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

V. S. K. Yadav, M. K. Purkait*

Department of Chemical Engineering, Indian Institute of Technology Guwahati-781089, Assam, India

*Corresponding Author: mihir@iitg.ernet.in

(Ph. No.: +91 361 2582262; Fax: +91 361 2582291)

Abstract

The reduction of CO_2 to products electrochemically (RCPE) using synthesized Pb_2O and Co_3O_4 electrocatalyst in various electrolytes was investigated under ambient condition. The catalyst (Pb_2O) was synthesized electrochemically using electrodeposition technique. Electrodes were prepared using synthesized electrocatalyst coated on graphite plate surface for RCPE. Pb_2O/(graphite plate) and Co_3O_4/(graphite plate) was used as cathode and anode respectively, in RCPE. The experiments were conducted at different applied voltages (1.5 to 3.5 V) and time intervals of 5, 10, 15, 20 and 25 min using both carbonates and bicarbonates of sodium and potassium electrolytes separately. Formic acid (HCOOH) was formed for all the applied voltages at different time interval in presence of four electrolytes considered herein. However, high Faradaic efficiencies were obtained for bicarbonate based solutions than carbonates. At 2 V, maximum Faradaic efficiencies of ~60 % and ~50 % for HCOOH were obtained after 10 min of reaction in $KHCO_3$ and $NaHCO_3$ electrolyte solution, respectively.

Keywords: Reduction of CO_2 to products electrochemically (RCPE); Faradaic efficiency; HCOOH; Pb_2O; electrodeposition.

1. Introduction

Emission of greenhouse gases in the atmosphere is very critical during combustion of fossil fuels for energy generation. CO_2 is one of the primary greenhouse gas causing global warming effect. A possible solution would be to find a suitable solution for the reduction of this gas back to fuels. Thus, reduction of CO_2 has become an important topic in the field of electrochemistry. However, various technologies like; thermochemical, photochemical, electrochemical were in existence for the reduction of CO_2 to various products including methanol, ethanol, formic acid and formaldehyde.[1-7] Due to its easy operation reduction of CO_2 to products electrochemically (RCPE) has received a great attention among the other techniques.[8] In RCPE, electrical energy can be stored in the form of chemical energy, which can be used more widely in the transportation applications.[9] In electrochemical process, different products are obtained depending on the material used for electrode, electrolytes (aqueous and non-aqueous) and applied voltage.[10-14] Based on electrocatalyst used various products like methanol, ethanol, formic acid, formaldehyde, acetic acid, methane and ethylene were reported.[15-18] Hori et al. described that efficiency and product selectivity mainly depended on the electrocatalyst crystal surfaces and operating conditions used for RCPE.[19] Electrocatalysts like Ag, Sn and Au were able to reduce CO_2 to CO, HCOOH and H_2 with some other liquid products.[15] The reduction of CO_2 was also investigated using Pb and Sn electrocatalysts.[20-22] The type of electrolytes used in RCPE also plays a major role in product formation. It was reported that products like CO, $H_2C_2O_4$, HCOOH were formed by using acetonitrile, N,N-dimethyl formamide, propylene carbonate as electrolytes.[23] It has been reported that if liquid products were made with high faradaic efficiencies from RCPE, that could become a sustainable approach for future liquid fuel production.[22]

Different products were reported from the reduction of CO_2 electrochemically. However, conversion of CO_2 to formic acid is the best process with respect to technical development and economic viability because of its requirement in paper, pharmaceuticals and pulp industries.[24-25]

Synthesis of HCOOH by hydrocarbon oxidation or thermochemical process bears adverse environmental effects and expensive.[22] It may be envisaged from the above literatures that different products were produced from the reduction of CO_2 electrochemically. However, conversion of CO_2 to formic acid may be an alternate one but needs detail investigations both on technical development and economic viability. Several studies have been reported towards the reduction of CO_2 to HCOOH.[26, 24] Subramanian et al. studied the RCPE using Iridium oxide as anode and Lead as cathode towards CO_2 reduction.[26] Platinum (Pt) was efficiently used as anode for water oxidation reaction[22]. Although the reaction is feasible, but multiple products are formed in presence of various catalysts. [16] Experimental conditions are also important on the type of product formation using different catalyst. [11, 27] Finding of an alternate catalyst to reduce CO_2 to a single product with high Faradaic efficiency is the ultimate goal of the current research. Co_3O_4 is abundant, cheap and efficient towards water oxidation reaction which might be better alternate electrocatalyst in place of Pt for RCPE. Use of Co_3O_4 as anode and Pb_2O as cathode towards RCPE is scant. This is focused on the RCPE using cheaper Co_3O_4 as anodic material. Pb_2O powder was prepared using electrodeposition method as it requires room temperature, low process time and cost effective.

The present work is to study 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 electrolytes. 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.

2. Experimental

2.1. 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.

2.2. Synthesis of Pb_2O and Co_3O_4 powder electrochemically

Lead oxide (Pb_2O) powder was synthesized by electrodeposition method.[28-30] The schematic for the synthesis of Pb_2O is shown in Figure 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. Catalyst was removed from the graphite surface using acetone. Further, catalyst solution was heated at the 100 ^oC for 1h to obtain Pb_2O powder. Co_3O_4 powder was synthesized using electrodeposition method. The process involved extraction of Co from its nitrate solution (0.1 M Co $(NO_3)_2.6H_2O$). A 2-elelctrode cell was used to conduct electrodeposition experiments using copper and graphite plates as anode and cathode, respectively. Deposition of Co on the surface of cathode takes place at constant applied current of 0.2A for 3 min between two electrodes. Acetone was used to remove deposited catalyst from the surface. Co_3O_4 powder was obtained by heating at 100°C for 1h.

2.3. 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° to 80° 2θ. Particle size analysis of synthesized electrocatalysts was done using Delsa nano (make: Beckman coulter; model: Delsa nano C) particle size analyzer.

2.4. 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 °C and dried for 2 h at 100 °C each to obtain fully prepared electrode.

2.5. 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 2. 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.

2.6. 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).

3. Results and discussion

3.1. Characterization and mechanism of Pb_2O electrocatalyst

FTIR spectrum of synthesized electrocatalyst was represented in Figure 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.[31] XRD patterns of synthesized electrocatalyst are shown in Figure 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.[32] Particle size distribution of synthesized catalyst is shown in Figure 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. 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. 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.

3.2. RCPE in different electrolytes solutions

3.2.1. 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 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 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.

3.*2.2. 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.[21] 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 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.[22] 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. 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 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.[22] 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.[21] 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 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.

3.2.3. 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.[22] Figure 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 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. RCPE studies show that HCOOH is formed in all experimental conditions, but low efficiencies were observed when compared to $KHCO_3$ electrolyte solution (Figure 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.[21] It is discussed in the preceding section (Fig. 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 Figs. 5, 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 (Figs. 5, 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.

3.2.4. 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.[21-22] 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 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. 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.[22] 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 8). Low efficiencies were observed, though high current density was obtained that may be due to hydrogen generation favors the reaction (Figure 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.[34] RCPE using electrocatalysts in sodium based salts shows good results towards HCOOH formation.

3.2.5. 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 9. The reduction of CO_2 to formic acid using Pb catalyst in carbonate based solution was reported.[22] 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 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 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.[22] 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.[21] 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 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.[32]

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.

4. Conclusion

Pb_2O and Co_3O_4 were synthesized to achieve enhanced RCPE performance. The effect of electrocatalyst towards CO_2 reduction is 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. For $KHCO_3$, at 1.5 V and 2 V high Faradaic efficiencies of 37 % and 60 % were observed which is the most optimum condition for RCPE. Similarly, Faradaic efficiencies of 17 % and 50 % were observed at reaction time of 5 and 10 min at applied voltages of 1.5 V and 2 V in $NaHCO_3$. This preliminary investigation will be helpful to improve RCPE towards high Faradic efficiency and electrode stability for future applications.

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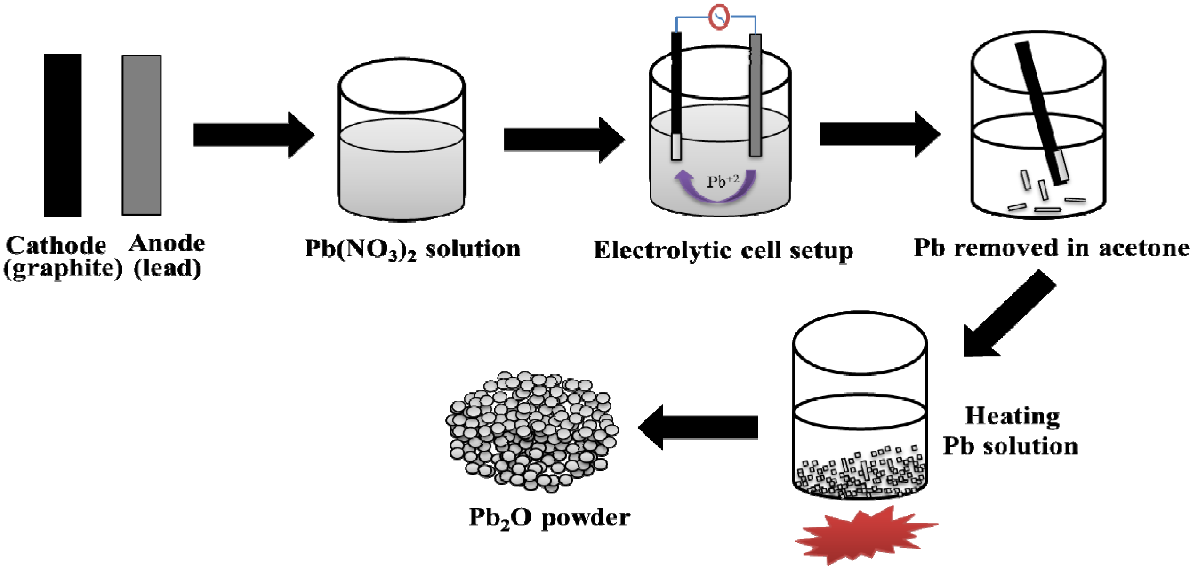

Figure 1. Schematic representation for the synthesis of Pb_2O powder

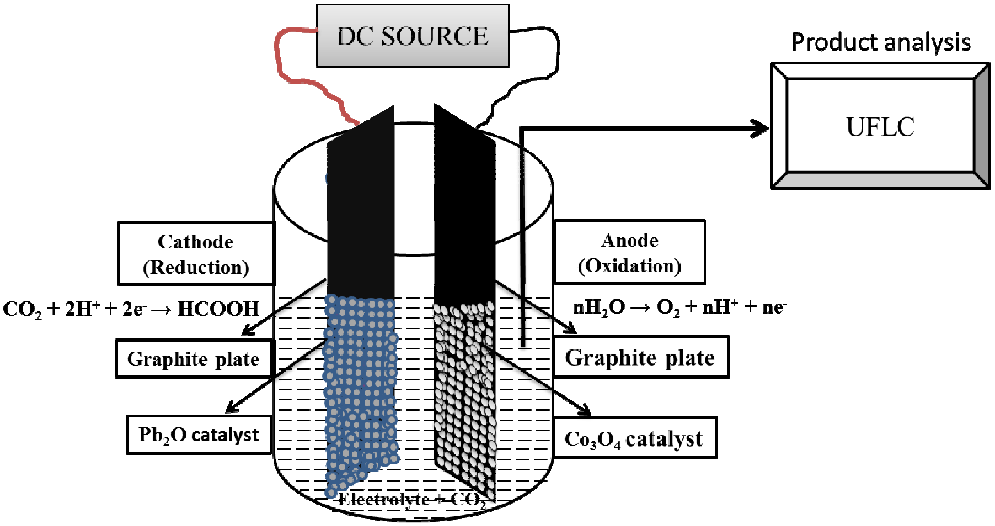

Figure 2. Schematic diagram of RCPE experimental setup

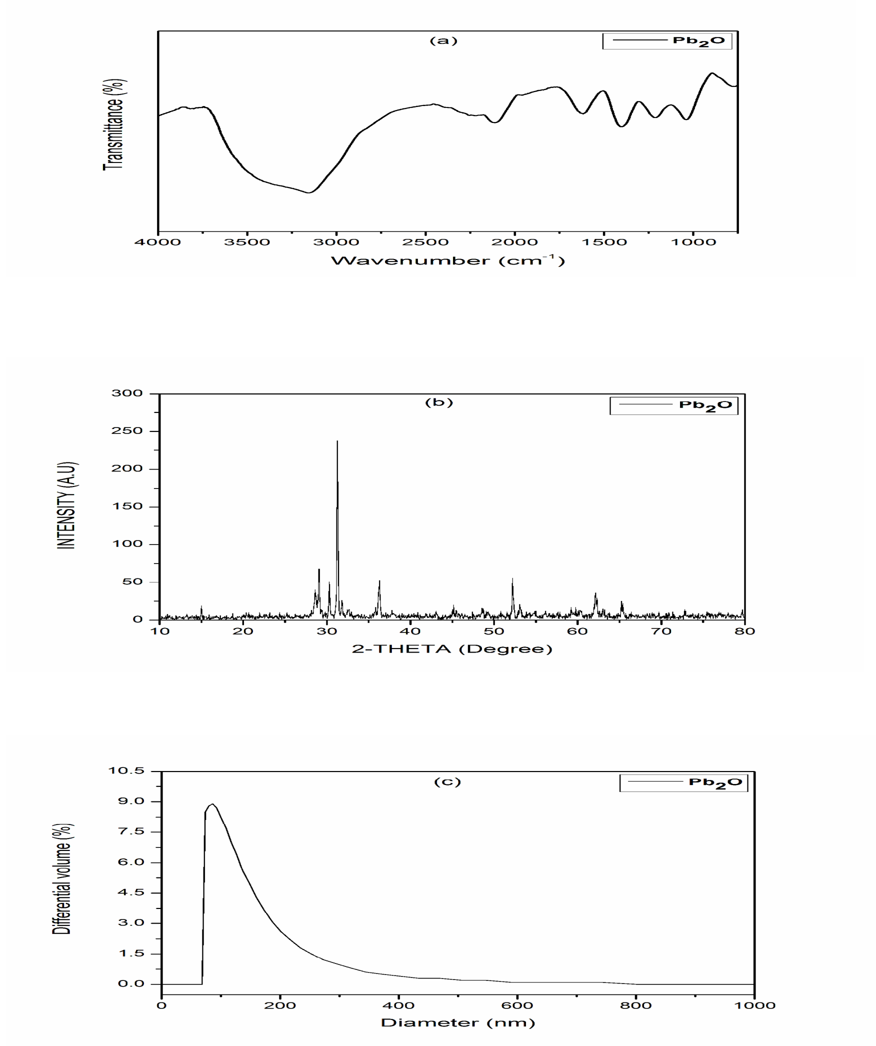

Figure 3. Characterization of synthesized Pb_2O electrocatalyst, (a) FTIR, (b) XRD, and (c) particle size analysis

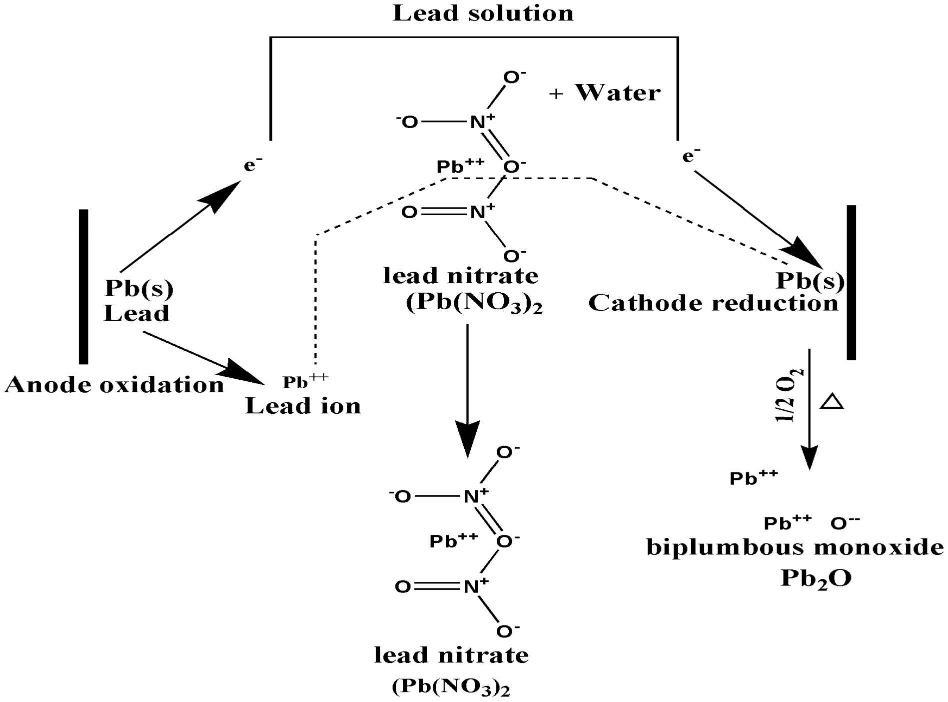

Figure 4. Mechanism for the formation of Pb_2O electrocatalyst

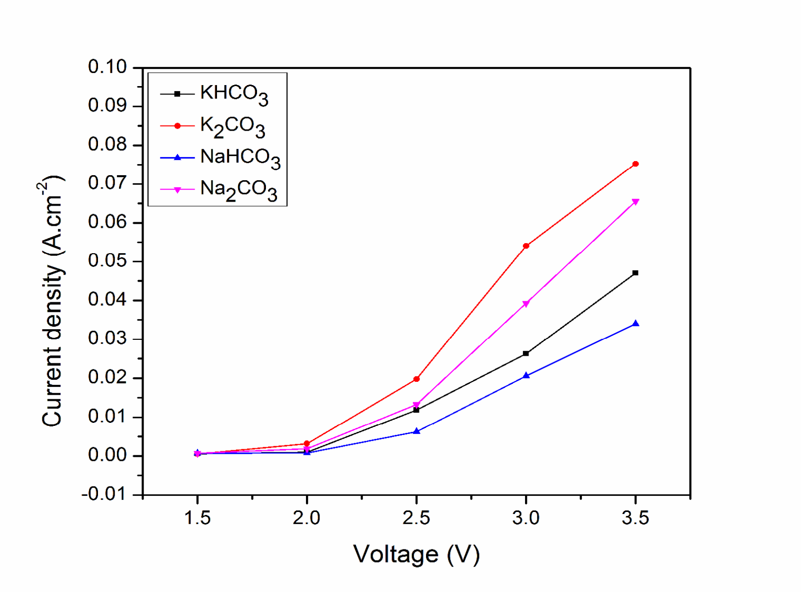

Figure 5. Variation of current density with applied voltage during RCPE using various electrolytes

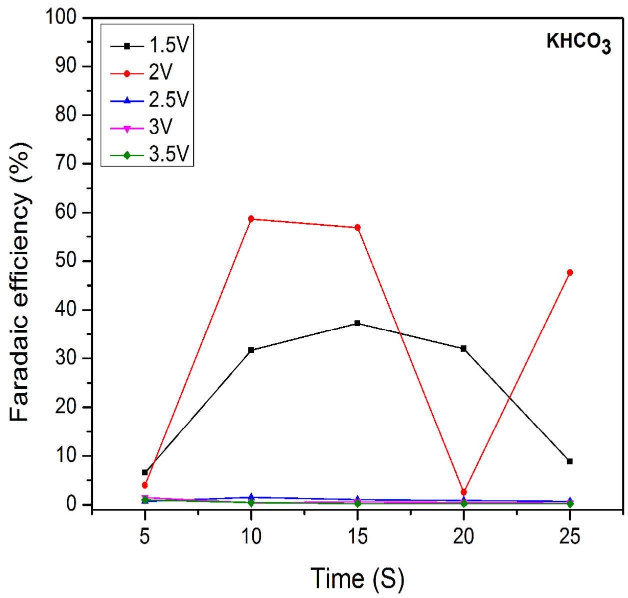

Figure 6. Effect of Faradaic efficiency Vs time for RCPE in $KHCO_3$ solution at different applied voltages

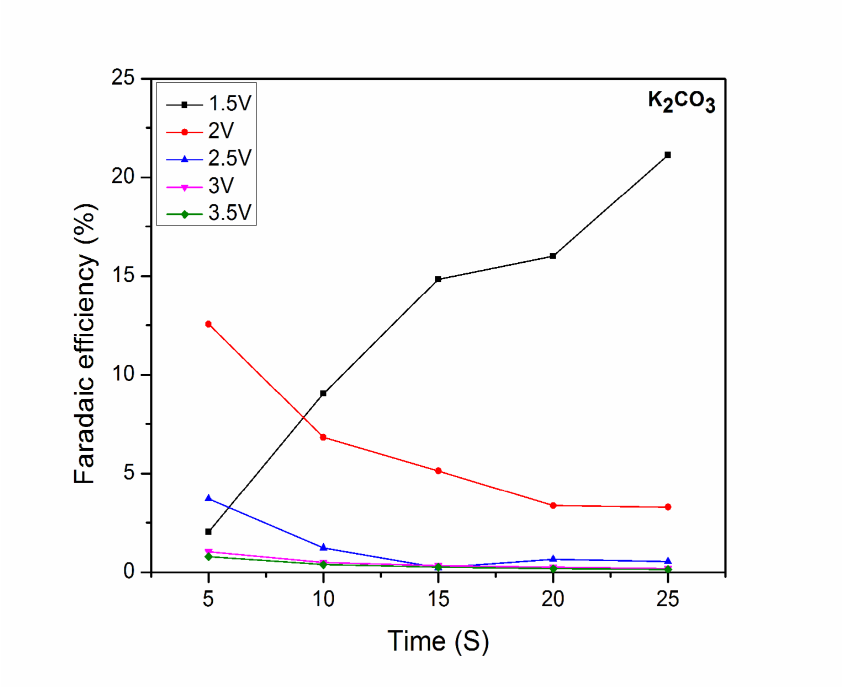

Figure 7. Effect of Faradaic efficiency Vs time for RCPE in K_2CO_3 solution at different applied voltages

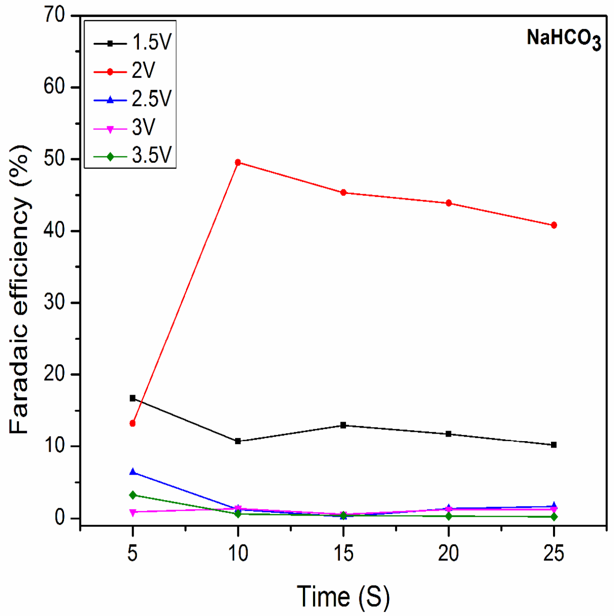

Figure 8. Effect of Faradaic efficiency Vs time for RCPE in $NaHCO_3$ solution at different applied voltages

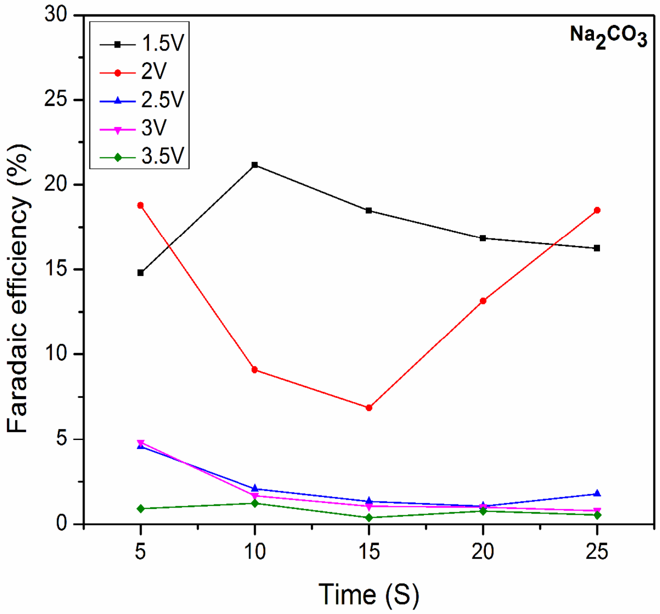

Figure 9. Effect of Faradaic efficiency Vs time for RCPE in Na_2CO_3 solution at different applied voltages

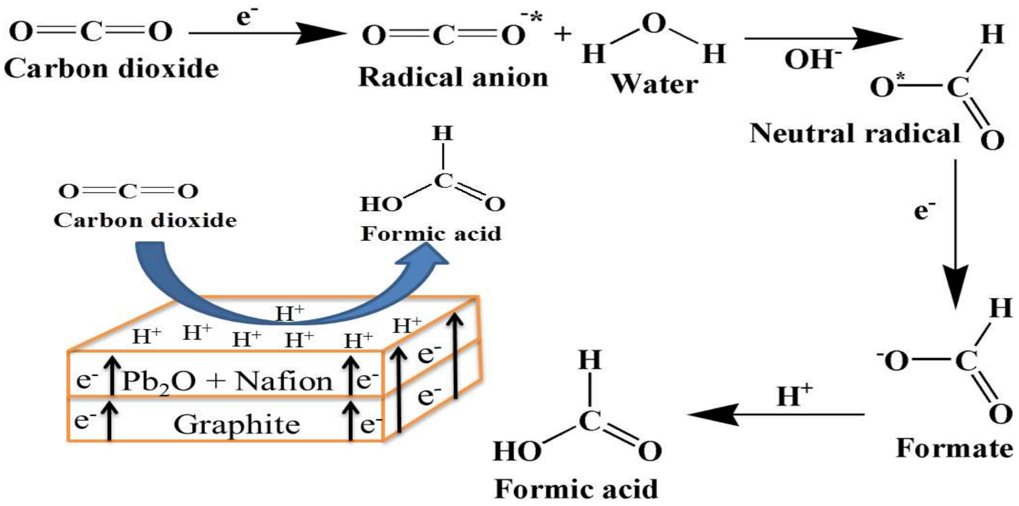

Figure 10. Proposed elementary mechanism for HCOOH formation from RCPE

Table 1: Maximum Faradaic efficiency of HCOOH obtained at different experimental conditions

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