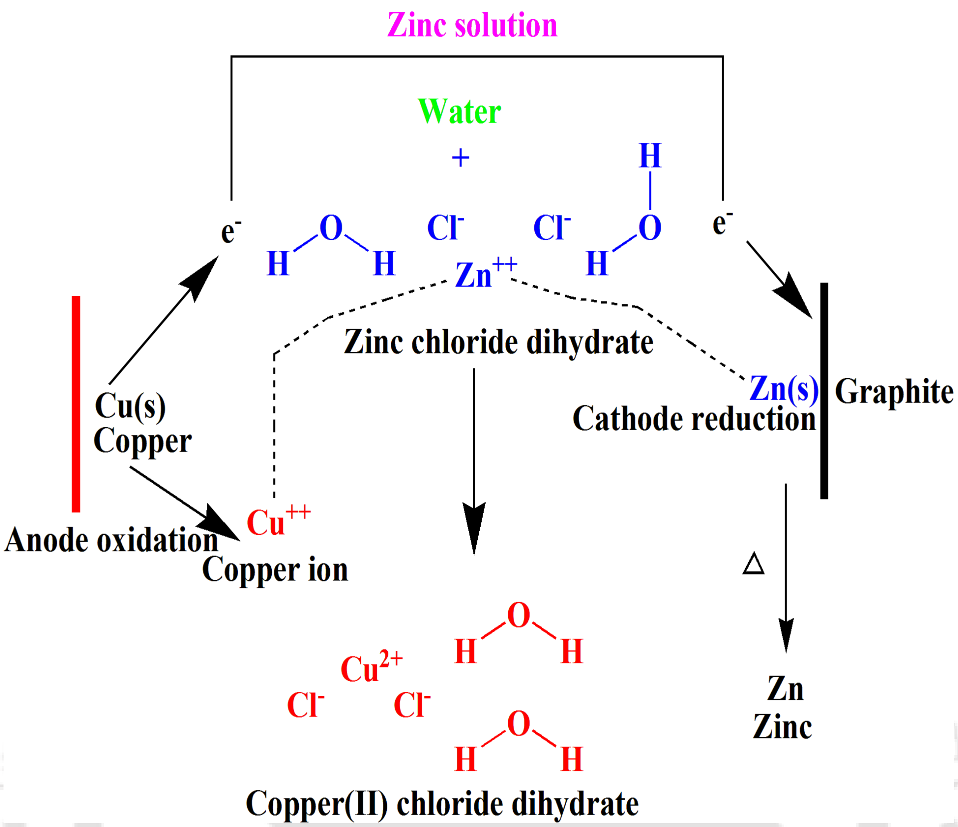

Figure 5.4. Mechanism for the Zn powder formation

5.3. Reduction CO_2 at Zn electrocatalyst

5.3.1. Variation of current density with applied voltage on Zn electrocatalyst

The experimental results shown in figure 5.5 illustrate that the applied voltage increases with the current density in all electrolyte conditions. However, carbonates show high current densities compared to respective bicarbonate electrolytes. Current density depicted the rate of reaction which signified that the increased current densities were due to high reaction rate either for CO_2 reduction or hydrogen evolution. Again, potassium electrolytes show high current densities than sodium electrolytes shown in figure 5.5. Overall, current densities for all experiments towards RCPE in various experimental conditions confirm that reaction occurs at the surface of the cathode.

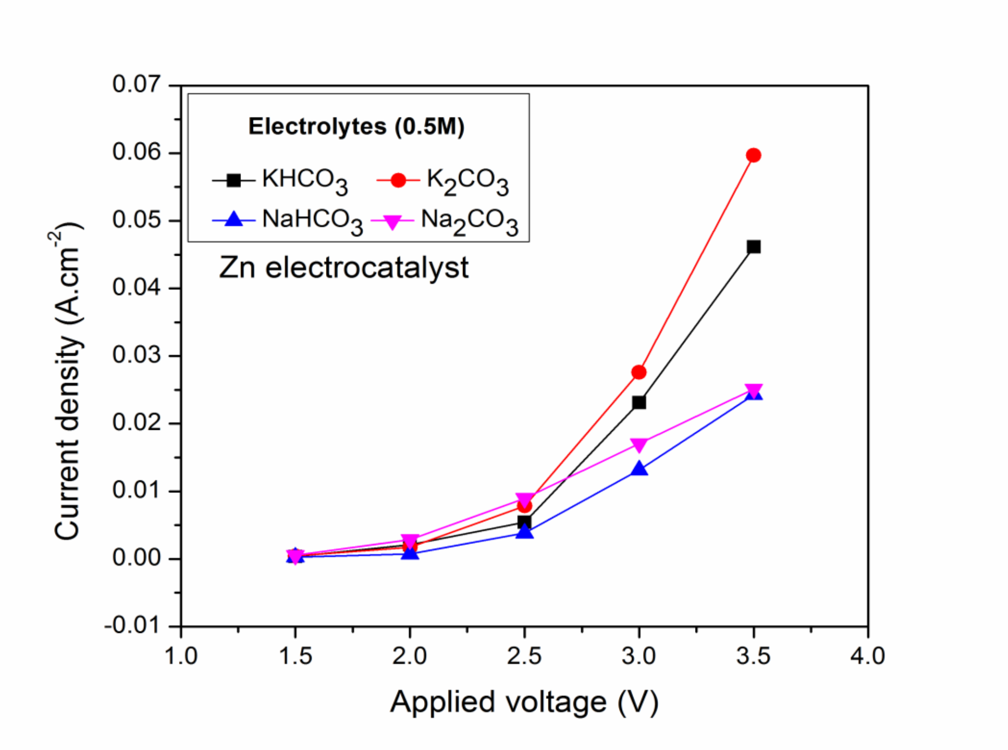

Figure 5.5. Current density during CO_2 reduction with applied voltage on Zn electrocatalyst

5.3.2. Faradaic efficiency of HCOOH with time from CO_2 reduction in $KHCO_3$ solution.

Faradaic efficiency of product was calculated with time for different applied voltages. It was observed from the figure 5.6a that, HCOOH was formed at all applied conditions from reduction of CO_2. Maximum Faradaic efficiencies were obtained at low applied voltage of 1.5 V. Efficiencies were calculated for reaction time of 5, 10, 15, 20 and 25 min at the same applied voltage were 78.5, 78.4, 29.3, 16.7 and 23 %, respectively. Reaction at 1.5 V shows significant results for HCOOH with high Faradaic efficiency of 78.5 % for 5 min reaction which is more optimized condition for RCPE. Hara et al. reported using 0.1M $KHCO_3$ at 1.7 V using Pt anode with 40.8% Faradaic efficiency.[67] Reduction of CO_2 at 2 V was occurred having Faradaic efficiencies of 6.48, 23.9, 3.96, 4.45 and 3.317 %, respectively (figure 5.6a). The obtained efficiencies were low compared with RCPE at 1.5 V which may be due to high hydrogen or CO evolution.[66]

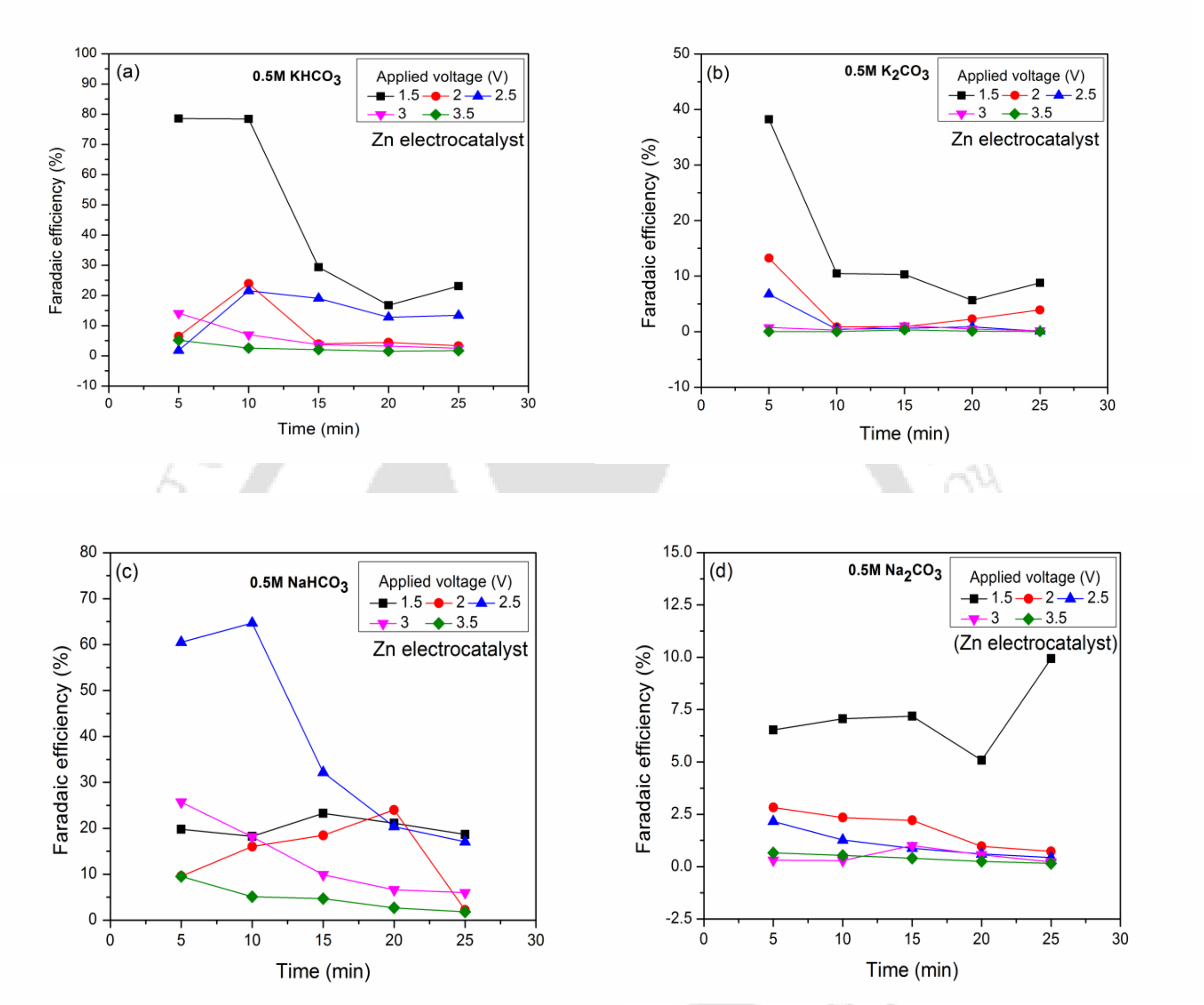

Figure 5.6. Variation of Faradaic efficiency of HCOOH with time using various electrolytes. a) $KHCO_3$, b) K_2CO_3, c) $NaHCO_3$ and d) Na_2CO_3 solution

Faradaic efficiencies of 1.7, 21.5, 19, 12.7 and 13.4 % were obtained at 2.5 V signify more favorable compared to that of at 2 V. The rate of CO_2 reduction at 3 V and 3.5 V, were also shown in figure 5.6a with low Faradaic efficiencies of (14.1, 6.99, 3.7, 3.2 and 2.48 %) and (5.1, 2.56, 2.03, 1.54 and 1.72 %), respectively. However, the current densities (reported in figure 5.5) were high at these applied voltages due to high proton generation than CO_2 reduction. Overall, RCPE at this electrolyte shows that HCOOH was formed as product at all conditions. The optimized voltage for CO_2 reduction was observed to be 1.5 V with maximum faradaic efficiencies. Finally, it may be inferred that HCOOH may be formed using synthesized electrocatalyst (Zn) in $KHCO_3$ solution.

5.3.3. Faradaic efficiency of HCOOH with time from CO_2 reduction in K_2CO_3 solution.

Results in figure 5.6b shows that high Faradaic efficiencies were obtained at low applied voltage of 1.5 V compared with other high voltages. The efficiencies for HCOOH at this voltage are obtained to be 38.2, 10.4, 10.3, 5.6 and 8.7 %, respectively. The maximum efficiency was obtained is 38.2 % for 5 min reaction. High efficiencies were also reported for CO than HCOOH at Zn electrocatalyst in potassium based electrolyte using Pt as anode.[66] RCPE at an applied voltage of 2V shows Faradaic efficiencies of 13.2, 0.84, 0.91, 2.28 and 3.91 %, with maximum efficiency of 13.2 % after 5 min. Faradaic efficiencies of 6.7, 0.44, 0.61, 0.85 and 0.08 % were observed at 2.5 V. Efficiencies at 2 and 2.5 V were low compared with 1.5 V as hydrogen evolution is competing with CO_2 reduction. The efficiencies at 3 V and 3.5 V were observed to be 0.75, 0.31, 1.07, 0.47 and 1.68 % and 0.03, 0.02, 0.34, 0.09 and 0.03 %, respectively. RCPE in potassium based salt have reported for HCOOH formation on Zn electrocatalyst and Pt as anodic material.[5] However HCOOH is formed in all experimental conditions with low efficiencies compared to $KHCO_3$ electrolyte solution, though current densities were high for carbonate based electrolyte than bicarbonate (shown in figure 5.5). This was due to the fact that high hydrogen evolution reaction was favorable in carbonate solutions than bicarbonates. Hence, the present electrocatalysts were able to reduce CO_2 to single produce (HCOOH) in the presence of K_2CO_3 but with reduced efficiency than $KHCO_3$.

5.3.4. Faradaic efficiency of HCOOH with time from CO_2 reduction in $NaHCO_3$ solution.

In 0.5M $NaHCO_3$ electrolyte solution the only product formed was HCOOH and the respective results were shown in figure 5.6c. Effect of CO_2 reduction using Zn electrocatalyst reported high reaction rates for HCOOH formation using Pt as anodic material.[60] For reaction time of 5, 10, 15, 20 and 25 min, Faradaic efficiencies were obtained as 19.7, 18.2, 23.2, 21 and 18.6 % at 1.5 V, respectively. However, maximum Faradaic efficiency of 23.27% for 15 min reaction is the optimized condition towards RCPE. Faradaic efficiencies for HCOOH at 2 V were obtained as 9.5, 16, 18.4, 24 and 2.2 %. High efficiency was observed to be 24 % for reaction time of 20 min. Maximum Faradaic efficiencies were observed as 60.4, 64.7, 32.1, 20.3 and 17 % at 2.5 V. Jin et al. reported CO_2 reduction to HCOOH with high yields for Zn catalyst using different concentrations of $NaHCO_3$ electrolyte solution.[60] RCPE at 3 V obtained Faradaic efficiencies of 25.7, 18.1, 9.9, 6.6 and 5.9 % towards HCOOH formation (figure 5.6c). At 3.5V, low efficiencies of 9.4, 5, 4.6, 2.6 and 1.8 %, respectively, were obtained which may due to high proton generation at Co_3O_4 electrode. Reduction of CO_2 to HCOOH favors at all applied voltages and maximum efficiencies were observed at 2.5 V. However, very low Faradaic efficiencies were obtained at 3.5 V. From the above results it was confirmed that synthesized electrocatalysts were able to reduce CO_2 to HCOOH in $NaHCO_3$ based salt efficiently.

5.3.5. Faradaic efficiency of HCOOH with time from CO_2 reduction in Na_2CO_3 solution

Results for reduction of CO_2 in 0.5M Na_2CO_3 solution in figure 5.6d showed that HCOOH was formed in all the conditions and respective Faradaic efficiencies were reported for 5, 10, 15, 20 and 25 min reaction. Though current densities were high compared with bicarbonate solution, low Faradaic efficiencies were obtained for this electrolyte (figure 5.5) which may be due to high proton generation. For reaction at 1.5 V, Faradaic efficiencies of 6.5, 7, 7.2, 5.1 and 9.9 % were obtained at various time. It was reported that the reaction time may affect the product formation in sodium based salt at Zn electrocatalyst for CO_2 reduction to HCOOH using Pt as anode.[60] At 2 V, Faradaic efficiencies of 2.8, 2.3, 2.2, 0.9 and 0.7 % were observed, respectively for various times (figure 5.6d). Faradaic efficiencies of 2.1, 1.2, 0.8, 0.6 and 0.4 % were obtained at 2.5 V which showed low efficiencies when compared to reaction at 1.5 V. At 3 V and 3.5 V, Faradaic efficiencies were reported to be (0.3, 0.29, 1, 0.56 and 0.23 %) and (0.6, 0.53, 0.4, 0.25 and 0.15 %) respectively. Low Faradaic efficiencies were observed in these experimental conditions which may be due to the high hydrogen or CO formation at the cathode surface with proton generation at anode surface.[73] High CO Faradaic efficiencies were reported when Zn electrocatalyst was used for CO_2 reduction.[67] However, the present catalyst was able to reduce CO_2 to HCOOH by the observed results.

Table 5.1 Optimized experimental conditions for RCPE on Zn electrocatalyst

Applied Voltage	**Maximum Faradaic efficiency (time)**							
	$KHCO_3$		**K_2CO_3**		**$NaHCO_3$**		**Na_2CO_3**	
(V)	**(%)**	**(min)**	**(%)**	**(min)**	**(%)**	**(min)**	**(%)**	**(min)**
1.5	78.5	5	38.2	5	23.2	15	9.9	25
2	23.9	10	13.2	5	24	20	2.8	5
2.5	21.5	10	6.7	5	64.7	10	2.1	5
3	14.1	5	1.07	20	25.7	5	1.0	15
3.5	5.1	5	0.34	15	9.4	15	0.6	5

The optimized conditions for RCPE using synthesized electrocatalyst with a maximum Faradaic efficiency of HCOOH at different times using various electrolytes is shown in Table 5.1. From the table it may be concluded that the bicarbonates are able reduce CO_2 with high Faradaic efficiencies that the carbonates salts of potassium and sodium. The elementary mechanism towards CO_2 reduction was shown in figure 5.7. Radical anion is formed by accepting electron from cathode (Zn). Water molecule may be protonated to form neutral radical from radical anion. The radical anions so formed were further gained electrons with some internal arrangements to form formate which accepts a proton to form HCOOH.[111]

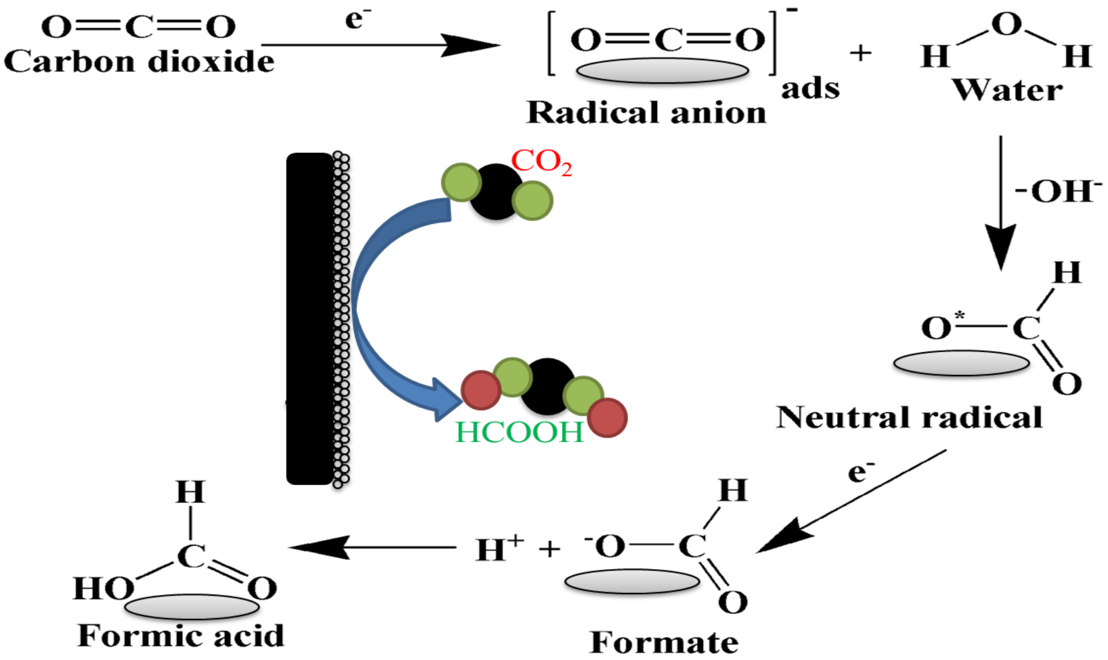

Figure 5.7. Proposed elementary mechanism for reduction of CO_2 to HCOOH

5.4. Summary

Effective synthesis of Zn electrocatalyst was done by electrodeposition method and utilized for CO_2 reduction experiment. Co_3O_4 was synthesized and used as electrocatalyst for H_2O oxidation to generate proton for CO_2 reduction to form HCOOH. At low applied voltages bicarbonate based electrolytes showed high Faradaic efficiencies than carbonate based electrolyte solutions. HCOOH was the only product formed at all applied voltages in different electrolyte solutions. These studies are helpful in selecting a cheap and effective electrocatalyst (Co_3O_4) that replaces Pt towards H_2O oxidation for CO_2 reduction on Zn electrocatalyst.

Chapter 6

Electrochemical reduction of CO_2 to HCOOH on a synthesized Sn electrocatalyst using Co_3O_4 anode

Chapter 6

Electrochemical reduction of CO_2 to HCOOH on a synthesized Sn electrocatalyst using Co_3O_4 anode

This chapter covers the synthesis of Tin (Sn) by electrodeposition method and its characterization. The synthesized catalyst was used for CO_2 reduction in potassium and sodium based electrolytes and described in detail.

6.1. Experimental

6.1.1. Materials, Characterization and product analysis

Graphite plates (1.5 × 2.5) cm^2 were purchased from Sunrise enterprises, Mumbai. Sodium bicarbonate ($NaHCO_3$), potassium bicarbonate ($KHCO_3$), sodium carbonate (Na_2CO_3), potassium carbonate (K_2CO_3), tin chloride dihydrate ($SnCl_2.2H_2O$), acetone (CH_3COCH_3) and isopropyl alcohol ($(CH_3)_2CHOH$) were procured from Merck, India. Nafion (5 wt %) solution was obtained from DuPont, USA and direct current (DC) source was purchased from Crown, India. All the chemicals were used without any further purification and deionized water was used in all experiments.

6.1.2. Synthesis of Sn powder electrochemically

Tin (Sn) powder was synthesized by electrodeposition method.[112] Schematic for the synthesis of Sn powder is shown in figure 6.1. Metal powder was extracted from the solution of 0.1M $SnCl_2.2H_2O$ by supplying energy between the metallic copper plate and graphite plate in an electrolytic cell. A constant current of 0.2 A for 3 min was applied by which the Sn deposition takes place on graphite plate. The deposited Sn powder was removed with using acetone. Further, catalyst solution was heated at the 100 ^oC for 1h to obtain Sn powder.

6.1.3. Characterization

Sn electrocatalyst was characterized using Fourier Transform Infrared Spectrophotometer (FTIR) (make: Shimadzu; model: IR Affinity-1). Peaks were recorded in the range of 500 - 4000 cm^{-1} by crushing the sample with KBr (IR grade). X-ray diffraction (XRD) analysis was done using X-ray diffractometer (make: Bruker; model: D8 advance) between 10^o to 80^o 2θ. Particle size analysis of synthesized electrocatalyst was done using Delsa nano (make: Beckman coulter; model: Delsa nano C) particle size analyzer.

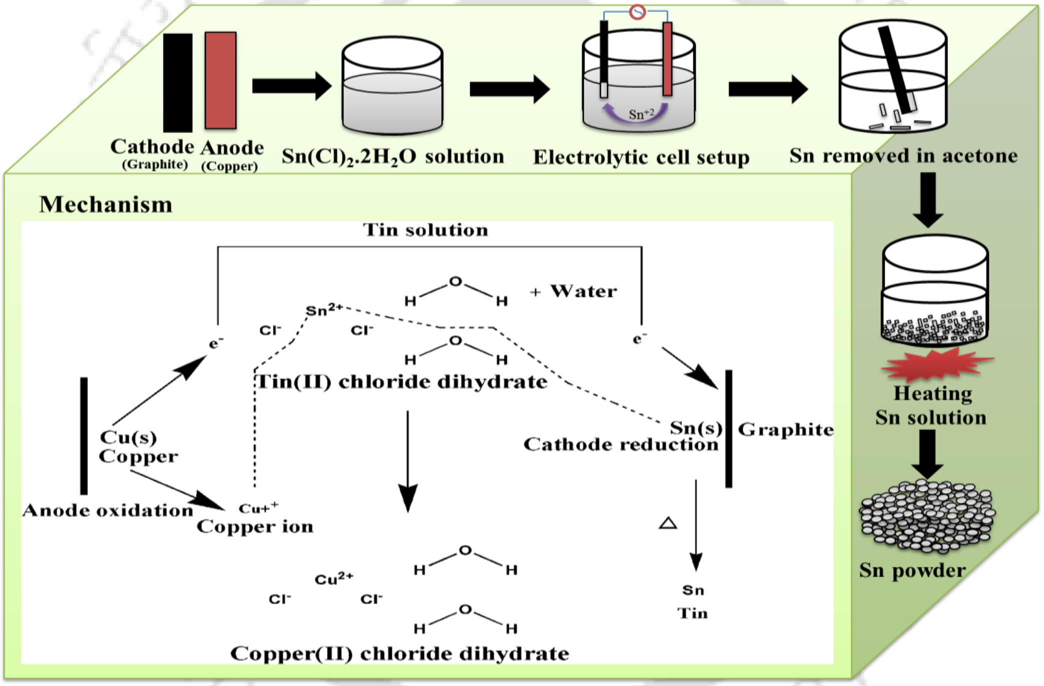

Figure 6.1. Schematic representation for the synthesis of Sn powder and its mechanism

6.1.4. Electrodes preparation

Electrodes were prepared by taking solution of 1:5 ratio of 200 µl of nafion + isopropyl alcohol (IPA) which acts as a binder. 7.5 mg of electrocatalyst (Co_3O_4 and Sn) was added to the binder solution separately, and sonicated for 30 min. The solution was coated on the graphite plate surface at 80 °C to get the electrodes at active area 2 mg/cm^2. Thereafter, electrodes were dried for 2 h in oven at 100 °C.

6.1.5. Electrochemical studies towards CO_2 reduction

Prepared electrodes were used in RCPE by using a 2-electrode homemade glass cell in order to study the effect of CO_2 reduction. Figure 6.2 shows the schematic of experimental setup used for RCPE using a two electrode cell.

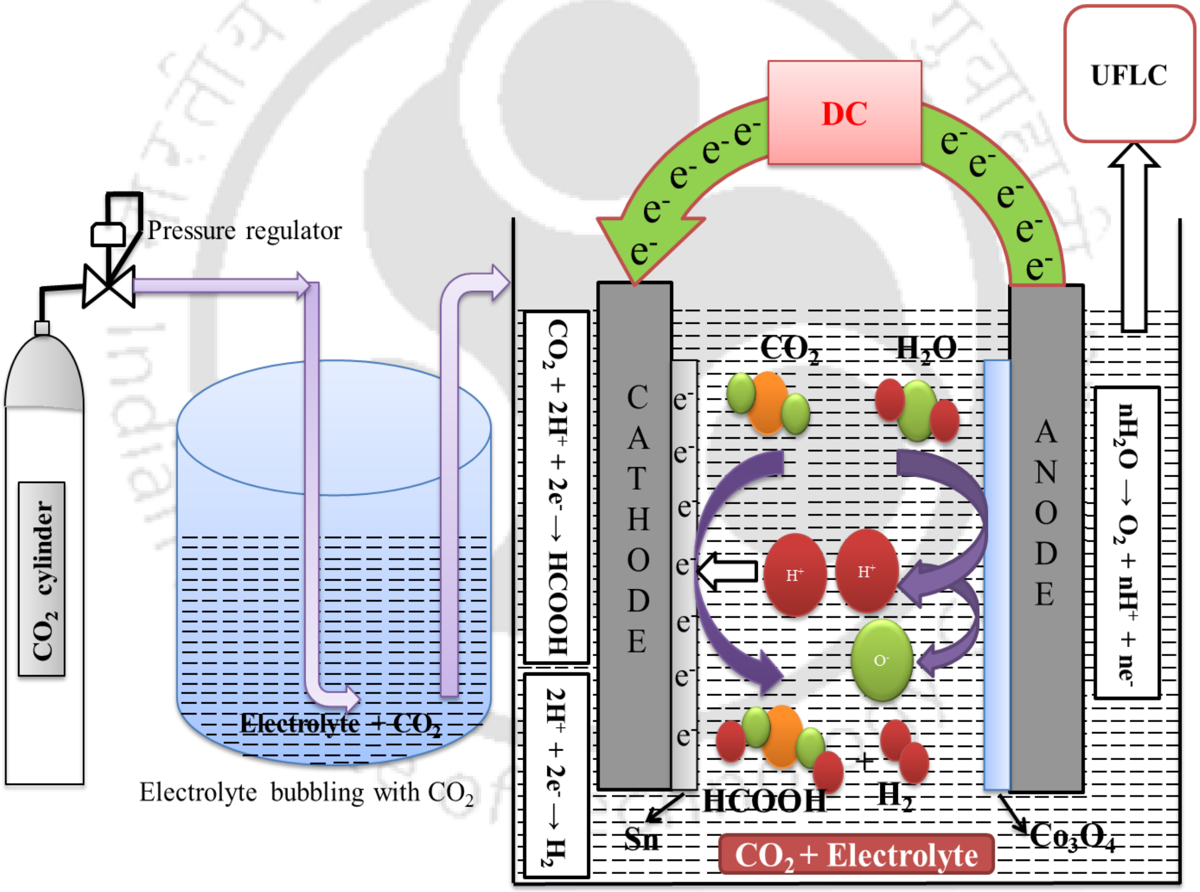

Figure 6.2. Experimental setup for the reduction of CO_2 to HCOOH on Sn electrocatalyst

The glass cell was filled with prepared 0.5 M electrolyte solution of 80 ml which was saturated with CO_2 by continuous bubbling for 50 min. RCPE experiments were conducted in CO_2

saturated solution by connecting the electrodes to the DC source. Experiments were conducted at potentials of 1.5, 2, 2.5, 3 and 3.5 V with reaction time of 0-5, 10, 15, 20 and 25 min for every applied voltage.

6.1.6. Product analysis

Product from CO_2 reduction was analyzed by ultra-fast liquid chromatography (UFLC, Shimadzu LC-20AD, UV-detector of deuterium lamp SPD-20A). The product was detected at 205 nm wavelengths by injecting 20 µl of reacting sample to the C-18 Column (10 X 4 mm). Tetrabutyl ammonium hydrogen sulfate (5 mM) was used as mobile phase at flow rate of 1 ml/min.

6.2. Results and discussion

6.2.1. Characterization of Sn electrocatalyst and its mechanism

FTIR spectrum of synthesized Sn electrocatalyst was represented in figure 6.3a. The broad band around 3000-3600 cm^{-1}, 1642 cm^{-1} corresponds to O-H stretching vibrations and O-H bending vibrations respectively, attributed to adsorbed water. Band at 1000-1250 cm^{-1} confirms the presence of Sn.[112] XRD pattern of synthesized Sn electrocatalyst was shown in figure 6.3b. Peak positions at 31.2^{o}, 32.1^{o}, 43.8^{o}, 44.9^{o}, 55.45^{o}, 62.5^{o}, 63.7^{o}, 64.5^{o}, 72.4^{o}, 73.1^{o} and 79.5^{o} are matched closely to Sn structure.[113] Particle size distribution of synthesized catalyst is shown in figure 6.3c. The particle size of Sn powder was found in the range of 156.7 – 278.9 nm. The distribution median size (D_{v50}) of Sn electrocatalyst particle was found to be 192.5 nm. A mechanism for the formation of Sn electrocatalyst is already shown in figure 6.1. Sn ion from the electrolyte solution was deposited on the cathode surface by accepting electrons generated at anode (oxidation). Copper ion formed at anode had a driving force for the deposition of Sn ion

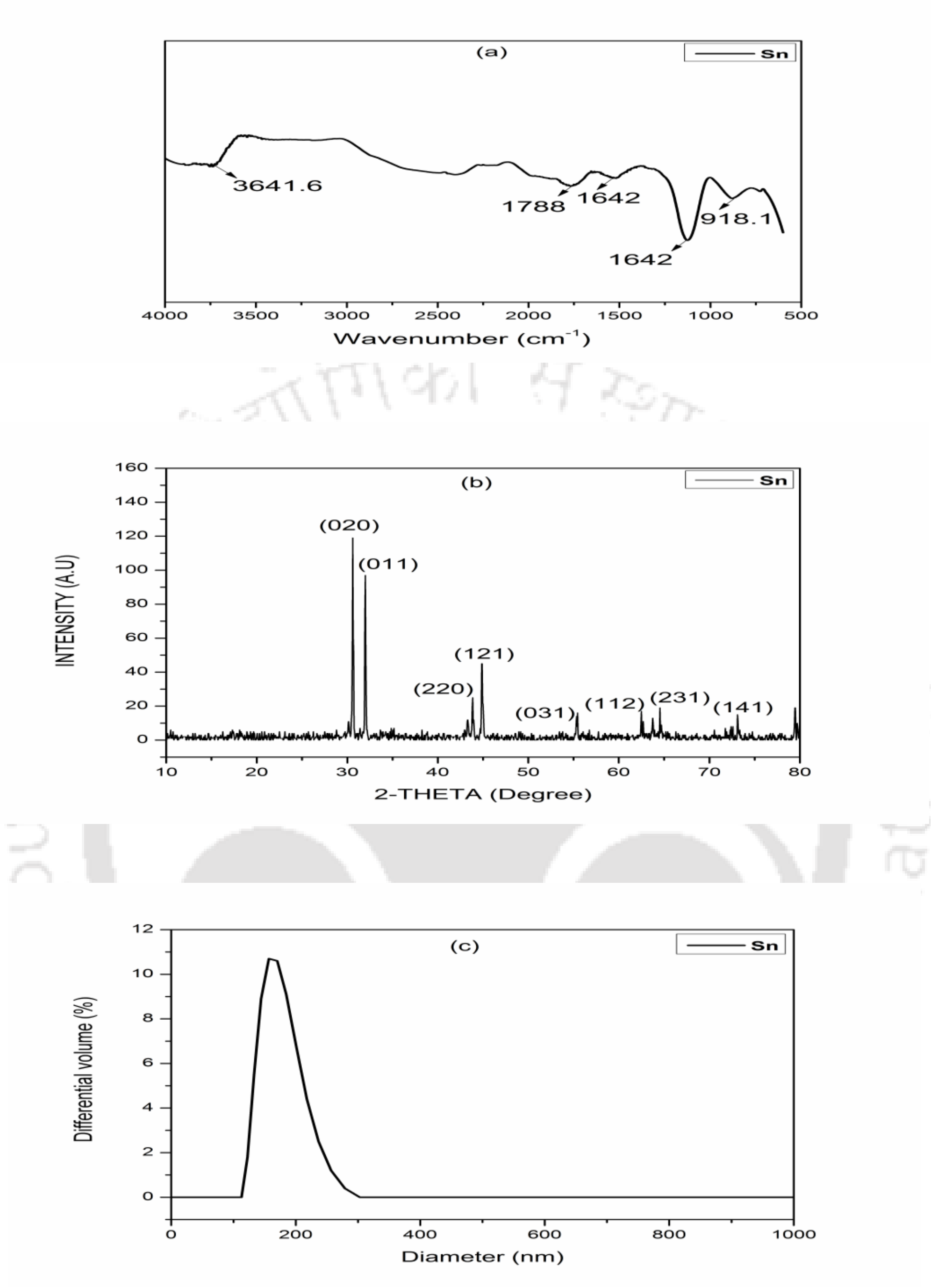

Figure 6.3. Characterization of Sn electrocatalyst (a) FTIR, (b) XRD, and (c) particle size analysis

on the surface of graphite plate. The deposition rate was proportional to the formation of a new copper chloride molecule in solution. Further, upon heating the deposited Sn powder on graphite gives Sn electrocatalyst.

6.3. RCPE studies at Sn electrocatalyst in different electrolyte solutions

6.3.1. Variation of current density with applied voltage during CO_2 reduction on Sn electrocatalyst

Experimental results for the variation of current density with applied voltage were shown in figure 6.4 for all the electrolytes. It was observed that the current density increased with increase in applied voltages for all the cases. Reduction of CO_2 signifies the increase of current density.

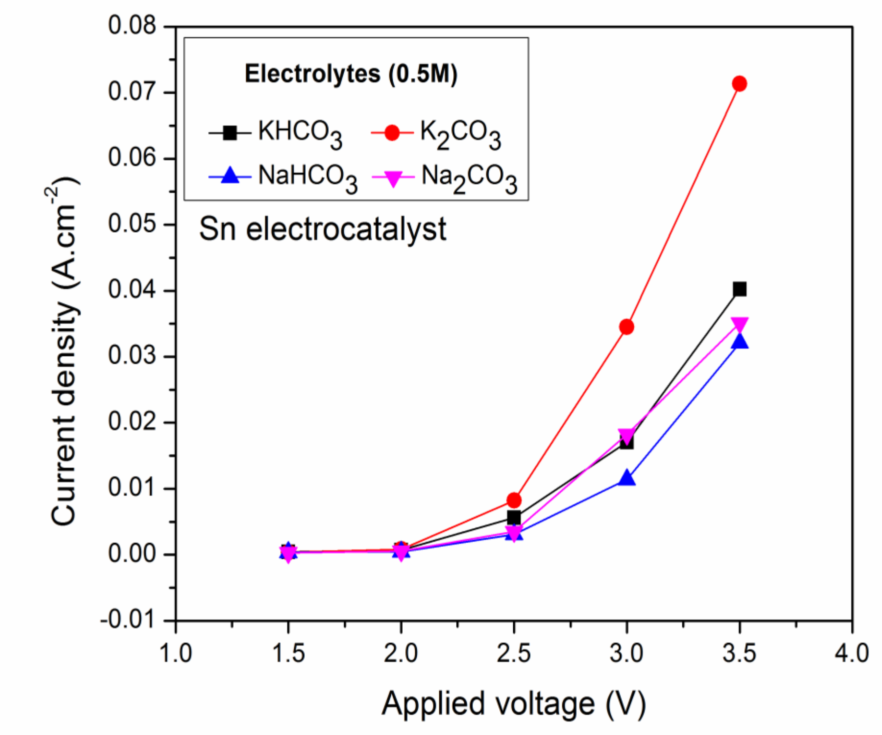

Figure 6.4. Variation of current density with applied voltage during CO_2 reduction using Sn electrocatalyst

Increase in current density dictates the high reaction rate for CO_2 reduction or hydrogen generation. Again, figure 6.4 shows that potassium carbonate electrolyte gives high current density compared to bicarbonates. This confirms that the rate of reaction is more for carbonates of potassium and sodium. It is also found that the potassium electrolytes show high current densities than sodium electrolytes. In summary, the increase in current density signifies the rate of reaction towards CO_2 reduction occurs at the surface of cathode in all conditions applied.

6.3.2. Reduction of CO_2 to HCOOH in $KHCO_3$ solution (time vs Faradaic efficiency)

In order to find the applied energy utilized towards CO_2 reduction, Faradaic efficiency was calculated with time for applied voltages in 0.5 M $KHCO_3$ electrolyte solution and shown in figure 6.5a. It was observed that the only product formed was HCOOH for the applied conditions. This signifies that synthesized electrocatalyst was able to reduce CO_2 to single products. Maximum Faradaic efficiencies were obtained at low applied voltages of 1.5 V and 2 V compared to others considered here. Faradaic efficiencies for the reduction of CO_2 to HCOOH at 1.5 V with reaction time of 5, 10, 15, 20 and 25 min were observed to be 8.28, 13.54, 52.2, 74.04 and 40.61 %, respectively. Overall, high efficiencies (74%) were observed for the applied voltage after 20 min reaction. Similar results were shown when Pt was used as the anode after a reaction time of 30 min.[58] High Faradaic efficiencies (92.6, 67.36, 10.17, 0.91 and 14.51% respectively) were obtained (figure 6.5a) at 2 V. RCPE at 2 V shows significant results for HCOOH with high Faradaic efficiency of 92.6 % for 5 min reaction. However, at this applied voltage maximum energy was utilized in reducing CO_2 to HCOOH. At 2 V a Faradaic efficiency of 47 % was reported[58] and maximum Faradaic efficiency of 92.3% was observed at Sn/Pt in 0.1M $KHCO_3$ solution.[67] Faradaic efficiencies at 2.5 V decrease with time to be 16, 5.33, 3.45, 7.77 and 1.09 %, of which maximum efficiency of 16 % was observed at reaction time of 5 min.

Low Faradaic efficiencies of 0.10, 0.83, 2.87, 1.22 and 0.23 % at 3 V and 0.43, 0.22, 0.21, 0.73 and 0.69 % at 3.5 V, respectively, were found (figure 6.5a). Considering the above results it may be envisaged that low efficiencies were obtained at 3 V and 3.5 V, which may be due to other side reactions, especially hydrogen evolution due to high proton generation at Co_3O_4 anode.

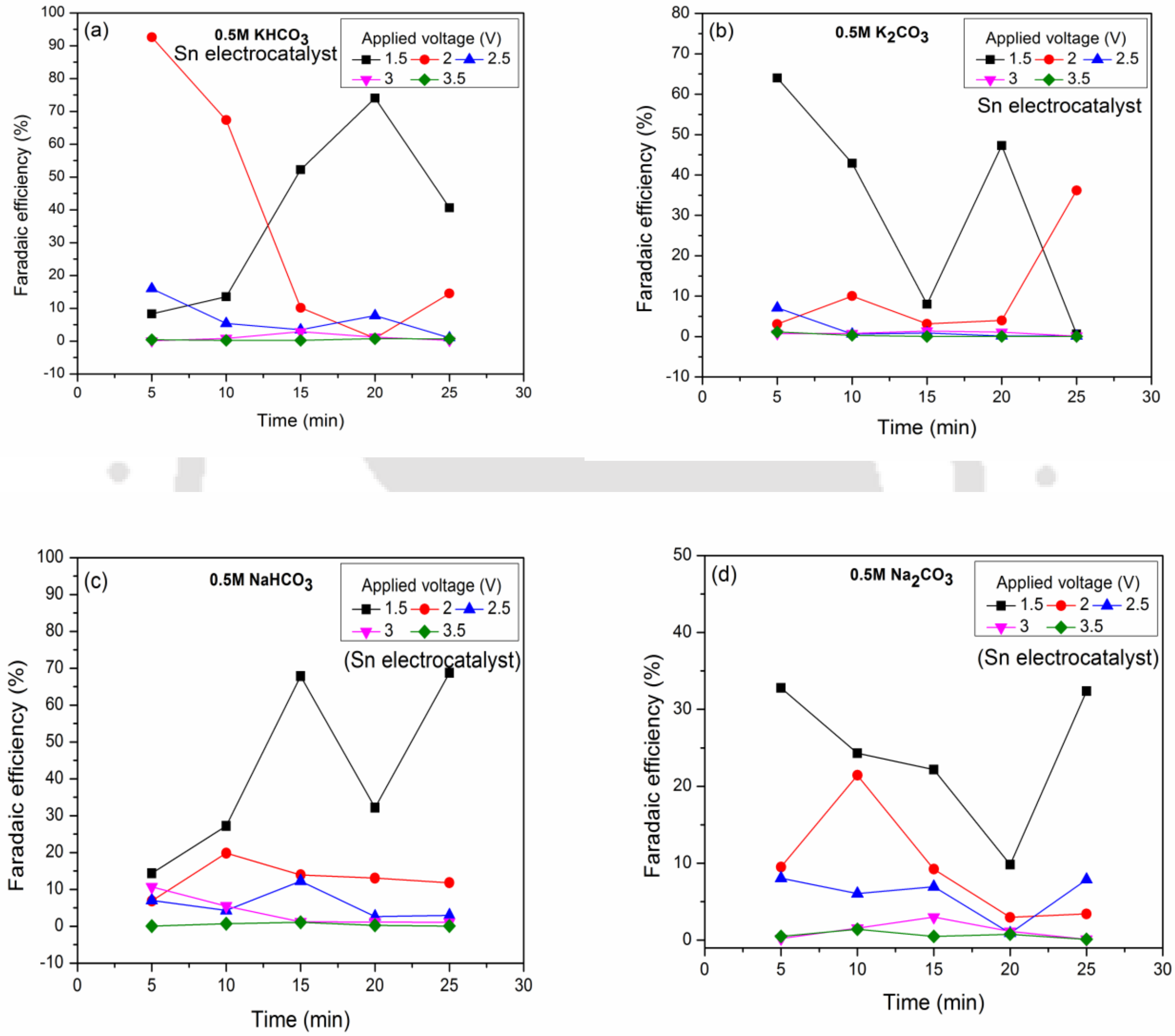

Figure 6.5. Variation of Faradaic efficiency with time during reduction of CO_2 to HCOOH using a) $KHCO_3$, b) K_2CO_3, c) $NaHCO_3$, and d) Na_2CO_3 electrolyte solutions.

The synthesized electrocatalyst was able to reduce CO_2 to HCOOH at all applied conditions. However, high efficiencies were obtained at low potentials compared with high potentials. The optimized conditions for RCPE were observed to be 1.5 V (20 min) and 2 V (5 min) towards HCOOH formation.

6.3.3. Reduction of CO_2 to HCOOH in K_2CO_3 solution

Reduction of CO_2 to HCOOH using Sn and Pt as cathode and anode material in 0.1 M K_2CO_3 solution was investigated and reasonable Faradaic efficiencies were obtained for different applied voltages.[58] Faradaic efficiencies towards HCOOH formation from RCPE using Co_3O_4 as anode at different applied voltages in presence of 0.5M K_2CO_3 electrolyte solution was investigated in this work and shown in figure 6.5b. Significant results were obtained towards RCPE at low applied voltages, particularly at 2 V than 1.5 V. However, comparing with $KHCO_3$ solution, the efficiencies obtained were low that may be due to high hydrogen formation.[114] For RCPE at 1.5 V, Faradaic efficiencies for HCOOH with reaction time of 5, 10, 15, 20 and 25 min were 64, 43, 8, 47.3 and 0.60 %, respectively. Faradaic efficiency of 39 % was reported at 1.5 V.[22] Overall, applied voltage is able to reduce CO_2 to HCOOH with good efficiencies and the optimized reaction condition at this potential is 64 % for 5 min reaction. RCPE at 2 V observed that efficiency increases with time and the obtained Faradaic efficiencies were 3, 10, 3, 4 and 36 %. Faradaic efficiency of 36 % for 25 min reaction was observed as optimized reaction at this particular applied voltage. The RCPE at 2.5 V shows low Faradaic efficiencies of 7.1, 0.62, 0.90, 0.15 and 0.12 %. Low efficiencies were observed with high current density, which may be due to other side reactions (figure 6.5b). At 3 V and 3.5 V, very low Faradaic efficiencies were obtained (for 5, 10, 15, 20 and 25 min reaction) as 0.73, 0.75, 1.36, 1.08 and 0.1 % and 1.14, 0.31, 0.02, 0.02 and 0.03 %, respectively. The RCPE results were also confirmed the formation of HCOOH in all the experimental conditions considered here. However, low efficiencies were obtained for carbonate compared to bicarbonate solutions. The high current densities so obtained may be due to competition in hydrogen evolution reaction. The synthesized catalyst Sn and effect of Co_3O_4 as anode in reducing the CO_2 to HCOOH is proven to be an efficient method.

6.3.4. Variation of Faradaic efficiency with time during reduction of CO_2 to HCOOH

The experimental results on reduction of CO_2 to HCOOH in 0.5M $NaHCO_3$ electrolyte solution is shown in figure 6.5c. High Faradaic efficiencies were observed at 1.5 V and low for the remaining applied voltages (figure 6.5c). However, the only product formed at all the applied conditions is HCOOH. At 1.5 V, the Faradaic efficiencies of 14.3, 27.2, 67.8, 32.2 and 68.7 %, respectively, were obtained after 5, 10, 15, 20 and 25 min. Decrease in efficiency at 40 min reaction may be due to the oxidation of HCOOH at Co_3O_4 anode.[73] However, maximum Faradaic efficiency of 68.7 % (25 min) and 67.8 % (15 min) reaction was observed as an optimum condition. Faradaic efficiencies of 6.8, 19.8, 13.9, 13 and 11.8 % were obtained for RCPE at 2 V. This potentially reduces CO_2 with low faradaic efficiency compared with applied voltage of 1.5 V in these experimental conditions. For reaction at 2.5 V low efficiencies were observed to be 7.02, 4.3, 12.26, 2.60 and 2.97 % (figure 6.5c). Lower efficiencies were observed as hydrogen generation favors the reaction (figure 6.5). The reduction of CO_2 to HCOOH at 3 V and 3.5 V were observed for which Faradaic efficiencies were 10.6, 5.4, 1.2, 1.1 and 1.05 % and 0.03, 0.67, 1.07, 0.26 and 0.06 %, respectively after the said time interval. It may be concluded from this section that RCPE favors at all applied voltages and maximum efficiency is observed at 1.5 V which is the most optimum potential towards HCOOH formation.

6.3.5. Reduction of CO_2 to HCOOH in Na_2CO_3 solution

RCPE study using Sn as electrocatalyst in 0.5M Na_2CO_3 solution towards HCOOH formation is shown in figure 6.5d. Formation of HCOOH at all applied conditions shows that low applied voltages are more favorable for high Faradaic efficiencies. Faradaic efficiencies of

32.8, 24.3, 22.2, 9.8 and 32.3 % were obtained at 1.5 V. Sudden decrease in efficiency after 15 min reaction was due to HCOOH oxidation at anode.[73] However, this voltage was more favorable for the reduction of CO_2 to HCOOH with efficiency of 32.3 % after 25 min. For the reaction at 2 V, Faradaic efficiencies of 9.5, 21.4, 9.2, 2.9 and 3.4 % were observed (figure 6.5d). It may be noted that efficiencies were low when compared with RCPE in $NaHCO_3$ electrolyte

Table 6.1 Comparison of HCOOH Faradaic efficiency at different experimental conditions with literature

Electrode		**Electrolyte**	**Applied Voltage (V)**	**Reaction Time (min)**	**Faradaic efficiency (HCOOH) (%)**	**References**
Anode	**Cathode**					
Pt	Sn	0.5 M $KHCO_3$	1.5	30	74	[22]
			2	30	47	
			1.5	120	20	
			2	120	20	
Pt	Sn	0.1 M K_2CO_3	1.5	30	-	
			2	30	14.2	
			1.5	120	-	
			2	120	13	
Pt	Sn	0.1 M $KHCO_3$	1.39	-	92.3	[34]
Pt	Sn	0.1 M $KHCO_3$	1.8	60	91	[25]
Co_3O_4	Sn	0.5 M $KHCO_3$	1.5	20	74.08	**Present work**
			2	5	92.6	
		0.5 M K_2CO_3	1.5	5	64.03	
			2	25	36.18	
		0.5 M $NaHCO_3$	1.5	25	68.72	
			2	10	19.83	
		0.5 M Na_2CO_3	1.5	10	32.82	
			2	10	21.44	

solution. Faradaic efficiencies of 8, 6, 6.9, 0.91 and 7.8 % were observed to be less at 2.5 V compared with above applied voltages. Low efficiencies were obtained at 3 V (0.20, 1.55, 2.98, 1.14 and 0.1 %) and 3.5 V (0.49, 1.40, 0.49, 0.76 and 0.10 %). This may be due to high proton generation at Co_3O_4 which leads to more hydrogen formation at the cathode surface.[73] RCPE using this electrolyte was able to form HCOOH from CO_2 at all applied voltages. However, optimum conditions for maximum efficiencies were low applied voltages towards RCPE. Finally, application of Co_3O_4 as anode for the reduction of CO_2 to HCOOH was proven. The optimized condition towards reduction of CO_2 to HCOOH on the synthesized catalyst was shown in Table 1. Experimental conditions to get high HCOOH Faradaic efficiency with time in RCPE is also shown with respect to the applied voltages. It is concluded that bicarbonates were able to reduce more CO_2 than carbonates electrolyte solutions.

6.4. Summary

A study on RCPE was done by synthesizing Sn electrocatalysts via electrodeposition method. Result showed that Co_3O_4 was able to oxidize H_2O efficiently for CO_2 reduction. However, high Faradaic efficiencies were obtained for bicarbonates than carbonate based electrolyte solutions at low applied voltages. The synthesized electrocatalyst was able to reduce CO_2 to HCOOH effectively at all applied voltages. This preliminary study will be helpful towards findings of a effective electrocatalyst for proton generation at anode for RCPE (alternate to expensive Pt).

Chapter 7

Solar cell driven electrochemical studies for CO_2 reduction on various electrocatalysts

Chapter 7

Solar cell driven electrochemical studies for CO_2 reduction on various electrocatalysts

This chapter discusses the application of all synthesized electrocatalysts towards CO_2 reduction using solar energy on Co_3O_4 anode. The studies were done using bicarbonate salt. Experimental procedure and analysis of results obtained is discussed in detail.

7.1. Experimental

7.1.1. Materials

A solar panel (8.8 V, 340 mA) was bought from Waare Energies Pvt. Ltd, Surat, India. Graphite plates (1.5 × 2.5) cm^2 were purchased from Sunrise Enterprises, Mumbai. $NaHCO_3$, $KHCO_3$ and Iso-propyl alcohol ($(CH_3)_2CHOH$) were procured (Merck, India). Nafion (5 wt.%) solution was purchased from DuPont, USA. No further purification was done for the chemicals used here and deionized water was used in all experiments.

7.1.2. Cathode and anode electrodes for photo electrochemical reduction of CO_2

The synthesis of electrocatalysts were done by electrodeposition method and reported in our previous publications.[115-116] The accurately weighed electrocatalyst (7.5 mg) was mixed with the binder solution (1:5 (nafion+IPA (Iso propyl alcohol))) of 200 µl for 30 min sonication to get fully prepared catalyst ink. The prepared ink was coated on the surface of graphite plate at 80 ^oC to get the plate in an active area of 2 mg/cm^2.[117] The coated graphite plate was dried for 2 h in oven at 100 ^oC to get electrode. Similar procedure was followed for all the three electrocatalyst (Cu_2O, Pb_2O and Co_3O_4).

7.1.3. Experimental studies on photo electrochemical CO_2 reduction

The prepared electrodes (Co_3O_4/G – Cu_2O/G, Co_3O_4/G – Pb_2O/G, Co_3O_4/G – Sn/G and Co_3O_4/G – Zn/G) were connected to solar cell by using a 2-electrode homemade glass cell for photo electrochemical studies. Schematic of experimental setup used for the CO_2 reduction was shown in figure 7.1. The electrolyte solutions ($NaHCO_3$ or $KHCO_3$) of 80 ml were prepared in different concentrations (0.2, 0.4, 0.6, 0.8, 1M). The solutions were bubbled with CO_2 for 1h to get completely saturated CO_2 solution. Experiments were conducted for two electrolyte solutions and reacted solutions were collected at 0, 10, 20, 30, 40 and 50 min for every electrolyte concentration.

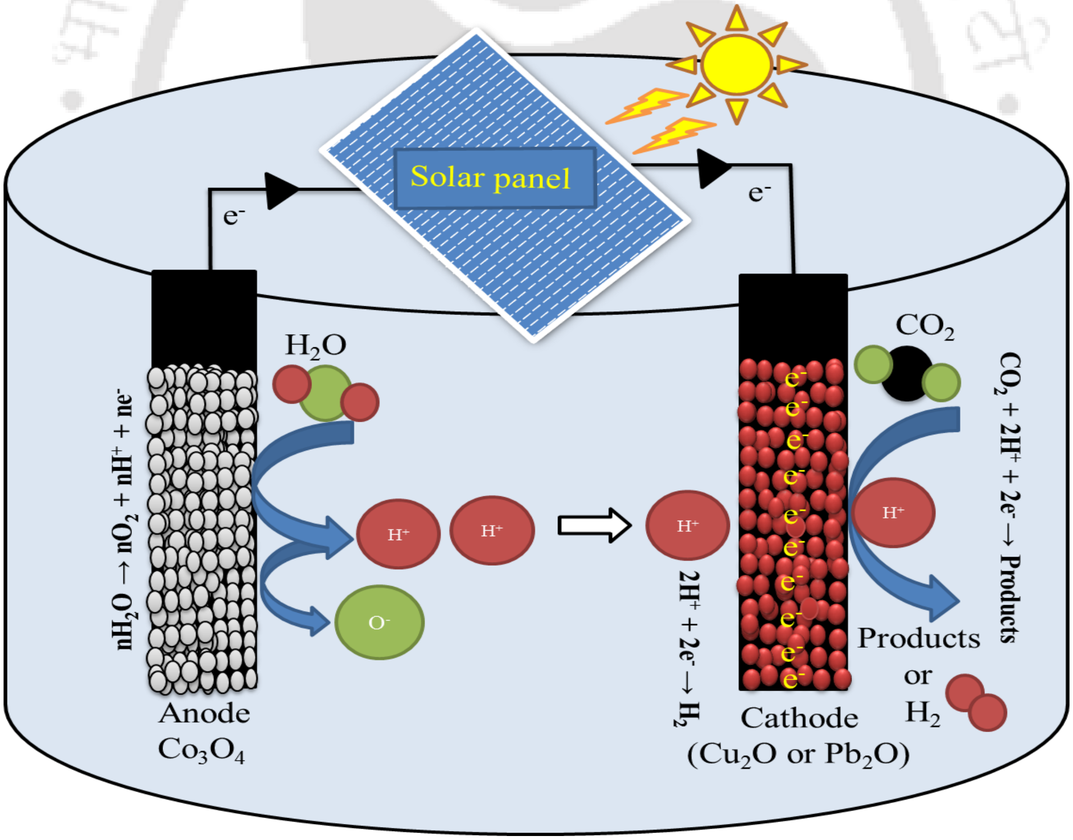

Figure 7.1. Photo electrochemical reduction of CO_2 experimental setup

7.1.4 Product analysis

The CO_2 reduction products were analyzed by ultra-fast liquid chromatography (UFLC), Shimadzu LC-20AD and UV-detector of deuterium lamp (SPD-20A). Analysis was done at 205 nm by injecting a 20 µl of reacting sample to the C-18 Column (10 × 4 mm), mobile phase (5mM Tetrabutyl ammonium hydrogen sulfate) was used at the flow rate of 1 ml/min.

7.2. Results and discussion

7.2.1. Photo electrochemical studies for the reduction of CO_2 on Cu_2O electrocatalyst

Reduction of CO_2 to store solar energy in the form of HCOOH was studied using two electrodes anode (Co_3O_4/G) and cathode (Cu_2O/G). The Photo electrochemical reduction of CO_2 was done in bicarbonate based solutions. The reduction studies were done using bicarbonate based electrolyte solutions and results were discussed in subsequent sections.

7.2.1.1. Photo electrochemical reduction of CO_2 at Cu_2O electrocatalyst in $KHCO_3$ electrolyte solution

Results in figure 7.2 shows the photo electrochemical reduction of CO_2 at Cu_2O electrocatalyst using Co_3O_4 (anode) as anode for H_2O oxidation reaction in $KHCO_3$ electrolyte. The proton that generates at anode reaches Cu_2O (cathode) to react with adsorbed CO_2 to give reduced products. The reactions take place at anode and cathode for CO_2 reduction were shown in figure 7.1. The photo electrochemical reduction of CO_2 in 0.2M $KHCO_3$ solution was shown in figure 7.2a. Different products like CH_3OH, C_2H_5OH and HCOOH were obtained with C_2H_5OH as major amount. Studies on CO_2 reduction electrochemically were performed using Copper (cathode) and expensive Platinum (anode) as catalyst in $KHCO_3$ electrolyte solution and similar products were reported.[98,54]

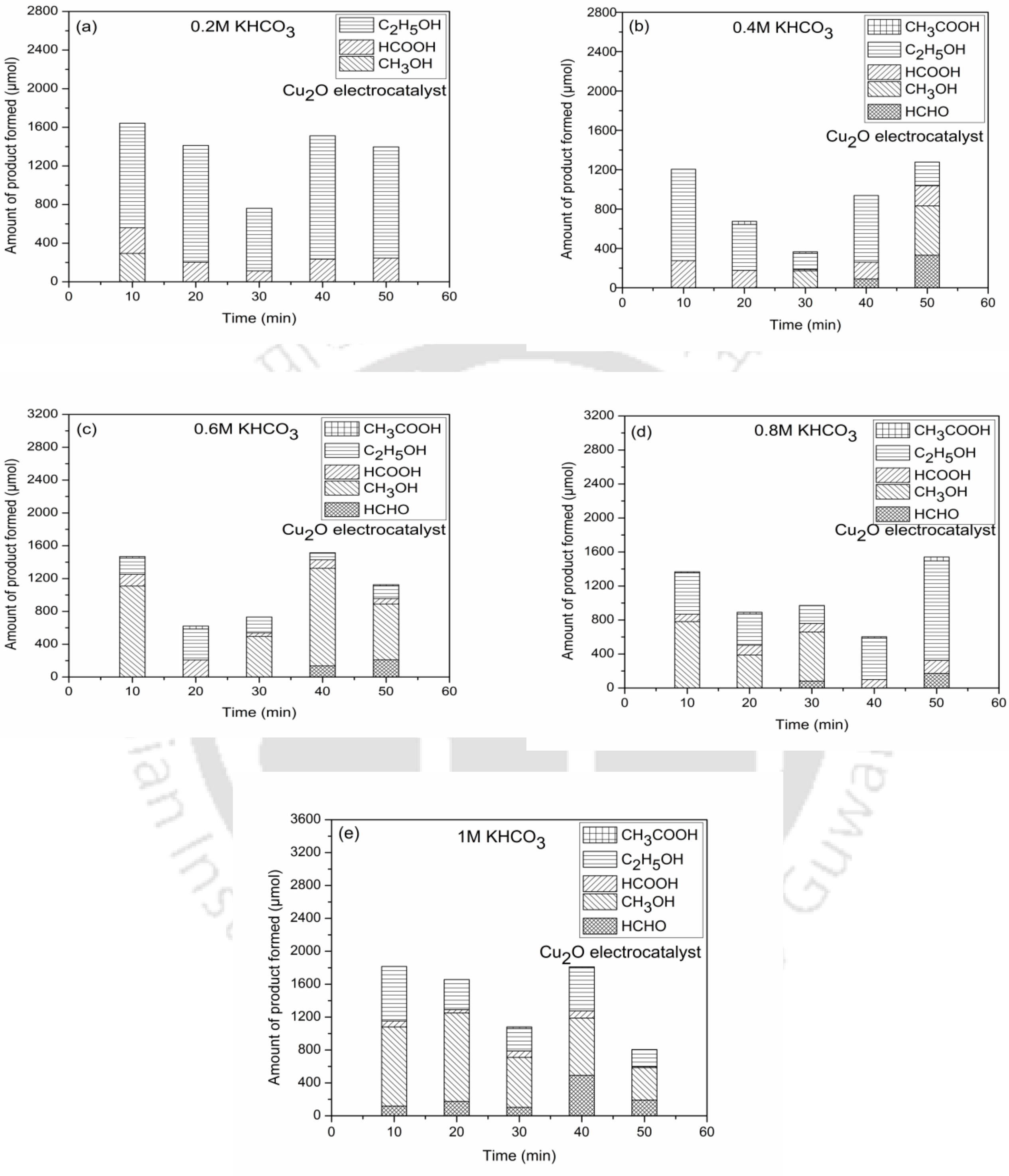

Figure 7.2. (a) Effect of Time vs amount of product formed during of CO_2 reduction in a) 0.2M b) 0.4M c) 0.6M d) 0.8M e) 1M $KHCO_3$ electrolyte solution

In the reaction time of 10, 20, 30, 40 and 50 min for all the cases, both C_2H_5OH and HCOOH were observed as a product. A small amount of CH_3OH was observed after a reaction time of 10 min. The optimized reaction conditions obtained for ethanol was 1277 µmol for 40 min reaction and HCOOH which was 265 µmol for 10 min reaction. The reduction in 0.4M was shown in figure. 7.2b. High concentration of C_2H_5OH was formed along with CH_3OH, HCHO, and CH_3COOH. However, the optimized reaction conditions were seen after reaction of 10 min for C_2H_5OH was 928 µmol and for HCOOH in the range of 176 µmol to 10 min. The electrochemical reduction of CO_2 showed results for formation of C_2H_5OH and HCOOH on copper based catalyst were studied in 0.5M $KHCO_3$ electrolyte solution.[101] The photo electrochemical reduction of CO_2 in 0.6M solution shows the formation of main products C_2H_5OH, CH_3OH, HCOOH and CH_3COOH with some amount of HCHO after 40 min (figure. 7.2c). The maximum reduction conditions for the products HCOOH and C_2H_5OH in this experimental condition was (208 µmol-10 min) and (377 µmol-10 min). Figure.7.2d represents the effect of photo electrochemical reduction of CO_2 in 0.8M electrolyte solution. It may be seen that the C_2H_5OH, CH_3OH, HCOOH and CH_3COOH are the main products along with small amounts of HCHO. The optimized reaction conditions for C_2H_5OH, and HCOOH are (1170 µmol-50 min) and (150 µmol-50 min). The ability of copper electrocatalyst in CO_2 reduction to different products like C_2H_5OH and CH_3OH were studied in $KHCO_3$ electrolyte solution using costly Platinum.[98] The reduction studies in 1M solution were studied and experimental results were shown in figure. 7.2e. All the products C_2H_5OH, CH_3OH, HCOOH and CH_3COOH and HCHO were obtained. The optimized conditions for CO_2 reduction photo electrochemically to C_2H_5OH and HCOOH after reaction times of 10 min and 40 min are 662 µmol and 88 µmol, respectively. From the obtained results it was confirmed that the selected electrocatalyst were able to reduce CO_2 photo electrochemically effectively.

Overall, the selected electrocatalysts were able to reduce CO_2 to different products in all different electrolyte concentrations. However, HCOOH and C_2H_5OH are the main products formed in applied conditions. Maximum C_2H_5OH formation was observed to be (1277 µmol-40 min) in 0.2M and for HCOOH was (276 µmol-10 min) in 0.4M.

7.2.1.2. Photo electrochemical reduction of CO_2 at Cu_2O electrocatalyst in $NaHCO_3$ electrolyte solution

The effect of CO_2 reduction photo electrochemically was studied in $NaHCO_3$ electrolyte solution and respective results were shown in figure.7.3. Different products were formed in different electrolyte concentrations for different sampling times. Reduction happens at cathode with a combination of proton generated at anode to form different reduction products from CO_2. The reduction studies were done in different electrolyte concentrations (0.2, 0.4, 0.6 and 1M) and the results were shown in figure. 7.3(a-e). The photo electrochemical reduction of CO_2 to C_2H_5OH and CH_3OH were studied in $NaHCO_3$ salts on Copper and expensive Platinum based electrocatalyst.[118] The photo electrochemical reduction of CO_2 in 0.2M electrolyte solutions were shown in figure.7.3a. Different products like C_2H_5OH, CH_3OH, HCHO, HCOOH and CH_3COOH were obtained. However, C_2H_5OH and HCOOH were the main products from CO_2 reduction. The optimum conditions for C_2H_5OH and HCOOH were found to be 960 and 178 µmol, respectively, for the reaction time of 50 min. The experimental results in 0.4M solution were shown in figure.7.3b. CH_3OH, C_2H_5OH and HCOOH were identified as main products and the optimized reaction conditions for the reduction of CO_2 to C_2H_5OH and HCOOH was 100 and 300 µmol for 10 min reaction time.

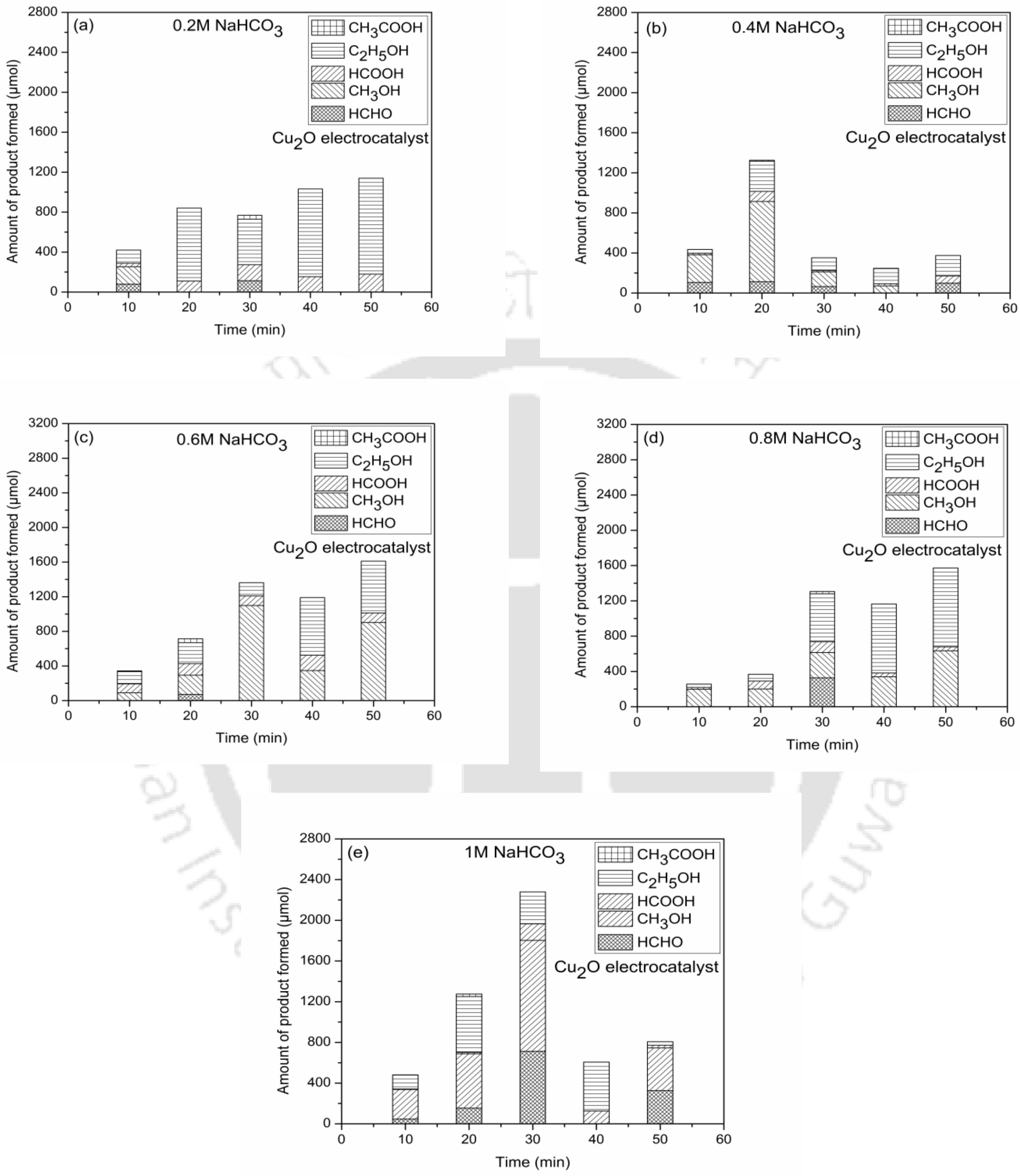

Figure 7.3. (a) Effect of Time vs amount of product formed during of CO_2 reduction in a) 0.2M b) 0.4M c) 0.6M d) 0.8M e) 1M $NaHCO_3$ electrolyte solution

The photo electrochemical studies were done for the reduction of CO_2 on Cu_2O/graphene oxide and reported the reduced product as CH_3OH.[86] The studies in 0.6M electrolyte solution shows the better condition for the products like CH_3OH, C_2H_5OH and HCOOH (Figure.7.3c). The maximum formation of these products mainly C_2H_5OH and HCOOH in reaction times of 40 min are 666 and 177 µmol, respectively. CH_3OH, C_2H_5OH and HCOOH were identified as main products during reduction of CO_2 in 0.8M electrolyte solution (Figure.7.3d). The maximum reduction was shown for ethanol, which was observed to be 894 µmol for the reaction time of 50 min. Won et al., studied the reduction of CO_2 photo electrochemically to HCOOH and CH_3OH on copper based electrocatalyst using costly Platinum.[119] All the discussed products as above were formed during the reaction in 1M solution (Figure.7.3e). Maximum yield was observed for CH_3OH and C_2H_5OH. The optimized condition for C_2H_5OH was found to be 548 µmol for 20 min reaction. By the above discussed results it was observed that electrolyte concentrations were also affecting the reduction rate towards different products which may be due to pH change for different electrolyte solutions. The studies found that mainly C_2H_5OH and HCOOH are mainly observed in all reaction conditions with CH_3OH at higher concentrations with other products in $NaHCO_3$ solution. The selected electrocatalyst reactions conditions were well enough to reduce CO_2 to different products effectively. Maximum formation for C_2H_5OH and HCOOH were observed to be 960 and 178 µmol for the reaction of 50 min in 0.2M electrolyte solution.

The photo electrochemical reduction of CO_2 on Cu_2O electrocatalyst was studied in $KHCO_3$ and $NaHCO_3$ electrolyte solutions. Different products were formed in different electrolyte concentrations with HCOOH and C_2H_5OH as main products confirms from previous sections. For the first time these studies were done using Co_3O_4 for H_2O oxidation and Cu_2O as a cathode for CO_2 reduction for photo electrochemical reduction of CO_2. The optimized conditions towards these two products in both electrolytes were given in Table 7.1.

Table 7.1 Optimized experimental conditions for HCOOH formation on Cu_2O electrocatalyst using solar energy

Molarity	C_2H_5OH				HCOOH			
	Electrolytes				Electrolytes			
	$KHCO_3$		$NaHCO_3$		$KHCO_3$		$NaHCO_3$	
M	**µmol**	**(min)**	**µmol**	**(min)**	**µmol**	**(min)**	**µmol**	**(min)**
0.2	1277	40	960	50	265	10	178	50
0.4	928	10	300	20	276	10	100	20
0.6	377	20	666	40	208	20	177	40
0.8	1170	50	783	40	152	50	122	30
1	662	10	548	20	78	30	161	30

7.3 Photo electrochemical studies for the reduction of CO_2 on Pb_2O electrocatalyst

The studies were done using two electrodes anode (Co_3O_4/G) and cathode (Pb_2O/G). The reduction studies were done in bicarbonates of sodium and potassium based electrolyte solutions and results were discussed in subsequent sections.

7.3.1. Photo electrochemical reduction of CO_2 at Pb_2O electrocatalyst in $KHCO_3$ electrolyte solution

Figure 7.4 shows the results for photo electrochemical reduction of CO_2 in $KHCO_3$ electrolyte solution. The selected electrocatalysts was able to convert CO_2 to HCOOH in all electrolyte concentrations. Low molar concentrations show high product formation than high electrolyte concentrations. The reduction of CO_2 in 0.2M solution was able to form HCOOH with 120.8, 157.3, 129.7, 109.2 and 100.9 µmol in reaction time of 10, 20, 30, 40 and 50 min. Solar energy

Solar energy can able store in the form of HCOOH in this experimental condition.

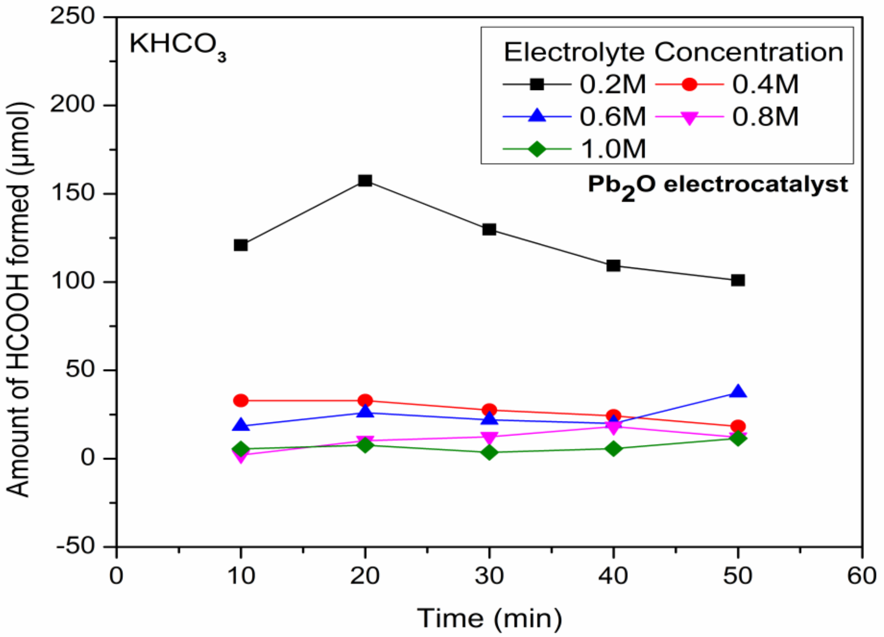

Figure 7.4. Photo electrochemical reduction of CO_2 to HCOOH on Pb_2O electrocatalyst in $KHCO_3$ electrolyte solution

Optimized reaction condition for high reduction is 157 µmol for 20 min. The reduction studies were done using Pb and Pt electrocatalysts as the anode and cathode for CO_2 reduction in $KHCO_3$ electrolyte.[54] The reduction of CO_2 in 0.4M solution shows the amount of HCOOH product formed was less compared with the reduction in 0.2M electrolyte solution which may be due to hydrogen evolution. Moles of HCOOH formed with respect to time are 32.9, 32.8, 27.5, 24.2 and 18.2 µmol. The feasible condition in this electrolyte concentration was 32.9 µmol after 10 min reaction. However, the rates of reduction in 0.6M electrolyte solutions were observed to be 18.4, 25.9, 21.9, 19.9 and 37.3 µmol. Though the reaction in this solution was able to reduce CO_2 to HCOOH, but rate of reduction was low compared with already discussed concentrations. Reduction studied were also done using Pb and Sn electrocatalysts for HCOOH acid generation in potassium based electrolytes.[58] Product moles of (2, 10.1, 12.3, 18.1 and 12.1 µmol) and (5.5, 7.6, 3.5, 5.7 and 11.4 µmol) were obtained in 0.8 and 1M electrolyte concentrations. Moles of HCOOH were observed lower in these concentrations which might be due to high hydrogen generation than CO_2 reduction. However, from the discussed results high reduction was observed in low molar concentrations which were most feasible conditions towards HCOOH formation.

7.3.2. Photo electrochemical reduction of CO_2 at Pb_2O electrocatalyst in $NaHCO_3$ electrolyte solution

The experimental results for photo electrochemical reduction of CO_2 in $NaHCO_3$ electrolyte was shown in figure 7.5. The results confirm the formation of HCOOH as reduction product using the Pb_2O electrocatalyst from CO_2 using solar energy. In different $NaHCO_3$ concentrations the effect of CO_2 reduction was studied. In 0.2M $NaHCO_3$ the moles of HCOOH formed in the reaction times of 10, 20, 30, 40 and 50 min was obtained to be 98.1, 179, 242, 163.6 and 202 µmol. The reduction rate was high in this electrolyte concentration and the maximum conversion (242 µmol) was observed at reaction time of 30 min. The reduction of CO_2 electrochemically on Pb-Pt electrocatalyst was studied and reported the formation of HCOOH.[120] At 0.4M CO_2 reduces to HCOOH and the obtained results were observed to be 58.9, 30.8, 22.6, 19.9 and 111.7 µmol. The optimized condition to conduct reduction reaction photo electrochemically in this electrolyte concentration was 111.7 µmol at reaction time of 50 min. The reduction in 0.6M solution shows low reduction rates comparing with the discussed molar concentrations which may be due to high hydrogen evolution reaction at the cathode surface. The moles of product formed to be 1.8, 4.3, 9.5, 17 and 54.4 µmol in 0.6M solution and optimized condition was observed after 50 min reaction was 54.4 µmol. The yield of HCOOH from CO_2 in bicarbonates based solutions were studied using Pb-Pt catalyst.[5,120] The reduction of CO_2 in 0.8M solution was 9, 13.6, 19.3, 36.2 and 42.5 µmol with maximum conversion after 50 min reaction was 42.5 µmol.

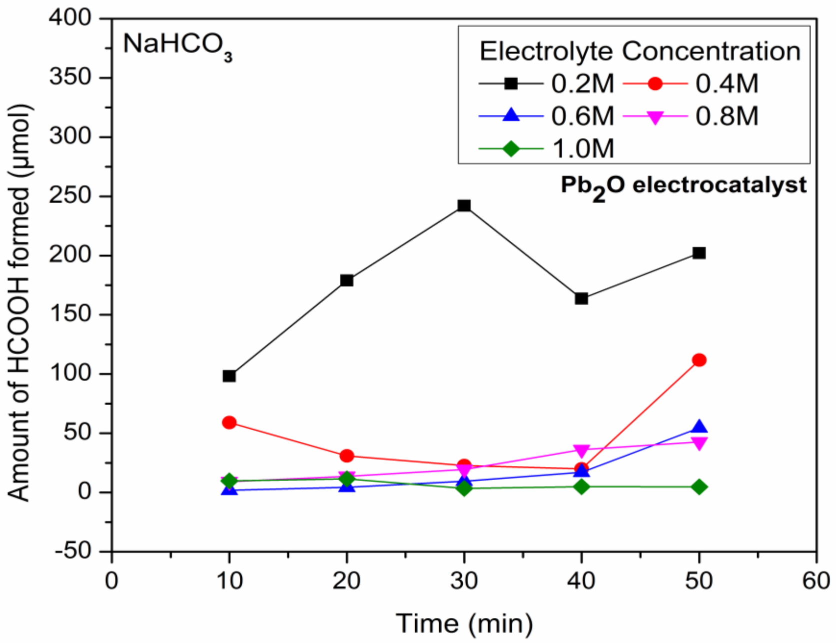

Figure 7.5. Photo electrochemical reduction of CO_2 to HCOOH on Pb_2O electrocatalyst in $NaHCO_3$ electrolyte solution

In 1M solution it was observed to be 9.7, 11.4, 3.3, 4.8, 4.7 µmol with maximum conversion of 11.4 µmol after 20 min reaction. From all the experimental results, conversion was more in low electrolyte concentrations, i.e., in 0.8M and 1M solutions conversion was observed to be low. This was due to the formation of hydrogen at cathode by the formed proton at anode.[115]

The effect of selected electrocatalysts towards photo electrochemical reduction of CO_2 in both $KHCO_3$ and $NaHCO_3$ electrolyte solutions showed the formation of HCOOH as a single product. For the first time using Co_3O_4 as anode and Pb_2O as a cathode for CO_2 reduction by using solar energy. Lower molar concentrations showed better HCOOH conversion than a highly concentrated electrolyte solution. The optimized reaction conditions for the maximum HCOOH formations were shown in Table 7.2.

Table 7.2 Optimized experimental conditions for HCOOH formation on Pb_2O electrocatalyst using solar energy

Molarity	**Electrolytes**			
	$KHCO_3$		**$NaHCO_3$**	
M	**µmol**	**(min)**	**µmol**	**(min)**
0.2	157	20	242	30
0.4	32.9	10	111.7	50
0.6	37.3	50	54.4	50
0.8	12.3	30	42.5	50
1	11.4	50	11.4	20

7.4. Photo electrochemical studies for the reduction of CO_2 on Sn electrocatalyst

The reduction of CO_2 using solar energy was done using anode (Co_3O_4/G) and cathode (Sn/G). Reduction is done in both different concentrations of $KHCO_3$ and $NaHCO_3$ electrolyte solutions and respective results were discussed in subsequent sections.

7.4.1. Photo electrochemical reduction of CO_2 at Sn electrocatalyst in $KHCO_3$ electrolyte solution

The experimental results for the reduction of CO_2 photo electrochemically in $KHCO_3$ is shown in figure 7.6. For the experimental conditions, HCOOH was the product formed in all different electrolyte concentrations, which signifies that electrocatalyst was able to reduce CO_2 to single product HCOOH selectively. From the figure it was observed that low molar solutions have more feasible towards the high HCOOH formation from CO_2 reduction than high concentrations. The reaction in 0.2M solution gives 430.04, 319.19, 372.35, 271.87 and 267.93 µmol in reaction time of 10, 20, 30, 40 and 50 min. However, the reaction in 0.2M shows the best performance of the selected electrocatalyst towards CO_2 reduction to HCOOH using solar energy. The optimized condition for high conversion is 430.04 for 10 min. Peng et al reported the reduction of CO_2 to HCOOH using solar energy in 0.1M $KHCO_3$ electrolyte on Cu catalyst different products like HCOOH, HCHO, CH_3OH, were reported.[27] The CO_2 reduction in 0.4M solution shows better reduction rate, but less compared to reaction in 0.2M electrolyte solution.

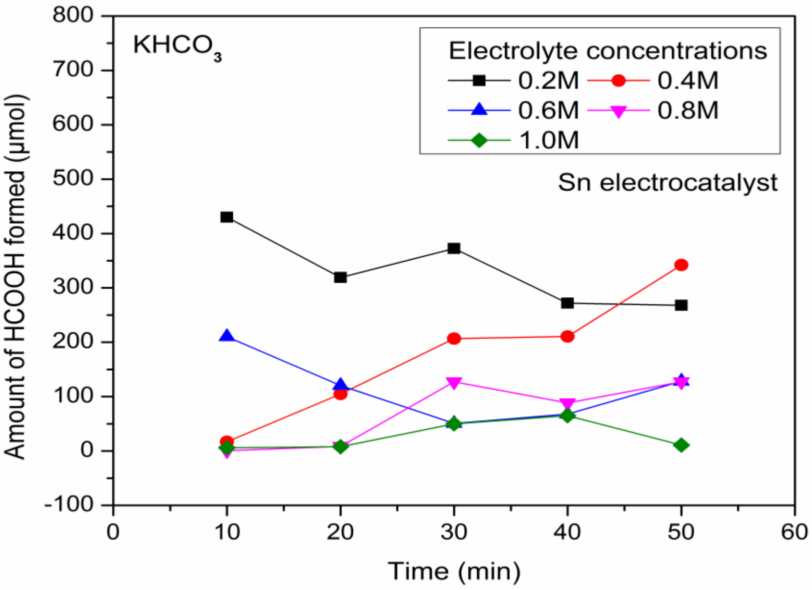

Figure 7.6. Photo electrochemical reduction of CO_2 to HCOOH on Sn electrocatalyst in $KHCO_3$ electrolyte

Amount of HCOOH formed with respect to time in solution is to be 16.85, 104.88, 206.73, 210.51 and 342.01 µmol. As time increases the reaction increases gives maximum conversion after a reaction time of 50 min is 342.01 µmol to be optimized condition. Though the reaction in 0.6M solution is good, but rate of reduction is low when compared to the above discussed conditions. 210.11, 120.38, 50.82, 67.75 and 128.21 µmol are observed for sampling times as shown in figure 7.6. Lower concentrations of HCOOH are observed which may be due to hydrogen evolution reaction more favorable than CO_2 reduction.[121] The reduction in 0.8 and 1M electrolyte solutions were low which may be due to high hydrogen evolution than CO_2 reduction. The moles of HCOOH formed is observed to be 0.68, 8.36, 127.21, 88.33 and 127.19 µmol at 0.8M & 5.72, 8.07, 49.94, 65.01 and 10.89 µmol at 1M. The rate of HCOOH formation from CO_2 is discussed in $KHCO_3$ electrolyte solution and the optimized condition for conversion rates to be low electrolyte solutions.

7.4.2. Photo electrochemical reduction of CO_2 at Sn electrocatalyst in $NaHCO_3$ electrolyte solution

The experimental results in the formation of HCOOH from photo electrochemical reduction of CO_2 with time in $NaHCO_3$ electrolyte solution is shown in figure 7.7. Experimental condition for the selected electrocatalyst was able to reduce CO_2 to HCOOH effective in different concentrations of $NaHCO_3$ solution. The reduction in 0.2M $NaHCO_3$ was obatined to be 494.6, 452.85, 339.27, 470.11 and 330.19 µmol for the reaction times of 10, 20, 30, 40 and 50 min. However, high conversions were observed in this condition and the optimized condition is 494.6 µmol for reaction time of 5 min. Photo electrochemical reduction of CO_2 to HCOOH in $NaHCO_3$ electrolyte solutions were reported.[60] In 0.4M concentration solution gives a possible reduction of CO_2 and moles of the product formed are obtained to be 25.9, 33.03, 29.73, 162.21, 13.61 µmol. Initial reaction shows low conversion after a reaction time of 40 min maximum conversion is obtained to be 162.21 µmol which is optimal in the electrolyte conditions. However, the rate of CO_2 reduction is lowest in 0.6, 0.8 and 1M electrolyte concentrations which may be due to high hydrogen evolution reaction at the cathode surface.[122] Moles of HCOOH formed in 0.6M solution was 3.1, 7.07, 6.42, 16.85, 27.75 µmol for reaction times and the optimized condition to be a reaction after 50 min which is 27.75 µmol. The CO_2 reduction in 0.8M solution is 3.19, 2.3, 14.31, 15.76 and 18.64 µmol as time increases the conversion rate is increasing, but the conversion rate is very low compared with reaction in 0.2M solution which may be too high hydrogen favorable reaction as shown in figure 7.7. Whereas in 1M solution the moles of HCOOH were obtained to be 3.03, 18.73, 10.04, 14.32 and 0.76 µmol and the optimized reaction condition to be 18.73 µmol for reaction time of 20 min.

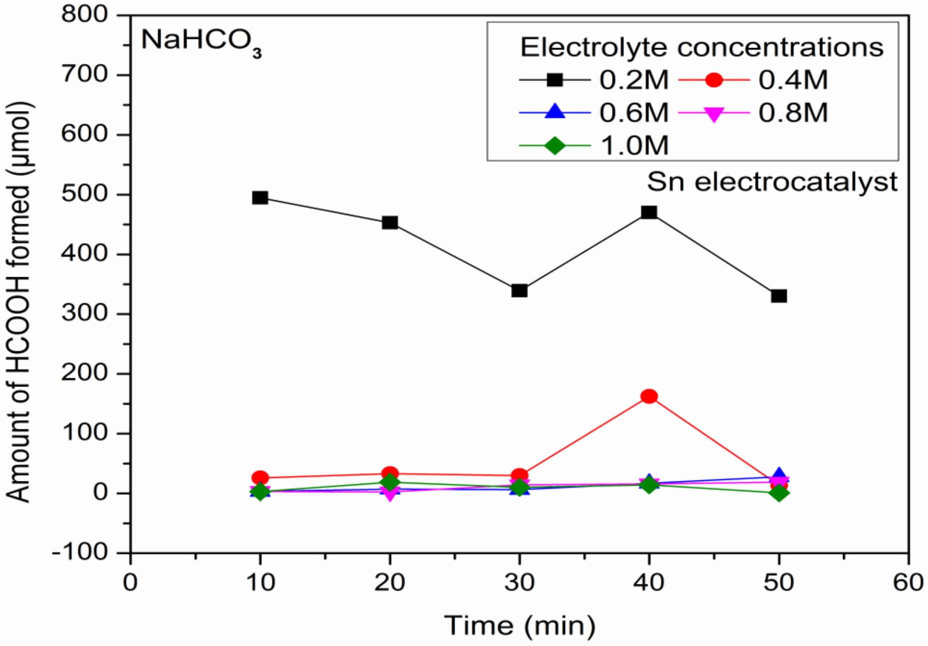

Figure 7.7. Photo electrochemical reduction of CO_2 to HCOOH on Sn electrocatalyst in $NaHCO_3$ electrolyte

The ability of the Co_3O_4 as anode and Sn as cathode towards photo electrochemical reduction of CO_2 is confirmed by results discussed in previous section. However, in both $KHCO_3$ and $NaHCO_3$ electrolyte solutions, low molar concentrations shows better conversion rates than a high concentrated electrolyte solution. The optimized reaction conditions for the photo electrochemical reduction of CO_2 to HCOOH were shown in Table 7.3.

Table 7.3 Optimized experimental conditions for reduction of CO_2 on Sn electrocatalyst using solar energy

Molarity	Electrolytes			
	$KHCO_3$		$NaHCO_3$	
M	**µmol**	**(min)**	**µmol**	**(min)**
0.2	430.04	10	494.60	10
0.4	342.01	50	162.21	40
0.6	210.11	10	27.75	50
0.8	127.21	30	18.64	50
1	65.01	40	18.73	20

7.5. Photo electrochemical studies for the reduction of CO_2 on Zn electrocatalyst

The photo electrochemical reduction of CO_2 was done using anode (Co_3O_4/G) and cathode (Zn/G). The experimental were studied in different concentrations of $KHCO_3$ and $NaHCO_3$ electrolytes respectively, and results in the formation of HCOOH as product were discussed in next sections.

7.5.1. Photo electrochemical reduction of CO_2 at Zn electrocatalyst in $KHCO_3$ electrolyte solution

Figure 7.8 confirms the only product formed during the photo electrochemical reduction of CO_2 on Zn electrocatalyst in different $KHCO_3$ solutions is HCOOH. The reduction of CO_2 in 0.2M electrolyte solution shows higher conversions than other molar concentration solutions. The moles of HCOOH formed at this condition are observed to be 400.02, 358.99, 355.01, 309.75 and 138.95 µmol for the reaction time of 10, 20, 30, 40 and 50 min. This shows high conversion rates towards CO_2 reduction in the applied experimental condition and the optimized condition is 400.02 µmol for 10 min reaction. The photo electrochemical reductions of CO_2 in 1M $KHCO_3$ electrolyte solutions were reported.[123] The reaction in 0.4M electrolyte solution shows the feasible conversion rate, but low compared with 0.2M solution. The moles of HCOOH formed are obtained to be 46.40, 36.14, 170.38, 208.41 and 74.26 µmol which confirms that electrolyte concentration affect the reduction rates which may be due to high hydrogen formation at the cathode.[117] The optimized condition at this electrolyte concentration is 208.41 µmol for 40 min reaction. Photo electrochemical reduction of CO_2 to HCOOH in 0.6M electrolyte solution shows that moles of product formed to be 27.19, 93.32, 22.62, 98.38 and 56.11 µmol which are low compared with reaction at 0.4M.

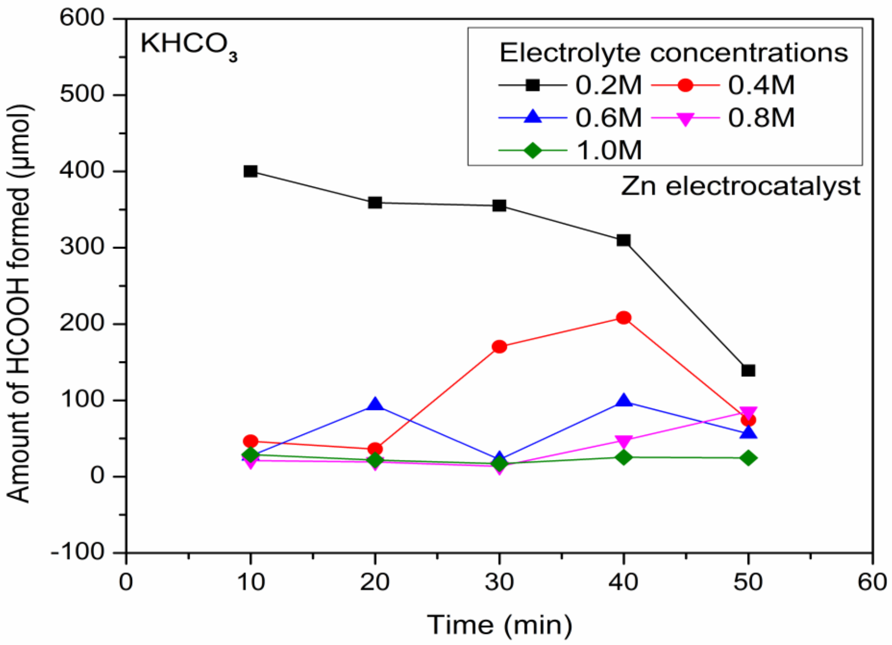

Figure 7.8. Photo electrochemical reduction of CO_2 to HCOOH on Zn electrocatalyst in $KHCO_3$ electrolyte

Optimized condition towards higher conversion is 98.38 for 40 min. Similarly, the reaction in 0.8M and 1M have shown low conversions comparing with low molar concentrations which may be due to high proton participation at the cathode for hydrogen formation.[124] Reaction in 0.8M electrolyte solution shows the formation of HCOOH to be 21.05, 19.25, 13.55, 47.53 and 85.31 µmol with high conversion at reaction time of 50 min is 85.31 µmol. The rate of HCOOH formation, with time in 1M solution is 28.81, 21.67, 17, 25.38 and 24.61 µmol. For a reaction time of 5 min shows high conversion rate towards HCCOH formation is 28.81 µmol. The results in figure 7.8 confirm that low molar concentrated solutions are more feasible for CO_2 conversion rates for the formation of HCOOH.

7.5.2. Photo electrochemical reduction of CO_2 at Zn electrocatalyst in $NaHCO_3$ electrolyte solution

Experimental results for the photo electrochemical reduction of CO_2 to HCOOH with time in $NaHCO_3$ electrolyte solution was shown in figure 7.9. The figure confirms the selected Co_3O_4 as anode and Zn as cathode is able to reduce CO_2 to HCOOH effectively in all molar solutions. For the reaction time of 10, 20, 30, 40 and 50 min the formation rates of HCOOH were obtained to be 146.23, 176.07, 187.06, 254.01 and 169.11 µmol. The optimized experimental condition towards the high HCOOH formation is 254.01 µmol for 40 min reaction. Solar driven reduction of CO_2 on Zn catalyst in $NaHCO_3$ electrolyte was reported.[60] Moles of HCOOH (51.68, 49.04, 37.13, 78.62 and 43.14 µmol) were formed from the reaction in 0.4M electrolyte solution. The rate of reaction towards HCOOH was low compared with 0.2M solution which may be due to high hydrogen evolution than CO_2 reduction. The photo electrochemical reduction of CO_2 to HCOOH (25.38, 6.71, 19.3, 41.88 and 81.85 µmol) was observed in 0.6M electrolyte solution. The optimized condition is 81.85 µmol for the reaction time of 50 min. Low conversions have observed in 0.8 and 1M solutions may be due to high hydrogen formation.[122] However, 30.69, 34.48, 55.67, 42.64 and 57.12 µmol in 0.8M solution, whereas 42.61, 19.13, 8.74, 28.63 and 45.71 µmol in 1M solution respectively in figure 7.9. The optimized conditions were 57.12 (50 min) and 45.71 (50 min) for 0.8 and 1M solutions. Similar results were observed for $NaHCO_3$ as $KHCO_3$ that low molar concentration shows high CO_2 conversions than others. The photo electrochemical reduction of CO_2 to HCOOH was studied using Co_3O_4 as anode and Zn as cathode. The selected electrocatalysts are able to reduce CO_2 by using solar energy is confirmed by results discussed in previous sections. The low molar electrolyte solutions show better conversions in both $KHCO_3$ and $NaHCO_3$ electrolyte based solutions. The optimized reaction conditions were shown in Table 7.4.

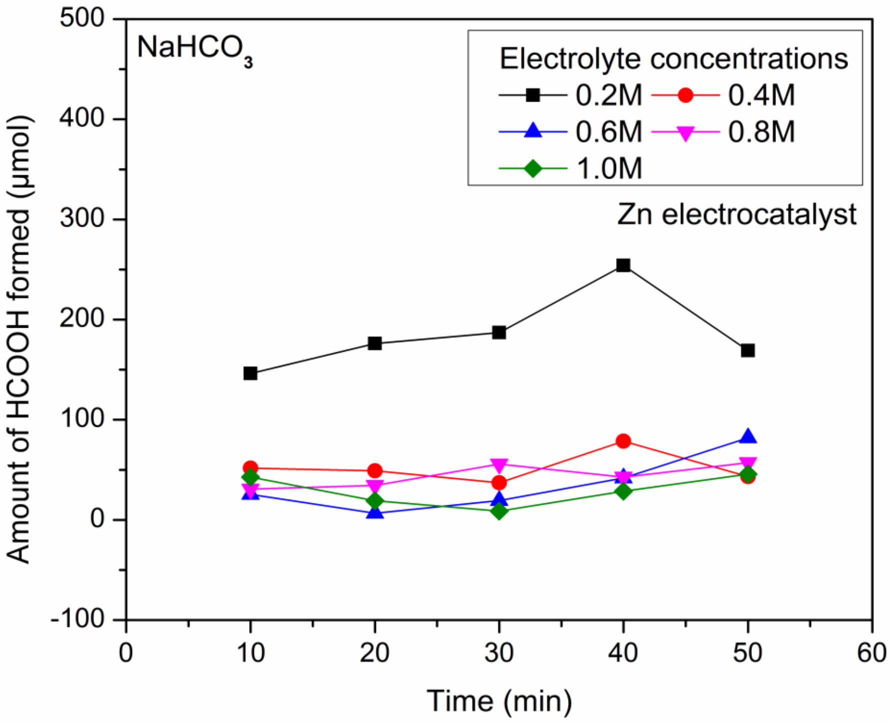

Figure 7.9. Photo electrochemical reduction of CO_2 to HCOOH on Zn electrocatalyst in $NaHCO_3$ electrolyte

Table 7.4 Optimized experimental conditions for reduction of CO_2 on Zn electrocatalyst using solar energy

Molarity	Electrolytes			
	$KHCO_3$		$NaHCO_3$	
M	µmol	(min)	µmol	(min)
0.2	400.02	10	254.01	40
0.4	208.41	40	78.62	40
0.6	98.38	40	81.85	50
0.8	85.31	50	57.12	50
1	28.81	10	45.71	50

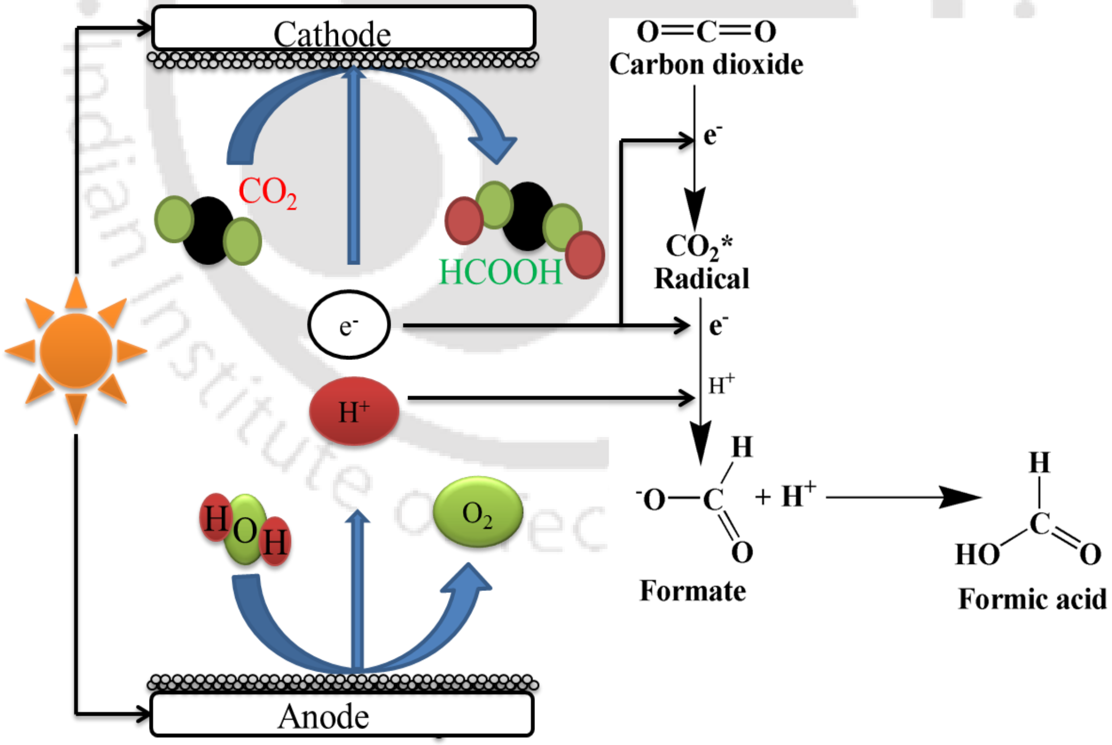

Figure 7.10. Proposed elementary mechanism for photo electroreduction of CO_2 to HCOOH

Elementary mechanism for HCOOH formation from CO_2 reduction is given in figure 7.10. The adsorbed CO_2 on cathode accepts electron to form radical. The radical reacts with proton and electron that are generated at anode due to water oxidation reaction to form formate with some internal arrangements. The new formate further accepts proton to form HCOOH.

7.6. Summary

In this work photo electrochemical studies were performed for the reduction of CO_2 to product. Cu_2O, Pb_2O, Sn and Zn were used as catalysts in the cathode whereas Co_3O_4 was used in anode for H_2O oxidation. The results confirmed the formation of different products (mainly C_2H_5OH and HCOOH) in all the electrolyte concentrations using Cu_2O electrocatalyst. For Pb_2O, Sn and Zn, the only product formed in all experimental conditions was HCOOH. This study discussed a brief about the importance in the use of cheap Co_3O_4 as an alternative of costly Platinum (Pt) electrocatalyst for effective CO_2 reduction photo electrochemically.

Chapter 8

Simultaneous CO_2 reduction and dye removal electrochemically on Sn and Zn catalysts using Co_3O_4 anode

Chapter 8

Simultaneous CO_2 reduction and dye removal electrochemically on Sn and Zn catalysts using Co_3O_4 anode

This chapter describes the application for simultaneous CO_2 reduction and removal of crystal violet (CV), methylene blue (MB) and brilliant green (BG) dye separately from aqueous medium. The studies were done using Sn and Zn electrocatalysts as cathode and Co_3O_4 as anode which were able to get high Faradaic efficiencies towards CO_2 reduction.

8.1. Experimental

8.1.1. Materials

Graphite plates of (1.5 × 2.5 cm^2, Sunrise Enterprises, Mumbai) were used base for catalyst coating. Bicarbonate salts ($NaHCO_3$ and $KHCO_3$), iso-propanol ($(CH_3)_2CHOH$) were purchased from Merck, India. Crystal violet, Methylene blue, Brilliant green were purchased from Qualigens, India whereas Nafion (5wt.%) solution was procured from DuPont, USA. All experiments were done with deionized water.

8.1.2. Preparation of catalyst coated graphite electrode

To coat the surface of graphite plate with the catalyst, the ink was prepared using binder (1:5 (nafion+IPA (Iso propanol)) of 200 µl solution) with mixing 7.5 mg of electrocatalyst (Co_3O_4, Zn & Sn) by 30 min sonication to get catalyst at a rate of 2 mg/cm^2. The preparation of electrocatalyst ink was based on electrocatalyst used to prepare electrode. The coating was done at 80 ^{o}C and dried at 100 ^{o}C for 2h to get the electrocatalyst coated electrode.

8.1.3. Electrochemical studies for RCPE and dye removal

In order to study the effect of electrocatalyst towards simultaneous CO_2 reduction and dye removal, a 2-electrode glass cell was used as shown in Figure 8.1.

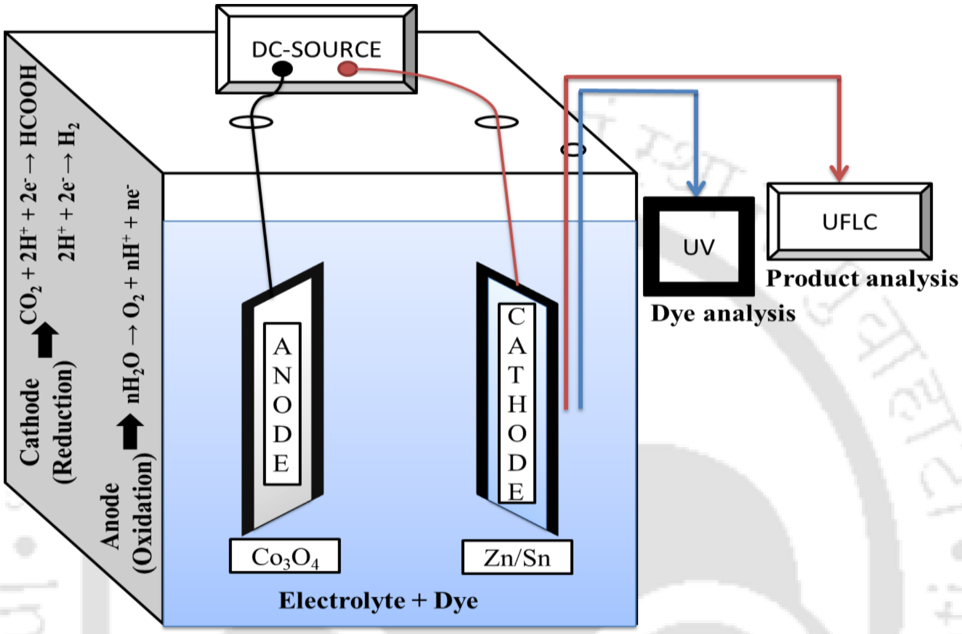

Figure 8.1. Schematic setup for simultaneous RCPE and CV dye removal

The electrolyte solutions of 0.5 M 80 ml (10 ppm dye) was prepared and saturated with CO_2 by bubbling for 50 min. The solution was dipped with the prepared electrodes either Co_3O_4/G – Zn/G or Co_3O_4/G – Sn/G to DC source. Experiments were conducted in 0.5 M (10 ppm CV) $KHCO_3$ and $NaHCO_3$ electrolyte solutions at different applied voltages with a reaction time of 0-5, 10, 15, 20 and 25 min.

8.1.4 Product and dye removal analysis

The product analysis was done by using ultra-fast liquid chromatography (UFLC), Shimadzu LC-20AD, UV-detector of deuterium lamp (SPD-20A) at 205 nm. 20 μl of reacting sample was injected into the C-18 column (10 × 4 mm), 5mM Tetrabutyl ammonium hydrogen sulfate used as mobile phase at the flow rate of 1 ml/min. A UV-Visible Spectrophotometer (Perkin Elmer, Model: Lambda 35) was used to determine the dye concentrations to find the % removal. The Faradaic efficiency of product was calculated by the charge utilized to form a particular product with respect to the overall charge utilized for the reaction. The % removal was calculated using initial and final concentrations of dye in the reaction.

8.2. Results and discussion

8.2.1. Simultaneous RCPE and CV removal using Sn and Co_3O_4 electrocatalyst

The studies were done using anode (Co_3O_4/G) and cathode (Sn/G). The reduction of CO_2 and % CV removal were analyzed in both $KHCO_3$ and $NaHCO_3$ electrolyte solutions and their respective results with applied voltages were discussed in subsequent sections.

8.2.1.1. Effect of current density at Sn electrocatalyst on applied voltage in CV solution

The results for current density in applied voltage in $KHCO_3$ and $NaHCO_3$ electrolytes at Sn electrocatalyst are shown in Figure 8.2a. As the applied voltage increases the current density increases in both the cases. Current density signifies rate of reaction with respect to applied voltage which is sigh for RCPE and hydrogen evolution. However, Figure 8.2 shows that $KHCO_3$ gives high current density compared with $NaHCO_3$ confirms the reaction rate of potassium based electrolyte is more. Overall, the rate of reaction towards RCPE and CV removal in various applied conditions with current density clearly discussed.

8.2.1.2. RCPE and CV dye removal at Sn cathode in $KHCO_3$ solution

The experimental results for RCPE and CV removal in 0.5 M (10 ppm CV) $KHCO_3$ solution are shown in Figure 8.2(b, d). HCOOH was formed as the only product during RCPE for all the applied voltages. It was observed from the figure that high Faradaic efficiencies were at low applied voltages compared with higher applied voltages. Similarly, high CV removal was observed at higher applied voltages than low applied voltages. From Figure 8.2(d-e) it may be seen that as time increases the CV removal percentage is increased. Faradaic efficiencies where changes with times which may be due to oxidation of the formed product after a certain time of reaction as shown in Figure 8.2(b-c).[115] The concurrent CO_2 reduction and methyl orange dye removal was studied in $KHCO_3$ electrolyte solution using copper as electrocatalyst.[27] High Faradaic efficiencies for HCOOH were obtained at 2 V at reaction time of 5, 10, 15, 20 and 25 min were 23.3, 24, 10.8, 10.4 and 6.8 % and CV removal are 11.9, 13.1, 14.4, 15 and 15.3 % respectively. Overall, for reaction at 2 V, significant results were observed for both HCOOH formation and CV removal and Faradaic efficiency was more compared to CV removal. Hori et al., reported the reduction of CO_2 towards HCOOH formation on Sn electrocatalyst in $KHCO_3$ electrolyte solution.[5] For reaction at 2.3 V, Faradaic efficiencies were 17.1, 8.7, 0.8, 1.6 and 1.7 % and CV removal was found to be 12.7, 18.3, 18.5, 23.5 and 25.9 %, respectively (Figure 8.2(b, d)). The results for RCPE and CV removal at 2.5 V were obtained to be (19.8, 8.9, 6.4, 3.8 and 3.6 %), (14.8, 17.2, 24.3, 28.8 and 38.7 %) respectively. Significant results for high CV removal than Faradaic efficiencies were obtained. Studies on Sn electrocatalyst towards HCOOH in potassium based salt was reported.[67] At 2.8 V, the Faradaic efficiency for HCOOH is 3.7, 1.2, 1.4, 0.4 and 1.3 % and CV removal was obtained with 13.6, 23.6, 31.1, 34.8 and 39.9 %. The Faradaic efficiencies obtained at 3.3 V (1.8, 2.6, 0.7, 1.1 and 1 %), 3.8 V (2.1, 1.1, 0.4, 0.5 and 0.4 %) and dye removal at 3.3 V (28.1, 34.1, 43.7, 48.7 and 53.7 %), 3.8 V (42.3, 52, 59.7, 65 and 71.5 %) respectively. From the experimental results in $KHCO_3$ electrolyte solution the applied voltages are proportional to CV removal.

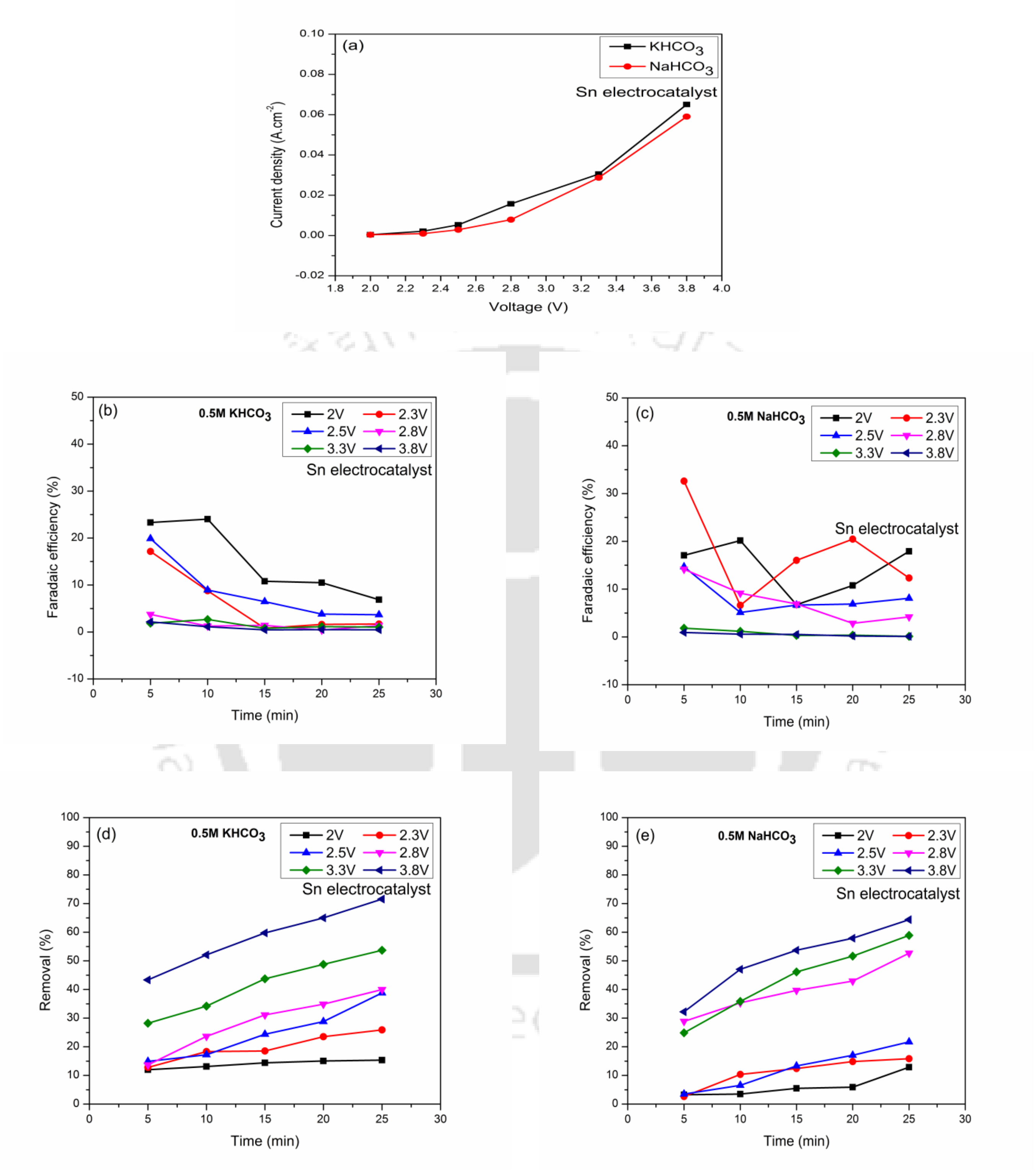

Figure. 8.2 (a) Voltage vs Current density, (b - c) FE vs Time and (d - e) CV Removal (%) vs Time at different applied voltages during RCPE in $KHCO_3$ and $NaHCO_3$ using Sn.

Faradaic efficiencies were reduced at high voltages which may be due to the high proton generation at anode (Co_3O_4) causes the formation of H_2 gas at the cathode (Sn).[125] However, from the above results it was known that electrocatalyst (Sn) was able to reduce CO_2 to HCOOH using Co_3O_4 as an anode for CV removal effective for all applied conditions.

8.2.1.3. RCPE and CV dye removal at Sn cathode in $NaHCO_3$ solution

The Faradaic efficiency of HCOOH formation and CV removal with time at different applied voltages in 0.5 (10 ppm CV) M $NaHCO_3$ electrolyte solutions were discussed in Figure 8.2(c, e). From the results it was observed that high CV removal and low Faradaic efficiencies were observed at high applied voltages and scenario is reversed for the case of low applied voltages as same as reaction in $KHCO_3$ electrolyte solution. The experimental results at 2 V were observed with 5, 10, 15, 20 and 25 min reaction was Faradaic efficiency (17, 20.1, 6.7, 10.7 and 17.9 %), CV removal (3.24, 3.4, 5.4, 5.8 and 12.7 %) respectively. For the applied condition removal was low compared with Faradic efficiency, which clearly sign for CV removal favorable at high applied voltage's compared with low applied voltages as discussed. The reduction of CO_2 to HCOOH at lead based electrocatalyst in $NaHCO_3$ electrolyte was reported.[115] Of reaction at 2.3 V, results were observed for Faradaic efficiency is 32.59, 6.6, 16, 20.4 and 12.3 % (Figure 8.2c) and CV removal to be 2.6, 10.34, 12.4, 14.8 and 15.8 % (Figure 8.2e). CV removal was increased as applied voltage's increases, which oxidation of the CV will be more at higher applied voltages whereas decrease in Faradaic efficiencies may be due to the oxidation of formed HCOOH as reaction time increases.[125] Faradaic efficiencies and CV removal of around 14.6, 5.1, 6.6, 6.8 and 8.1 % and 3.4, 6.5, 13.2, 17 and 21.7 % at 2.5 V were obtained in the reaction time of 5, 10, 15, 20 and 25 min respectively. However, results depict that Faradaic efficiencies were decreased compared with an above discussed conditions which may be due to high hydrogen at the cathode by protons generated at anode.[116] The formation of HCOOH from CO_2 in $NaHCO_3$ electrolyte solution using oxides of Sn electrolcatalyst.[114] The reaction at 2.8 V, Faradic efficiencies of 14.1, 9.1, 6.8, 2.8 and 4.1 % whereas for CV removal was obtained as 28.8, 35.3, 39.6, 42.9 and 52.6 % says that low Faradaic efficiencies were obtained at this applied voltage with high CV removal. Low Faradaic efficiencies were obtained at 3.3 and 3.8 V with CV removal up to 64.3 % at 3.8 V after reaction time of 25 min. The results say that higher applied voltages were favorable for CV removal, low applied voltage for high Faradaic efficiency. The RCPE and CV removal in $NaHCO_3$ electrolyte solution shows that the selected experimental condition was able to reduce CO_2 to HCOOH and CV removal. However, 2 V is favorable for high Faradaic efficiency of HCOOH and 3.8 V favorable for maximum CV removal which is same as reaction in $KHCO_3$ electrolyte.

8.2.2. Simultaneous RCPE and CV removal using Zn electrocatalyst

The reaction was conducted using anode (Co_3O_4/G) and cathode (Zn/G). RCPE and % CV removal were studied in both bicarbonates of sodium and potassium electrolytes and the results were discussed.

8.2.2.1. Effect of current density at Zn electrocatalyst on applied voltage in CV solution

The experimental results for CO_2 reduction and CV dye removal on Zn electrocatalyst is shown in figure 8.3. The reaction in $KHCO_3$ and $NaHCO_3$ electrolytes with respect to current density and applied voltages are shown in Figure 8.3a. Current density is signed for the rate of reaction towards RCPE or CV dye removal. The current density increases with applied voltage in both electrolytes which means high reaction rate either due to RCPE or hydrogen evolution. However, figure 8.3 shows that current densities in $NaHCO_3$ are slightly higher than $KHCO_3$ confirmed high reaction in $NaHCO_3$ electrolyte.

8.2.2.2. RCPE and CV dye removal at Zn cathode in $KHCO_3$ solution

Reduction of CO_2 and CV removal in 0.5 M (10 ppm CV) $KHCO_3$ solutions towards HCOOH formation is shown in figure 8.3. HCOOH was obtained at all applied conditions as above and respective Faradaic efficiencies and CV removal were observed for reaction time of 5, 10, 15, 20 and 25 min reaction. For reaction at 2 V, Faradaic efficiencies (14.9, 6.3, 29.1, 7.6 and 3 %) and CV removal (8.75, 9.1, 9.3, 9.6 and 10 %) were obtained and shown in figure 8.3 (b-d)). High Faradaic efficiency of 29.1 % was obtained at the reaction of 15 min, whereas dye removal was low which may be due to lower applied voltages. Synthesis of Zn electrocatalysts towards RCPE in different electrolyte solutions was reported and for all the conditions it was reported that HCOOH is the only product formed.[117] At 2.3 V, HCOOH Faradaic efficiencies along with CV removal were observed as (45.1, 9.7, 16.4, 3 and 4.2 %) and (8.4, 11.2, 13.3, 16.4 and 17.8 %) respectively. Comparing with reaction at 2 V, Faradaic efficiencies towards HCOOH formation was high and optimized reaction condition is 45.1 % for 5 min. Similarly the percentage dye removal is increasing which shows that high applied voltage's is favorable for better dye removal. Faradaic efficiencies and CV removal of around 7, 2.3, 6.5, 7.9 and 1.8 % (Figure 8.3b), 2.3, 6.7, 14.4, 16.8 and 20.2 % (Figure 8.3d) were obtained at 2.5 V. Faradaic efficiencies were reduced compared with above applied voltage's which may be due to high hydrogen evolution than CO_2 reduction as proton generation is high due to water oxidation reaction at anode.[117] Maximum CV removal of 33.7, 36.1, 38.3, 42, 47.3 % and minimum Faradaic efficiencies of 3.6, 2.2, 4.1, 0.69 and 0.62 % were obtained at 2.8 V. HCOOH from CO_2 reduction in $KHCO_3$ electrolyte solution was reported using Pt as electrocatalyst.[5,67] At 3.3 and 3.8 V, Faradaic efficiencies of (1.6, 2.21, 0.47, 0.9, 0.22 %), (2.2, 0.51, 0.29, 0.33, 0.16 %) were obtained with CV removal up to 60.9% at 3.8 V. When applied high voltages may be maximum

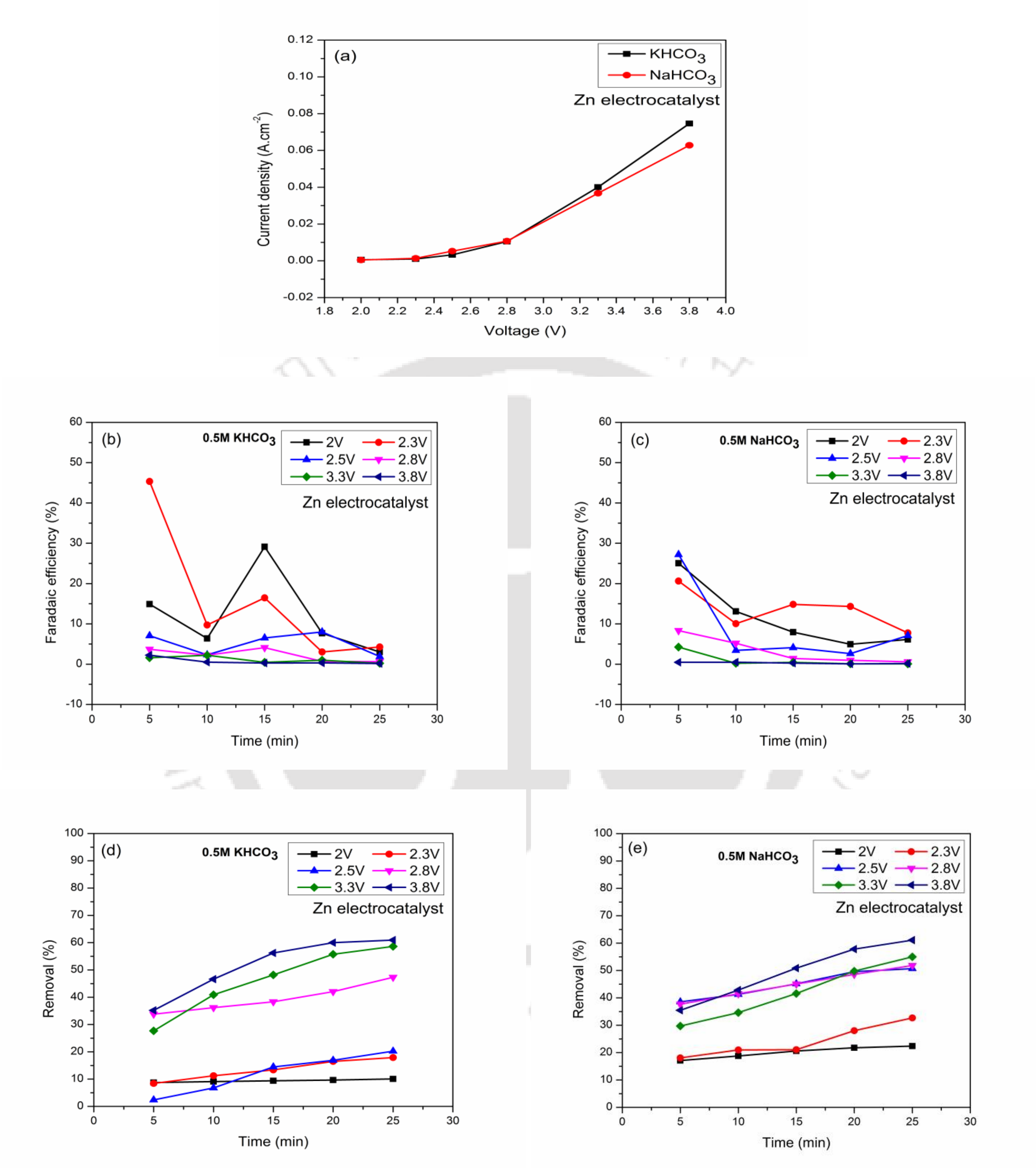

Figure. 8.3 (a) Voltage vs Current density, (b - c) FE vs Time and (d - e) CV Removal (%) vs Time at different applied voltages during RCPE in $KHCO_3$ and $NaHCO_3$ using Zn.

oxidation of CV dye taking place at anode which causes an increase in hydrogen evolution and hinders the CO_2 reduction.[117] From the above results it is depicted that higher applied voltages are favorable for CV removal and low applied voltages are for CO_2 reduction. The selected Zn as cathode and Co_3O_4 as anode were significant towards reduction of CO_2 to HCOOH as a single product and CV removal at all applied voltages.

8.2.2.3. RCPE and CV dye removal at Zn cathode in $NaHCO_3$ solution

The result in Figure 8.3(c, e) shows for simultaneous CO_2 reduction to HCOOH and CV removal in 0.5M (10 ppm CV) $NaHCO_3$ electrolyte solutions. The reactions were done at different applied voltages of 2, 2.3, 2.5 and 2.8 V for the reaction times of 5, 10, 15, 20 and 25 min. The reduction of CO_2 in $NaHCO_3$ based electrolyte solution using Zn electrocatalyst was reported for HCOOH formation.[60] The reaction at 2 V, with Faradaic efficiencies and CV removal were obtained as (25, 13.1, 7.9, 4.9 and 6.1 %) and (17.1, 18.7, 20.5, 21.7 and 22.3 %) respectively. The optimum reaction condition towards high HCOOH Faradaic efficiency and CV removal were 5 min and 25 min. As time increases the removal percentage is increasing, whereas Faradaic efficiency is decreasing, which may be due to the HCOOH oxidation at Co_3O_4 anode.[125] The obtained results at 2.3 V were 20.63, 10, 14.8, 14.3 and 7.7 % for HCOOH Faradaic efficiency and 18, 20.9, 21, 27.9 and 32.6 % for CV removal. The experimental studies were done using Zn electrocatalyst towards HCOOH formation in sodium based salts were reported.[117] The optimum condition for RCPE towards HCOOH is 20.63 for the reaction time of 5 min. At 2.5 V, Faradaic efficiencies (27.2, 3.4, 4.1, 2.6 and 7.09 %), CV removal (38.5, 41.2, 45.1, 49.5 and 50.6 %) respectively were obtained. The results show that CV removal is increased compared with 2 and 2.3 V. At 2.8 V the HCOOH Faradaic efficiency was observed to be 8.33, 5.18, 1.4, 0.96 and 0.59 % whereas CV removal is 37.6, 41.4, 45.04, 48.5 and 51.8 %

respectively. Faradaic efficiencies were obtained to be at 3.3 V (4.2, 0.23, 0.44, 0.1 and 0.07 %), 3.8 V (0.46, 0.48, 0.27, 0.07 and 0.17 %) with CV removal of (27.6, 40.9, 48.1, 55.7, and 58.6 %), (35.1, 46.6, 56.2, 59.9 and 60.9 %) at 3.3, 3.8 V (Figure 8.3) respectively. For a reaction at 3.8 V, shows high CV removal which shows that higher applied voltages were favorable for maximum dye removal. But Faradaic efficiencies were reduced at this voltage which may be due to high concentrations of protons at cathode compared with CO_2.[125] The applied conditions were able to reduce CO_2 to HCOOH and CV removal. From the results, the favorable conditions towards high Faradaic efficiency were low applied voltages and for maximum CV removal is obtained at higher applied voltages. The experimental results towards RCPE and dye removal state that the selected reaction conditions were able to do so.

Table 8.1 Optimized conditions towards HCOOH Faradaic efficiency in different catalysts

Applied Voltage	**Maximum Faradaic efficiency (time)**							
	Sn				**Zn**			
	$KHCO_3$		**$NaHCO_3$**		**$KHCO_3$**		**$NaHCO_3$**	
(V)	**(%)**	**(min)**	**(%)**	**(min)**	**(%)**	**(min)**	**(%)**	**(min)**
2	24	10	20.1	10	29.1	15	25	5
2.3	17.1	5	32.59	5	45.1	5	20.63	5
2.5	19.8	5	14.6	5	7.9	20	27.2	5
2.8	3.7	5	14.1	5	3.6	5	8.33	5
3.3	2.6	10	1.8	5	2.21	10	4.2	5
3.8	2.1	5	0.9	5	2.23	5	0.48	10

However, the optimized conditions towards CO_2 reduction and dye removal are shown in Table 8.1 and Table 8.2, respectively, for different electrolytes conditions. From the table it may be concluded that HCOOH is the formed product at high Faradaic efficiency at low applied potentials and high dye removal at higher applied voltages.

Table 8.2 Optimized conditions towards CV removal in different catalysts

Applied Voltage	**CV removal (time)**							
	Sn				**Zn**			
	$KHCO_3$		**$NaHCO_3$**		**$KHCO_3$**		**$NaHCO_3$**	
(V)	**(%)**	**(min)**	**(%)**	**(min)**	**(%)**	**(min)**	**(%)**	**(min)**
2	15.3	25	12.7	25	10	25	22.3	25
2.3	25.9		15.8		17.8		32.6	
2.5	38.7		21.7		20.2		50.6	
2.8	39.9		52.6		47.3		51.8	
3.3	53.7		58.8		58.6		54.9	
3.8	71.5		64.3		60.9		61	

8.2.3 Simultaneous RCPE and MB removal using Sn and Co_3O_4 electrocatalyst

Tin (Sn) as cathode and Co_3O_4 as anode were used to study the effect of CO_2 reduction and MB removal in potassium and sodium bicarbonate electrolytes. The reduction and removal with applied voltage and time were discussed clearly in further sections.

8.2.3.1. Effect of current density at Sn electrocatalyst on applied voltage in MB solution

In both electrolyte solutions, the current density results on applied voltages are given in figure 8.4a. The current densities are proportional to applied voltages in $KHCO_3$ and $NaHCO_3$ electrolyte solutions. Increasing applied voltages shows higher rate of reaction which confirms by the obtained current densities. The reaction rate corresponded to either hydrogen removal or CO_2 reduction. Higher current densities were obtained in $KHCO_3$ than $NaHCO_3$ at higher applied voltages which shows that the reaction rate is high in potassium based electrolyte solution (figure 8.4a). The CO_2 reduction reaction and MB dye removal for different time intervals for applying voltages are discussed subsequently.

8.2.3.2. RCPE and MB dye removal at Sn cathode in $KHCO_3$ solution

The results for simultaneous CO_2 reduction and MB dye removal in 0.5 M $KHCO_3$ (10 ppm MB) solution is shown in figure 8.4(b, d). Experimental process shows that HCOOH was the only product formed in RCPE at different applied voltages. Low applied voltages were able to get high Faradaic efficiencies compared with high voltages which may be due to high hydrogen evolution at higher voltages.[5] Similarly, higher applied voltages were favorable for high MB removal than low voltages. MB removal (%) was increasing with time as shown in figure 8.4(d-e). The reaction at 2 V was obtained with HCOOH Faradaic efficiencies in 28.2, 38.4, 57.9, 4.7 and 5.5% by MB removal (12.5, 13.33, 13.39, 13.5 and 14.1 %) for reaction time of 5, 10, 15, 20 and 25 min. The optimized condition towards maximum CO_2 reduction was 57.9% of reaction of 15 min. Similar studies were done at same experimental conditions without MB dye which shows the formation of HCOOH as a product.[116] The simultaneous dye removal and CO_2 reduction at 2.3 V was shown in Figure 8.4(b, d) with Faradaic efficiencies (7.7, 4.6, 6.8, 2.2 and 1.4 %) and MD dye removal (17.8, 18.08, 18.4, 18.8 and 19.2 %) respectively. The Faradaic efficiencies were decreased at this applied voltage compared with 2 V may be due to high H^+ generation at anode which reduced to hydrogen at the cathode.[115] The MB dye removal increasing as applied voltages increased with maximum removal of 19.2 % after 25 min reaction. Maximum Faradaic efficiency of 6.6% after 5 min reaction after that a drastic decrease in efficiency shows that HCOOH oxidation at Co_3O_4 anode. The change in Faradaic efficiency with time may be due to the oxidation of forming product at anode.[125]

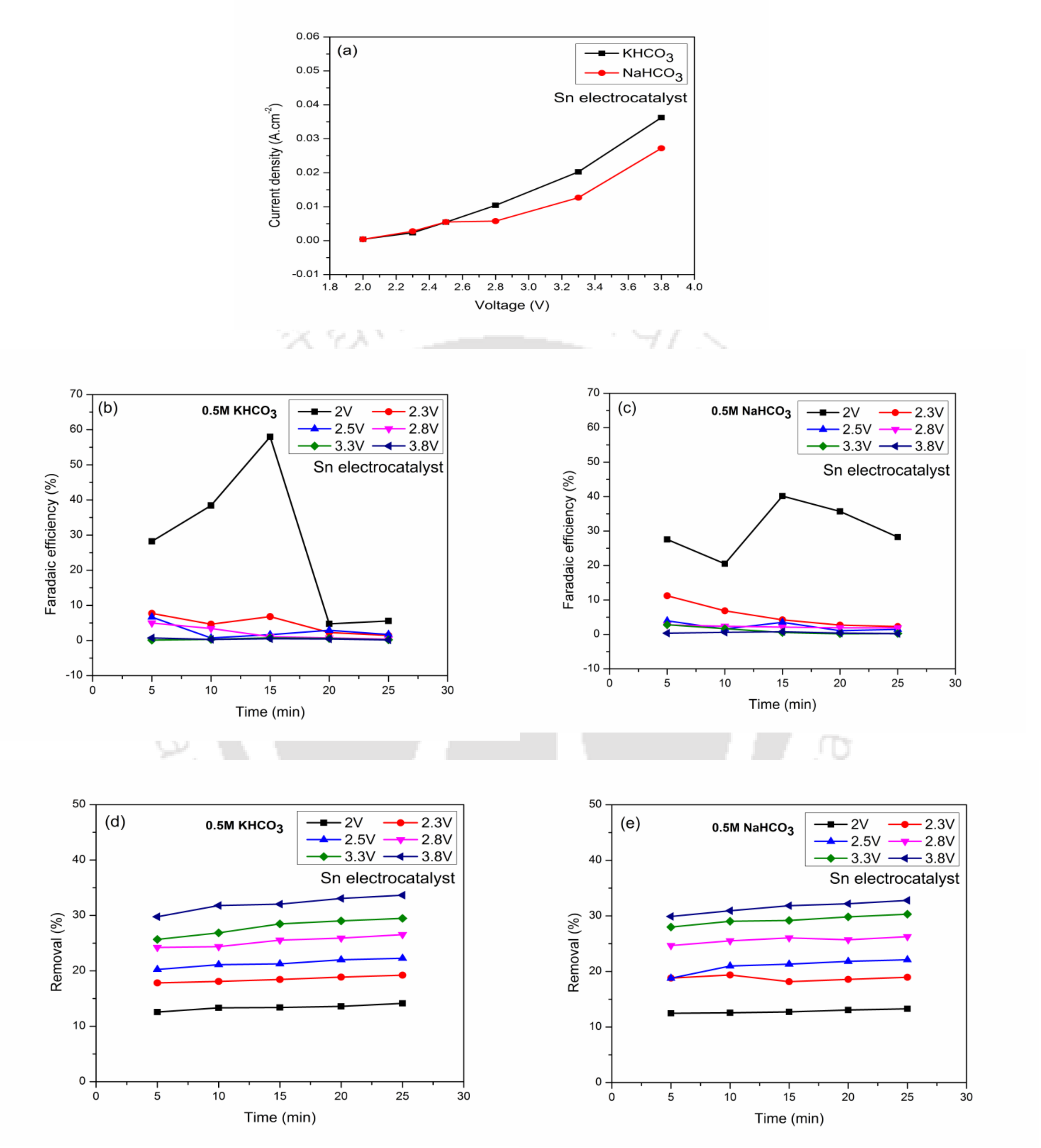

Figure. 8.4 (a) Voltage vs Current density, (b - c) FE vs Time and (d - e) MB Removal (%) vs Time at different applied voltages during RCPE in KHCO$_3$ and NaHCO$_3$ using Sn.

The optimized reaction condition for RCPE and MB removal was 4.9 % (5 min) and 26.5 % (25min). Faradaic efficiencies (0.72, 0.29, 0.5, 0.4, 0.17 %) and MB dye removal (29.7, 31.7, 32, 33 and 33.6 %) was obtained at 3.8 V. Overall, the reaction in $KHCO_3$ was able to reduce CO_2 to HCOOH and MB dye removal simultaneously. High applied voltages were able to remove maximum MB dye removal whereas low applied voltages were favorable for high Faradaic efficiencies.

8.2.3.3. RCPE and MB dye removal at Sn cathode in $NaHCO_3$ solution

The experimental results towards RCPE and MB dye removal in 0.5M $NaHCO_3$ (10 ppm MB) $NaHCO_3$ electrolyte solution for different applied voltages are shown in Figure 8.4(c, e). It was observed that low applied voltage give high Faradaic efficiency and high applied voltages favor maximum MB dye removal. At 2 V, Faradaic efficiencies (27.5, 20.5, 40.1, 35.6 and 28.2 %), MB removal (12.4, 12.5, 12.7, 13 and 13.2 %) were obtained in the reaction time of 5, 10, 15, 20 and 25 min. The maximum Faradaic efficiency of 40.1 % (15 min) and dye removal 13.2 % (25 min) were the optimized reaction conditions at this applied voltage. The reduction studies were done in $NaHCO_3$ electrolyte solution with same experimental conditions without dye.[116] For reaction at 2.3 V, the Faradaic efficiencies and MB dye removal were obtained to be (11.2, 6.8, 4.2, 2.7 and 2.2 %) and (18.8, 19.3, 18.1, 18.5 and 18.9 %) respectively, at the aforementioned time. At 3.3 V, Faradaic efficiencies (2.79, 1.6, 0.5, 0.19 and 0.2 %) and MB removal of around 27.9, 29, 29.1, 29.8 and 30.3 % (Figure 8.4e) was observed with maximum dye removal of 30.3 % after 25 min reaction. The decrease in Faradaic efficiency may be due to high proton generation at anode which forms hydrogen at the cathode than participating in CO_2 reduction.[125] From the discussion, high applied voltage of 3.8 V shows more dye removal and low voltage 2 V favors high HCOOH efficiencies.

8.2.4. Simultaneous RCPE and MB removal using Zn and Co_3O_4 electrocatalyst

The experimental studies were done to study the performance of electrocatalysts using (Co_3O_4/G) and (Zn/G) as the anode and cathode, respectively. The effect of electrolyte on RCPE and dye removal was clearly explained for different voltages with time intervals and discussed detail in subsequent sections.

8.2.4.1. Effect of current density at Zn electrocatalyst on applied voltage in MB solution

Results related to RCPE and MB dye removal using Zn electrocatalyst as cathode was shown in Figure 8.5. Increase of applied voltages in $KHCO_3$ and $NaHCO_3$ electrolytes shows high current densities (figure 8.5a). Maximum current represents a high reaction rate, which comprises of CO_2 reduction or hydrogen evolution at anode. The reaction in $KHCO_3$ electrolyte shows maximum current density compared with $NaHCO_3$ solution.

8.2.4.2. RCPE and MB dye removal at Zn cathode in $KHCO_3$ solution

The reaction in 0.5 M $KHCO_3$ (10 ppm MB) using Zn electrocatalyst for Faradaic efficiencies of HCOOH formation and MB dye removal is shown in Figure 8.5. The only product formed in experimental conditions is HCOOH and respective MB dye removal was reported for reaction time interval of 5, 10, 15, 20 and 25 min. Faradaic efficiencies (31.7, 12.1, 12.3, 11.5 and 18.1 %) and MB removal (7.7, 7.9, 8.1, 8.3 and 8.3 %) were obtained at 2 V(Figure 8.5 (b-d)). Maximum Faradaic efficiency of 31.7 % for reaction time of 5 min with low dye removal of this applied voltage. Experimental studies were reported using Zn as electrocatalyst for the formation of HCOOH as the only product from CO_2 in the absence of MB dye.[117] The reaction at 3.3 and 3.8 V shows very low Faradaic efficiencies of (2.02, 0.76, 0.5, 0.8 and 0.3 %), (1.4, 0.6,

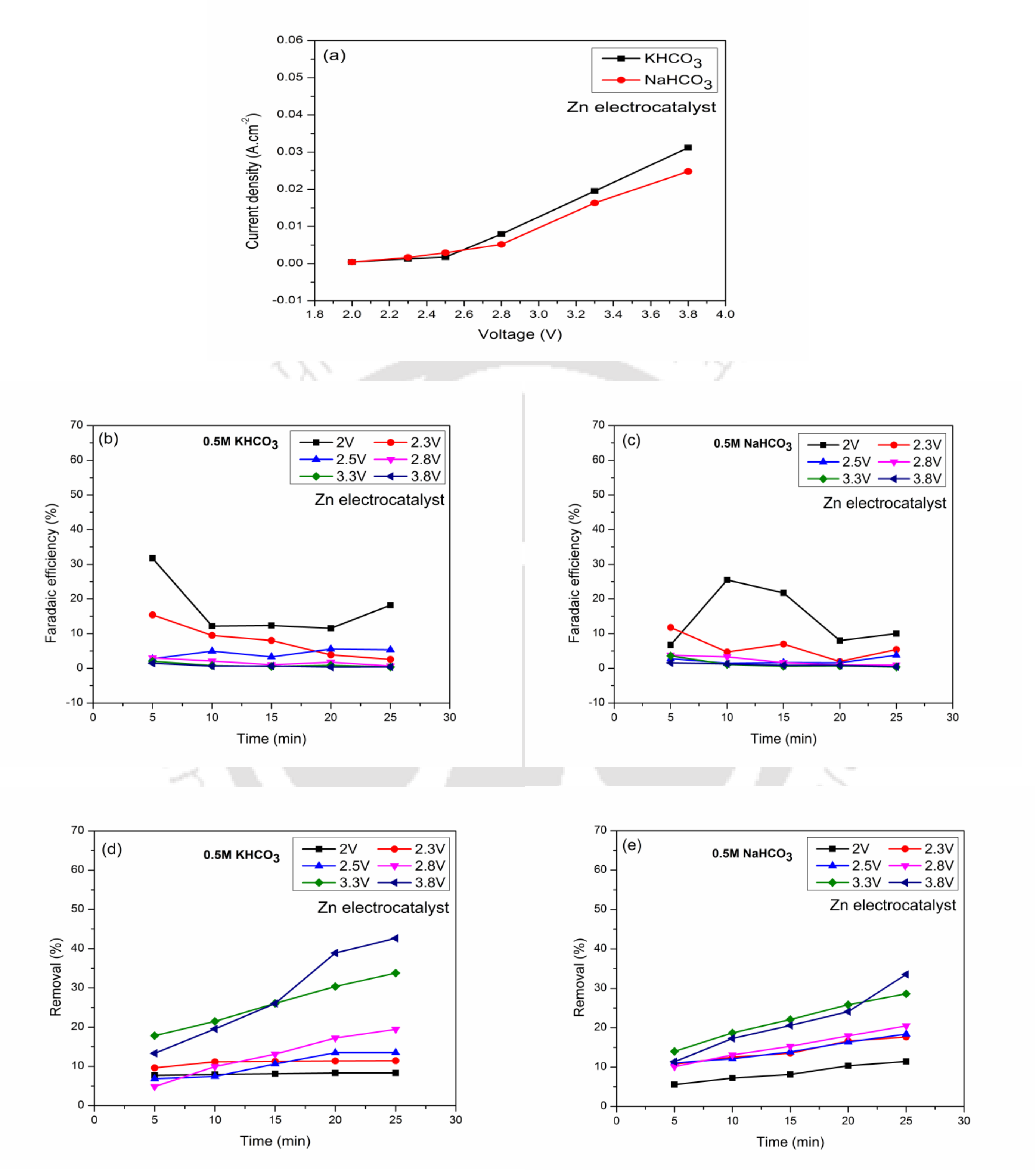

Figure. 8.5 (a) Voltage vs Current density, (b - c) FE vs Time and (d - e) MB Removal (%) vs Time at different applied voltages during RCPE in KHCO$_3$ and NaHCO$_3$ using Zn.

0.62, 0.35, 0.4) with high MB dye removal (17.8, 21.4, 26.07, 30.3 and 33.79), (13.3, 19.5, 26, 38.9 and 42.6 %) respectively. The decrease in Faradaic efficiencies may be due to high hydrogen evolution reaction is competing with CO_2 reduction at the cathode.[5]

8.2.4.3. RCPE and MB dye removal at Zn cathode in $NaHCO_3$ solution

Figure 8.5(c, e) shows the results for simultaneous reduction of CO_2 and MB dye removal in 0.5M $NaHCO_3$ (10 ppm MB) electrolyte solution. The experimental studies were done at different applied voltages of 2, 2.3, 2.5, 2.8, 3.3 and 3.8 V with reaction time of 5, 10, 15, 20 and 25 min. For reaction at 2 V, with Faradaic efficiencies (6.7, 25.4, 21.7, 7.9 and 9.99 %) and MB dye removal (5.5, 7.19, 8.1, 10.3 and 11.4 %) (Figure 8.5e) were obtained. The maximum Faradaic efficiency of 25.4 % for the reaction of 10 min was obtained which is the best optimized condition for HCOOH formation.

Table 8.3 Optimized conditions for HCOOH Faradaic efficiency in different electrolytes

Applied Voltage	**Maximum Faradaic efficiency (time)**							
	Sn				**Zn**			
	$KHCO_3$		**$NaHCO_3$**		**$KHCO_3$**		**$NaHCO_3$**	
(V)	**(%)**	**(min)**	**(%)**	**(min)**	**(%)**	**(min)**	**(%)**	**(min)**
2	57.9	15	40.1	15	31.7	5	25.4	10
2.3	7.7	5	11.2	5	15.4	5	11.7	5
2.5	6.6	5	3.9	5	5.5	20	3.7	25
2.8	4.9	5	2.76	5	3	5	3.77	5
3.3	0.75	15	2.79	5	2.02	5	3.5	5
3.8	0.72	5	0.76	15	1.4	5	1.5	5

The experimental results show that with the increase in time the Faradaic efficiencies were varying which may due oxidation of formed HCOOH anode.[116] The Faradaic efficiency of HCOOH (1.5, 1.2, 0.85, 0.83 and 0.43 %) and MB dye removal (11.3, 17.2, 20.5, 24.05, and 33.55 %) were obtained at 3.8 V. The Faradaic efficiencies were decreased compared with low applied voltages which may be due to high proton generation at anode such that the maximum number of protons was at the cathode than CO_2 molecules.[5, 117] The optimized conditions for both electrocatalyst Sn and Zn are given in Table 8.3 and MB removal in Table 8.4 in both potassium and sodium based solutions.

Table 8.4 Optimized conditions for MB removal in different electrolytes

Applied Voltage	MB removal (time)							
	Sn				Zn			
	$KHCO_3$		$NaHCO_3$		$KHCO_3$		$NaHCO_3$	
(V)	(%)	(min)	(%)	(min)	(%)	(min)	(%)	(min)
2	14.1	25	13.2	25	8.3	25	11.4	25
2.3	19.2		18.9		11.4		17.6	
2.5	22.2		22.1		13.5		18.3	
2.8	26.5		26.2		19.4		20.4	
3.3	29.4		30.3		33.7		28.6	
3.8	33.6		32.7		42.6		33.5	

8.2.5. Simultaneous RCPE and BG removal using Sn and Co_3O_4 electrocatalyst

The reduction of CO_2 and BG dye removal was studied using the Sn (cathode) and Co_3O_4 (anode) electrocatalysts in bicarbonate based electrolytes. Maximum dye removal was observed along with higher Faradaic efficiencies for different applied voltages and results were shown clearly. For all reaction studies, 0.5 M (10 ppm BG) concentration was used as electrolyte solution to conduct reaction.

8.2.5.1. Effect of current density at Sn electrocatalyst on applied voltage in BG solution

Based on the applied voltages, current densities were shown which corresponds to rate of reaction. The results in different electrolyte solutions are shown in Figure. 8.6a. Current densities were observed to be increasing with increasing voltages. It shows that the reaction rate is more at high applied voltages which may be due to CO_2 reduction or hydrogen evolution. The effect of current density with different voltages shows the ability of selected electrocatalysts towards BG due removal CO_2 reduction.

8.2.5.2. RCPE and BG dye removal at Sn cathode in $KHCO_3$ solution

The simultaneous CO_2 reduction to HCOOH and dye removal in $KHCO_3$ solution is shown in Figure. 8.6. For all the applied voltages HCOOH was obtained as product with maximum dye removal. The reaction at 2V for reaction time of 5,10,15,20 and 25 min shows high efficiencies of 40.6, 29.4, 22.1, 36.6 and 22.8 % with dye removal of 94.1, 94.6, 94.3, 94.3 and 94.2 %, respectively. The variation in product concentrations with respect to time may due to the oxidation of HCOOH at anode.[125] At 2.3 V, Faradaic efficiencies (7.2, 14.7, 40.4, 6.64 and 8.6 %) and BG dye removal (93, 93.1, 93.1 and 93.44 %) were observed with optimized condition for HCOOH formation is 40.4 % for reaction of 15 min. Lv et al., studied on HCOOH formation from reduction of CO_2 on Sn electrode in $KHCO_3$ solution without any dye using Pt anode.[73] The high applied voltages were not favorable for CO_2 reduction may be due to low CO_2 molecule concentration than hydrogen ions.[116] High efficiencies were observed at 2V which is the most optimized condition for simultaneous CO_2 reduction effective dye removal.

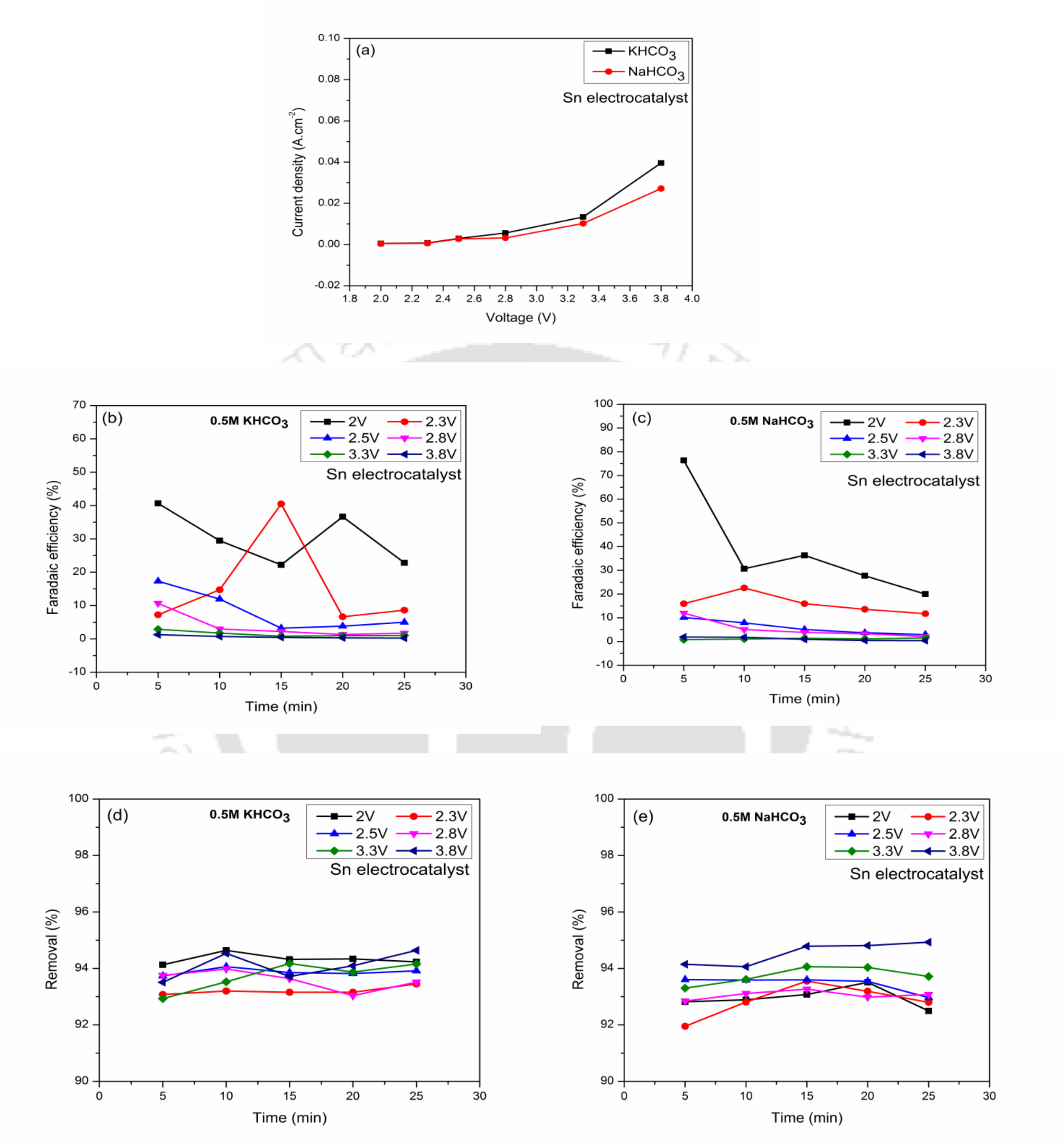

Figure. 8.6 (a) Voltage vs Current density, (b - c) FE vs Time and (d - e) BG Removal (%) vs Time at different applied voltages during RCPE in KHCO$_3$ and NaHCO$_3$ using Sn.

8.2.5.3. RCPE and BG dye removal at Sn cathode in $NaHCO_3$ solution

Figure 8.6 shows the effective results for CO_2 reduction and BG dye removal in sodium based solution. High Faradaic efficiencies were obtained for HCOOH formation compared with Potassium based solution with maximum dye removal. Faradaic efficiencies (76.3, 30.6, 36.3, 27.7 and 20.1 %) with BG removal of (92.8, 92.8, 93, 93.5 and 92.4 %) were obtained at 2 V reactions at varying time mentioned previously. The optimized reaction for maximum HCOOH formation is 76.3 % after 5 min. Variation of efficiencies may be due to formed product oxidation at Co_3O_4 which leads to hydrogen evolution at cathode.[5,117] The low efficiencies for HCOOH may be due to high hydrogen evolution at Sn electrode.[125] Faradaic efficiency (1.89, 1.8, 0.9, 0.46 and 0.39 %) and BG removal (94.1, 94.06, 94.7, 94.8 and 94.9 %) were shown for reaction at 3.8 V. The optimized condition was 5 min reaction at which maximum efficiency of 1.89 % was obtained. The efficiencies were high in sodium based solution with effective reduction in low applied voltages and dye removal.

8.2.6. Simultaneous RCPE and BG removal using Zn and Co_3O_4 electrocatalyst

The simultaneous CO_2 reduction with BG dye removal was studied using Zn electrocatalyst as cathode.

8.2.6.1. Effect of current density at Zn electrocatalyst on applied voltage in BG solution

The results for current density with respect to applied voltages for HCOOH Faradaic efficiencies in both electrolytes solutions are shown in Figure. 8.7. In particular the Current densities were increasing with applied voltage increase as shown in Figure. 8.7a. Electrolyte concentration of 0.5 M (10 ppm CV) was used to conduct electrochemical studies for all applied conditions. The current densities represent high reaction rates with maximum in $NaHCO_3$ electrolyte solution than $KHCO_3$.

8.2.6.2. RCPE and BG dye removal at Zn cathode in $KHCO_3$ solution

The effect of CO_2 reduction and BG dye removal in potassium based solutions is shown in figure.8.7(b, d). Hori et al., studied the reduction of CO_2 for HCOOH formation on Zn electrocatalyst in $KHCO_3$ solution using Pt anode.[5] In all applied voltages, HCOOH was observed as an only product with maximum BG removal at different reactions of 5, 10, 15, 20 and 25 min. Faradaic efficiencies (45.2, 69.9, 23.9, 20.4 and 15.07 %) and BG removal (95.1, 95.03, 94.6, 94.4 and 94.8 %) were obtained at 2 V after the afore mentioned time span. Faradaic efficiencies (45.2, 69.9, 23.9, 20.4 and 15.07 %) and BG removal (95.1, 95.03, 94.6, 94.4 and 94.8 %) were obtained at 2 V after the afore mentioned time span. Maximum efficiencies were obtained at this voltage which is clear sign for the best reaction condition. The change in efficiencies with time (Figure. 8.7(b)) may be due to oxidation of product (HCOOH) at anode.[125,117] For reaction at 2.3 V, Faradic efficiency of 15.01, 11.2, 8.8, 12.3 and 7.5 % along with BG removal of 92, 92.5, 92.8, 92.9 and 93 % was observed after the said time interval. The optimized condition at this voltage is 15.01 % for 5 min reaction. Low efficiencies were seen at low applied voltages which may not be better reaction condition towards CO_2 reduction for HCOOH formation. Electrochemical studies for HCOOH as product in CO_2 reduction on Zn electrocatalyst without dye in potassium salts were reported.[117] From the results it may be concluded that high applied voltages were not favorable for maximum HCOOH efficiencies. The result proves the capability of electrocatalyst towards CO_2 reduction to HCOOH and maximum dye removal.

8.2.6.3. RCPE and BG dye removal at Zn cathode in $NaHCO_3$ solution

Faradaic efficiencies of 50.7, 26.9, 32.1, 19.3 and 28.1 % and BG dye removal of 93.5, 93.3, 93.5, 93.5 and 93.5 % were obtained at said reaction time of 2 V.

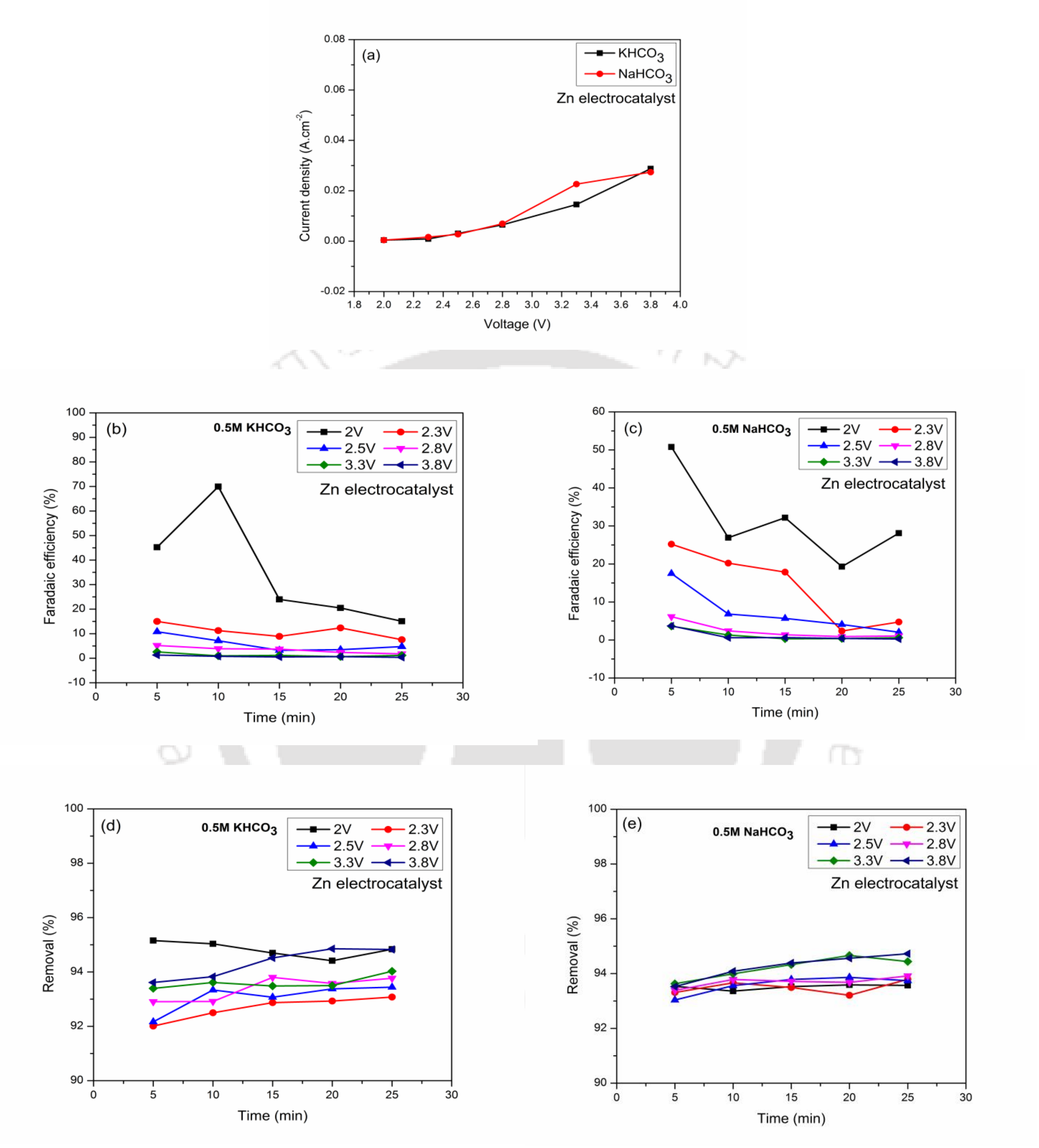

Figure. 8.7 (a) Voltage vs Current density, (b - c) FE vs Time and (d - e) BG Removal (%) vs Time at different applied voltages during RCPE in $KHCO_3$ and $NaHCO_3$ using Zn.

Table 8.5 Maximum Faradaic efficiencies for HCOOH at different applied conditions

Applied Voltage	Maximum Faradaic efficiency (time)							
	Sn				Zn			
	$KHCO_3$		$NaHCO_3$		$KHCO_3$		$NaHCO_3$	
(V)	(%)	(min)	(%)	(min)	(%)	(min)	(%)	(min)
2	40.6	5	76.3	5	69.9	10	50.7	5
2.3	40.4	15	22.5	10	15	5	25.2	5
2.5	11.9	10	10.1	5	10.8	5	17.4	5
2.8	10.6	5	11.9	5	5.1	5	6.1	5
3.3	2.8	5	1.5	25	2.5	5	3.6	5
3.8	1.2	5	1.89	5	1.2	5	3.7	5

Table 8.6 Maximum BG dye removal at different applied conditions

Applied Voltage	BG removal (time)							
	Sn				Zn			
	$KHCO_3$		$NaHCO_3$		$KHCO_3$		$NaHCO_3$	
(V)	(%)	(min)	(%)	(min)	(%)	(min)	(%)	(min)
2	94.6	15	93.5	20	95.1	5	93.58	20
2.3	93.4	25	93.5	15	93	25	93.7	25
2.5	94	10	93.6	5	93.4	25	93.8	20
2.8	93.9	10	93.2	20	93.8	15	93.9	25
3.3	94.17	15	94.06	15	94	25	94.6	20
3.8	94.6	25	94.9	25	94.85	20	94.7	25

The optimized condition towards maximum HCOOH formation was 50.7% for reaction time of 5 min. The results showed that efficiencies were changing with reaction times. This is due to

HCOOH oxidation at anode. Jin et al., studied the effect of CO_2 reduction on Zn electrocatalyst for HCOOH and similar product was reported.[60] The experimental results for CO_2 reduction and BG dye removal at different reaction times with applied voltages are shown in Table 8.5 and Table 8.6, respectively. For all the cases low voltages were shown high Faradaic efficiencies for HCCOH formation.

8.3 Summary

The experimental study describes the ability of the Zn and Sn electrocatalysts as cathode and Co_3O_4 as anode towards CV, MB and BG dye removal and reduction of CO_2 to HCOOH. The reaction was done in both $KHCO_3$ and $NaHCO_3$ electrolyte solutions. High HCOOH Faradaic efficiency was obtained in $KHCO_3$ electrolyte solution using Zn electrocatalyst. The high applied voltage was favorable for all three dye removal whereas low voltages are for maximum Faradaic efficiencies. The preliminary studies will help the simultaneous dye removal and CO_2 reduction for future applications.

Chapter 9

A photo electrochemical study on CO_2 reduction for solar energy storage and dye removal on Sn and Zn catalysts using Co_3O_4 anode

Chapter 9

A photo electrochemical study on CO_2 reduction for solar energy storage and dye removal on Sn and Zn catalysts using Co_3O_4 anode

This chapter elaborates the application of solar energy for simultaneous water purification by dye removal and CO_2 reduction. The studies were done using Zn and Sn electrocatalysts as cathode and Co_3O_4 anode in bicarbonates of sodium and potassium electrolytes and discussed in detail.

9.1. Experimental

9.1.1. Materials

Solar panel of 8.8 V, 340 mA was purchased from Waare Energies Pvt. Ltd, Surat, India. Graphite plates, dyes (CV, MB and BG), and Nafion solutions were also purchased and reported details in Chapter 2.

9.1.2. Preparation of Sn, Zn and Co_3O_4 coated graphite electrodes

Preparation of electrodes is discussed in chapter 8.

9.1.3. Photo electrochemical reduction of RCPE and Dye removal

The experimental setup used to study the effect of both photo electrochemical CO_2 reduction and dye removal is shown in figure 9.1. A 2-electrode glass cell was used with different concentrations (0.2, 0.4, 0.6 and 0.8M) of 80 ml (10 ppm dye). Electrolyte solutions were prepared using both $KHCO_3$ and $NaHCO_3$ salts. The solutions were saturated with CO_2 by bubbling for 50 min. The two electrodes of either Co_3O_4/G – Zn/G or Co_3O_4/G – Sn/G were connected to solar panel and dipped in the electrolyte solution to perform the photo electrochemical studies. Experiments were performed for both the solutions and samples were collected for every time interval of 5, 10, 15, 20 and 25 min for analysis.

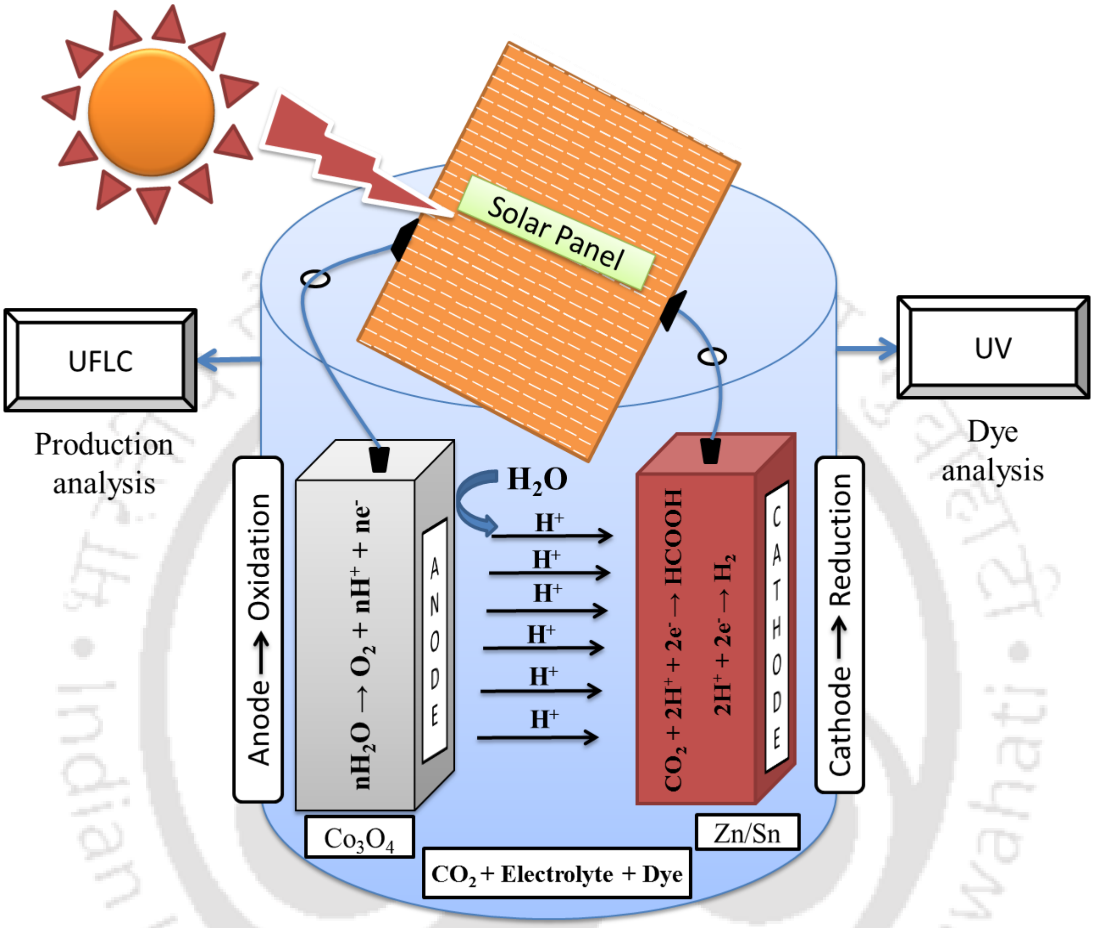

Figure. 9.1. Schematic setup for simultaneous Photo electrochemical CO_2 reduction and dye removal

9.2. Results and discussion

9.2.1. Simultaneous photo electrochemical CO_2 reduction and CV removal on Sn electrocatalyst

The photo electrochemical studies were done using Co_3O_4/G as anode for water oxidation and Sn/G as cathode for CO_2 reduction. The effect of CO_2 reduction and CV removal in both $KHCO_3$ and $NaHCO_3$ electrolyte solutions were discussed in detail in further sections.

9.2.1.1. Photo electrochemical studies on CO_2 reduction and CV removal in $KHCO_3$ electrolyte on Sn electrocatalyst

The photo electrochemical reduction of CO_2 and CV dye removal in bicarbonates of potassium and sodium based salts is shown in figure 9.2. The product formed from CO_2 reduction was HCOOH in all different concentrations of $KHCO_3$ electrolyte solutions. This depicted that the selected environment was able to reduce CO_2 effectively (figure 9.2a). The CV dye removal increased with time for different concentrations was clearly shown from figure 9.2c. From the figure it may be observed that the formation of HCOOH varying with time and electrolyte concentrations. The moles of HCOOH formed in 0.2M solution were obtained to be 188.5, 254, 151.5, 166.5 and 137.6 µmol at different reaction time intervals of 5, 10, 15, 20 and 25 min. The % CV removals for same time intervals were obtained to be 60.4, 68.1, 69.5, 69.8 and 72.5 % respectively. The change in product concentration with time may be due to oxidation of forming HCOOH product.[73] The optimum condition in this concentration was 254 µmol for reaction time of 10 min. The reaction in 0.8M solution was found to be 173.3, 34.5, 68.9, 137.9 and 218.5 µmol (figure 9.2a) with CV removal of 45.6, 47.6, 50.1, 53.8 and 57.2 % (figure 9.2c). The reduction was decreased compared with other solutions which may be due to more hydrogen evolution at cathode due to high proton generation at anode.[115] The optimized condition towards high CO_2 reduction was 218.5 µmol after 25 min reaction. The reaction here shows low reduction rate compared with other electrolyte concentrations.

9.2.1.2. Photo electrochemical studies on CO_2 reduction and CV removal in $NaHCO_3$ electrolyte on Sn electrocatalyst

The photo electrochemical CO_2 reduction and CV removal reaction in $NaHCO_3$ electrolyte is shown in figure 9.2 (b, d). The results show that HCOOH was formed in all different electrolyte concentrations. In 0.4M solution, the moles of product HCOOH formed were 309.5, 268.7, 532, 267.7 and 304.6 µmol (figure 9.2b) with CV dye removal of 17.9, 35.9, 48.4, 56.1 and 61.7 % (figure 9.2d).

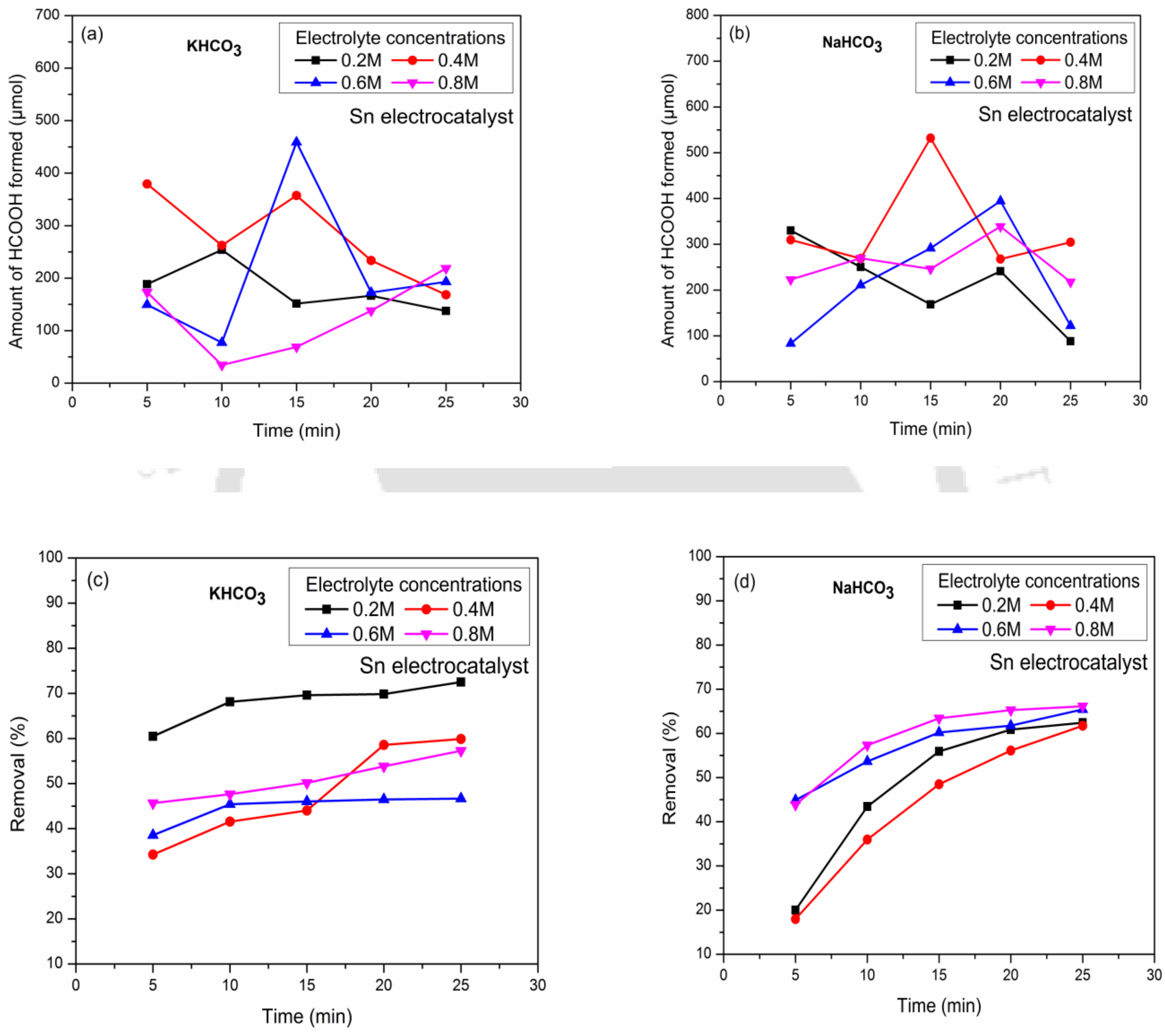

Figure. 9.2 Photo electrochemical CO_2 reduction with time in (a) $KHCO_3$ (b) $NaHCO_3$ and CV removal (%) vs Time in (c) $KHCO_3$ (d) $NaHCO_3$ using Sn.

HCOOH formation was increased in this concentration with maximum value of 532 µmol after 15 min reaction. The reaction in 0.6M solution, for CO_2 reduction was obtained as 83.1, 210.9, 291.2, 394.4 and 121.9 µmol and for CV removal was 44.8, 53.6, 60.2, 61.7 and 65.4 %, respectively. The reduction rate was decreased here may be due to high hydrogen evolution compared with CO_2 reduction at cathode and proton generation at anode.[116] The experimental results show the ability of selected experimental condition was able to reduce CO_2 to HCOOH with effective dye removal. In both electrolyte solutions, HCOOH was formed and dye removal was increased with time in all different electrolyte concentrations.

9.2.2. Simultaneous photo electrochemical CO_2 reduction and CV removal on Zn electrocatalyst

The studies were performed using Co_3O_4/G as anode and Zn/G as a cathode for simultaneous CO_2 reduction and CV removal in bicarbonate salts of potassium and sodium. The obtained results were shown clearly in further sections in detail.

9.2.2.1. Photo electrochemical studies on CO_2 reduction and CV removal in $KHCO_3$ electrolyte on Zn electrocatalyst

The results in figure 9.3 confirm the ability of the selected electrocatalyst towards the formation of HCOOH and effective CV dye removal. The photo electrochemical reduction of CO_2 and CV removal in different $KHCO_3$ electrolyte concentrations was shown in figure 9.3 (a, c). In 0.2M electrolyte solution the moles of HCOOH formed to be 78, 42.5, 30.4, 15.9 and 43 µmol with CV removal of 34.9, 47.5, 48.8, 53.8 and 58.9 % respectively. The optimized reaction condition for the maximum CO_2 reduction was 43 µmol after 25 min reaction. The reaction in 0.4M electrolyte solution obtained for CO_2 reduction was 147.2, 47.2, 24.4, 33.8 and 26.9 µmol (figure 9.3a) and CV removal with 29.2, 47.2, 56, 61.2 and 66.3 % (figure 9.3c). The optimized condition for HCOOH formation was 147.2 µmol for the reaction of 5 min. The product concentration was varied with time may be due to oxidation of the formed product at anode generating high hydrogen.[117] The experimental studies were reported for the electrochemical reduction of CO_2 to HCOOH on Zn electrocatalyst in $KHCO_3$ solution.[117] Photo electrochemical reduction of CO_2 to HCOOH and CV dye removal in a 0.6M solution was found to be (70.9, 350.1, 469.2, 207.2 and 179.1 μmol), (26.9, 44.4, 53.5, 55.4 and 56.4 %) respectively. The optimized reaction condition was found to be 469.2 (15min) and the moles of HCOOH was reduced after 15 min reaction may be due to oxidation of HCOOH at Co_3O_4 anode.[73] The reaction in 0.8 M solution was found as 134.1, 495.8, 116.4, 265.4 and 225.9 μmol for HCOOH and CV removal of 29.3, 41.8, 53.6, 59.8 and 64.4 %, respectively. The optimized reaction condition for maximum reduction of CO_2 was 495.8 μmol for 10 min reaction. The results in figure 9.3 (a, c) confirmed the formation of HCOOH with dye removal in different solutions of $KHCO_3$ electrolyte.

9.2.2.2. Photo electrochemical studies on CO_2 reduction and CV removal in $NaHCO_3$ electrolyte on Zn electrocatalyst

The results for photo electrochemical CO_2 reduction and CV removal with time in different $NaHCO_3$ electrolyte solutions were shown in figure 9.3 (b, d). The selected electrocatalyst were able to reduce CO_2 to HCOOH along with CV dye removal. The reacted samples were studied for reaction time of 5, 10, 15, 20 and 25 min in 0.2M solution, results in formation of HCOOH was 34, 62.2, 72.2, 76.6 and 91.2 μmol with CV removal of 38.5, 42.3, 46.5, 50.8 and 53.1 %. The formation rate is low which may be due to high hydrogen evolution at the cathode with maximum proton generation at anode due to oxidation of water.[116,122] The rate of HCOOH formation and CV dye removal in a 0.8M solution were observed as (393.6, 297, 361.7, 263.5 and 301.6 μmol) and (22.3, 31.4, 37.1, 43.2, 48 %), respectively. Maximum reduction takes place after 25 min reaction was found to be 175 μmol.

The optimized reaction conditions for HCOOH formation was given in Table 9.1 and CV removal is shown in Table 9.2.

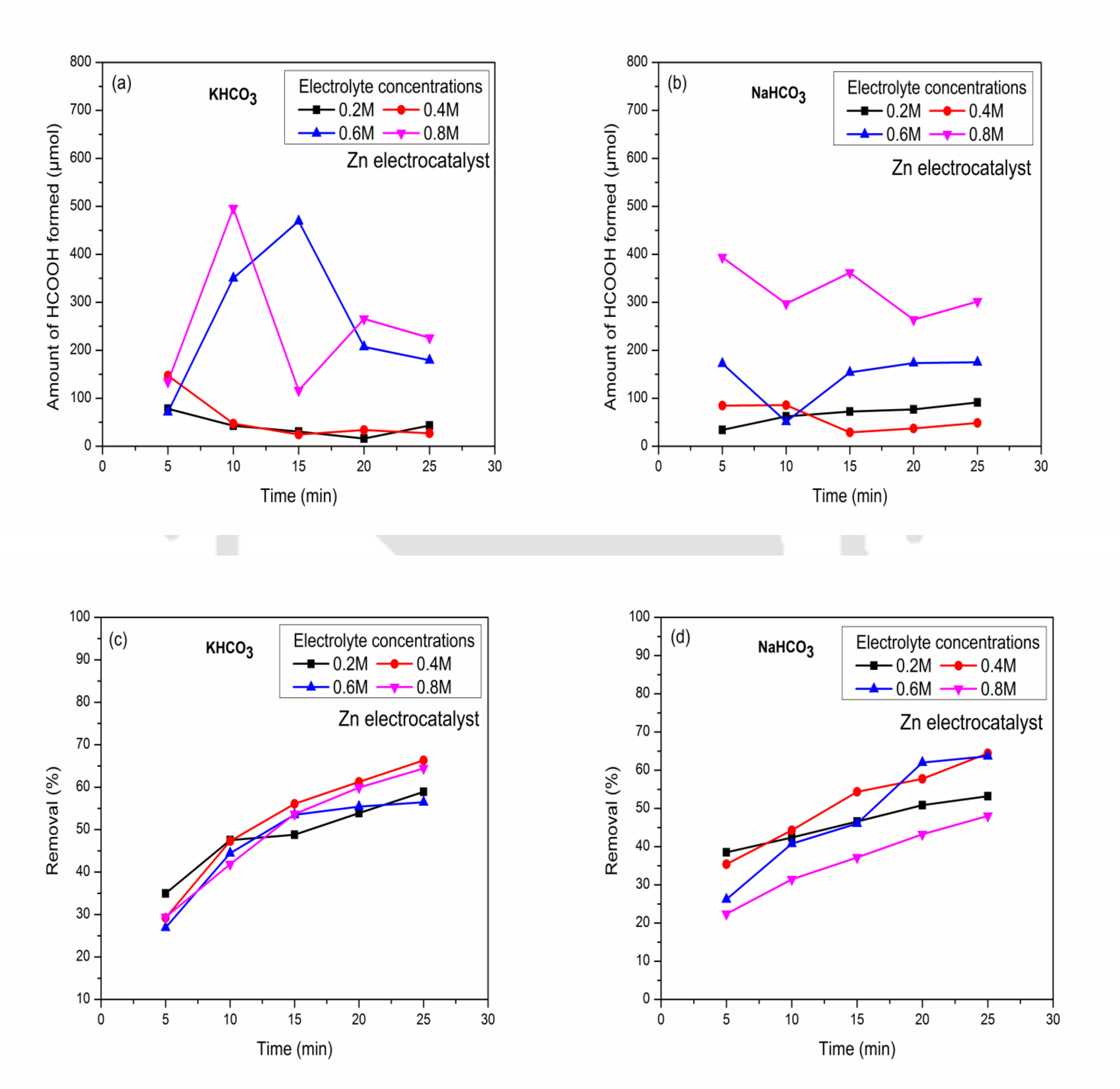

Figure. 9.3. Photo electrochemical CO_2 reduction with time in (a) $KHCO_3$ (b) $NaHCO_3$ and CV removal (%) vs Time in (c) $KHCO_3$ (d) $NaHCO_3$ using Zn.

Table 9.1 Optimized conditions towards HCOOH formation using solar energy

Molarity	Moles of HCOOH							
	Sn				Zn			
	$KHCO_3$		$NaHCO_3$		$KHCO_3$		$NaHCO_3$	
(M)	μmol	(min)	μmol	(min)	μmol	(min)	μmol	(min)
0.2	254	20	330.1	5	78	5	91.2	25
0.4	379.3	5	532	15	147.2	5	85.6	10
0.6	458.8	15	394.4	20	469.2	15	175	25
0.8	218.5	25	338.8	20	495.8	10	393.6	5

Table 9.2 Optimized conditions for CV removal using solar energy

Molarity	CV removal (time)							
	Sn				Zn			
	$KHCO_3$		$NaHCO_3$		$KHCO_3$		$NaHCO_3$	
(M)	(%)	(min)	(%)	(min)	(%)	(min)	(%)	(min)
0.2	72.5	25	62.4	25	58.9	25	53.1	25
0.4	59.8		61.7		66.3		64.4	
0.6	46.6		65.4		56.4		63.6	
0.8	57.2		66.1		64.4		48	

9.2.3. Simultaneous photo electrochemical CO_2 reduction and MB removal on Sn electrocatalyst

Here anode (Co_3O_4/G) and cathode (Sn/G) were used as electrodes to study the photo electrochemical studies of CO_2 reduction and MB dye removal in $KHCO_3$ and $NaHCO_3$ electrolytes. The results were explained in detail with time and concentrations of electrolyte solutions.

9.2.3.1. Photo electrochemical studies on CO_2 reduction and MB removal in $KHCO_3$ electrolyte on Sn electrocatalyst

The results of photo electrochemical studies in $KHCO_3$ solution towards HCOOH formation and MB dye removal are shown in figure 9.4. The results showed that the selected catalyst was able to reduce CO_2 to HCOOH and MB dye effectively in all different electrolyte concentrations (figure 9.4 (a, c)). The photo electrochemical reaction for HCOOH formation in 0.2 M solution was found to be 51.7, 6.54, 84.09, 166.4 and 217.4 µmol along with MB dye removal of 28, 34.5, 51.8, 62.5 and 76.8 % for the reaction time of 5, 10, 15, 20 and 25 min. After 10 min reaction the decrease in formation of product concentration may be due to the oxidation of HCOOH at Co_3O_4 anode.[73] The dye removal gradually increases with time with maximum at 25 min reaction with 76.8%. Peng et al., studied the simultaneous CO_2 reduction and the methyl orange dye removal on copper catalyst using solar energy and reported different products like HCOOH, HCHO, CH_3OH and CH_4.[89] For reaction in a 0.4 M solution, the HCOOH formation and MB dye removal was obtained as (12.7, 93.8, 35.7, 80.5 and 261.5 µmol) and (28, 39.8, 50.6, 61.5 and 71.3 %), respectively. The optimized reaction condition was 261.5 µmol for 25 min reaction. HCOOH (53.9, 104.6, 64.8, 206.4 and 84.8 µmol) and MB dye removal (32, 45.4, 51.3, 60.1 and 64.8 %) were observed during the photo electrochemical reduction reaction in 0.6 M electrolyte solution. The decrease in HCOOH formation after 25 min reaction may be due to the oxidation of reacting product after 20 min reaction.[115] The results showed that the selected electrocatalyst combination was able to reduce CO_2 and dye removal effectively.

9.2.3.2. Photo electrochemical studies on CO_2 reduction and MB removal in $NaHCO_3$ electrolyte on Sn electrocatalyst

The photo electrochemical studies for HCOOH formation and MB dye removal in different concentrations of $NaHCO_3$ solution is shown in figure 9.4 (b, d).

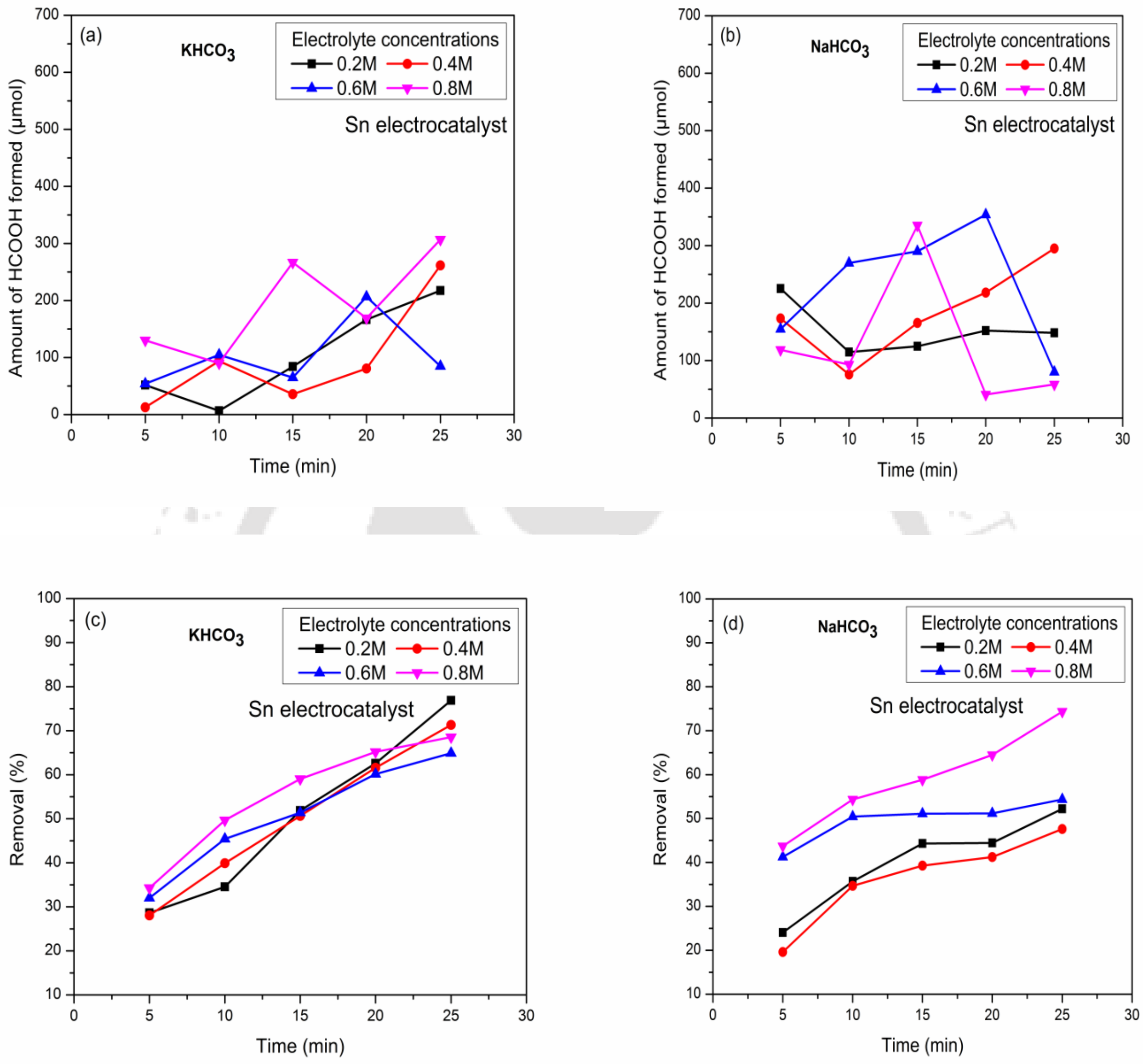

Figure. 9.4. Photo electrochemical CO_2 reduction with time in (a) $KHCO_3$ (b) $NaHCO_3$ and MB removal (%) vs Time in (c) $KHCO_3$ (d) $NaHCO_3$ using Sn.

For reaction 0.2 M solution, MB dye removal and HCOOH formation were observed as (24, 35.6, 44.3, 44.4 and 52.2 %) and (225, 114.6, 124.8, 152.2 and 148.1 μmol), respectively. The change in product HCOOH concentration with reaction time may be due to oxidation of HCOOH at anode.[125] HCOOH formation (118.7, 92.9, 335.2, 40.9 and 58.4 μmol) and MB dye removal (43.6, 54.3, 58.8, 64.4 and 74.3 %) was observed when photo electrochemical studies were done in a 0.8 M solution. The change in amount of product formation with time is may be due to oxidation of HCOOH at anode.[122] Maximum MB dye removal was observed in this electrolyte concentration by 74.3 % after 25 min reaction. The effect of Sn electrocatalyst in both electrolytes shows a better performance in reducing CO_2 to HCOOH and MB dye removal.

9.2.4. Simultaneous photo electrochemical CO_2 reduction and MB removal on Zn electrocatalyst

The electrodes used here for photo electrochemical studies towards CO_2 reduction and MB dye removal in bicarbonates of sodium and potassium electrolytes are anode (Co_3O_4/G) and cathode (Zn/G) respectively. Results in respective electrolytes with time are analyzed below.

9.2.4.1. Photo electrochemical studies on CO_2 reduction and MB removal in $KHCO_3$ electrolyte on Zn electrocatalyst

Figure 9.5 (a,c) shows the results in formation of HCOOH and MB dye removal in different $KHCO_3$ concentrations on Zn electrocatalyst. The reaction in 0.2 M shows the ability of electrocatalyst towards the formation of HCOOH (204.6, 165.5, 186.9, 178.7 and 245.6 μmol) and MB dye removal (14, 21.3, 38.9, 53.9 and 65.3 %). The optimized condition towards maximum CO_2 reduction is 245.6 μmol after 25 min reaction. In 0.8 M solution, 90.5, 247.6, 256.2, 282.5 and 189.9 μmol for HCOOH was formed (figure 9.5a) and MB dye removal of 49.6, 58.5, 65.8, 77.2 and 86.5 % was obtained after the said time interval. Maximum dye removal of 86.5 % was observed using Zn electrocatalyst after 25 min reaction. The results confirmed the simultaneous dye removal and CO_2 reduction.

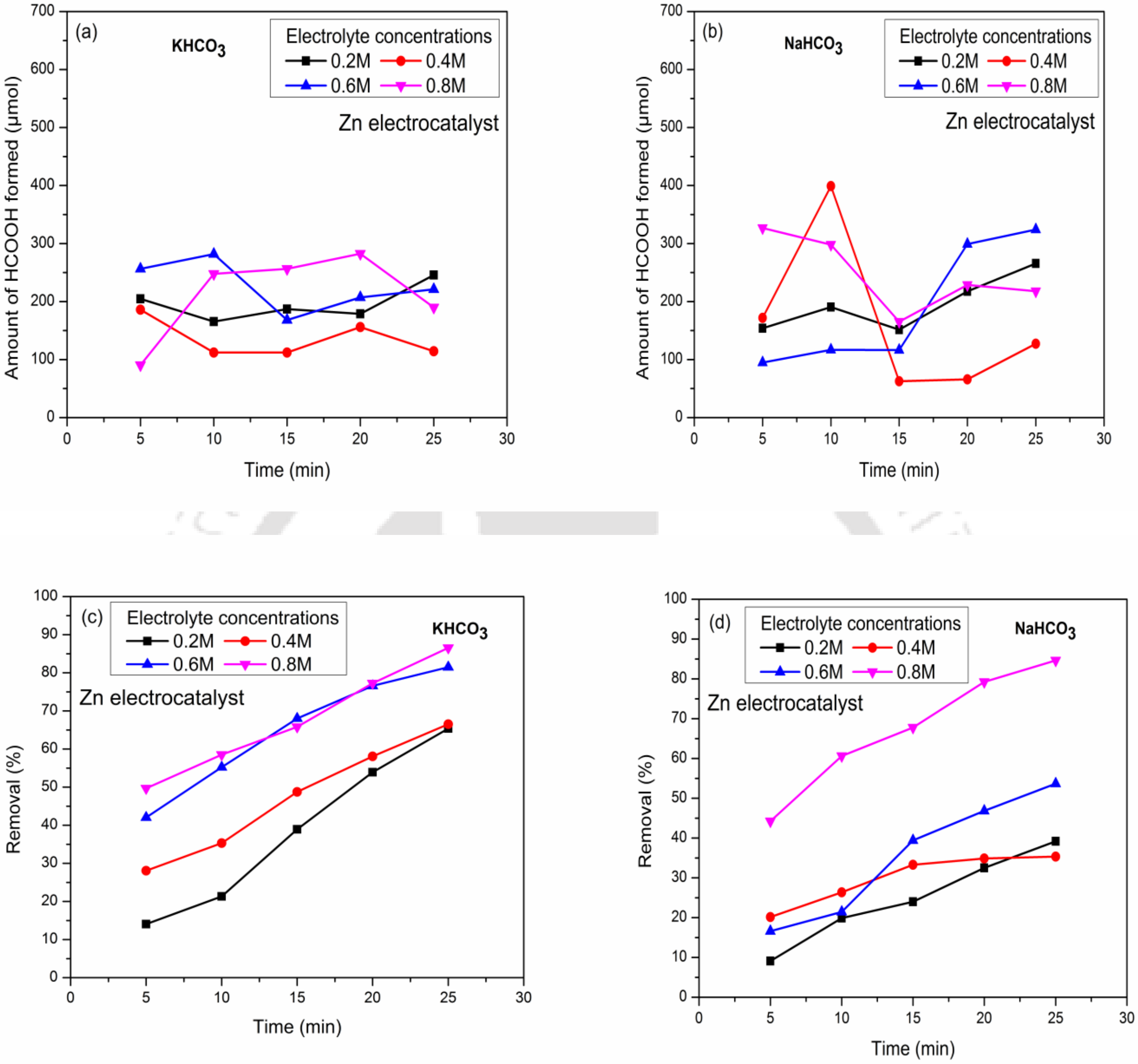

Figure. 9.5 Photo electrochemical CO_2 reduction with time in (a) $KHCO_3$ (b) $NaHCO_3$ and MB removal (%) vs Time in (c) $KHCO_3$ (d) $NaHCO_3$ using Zn.

9.2.4.2. Photo electrochemical studies on CO_2 reduction and MB removal in $NaHCO_3$ electrolyte on Zn electrocatalyst

The photo electrochemical studies in different concentrations of $NaHCO_3$ electrolyte Solutions on Zn electrocatalyst are shown in figure 9.5 (b, d). HCOOH was the only product formed in all applied conditions with MB dye removal. The photo electrochemical studies in a 0.4 M solution depicted the formation of HCOOH as 171.7, 399, 62.6, 65.9 and 127.2 µmol with MB dye removal of 20.1, 26.3, 33.2, 34.8 and 35.3 % (figure 9.5d). Variation in HCOOH formation with time may be due to the oxidation of forming product at anode to produce hydrogen at the cathode.[116]Experimental studies in a 0.8 M solution shows a maximum dye removal of about 84.6 % after 25 min reaction. The results for HCOOH formation was 326.7, 298.1, 165.2, 228.5 and 217.8 µmol (figure 9.5b) with dye removal of 44.2, 60.6, 67.7, 79.2 and 84.6 %, respectively. The optimized condition's for photo electrochemical reduction of CO_2 with MB dye removal using Sn, Zn as cathode and Co_3O_4 as anode in bicarbonates of sodium and potassium electrolyte solution were shown in Table 9.3 and Table 9.4 respectively.

Table 9.3 Optimized conditions towards CO_2 to HCOOH formation

Molarity	**Moles of HCOOH**							
	Sn				**Zn**			
	$KHCO_3$		**$NaHCO_3$**		**$KHCO_3$**		**$NaHCO_3$**	
(M)	**µmol**	**(min)**	**µmol**	**(min)**	**µmol**	**(min)**	**µmol**	**(min)**
0.2	217.4	25	225	5	245.6	25	265.5	25
0.4	261.5	25	294.8	25	186	5	399	10
0.6	206.4	20	353.8	20	281.8	10	324	25
0.8	306.9	25	335.2	15	282.5	20	326.7	5

Table 9.4 Optimized conditions for MB dye removal

Molarity	MB dye removal (time)							
	Sn				Zn			
	$KHCO_3$		$NaHCO_3$		$KHCO_3$		$NaHCO_3$	
(M)	(%)	(min)	(%)	(min)	(%)	(min)	(%)	(min)
0.2	76.8	25	52.2	25	65.3	25	39.1	25
0.4	71.3		47.6		66.5		35.3	
0.6	64.8		54.3		81.4		53.6	
0.8	68.5		74.3		86.5		84.6	

9.2.5. Simultaneous photo electrochemical CO_2 reduction and BG removal on Sn electrocatalyst

The photo electrochemical studies were done using anode (Co_3O_4/G) and cathode (Sn/G) electrodes for reduction of CO_2 and BG dye removal using sodium and potassium based electrolyte solutions. Different electrolyte concentrations of 0.2, 0.4, 0.6 and 0.8 M of CO_2 saturated solutions were used to study the electrocatalysts for reaction time of 5, 10, 15, 20, and 25 min. Results are analyzed subsequently.

9.2.5.1. Photo electrochemical studies on CO_2 reduction and BG removal in $KHCO_3$ electrolyte on Sn electrocatalyst

The results for simultaneous CO_2 reduction and BG dye removal photo electrochemically in $KHCO_3$ solution is shown in figure 9.6 (a, c). For a reaction in 0.2 M, the HCOOH formation of 245.9, 102.3, 247.2, 231.5 and 193.5 µmol was obtained with BG dye removal of 95.4, 95.9, 95.06, 95.4and 93.3 %, respectively. The optimized reaction condition for the maximum HCOOH formation is 247.2 µmol for reaction time of 15 min.

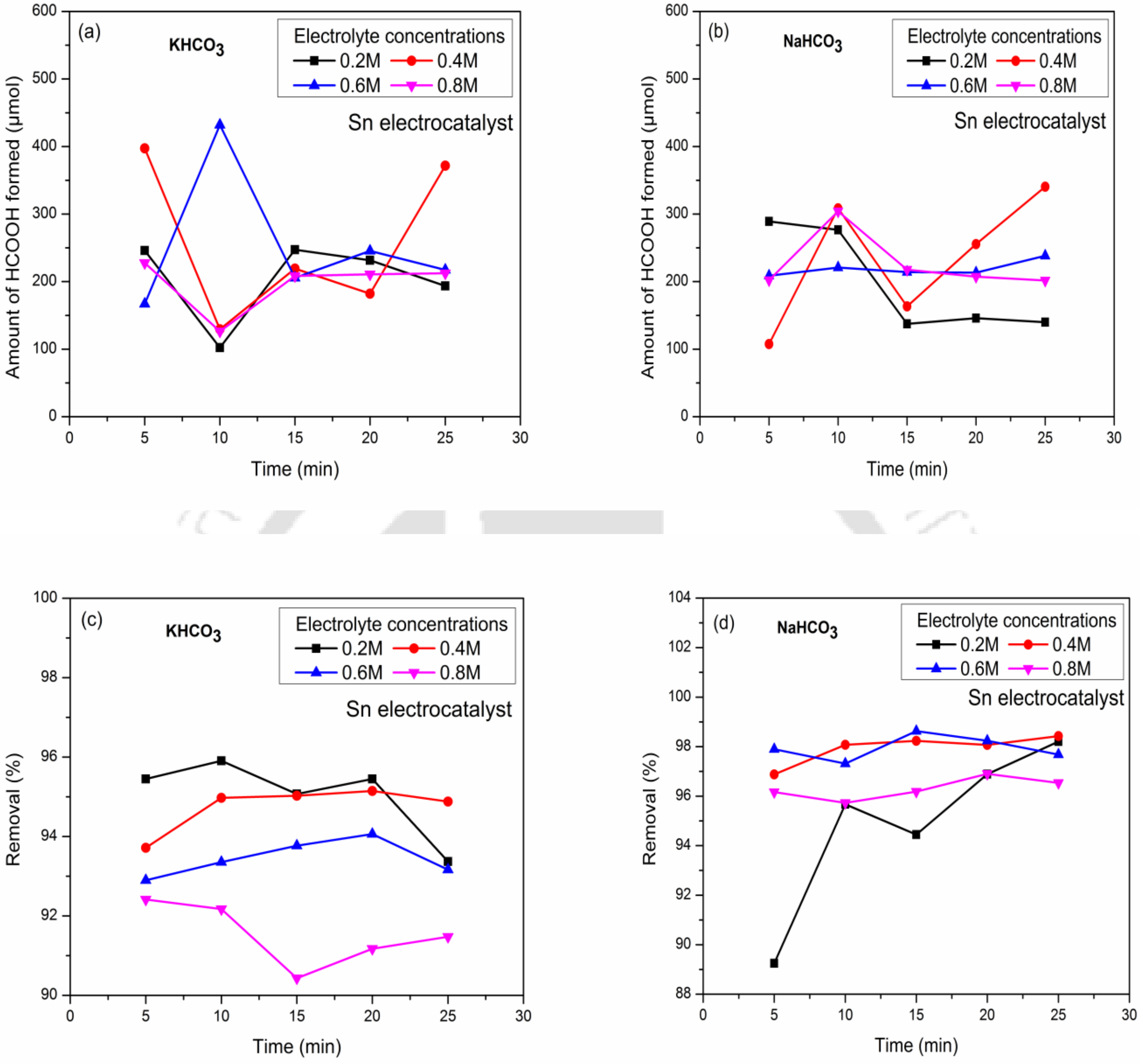

Figure. 9.6 Photo electrochemical CO_2 reduction with time in (a) $KHCO_3$ (b) $NaHCO_3$ and BG removal (%) vs Time in (c) $KHCO_3$ (d) $NaHCO_3$ using Sn.

Moles of HCOOH formation are varying with time, which may be due to the oxidation of product at Co_3O_4 anode.[117] In case of photo electrochemical studies at 0.4 M solution, 397.2, 129, 219.1, 182.07 and 371.5 μmol (figure 9.6 a) of HCOOH were obtained. For the same condition, removal of BG was found as 93.7, 94.9, 95.02, 95.1 and 94.8 %, respectively. Moles of HCOOH (166.9, 431.9, 205.5, 245.4 and 217.3 µmol) and BG removal (92.8, 93.3, 93.7, 94.06 and 93.1 %) were obtained from the photo electrochemical reaction in 0.6 M electrolyte solution. The maximum BG removal was observed in reaction time of 20 min with 94.06 %. The formation of product at different concentrations was changing due to the conductivity of the electrolyte solution. The low product formation corresponds to the availability of more protons at the cathode than CO_2 molecules as formation corresponds discussed in the preceding chapter.

9.2.5.2. Photo electrochemical studies on CO_2 reduction and BG removal in $NaHCO_3$ electrolyte on Sn electrocatalyst

The results in $NaHCO_3$ electrolyte solution for simultaneous BG removal and HCOOH formation are shown figure 9.6 (b, d). HCOOH (289.1, 276.6, 137.4, 145.8 and 139.8 µmol) and BG dye removal (89.2, 95.6, 94.4, 96.8 and 98.2 %) was obtained for a reaction at 0.2 M electrolyte solution. For reaction in a 0.4 M solution, mole of HCOOH formed was 107.5, 308.4, 163.2, 255.5 and 340.4 µmol (Figure 9.6b) with BG dye removal (96.8, 98.07, 98.2, 98.06 and 98.4 %). The change in HCOOH formation with time was due to oxidation of forming product at anode and generation of hydrogen gas at anode.[125] HCOOH (202.1, 303.9, 217.6, 207.2 and 201.7 µmol) and BG removal (96.1, 95.7, 96.1, 96.8 and 96.5 %) were observed in 0.8 M electrolyte solution.

9.2.6. Simultaneous photo electrochemical CO_2 reduction and BG removal on Zn electrocatalyst

The effect of using Zn as a cathode and Co_3O_4 as anode for simultaneous CO_2 reduction and BG dye removal was studied in $KHCO_3$ and $NaHCO_3$ electrolyte solutions. HCOOH was observed as the only product in all applied conditions with maximum BG dye removal. Results are shown below.

9.2.6.1. Photo electrochemical studies on CO_2 reduction and BG removal in $KHCO_3$ electrolyte on Zn electrocatalyst

The photo electrochemical studies in different $KHCO_3$ electrolyte solutions were shown in figure 9.7 (a,c). In 0.2 M solution, 408.2, 372.7, 328.3, 281.1 and 151.5 µmol of HCOOH was formed and simultaneously (99.3, 99.72, 99.72, 99.6 and 99.3 %) BG dye was removed. The change in product moles with time was due to HCOOH oxidation at anode.[116] The photo electrochemical studies in 0.6 M electrolyte solution were observed with HCOOH formation (271.8, 279.6, 464.1, 203.4 and 218.5 µmol) and BG removal (99.5, 99.6, 99.7, 99.7 and 99.6 %), (figure 9.7a,c). The maximum HCOOH formation of 464.1 µmol in 15 min reaction is the better one. For a reaction in 0.8 M electrolyte solution low HCOOH formation (210.7, 312.4, 243.1, 299.02 and 222.5 µmol) with BG dye removal of 99.4, 99.6, 99.6, 99.5 and 99.5 % (Figure 9.7c) were obtained. Low product formation may be due to the hydrogen evolution at cathode by the generation of protons at anode.[115]

9.2.6.2. Photo electrochemical studies on CO_2 reduction and BG removal in $NaHCO_3$ electrolyte on Zn electrocatalyst

The experimental results for CO_2 reduction and BG dye removal in $NaHCO_3$ solution using Zn as cathode is shown in figure 9.7 (b,d). HCOOH was the only product formed in all electrolyte concentrations. The photo electrochemical studies in 0.2 M electrolyte solution for BG dye removal (86.06, 94.9, 91.7, 98.9 and 99.3 %) and HCOOH (208.05, 289.1, 89.08, 190.7 and 303.2 µmol) were obtained. The sudden decrease in HCOOH formation after 15 min reaction was due to the oxidation of forming product at anode for proton generation.[117] In 0.8 M electrolyte concentration, 287.2, 319.5, 227.3, 273.9 and 345.9 µmol of HCOOH formation and 98.7, 97.5, 99.6, 99.98 and 99.92 % of BG dye removal was found (figure 9.7d).

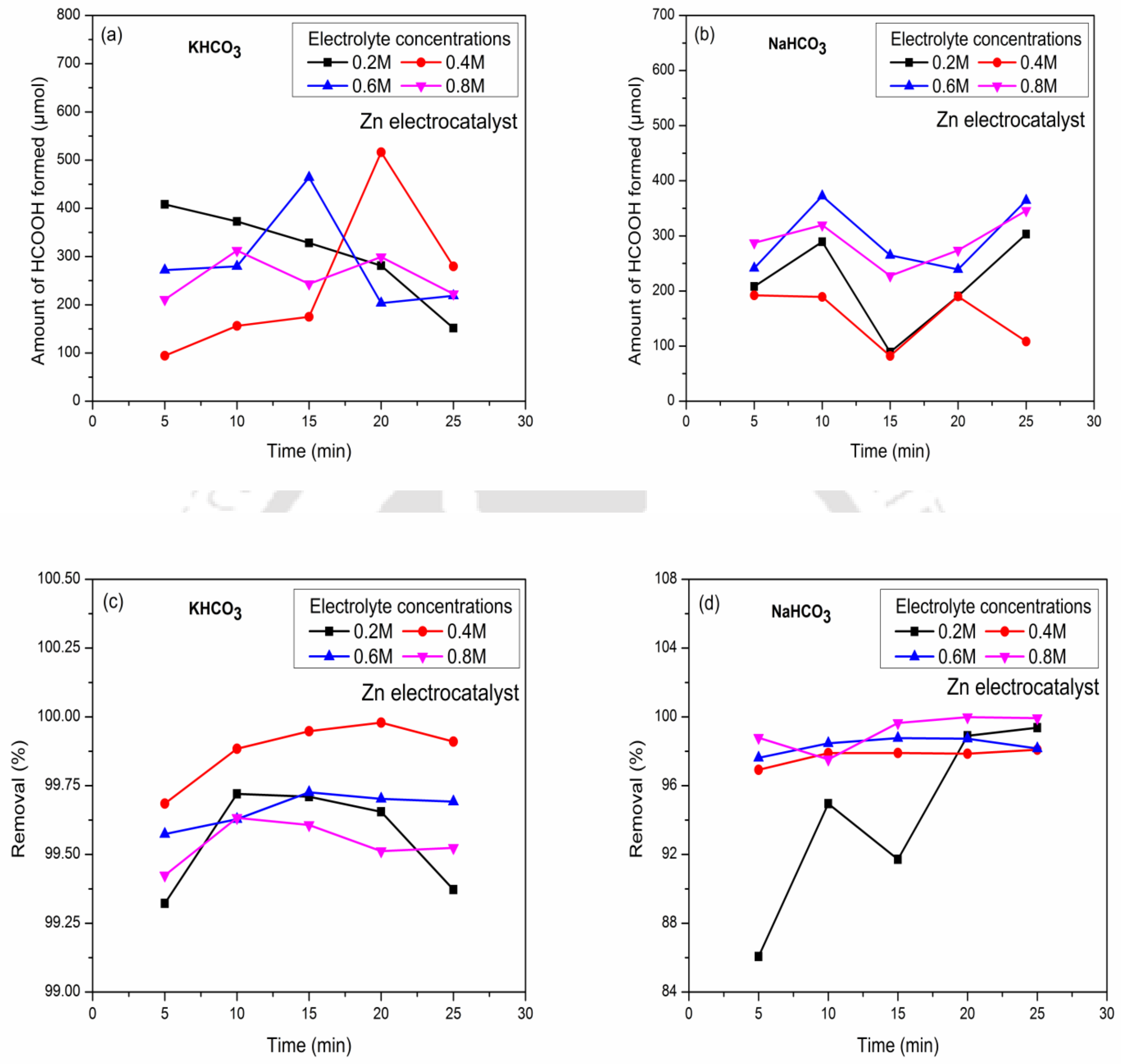

Figure. 9.7. Photo electrochemical CO_2 reduction with time in (a) $KHCO_3$ (b) $NaHCO_3$ and BG removal (%) vs Time in (c) $KHCO_3$ (d) $NaHCO_3$ using Zn.

Low product formation was due to the hydrogen evolution at cathode with high proton generation at anode.[115] The effect of electrocatalysts was studied for HCOOH formation with maximum BG dye removal. The maximum HCOOH formation and BG dye removal using different electrocatalyst of Sn, Zn as cathode to Co_3O_4 anode in sodium and potassium based solutions were given in Table 9.5 and Table 9.6 respectively.

Table 9.5 Maximum HCOOH formation in different electrolytes

Molarity	**Moles of HCOOH**							
	Sn				**Zn**			
	$KHCO_3$		**$NaHCO_3$**		**$KHCO_3$**		**$NaHCO_3$**	
(M)	**µmol**	**(min)**	**µmol**	**(min)**	**µmol**	**(min)**	**µmol**	**(min)**
0.2	247.2	15	589.1	5	408.2	5	303.2	25
0.4	397.2	5	340.4	25	516.3	20	192.1	5
0.6	431.9	10	238.1	25	464.1	15	364.2	25
0.8	227.6	5	303.9	10	312.4	10	345.9	25

Table 9.6 Maximum BG dye removal in different electrolytes

Molarity	**BG dye removal (time)**							
	Sn				**Zn**			
	$KHCO_3$		**$NaHCO_3$**		**$KHCO_3$**		**$NaHCO_3$**	
(M)	**(%)**	**(min)**	**(%)**	**(min)**	**(%)**	**(min)**	**(%)**	**(min)**
0.2	95.9	10	98.2	25	99.72	10	99.3	25
0.4	95.1	20	98.4	25	99.97	20	98.08	25
0.6	94	20	98.6	15	99.72	15	98.76	15
0.8	92.4	5	96.8	20	99.63	10	99.98	20

9.3. Summary

The photo electrochemical studies were performed first time for the simultaneous reduction of CO_2 to HCOOH and dye (CV, MB and BG) removal using Zn and Sn as cathode electrocatalysts with Co_3O_4 anode. The formation of HCOOH was studied in different concentrations of bicarbonates of potassium and sodium salts. The effect of dye removal with CO_2 reduction in different electrolyte concentrations was discussed to obtain the reaction efficiency. This study will be helpful in improving simultaneous water purification and CO_2 reduction with solar energy for future applications.

Chapter 10

Conclusions and Future Scope

Chapter 10

Conclusions and Future Scope

10.1. Conclusions

In this study, various electrocatalysts were synthesized by using a simple electro deposition method. The prepared electrocatalysts were characterized and used for the reduction of CO_2 electrochemically (chapters 3 to 6 and 8) and photo electrochemically (chapters 7 and 9). Co_3O_4 was used as the anode for water oxidation reaction with four different electrocatalysts (Cu_2O, Pb_2O, Zn and Sn) as a cathode. The effect of these electrocatalysts was also studied in different electrolytes for the simultaneous dye removal and CO_2 reduction (chapters 8, 9). The major conclusion obtained is given below chapter wise.

Chapter 3: Electrochemical studies for CO_2 reduction using synthesized Co_3O_4 (anode) and Cu_2O (Cathode) in different electrolytes

- Multiple products (C_2H_5OH, CH_3OH, HCOOH, HCHO, CH_3COOH and C_3H_7OH) were formed when Cu_2O and Co_3O_4 was used as cathode and anode, respectively.
- It was observed that bicarbonate salts are showing better Faradaic efficiency of product formation than that of carbonate salts.
- For ethanol, high Faradaic efficiencies of 76.31 % and 96.15 % were observed at 1.5 V and 2 V respectively, after 5 min of RCPE in $KHCO_3$.
- In $NaHCO_3$ solution, maximum Faradaic efficiency for ethanol was 98.1 % at 2 V after 5 min.

Chapter 4: Synthesis of Pb_2O electrocatalyst and its application towards the reduction of CO_2 electrochemically to HCOOH in various electrolytes

- HCOOH was the only product formed at all applied conditions when Pb_2O (cathode) and Co_3O_4 (anode) was used as electrocatalyst.
- RCPE in bicarbonate based solutions shows better results towards HCOOH formation.
- For $KHCO_3$, at 1.5 V and 2 V high Faradaic efficiencies of 37 % and 60 % were observed after 5 min and 10 min, respectively.
- In case of $NaHCO_3$, Faradaic efficiencies of 17 % and 50 % were observed for 1.5 V and 2 V after 5 min and 10 min, respectively.

Chapter 5: Electrochemical reduction of CO_2 to HCOOH using Zinc and Cobalt oxide as electrocatalysts

- HCOOH was the only product formed at all applied conditions when Zn (cathode) and Co_3O_4 (anode) were used for RCPE.
- Maximum Faradaic efficiencies of 78.5 % and 78.4 % for HCOOH were obtained for reaction time of 5 and 10 min at 1.5 V in $KHCO_3$ electrolyte solution.
- In the case of $NaHCO_3$ electrolyte solution, high Faradaic efficiencies of 60.4% and 64.7% were observed at reaction time of 5 and 10 min at 2.5 V.

Chapter 6: Electrochemical reduction of CO_2 to HCOOH on a synthesized Sn electrocatalyst using Co_3O_4 anode

- HCOOH was obtained as the only product in all electrolyte solutions for different applied voltages using Sn (cathode) and Co_3O_4 (anode) as electrocatalysts.
- Maximum Faradaic efficiency of 92.6% was observed at 2 V for reaction time of 5 min and 74.06 % at 1.5 V for 20 min in $KHCO_3$ solution.
- For $NaHCO_3$, Faradaic efficiencies of 68.72% were observed at 1.5 V after 25 min.

Chapter 7: Solar cell driven electrochemical studies for CO_2 reduction on various electrocatalysts

- Multiple products (CH_3OH, C_2H_5OH, HCOOH, HCHO and CH_3COOH) were obtained during when Cu_2O was used as electrocatalyst in the cathode.
- HCOOH was the only product obtained when Pb_2O, Zn and Sn were used as electrocatalyst in the cathode.
- Using Cu_2O as electrocatalyst, maximum C_2H_5OH formation was observed to be 1277 µmol for 40 min reaction in 0.2M $KHCO_3$ electrolyte solution.
- The optimized conditions towards HCOOH formation on Pb_2O electrocatalyst was 242 µmol for 30 min reaction in 0.2M $NaHCO_3$ and 157 µmol of HCOOH formed for 10 min reaction in 0.2M $KHCO_3$.
- For Sn based reduction, maximum product formed was 430.04 µmol and 494.60 µmol after 10 min using 0.2 M of $KHCO_3$ and $NaHCO_3$, respectively.
- In case of Zn electrocatalyst, 400µmol (10 min) and 254 µmol (40 min) of product was formed for $KHCO_3$ and $NaHCO_3$, respectively.

- The results from the electrochemical and photo electrochemical studies were found that better performances were obtained for Zn and Sn electrocatalysts for single HCOOH production with high Faradaic efficiency.

Chapter 8: Simultaneous CO_2 reduction and dye removal electrochemically on Sn and Zn catalysts using Co_3O_4 anode

- HCOOH was the product towards RCPE along with dye removal for all CO_2 saturated bicarbonate electrolyte solutions with different dyes (Crystal violet, Methylene blue and Brilliant green).

- Maximum CV dye removal for Sn and Zn electrocatalyst were observed as 64.3% and 61% in $NaHCO_3$ electrolyte solution. Similarly, removal of 71.5% and 60.9% were obtained in $KHCO_3$ electrolyte at 2.8V for 25 min. High HCOOH Faradaic efficiency of 45.3% was obtained in $KHCO_3$ electrolyte solution using Zn electrocatalyst at 2.3V for 5 min.

- Maximum MB removal for Sn electrocatalyst was obtained to be 33.6 % and 32.7 % for $KHCO_3$ and $NaHCO_3$, respectively. For Sn as electrocatalyst maximum Faradaic efficiencies of 57.9 % and 40.6 % were obtained after 15 min for the two electrolytes.

- BG dye removal was observed for all conditions for both (Zn and Sn) as electrocatalysts. HCOOH formation is favorable at low applied voltages compared with higher voltages. Maximum Faradaic efficiency of 76.3 % (5 min)–2 V and BG dye removal of 94.9 % (25 min) – 3.8 V was observed for Sn electrocatalysts in $NaHCO_3$ solutions.

- For Zn as electrocatalyst, maximum Faradaic efficiency of 69.9 %(10 min)-2 V and BG dye removal 95.1 %(5 min)-2 V was observed in $KHCO_3$ electrolyte solution.

Chapter 9: A photo electrochemical study on CO_2 reduction for solar energy storage and dye removal on Sn and Zn catalysts using Co_3O_4 anode

- HCOOH was the product obtained after reaction along with dye (Crystal violet, Methylene blue and Brilliant green) removal for all applied conditions in different concentrations of $KHCO_3$ and $NaHCO_3$.
- The maximum product formation was 532 µmol (15 min) in 0.4 M $NaHCO_3$ solution with CV removal of 72.7 % (25 min) using Sn as electrocatalyst. Using a Zn electrocatalyst as cathode, the formation of HCOOH was 495.8 µmol (10 min) in 0.8 M $KHCO_3$ with CV removal of 66.3 % (25 min) in 0.4 M $KHCO_3$ solution.
- For MB with CO_2 reduction maximum dye removal of 74.3 % (0.8 M $NaHCO_3$) and HCOOH formation of 335.2 µmol in 15 min (0.8 M $NaHCO_3$) was obtained on Sn electrocatalyst.

10.2. Future scope

This section highlights some of the new areas of research, that can be carried out to further the preparation and applicability of electrocatalysts for the production of single product from CO_2 economically. Some of the important areas of recommended research are suggested as an extension of the present study:

- Electrokinetics and mass transfer limitation of CO_2 at catalyst-electrolyte interface need to be studied for the effective CO_2 reduction electrochemically and or photo electrochemically to get high energy efficiencies.

- Study of CO_2 reduction in continuous electrochemical reactor system for gas and liquid phase reactions.

- The studies of continuous photo electrochemical reactor system for solar energy storage by CO_2 reduction.

- Pilot scale investigation of RCPE using the real gaseous (CO_2) stream and dye containing effluent.

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Research Output

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Papers published in peer reviewed international journals

1. **V. S. K. Yadav**, M. K. Purkait, Electrochemical Studies for CO_2 Reduction Using Synthesized Co_3O_4 (Anode) and Cu_2O (Cathode) as Electrocatalysts, ***Energy and Fuels***, 2015, 29, 6670-6677.
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