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

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Abstract

The present work investigates the electrocatalytic effect of tin (Sn) and cobalt oxide (Co_3O_4) towards reduction of CO_2 to products electrochemically (RCPE). Electrocatalyst (Sn) powder was synthesized by electrodeposition method from $SnCl_2$. $2H_2O$ solution. Experiments were conducted using Co_3O_4 and Sn electrodes as anode and cathode, respectively, in 0.5M carbonates and bicarbonates of potassium and sodium solutions. Electrodes were prepared by coating electrocatalysts on graphite plate surface. The experiments were conducted at different applied voltages (1.5 to 3.5 V) and time intervals (5, 10, 15, 20 and 25 min) at various electrolyte solutions. It was observed that HCOOH acid was the only product formed for all the applied conditions. At 1.5 V and 2 V, maximum Faradaic efficiencies of 74.04 % and 92.6 % for HCOOH were obtained at 20 and 5 min reaction in $KHCO_3$ electrolyte solution. The ability of Co_3O_4 for water oxidation and Sn electrocatalyst towards reduction of CO_2 to HCOOH was established from the obtained results. Optimized reaction conditions to get high Faradaic efficiencies were explained in detail.

Keywords: Faradaic efficiency; Reduction of CO_2 to products electrochemically (RCPE); Sn; Electrodeposition; Co_3O_4.

1. Introduction

Fossil fuels are used as world's primary energy source. Since energy produced from fossil fuel is cheap, most of the energy generating in present's technology is by using fossil fuels. The process of energy generation deals with combustion of fossil fuels like coal, natural gas and petroleum. Mainly CO_2 and some other gases like nitrous oxide, methane and other halocarbons were evolved into the atmosphere as greenhouse gases during combustion. Utilization of fossil fuel energy is drastically increasing due to rapid rise in population. The emissions of greenhouse gases mainly CO_2 is proportional to the energy generation and is the main cause for global warming.[1-3] Most of the environmentally challenging issues arise due to CO_2 in all the countries. Hence, it is highly recommended to control this greenhouse gases before its release into the environment. Many methods were in existence for the reduction of CO_2 to various products, but reduction of CO_2 to products electrochemically (RCPE) is promising method because of its several advantages. Firstly, RCPE in the aqueous systems has yielded high selectivity at low cost by using heterogeneous catalyst.[4-7] Secondly, the entire reaction process can be done at ambient temperature and pressures.[8] Thirdly, it can be done using solar energy as a source.[9-11] Fourthly, energy generated for RCPE can be stored in the form of fuels.[12-13] Fifthly, generation of the proton source of wastewater decreases the overall chemical consumption. Finally, RCPE systems have compact design and easy to scale up for industrial application.

It is envisaged from the above literatures that the RCPE is going to be a promising technology for the reduction of CO_2 to produce several products. Reduction of CO_2 mainly depends on electrocatalyst used in the reaction and applied potentials. However, work is going on to improve the reduction rates by improving stability and efficiency of electrocatalyst. The main attention is focused to study the extent of catalyst deactivation in order to find developed electrocatalyst of high stability.[14] Electrolytes[15], pH[16] and catalyst structure[17-19] plays a major role for product selectivity in RCPE. Copper is well known electrocatalyst in RCPE as various products like; methane, ethylene and other hydrocarbons are formed with significant efficiencies. However, due to formation of multiple products, process becomes more complex.[20] In order to reduce this complexity; CO_2 has to be reduced to single product with high Faradaic efficiency. If liquid product is formed in RCPE with high Faradaic efficiencies, this could be sustainable approach for future liquid fuel production. Some studies were done for RCPE at Pb and Sn electrocatalysts to form HCOOH.[21-25] In most of the RCPE processes platinum (Pt) was used as anode for oxidation of water.[26-27] However, few authors investigated the effect of water oxidation using Co_3O_4 electrocatalyst for hydrogen evolution reactions.[28–31]

From the extensive literature survey, it was observed that Pt was used as anode electrocatalyst for the oxidation reaction in most of the cases. Use of Co_3O_4 as electrocatalyst in place of Pt for RCPE is scant and might be a better alternative. Present work explores the use of Co_3O_4 as anode and Tin (Sn) as cathode material in RCPE for the reduction of CO_2 to HCOOH as a single liquid product. The role of electrocatalyst for an anode (Co_3O_4) and cathode (Sn) towards RCPE is explained with respect to rate of reaction for all applied voltages using a 2-electrode glass cell. To the best of our knowledge, no studies have been reported using Co_3O_4 as anode for RCPE on Sn electrocatalyst. Therefore, data generated in this investigation might be of useful in the field of RCPE during selection of low cost and appropriate electrocatalyst.

2. Experimental

2.1. Materials, characterization and product analysis

Materials: 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.

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.

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.

2.2. Synthesis of Sn powder electrochemically

Tin (Sn) powder was synthesized by electrodeposition method.[32] Schematic for the synthesis of Sn powder is shown in Figure 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.

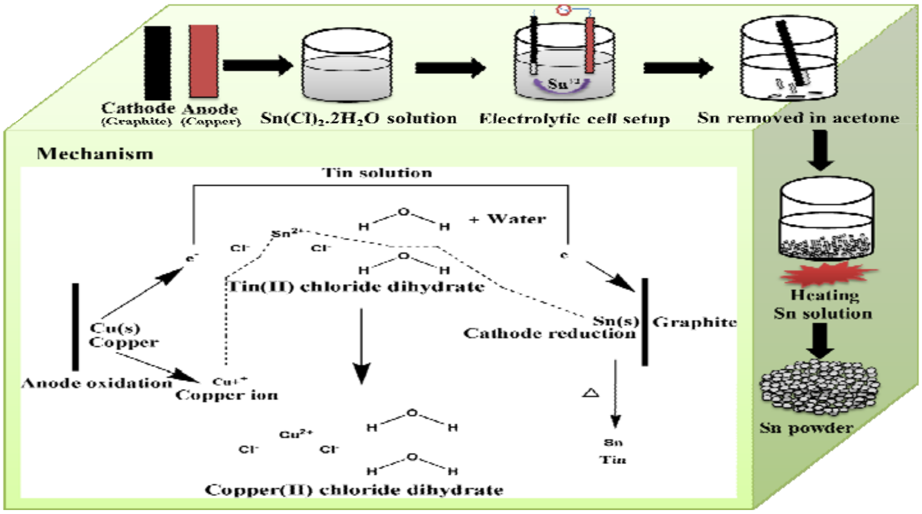

Figure 1. Schematic representation for the synthesis of Sn powder and its mechanism

2.3. 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 ^{o}C to get the electrodes at active area 2 mg/cm^2. Thereafter, electrodes were dried for 2 h in oven at 100 ^{o}C.

2.4. 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 2 shows the schematic of experimental setup used for RCPE using a two electrode cell. 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.

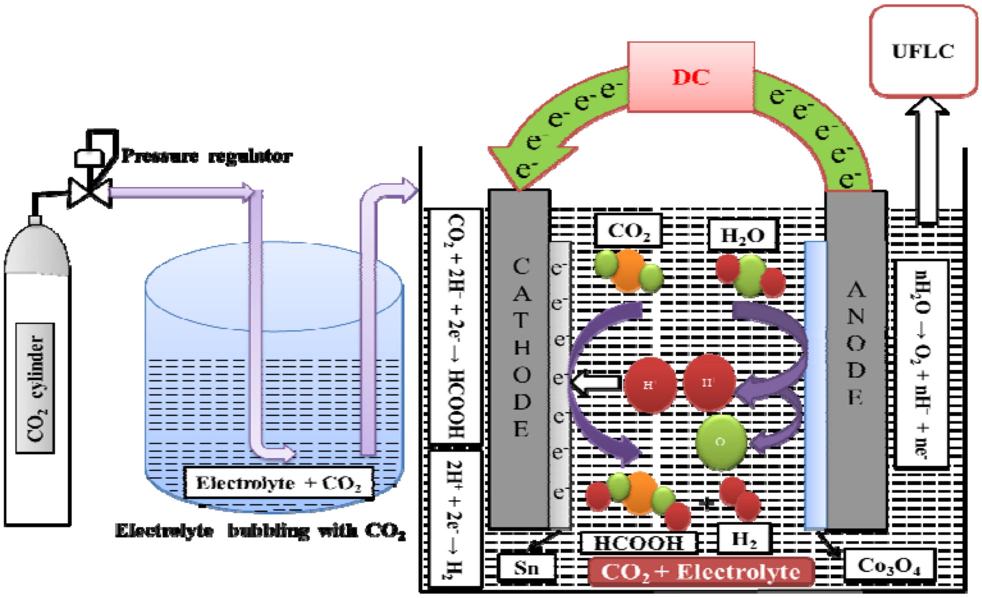

Figure 2. Experimental setup for the reduction of CO_2 to HCOOH on Sn electrocatalyst

3. Results and discussion

3.1. Characterization of Sn electrocatalyst and its mechanism

FTIR spectrum of synthesized Sn electrocatalyst was represented in figure 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.[32] XRD pattern of synthesized Sn electrocatalyst was shown in figure 3b. Peak positions at 30.7°, 32.08°, 43.97°, 45.0°, 55.46°, 62.67°, 63.93°, 64.73°, 72.59°, 73.34° and 79.7° are matched closely to Sn structure.[33] The particle size analysis was performed using Delsa nano (make: Beckman coulter; model: Delsa nano C) particle size analyzer and the particle size distribution data for synthesized catalyst is shown in Figure 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.

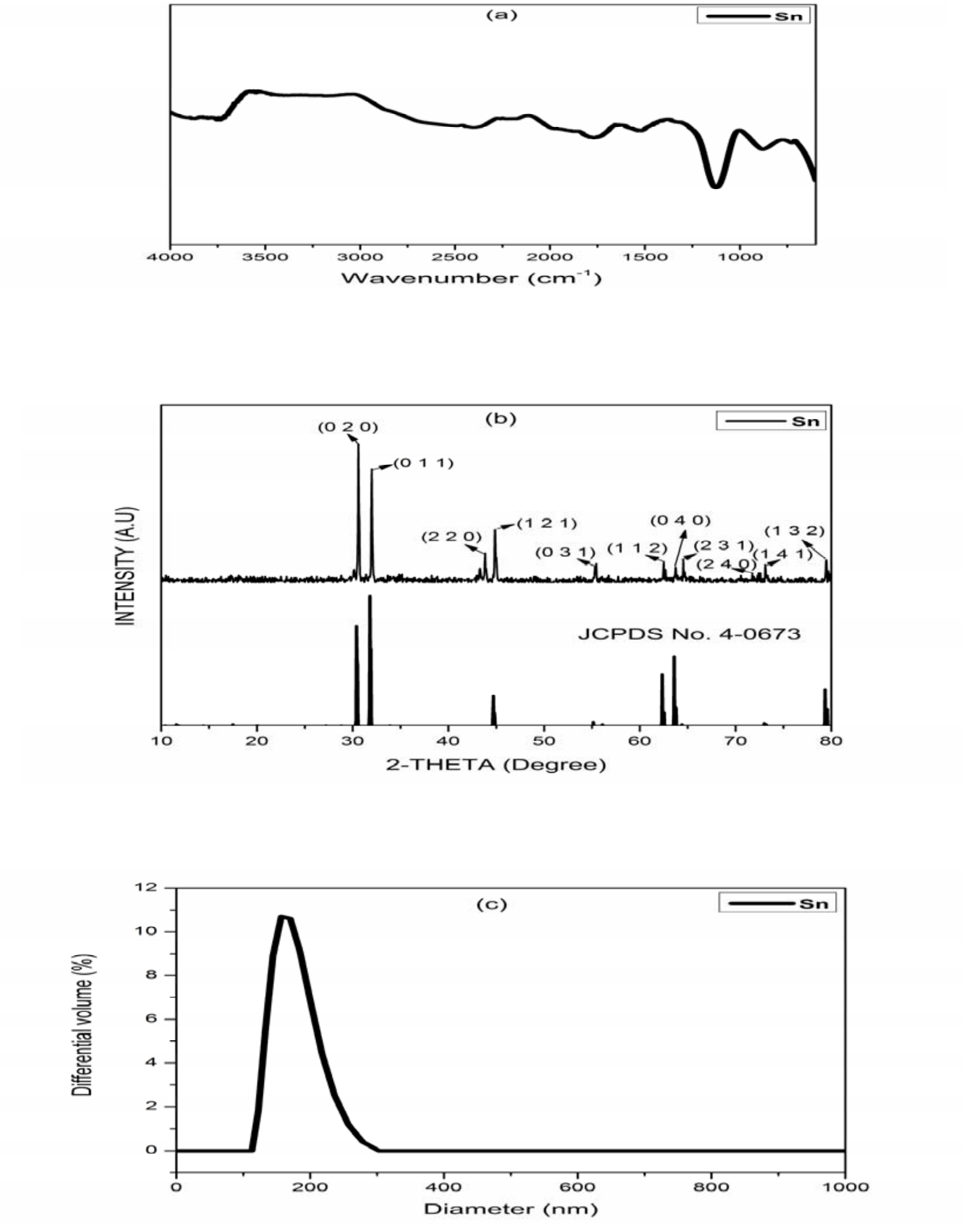

Figure 3. Characterization of Sn electrocatalyst (a) FTIR, (b) XRD, and (c) particle size analysis

A mechanism for the formation of Sn electrocatalyst is shown in figure 1. Oxidation of Copper (Cu(s) $\longrightarrow$ $Cu^{2+} + 2e^{-}$ (0.34 V)) and reduction of Tin ($Sn^{2+} + 2e^{-} \longrightarrow Sn$ (0.14 V)) is taking place at anode and cathode, respectively. Sn ion from the electrolyte solution was deposited on the cathode surface by accepting electrons generated at anode due to oxidation of Copper. Copper ion formed at anode had a driving force for the deposition of Sn ion 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.

3.2. RCPE studies at Sn electrocatalyst in different electrolyte solutions

3.2.1. 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 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. Increase in current density dictates the high reaction rate for CO_2 reduction or hydrogen generation.

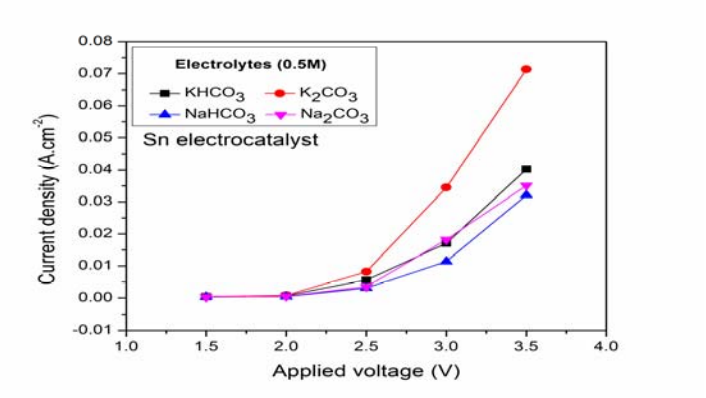

Figure 4. Variation of current density with applied voltage during CO_2 reduction using Sn electrocatalyst.

Again, figure 4 show 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.

3.2.2. 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 5a.

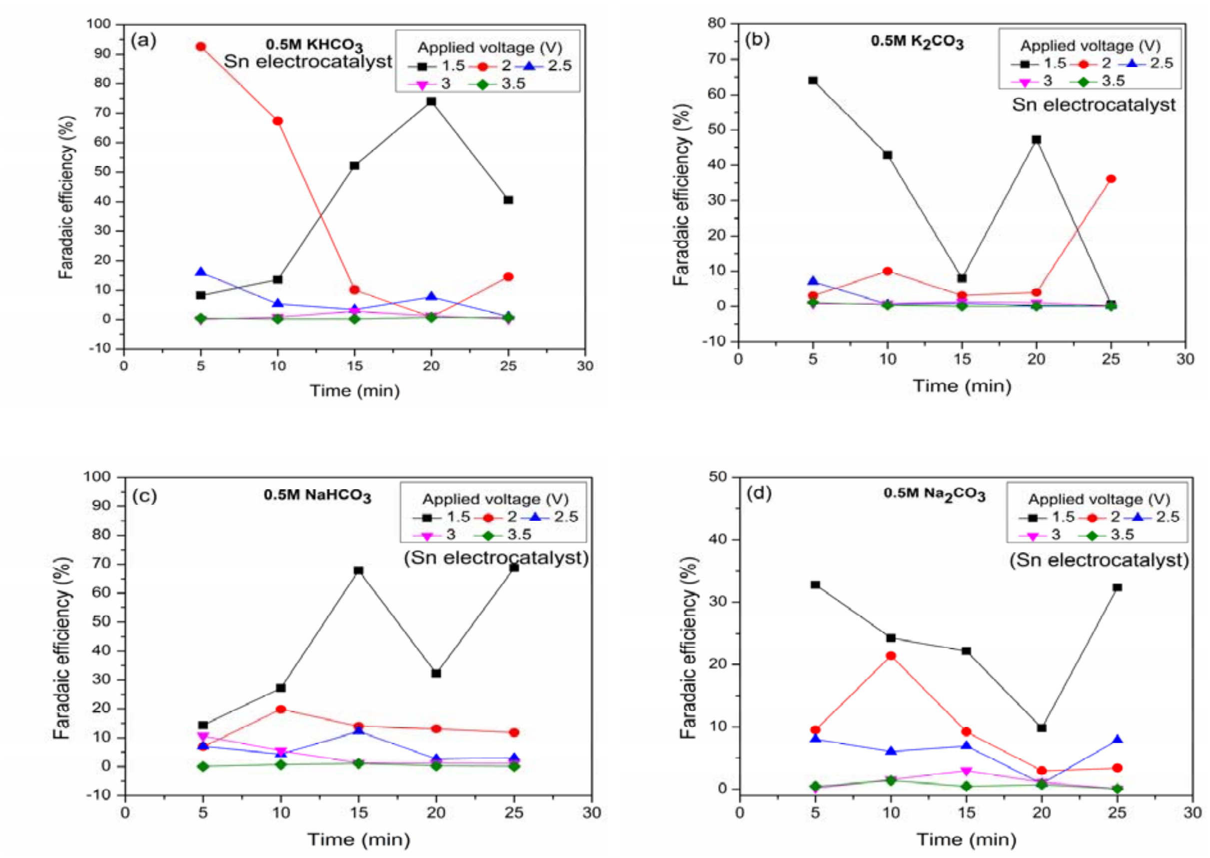

Figure 5. Variation of Faradaic efficiency with time during reduction of CO_2 to HCOOH using a) $KHCO_3$, b) K_2CO_3, c) $NaHCO_3$, and d) Na_2CO_3 electrolyte solutions.

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 (Table 1) after a reaction time of 30 min.[22] High Faradaic efficiencies (92.6, 67.36, 10.17, 0.91 and 14.51% respectively) were obtained (figure 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[22] and maximum Faradaic efficiency of 92.3% was observed at Sn/Pt in 0.1M $KHCO_3$ solution.[34] 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 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. 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.

3.2.3. *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.[22] 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 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 (Table 1), the efficiencies obtained were low that may be due to high hydrogen formation.[23] 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 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.

3.2.4. 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 5c. High Faradaic efficiencies were observed at 1.5 V and low for the remaining applied voltages (figure 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.[25] However, maximum Faradaic efficiency of 68.7 % (25 min) and 67.8 % (15 min) reaction was observed as an optimum condition. 19 % Faradaic efficiency was reported in 0.5M $NaHCO_3$ solution for Sn/SnO_x catalyst at 0.7 V.[23] 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 5c). Lower efficiencies were observed as hydrogen generation favors the reaction (figure 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.

3.2.5. 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 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.[25] 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 5d). It may be noted that efficiencies were low when compared with RCPE in $NaHCO_3$ electrolyte solution. RCPE in Na based electrolyte solution was able to reduce effectively in Sn/SnO_x electrode.[23] 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. 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. Comparison of HCOOH Faradaic efficiency at different experimental conditions with literature was shown in Table 1. From the table it may be concluded that the use of Co_3O_4 as an alternative to Pt for anode during RCPE is economically favorable. 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.

Table 1: Comparison of HCOOH Faradaic efficiency at different experimental conditions with literature.

Electrode		**Electrolyte**	**Applied voltage**	**Reaction time**	**Faradaic efficiency (HCOOH)**	**References**
Anode	Cathode		(V)	(min)	(%)	
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	

4. Conclusion

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. A 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 $NaHCO_3$, at 1.5 V high Faradaic efficiencies of 68.72% were observed at reaction time of 25 min which is the most optimum condition for RCPE. This preliminary study will be helpful towards findings of cheap and effective electrocatalyst for RCPE (alternate to expensive Pt).

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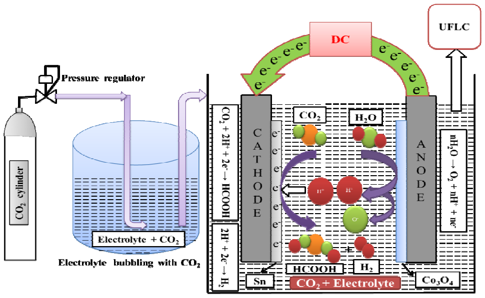
Graphical abstract



Reduction of CO_2 to HCOOH on Sn electrocatalyst

Research highlights

- Co_3O_4 is used as an alternative to Pt for the reduction of CO_2 to HCOOH using Sn electrocatalyst.