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Electrochemical reduction of CO$_2$ to HCOOH using zinc and cobalt oxide as electrocatalysts

Viyyapu Shyam Kumar Yadav and Mihir Kumar Purkait[*]

Department of Chemical Engineering

Indian Institute of Technology Guwahati

Guwahati - 781039, Assam, India

[*] Corresponding author

Tel: + 91 - 361 - 2582262

Fax: +91 - 361 - 2582291

E. Mail: mihir@iitg.ernet.in   (M K Purkait)

Abstract

Present work studies the effect of synthesized Zinc (Zn) electrocatalyst towards reduction of CO_2 to products electrochemically (RCPE) using Cobalt oxide (Co_3O_4) for water oxidation. Zn catalyst was prepared using electrodeposition method of zinc chloride dihydrate ($ZnCl_2.2H_2O$) solution. The synthesized electrocatalyst was characterized by XRD, FTIR and particle size analysis, which confirms the formation of Zn particles. Electrodes were prepared by depositing synthesized Zn and Co_3O_4 on graphite plates and used as cathode and anode, respectively. The effects of applied voltage with time for RCPE were studied in carbonates and bicarbonates of sodium and potassium electrolytes. Ultra-fast liquid chromatography (UFLC) was used for the detection of end products from RCPE. However, HCOOH was the only product formed at all applied conditions. Maximum efficiencies were observed in bicarbonates than carbonates. 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 5 min and 10 min duration were obtained at 2.5 V. Ability of synthesized electrocatalyst towards RCPE was explained for all the applied conditions in detail.

Keywords: CO_2 reduction; Faradaic efficiency; Zn; Electrodeposition; Co_3O_4.

1. Introduction

A simultaneous increase in energy utilization and environmental problems are two main challenges for researchers around the globe. Increase in energy utilization is proportional to greenhouse gas emissions because most of present energy generated is by the combustion of fossil fuels like petroleum, coal and natural gas. During the process of combustion, greenhouse

gases were emitted with CO_2 as major emission. This increases the CO_2 concentrations in atmosphere drastically from past few decades, which is the main cause for global warming effect.[1] In order to reduce these concentrations different techniques like photochemical [2], electrochemical [3-6], chemical [7], biochemical [7] and radiochemical [7] were used and reported well. However, reduction of CO_2 electrochemically (RCPE) is considered as one of the promising methods for the elimination and conversion of atmospheric CO_2 to products.[8-10]

Researchers are working on the RCPE for past few decades, mainly on electrocatalyst and its effect in different electrolytes.[3,11] Operating conditions and type of electrocatalyst plays a major role on the efficiency of RCPE and product selectivity. Electrocatalysts like Ag, Sn, and Au were used as electrodes for the reduction of CO_2 and various products including CO, HCOOH, H_2 and some liquid products were formed.[3] Electrolytes play a major role in RCPE, and their effects on reduction of CO_2 to carbon monoxide, oxalic acid, formic acid were reported.[12] Moreover, copper is accepted a suitable electrocatalyst in reducing CO_2 to hydrocarbons by several studies.[13] Ohya et al studied the effect of RCPE in methanol based electrolytes to evaluate the performance of copper oxides electrocatalyst.[14] Brito et al. reported the effect of photochemical reduction of CO_2 dissolved in carbonate electrolytes at Cu/Cu_2O electrocatalyst and reported the formation of methanol and ethanol as products.[15] The reduction of CO_2 on copper electrode was studied and 16 different reaction products were reported. Out of these, methane and ethylene were identified with high efficiencies of current and remaining 14 products were reported as oxygenates.[16] Li et al. reported the reduction of CO_2 on copper particles to CO and HCOOH in 0.5M $NaHCO_3$ at high Faradaic efficiencies.[17] RCPE was studied in 0.1M $KHCO_3$ on different copper electrodes in single series orientations. Based on used catalyst orientation, different products like acetic acid, ethanol, acetaldehyde, methane and

ethylene were reported.[18] Though copper is accepted as the best catalyst towards RCPE, the process becomes complex due to formation of multiple products.[19] To reduce this complexity, authors were worked on reduction of CO_2 to single products. Reduction of CO_2 resulting in a single liquid product with higher efficiencies would become a sustainable approach for future liquid fuel production. HCOOH from RCPE was studied using Pb, Sn, and Zn electrocatalysts.[20-28] This is to be mentioned here that Pt was used for water oxidation in all the literatures mentioned above. To the best of our knowledge, work related to replacement of expensive Pt electrocatalyst with a cheap and easily available material for RCPE was scant. Therefore, this work focused on the identification and synthesis of low cost and easily available electrocatalyst for RCPE. Co_3O_4 was used for the oxidation reactions.[33-35] In the present work, Co_3O_4 was chosen first time as an electrocatalyst for the RCPE experiment and results were compared with that of Pt.

This study reports the synthesis of electrocatalyst and its applications in RCPE using various electrolyte solutions to produce single liquid product. RCPE studies were performed using 2-electrode glass cell at different applied voltages in order to find the optimum conditions towards maximum Faradaic efficiency. This study will be helpful to assess the ability of present electrocatalysts towards HCOOH formation by RCPE.

2. Experimental

2.1. 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 (1.5×2.5) cm^2 were procured from Sunrise enterprises, Mumbai. Nafion (5 wt.%) solution and DC (direct current) source were purchased from DuPont, USA) and Crown, India, respectivelly. All the chemicals were used without any further purification and deionized water was used for all the cases.

2.2. Synthesis of Zn and Co₃O₄ powder

Zinc (Zn) powder was synthesized by electrodeposition method.[36] Synthesis for Zn powder starts with deposition of Zn on surface of graphite plate from 0.1M $ZnCl_2.2H_2O$ solution (Figure 1). 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 ^{o}C for 1h to obtain Zn powder. Co_3O_4 powder was prepared from its nitrate solution (0.1M Co $(NO_3)_2.6H_2O$) by electrodeposition method and reported elsewhere in our previous work.[37] Constant current of 2A for 3 min was applied between two electrodes (copper and graphite) in electrolyte solution. Deposition of Co takes place at the surface of graphite plate which was removed with acetone solvent. Catalyst solution was heated at 100°C for 1h to get Co_3O_4 powder.

2.3. 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° to 80° 2θ. Particle size analysis was done by Delsa nano (make: Beckman coulter; model: Delsa nano C) particle size analyzer.
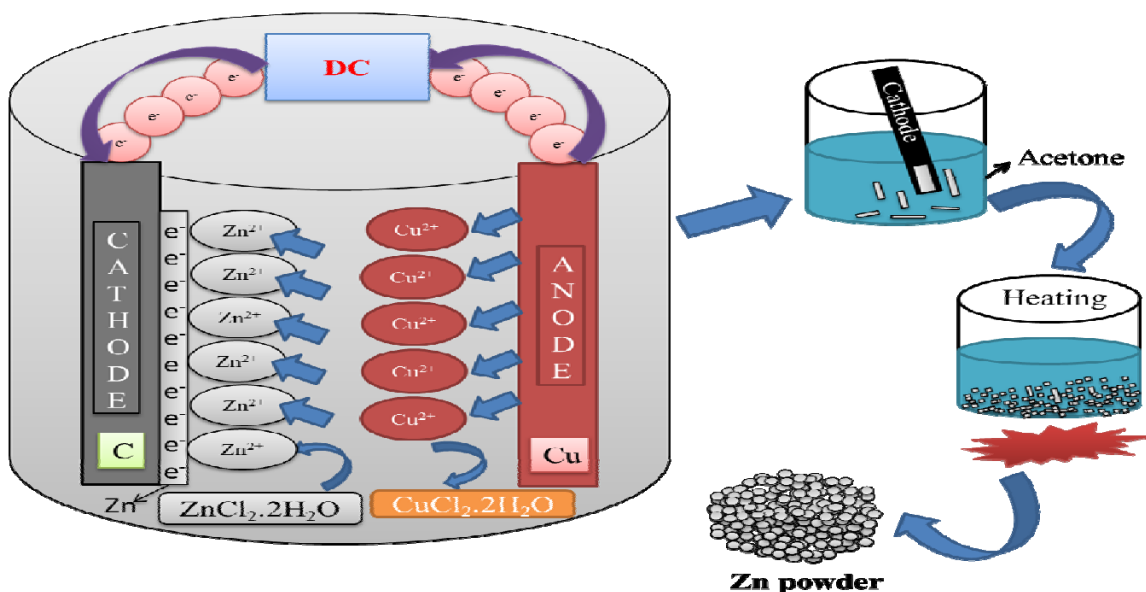
Figure 1. Schematic for the Zn powder synthesis by electrodeposition method

2.4. Preparation of anode and cathode electrodes

The cathode and anode were prepared by coating the Co_3O_4 and Zn electrocatalysts on the surface of graphite plates, respectively. The binder was 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 ^{o}C to get electrode of 2 mg/cm^2. Coated electrodes were dried at the 100 ^{o}C for 2h to form finished electrode.

2.5. Electrochemical reduction of CO_2

RCPE experiments were conducted in a two electrode glass cell. Co_3O_4 and Zn electrodes were 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. Saturated solution was taken in a glass cell and experiments were conducted by connecting two electrodes to DC source as shown in figure 2. RCPE was done at different potentials (1.5, 2, 2.5, 3 and 3.5 V) with varying reaction time (0-5, 10, 15, 20, and 25 min) using different electrolyte solutions.
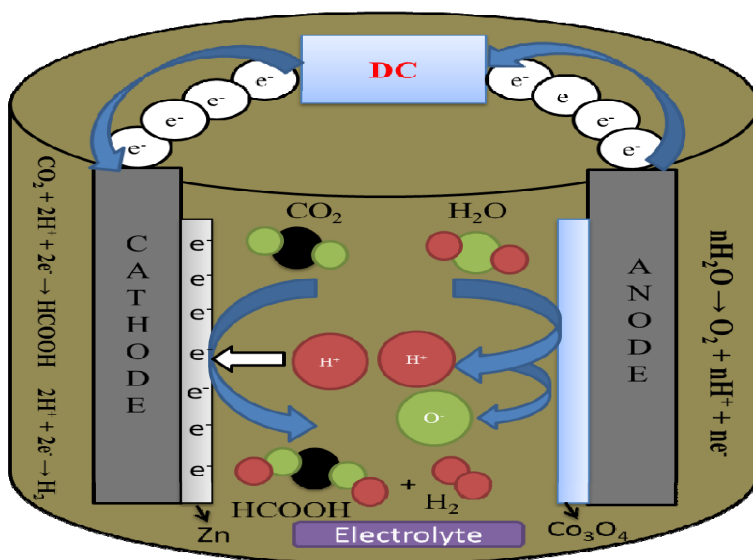

Figure 2. Schematic diagram for reduction of CO_2 to HCOOH on Zn electrocatalyst

2.6 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 the 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.

3. Results and discussion

The Zn and Co_3O_4 were synthesized separately by using electrodeposition technique and used for the RCPE as electrocatalyst. Experimental results for Zn and Co_3O_4 electrocatalysts on RCPE were discussed in the subsequent sections.

3.1. Characterization of Zn electrocatalyst and its formation mechanism

FTIR spectrum of Zn catalyst is shown in figure 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.
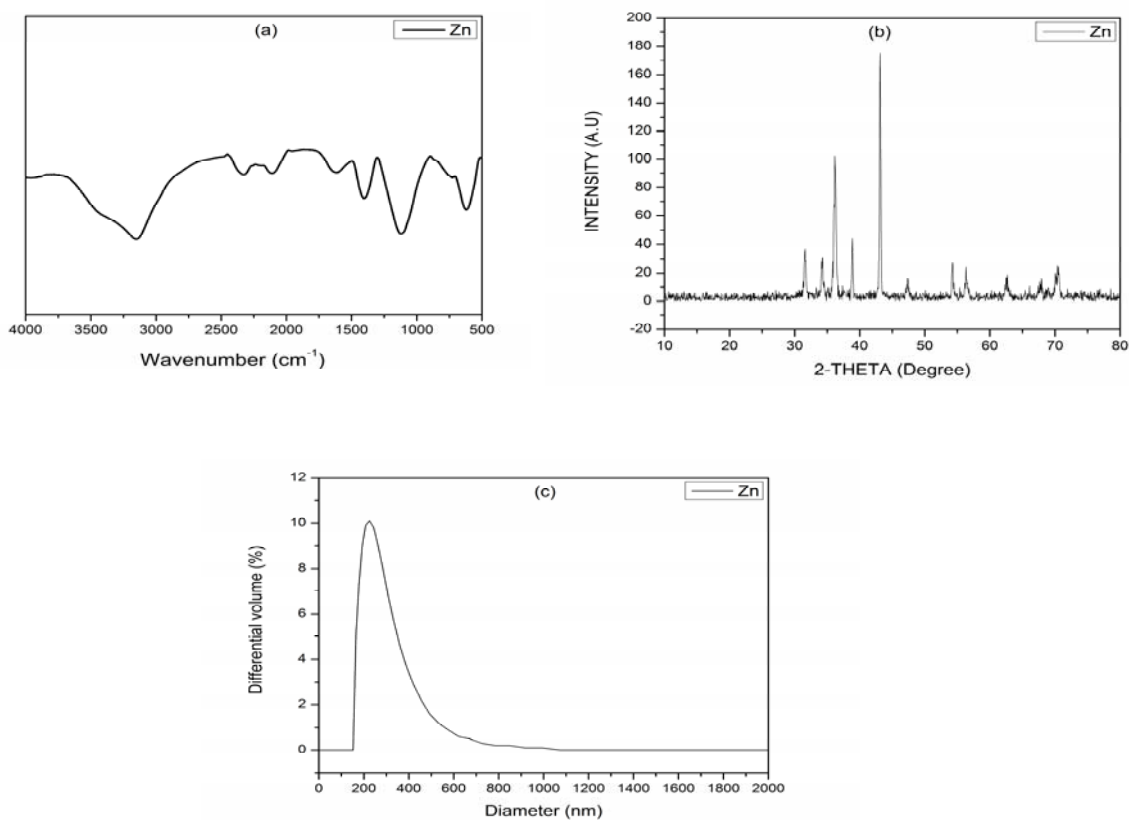

Figure 3. Characterization Zn electrocatalyst, (a) FTIR, (b) XRD, and (c) particle size analysis

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.[38] XRD pattern of Zn catalyst is shown in figure 3. Peak positions at 36.15^o, 38.85^o, 43.15^o, 54.25^o, 67.95, 70.5 and 76.9^o are matching closely with Zn structure.[39] Particle size distribution of Zn is represented in figure 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. Under the application of voltage between two electrodes as shown in figure 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.
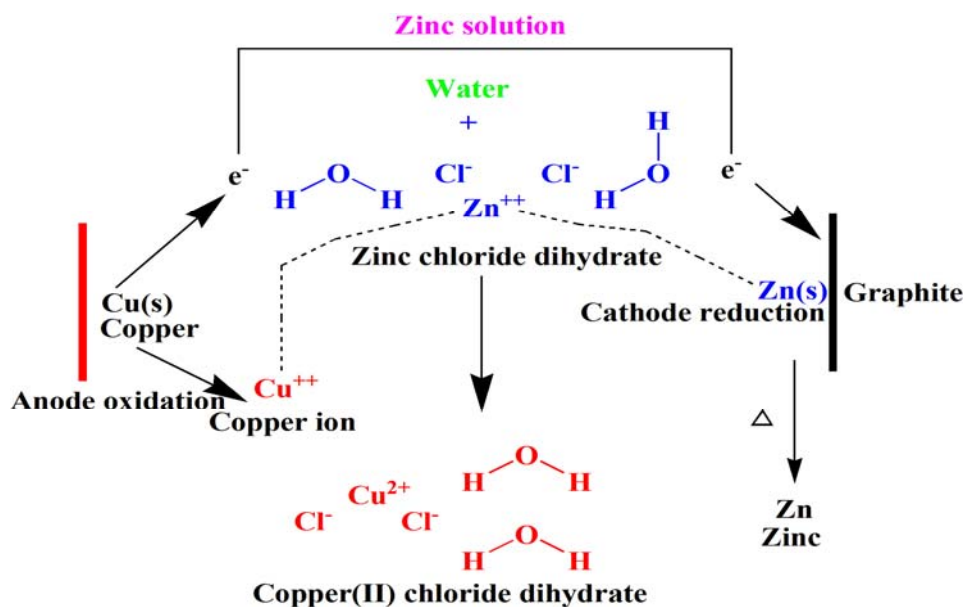

Figure 4. Mechanism for the Zn powder formation

3.2. Reduction CO$_2$ at Zn electrocatalyst

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

The experimental results shown in figure 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 showed high current densities than sodium electrolytes as shown in figure 5. Overall, current densities for all experiments towards RCPE in various experimental conditions confirmed that reaction occurred at the surface of the cathode.
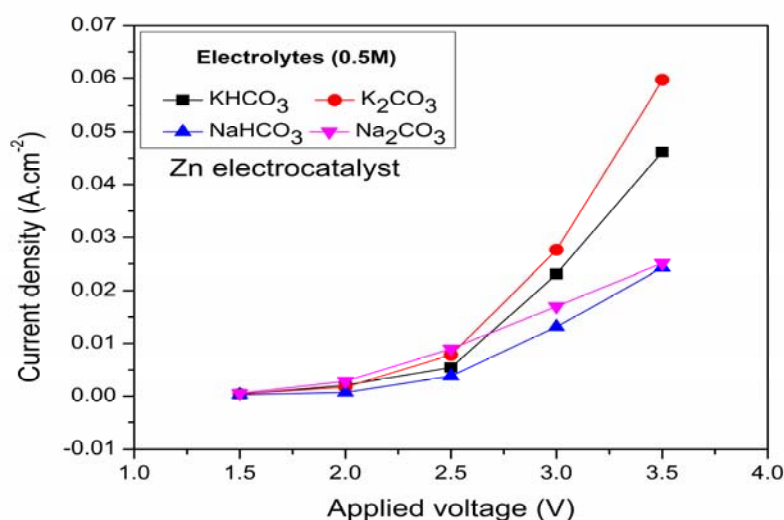

Figure 5. Current density during CO_2 reduction with applied voltage on Zn electrocatalyst

3.2.2. 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 6a that, HCOOH was formed at all applied conditions from the 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 as 78.5, 78.4, 29.3, 16.7 and 23%, respectively. Reaction at 1.5 V showed significant results for HCOOH with high Faradaic efficiency of 78.5% for 5 min reaction which was more optimized condition for RCPE. Hara et al. reported 40.8% Faradaic efficiency in 0.1M $KHCO_3$ at 1.7 V using Pt anode.[27] 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 6a). The obtained efficiencies were low compared with RCPE at 1.5 V which might be due to high hydrogen or CO evolution.[28] 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 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) 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.

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

High Faradaic efficiencies were obtained at low applied voltage of 1.5 V compared with other high voltages (Figure 6b). 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 as 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.[28] RCPE at an applied voltage of 2V showed

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 was 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 was reported for HCOOH formation on Zn electrocatalyst and Pt as anodic material.[26] However, HCOOH was 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). 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 product (HCOOH) in the presence of K_2CO_3 but with reduced efficiency than $KHCO_3$.

3.2.4. 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 6c. Effect of CO_2 reduction using Zn electrocatalyst was reported high reaction rates for HCOOH formation using Pt as anodic material.[20] 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.[20] RCPE at 3 V obtained Faradaic

efficiencies of 25.7, 18.1, 9.9, 6.6 and 5.9% towards HCOOH formation (figure 6c). At 3.5V,

low efficiencies of 9.4, 5, 4.6, 2.6 and 1.8%, respectively, were obtained which may be due to

high proton generation at Co_3O_4 electrode. Reduction of CO_2 to HCOOH was favored 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

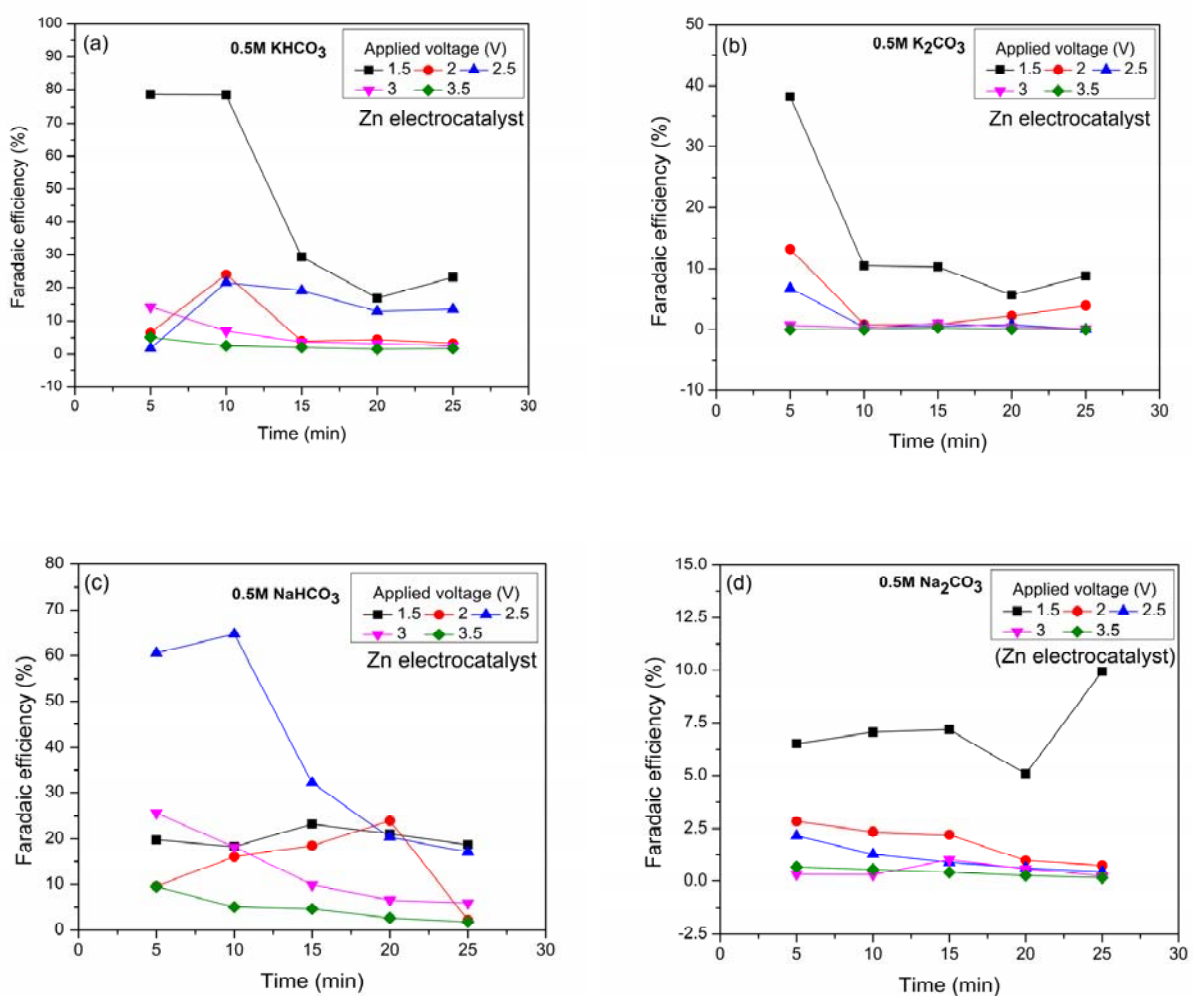electrocatalysts were able to reduce CO_2 to HCOOH in $NaHCO_3$ based salt efficiently.

Figure 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

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

Results for the reduction of CO_2 in 0.5M Na_2CO_3 solution (figure 6d) showed that HCOOH was formed in all the conditions and respective Faradaic efficiencies were reported for 5, 10, 15, 20 and 25 min of reactions. Though current densities were high compared with bicarbonate solution, low Faradaic efficiencies were obtained for this electrolyte (figure 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.[20] At 2 V, Faradaic efficiencies of 2.8, 2.3, 2.2, 0.9 and 0.7% were observed, respectively for various times (figure 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. High CO Faradaic efficiencies were reported when Zn electrocatalyst was used for CO_2 reduction.[27] However, the present catalyst was able to reduce CO_2 to HCOOH by the observed results.

3.2.6. Mechanism of HCOOH formation

The optimized conditions for RCPE using synthesized electrocatalyst with a maximum Faradaic efficiency of HCOOH at different time using various electrolytes are shown in Table 1. From the table it may be concluded that the bicarbonates are able to reduce CO_2 with high Faradaic efficiencies than that of carbonates salts of potassium and sodium. The elementary mechanism towards CO_2 reduction is shown in figure 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.[40]

Table 1: Optimized experimental conditions for RCPE

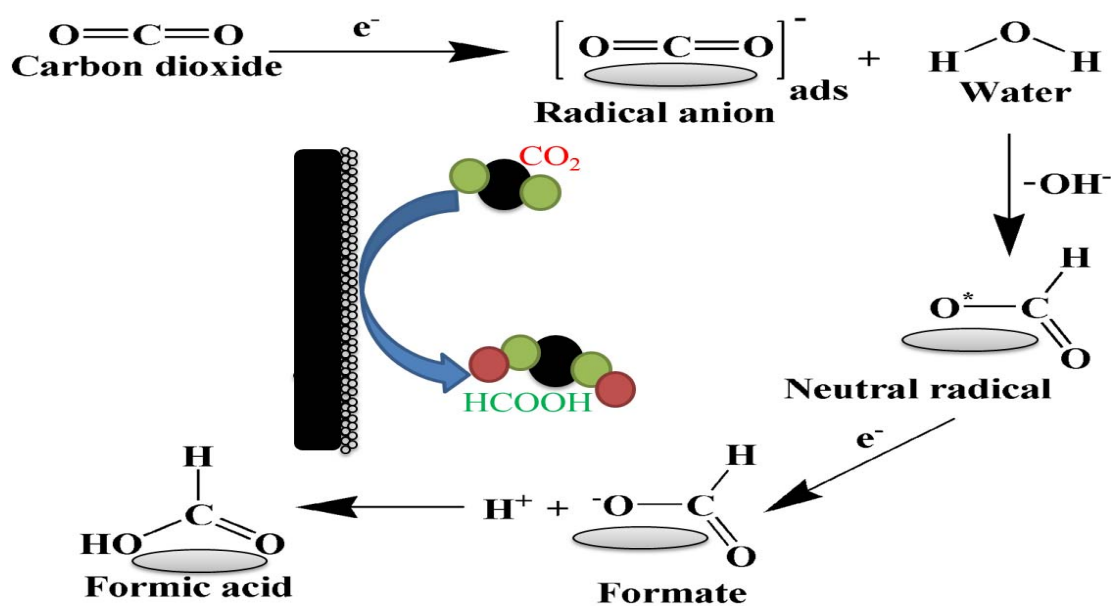| Voltage | Maximum Faradaic efficiency (time) | | | | | | | |
| | $KHCO_3$ | | K_2CO_3 | | $NaHCO_3$ | | Na_2CO_3 | |
(V)	(%)	(min)	(%)	(min)	(%)	(min)	(%)	(min)
1.5	78.5	5	38.2	5	23.2	15	9.9	25
2	23.9	10	13.2	5	24	20	2.8	5
2.5	21.5	10	6.7	5	64.7	10	2.1	5
3	14.1	5	1.07	20	25.7	5	1.0	15
3.5	5.1	5	0.34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

Figure 7. Proposed elementary mechanism for reduction of CO_2 to HCOOH

4. Conclusions

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 shows high Faradaic efficiencies than carbonate based electrolyte solutions. HCOOH was the only product formed at all applied voltages in different electrolyte solutions. 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 which was the most optimum condition for CO_2 reduction. 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.

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