Electrochemical reduction of CO₂ on Pb–Bi–Sn metal mixtures: importance of eutectics

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Abstract

Pure phases of Pb, Sn and Pb₇₀Bi₃₀, their combinations and the eutectics (Pb₂₅Sn₇₅, Pb₄₄Bi₅₆ and Pb₂₉Bi₄₆Sn₂₅) of the Pb–Bi–Sn system were prepared and evaluated for electrochemical reduction of CO₂ at –2.0 V (vs Hg/HgO). The bulk composition, the phase structure and the surface composition were characterized by inductively ICP-AES, XRD and XPS respectively. The phases obtained from XRD data matches well with the ternary phase diagram of Pb, Bi and Sn. The electrochemical characterization was done by CV and LSV. The formation rate of formate ions was compared for all the alloy catalysts at –2.0 V (vs Hg/HgO) in CO₂ saturated 0.5 M NaHCO₃. It was observed that addition of both Bi and Sn individually or both concurrently to Pb increases the rate of formate ion production for Pb–Bi, Pb–Sn binary systems and the Pb–Bi–Sn ternary system respectively. Interestingly, it was found out that the eutectic compositions of each alloy system (both binary and ternary) were electrocatalytically superior (Pb–Bi–Sn eutectic (Pb₂₉Bi₄₆Sn₂₅) > Pb–Sn eutectic (Pb₂₅Sn₇₅) > Pb–Bi eutectic (Pb₄₄Bi₅₆)). Further, on these high performing eutectics, the hydrogen evolution is greatly suppressed.

Keywords CO₂ electroreduction · Metal alloy catalysts · Metal eutectic compositions · Formate ion production · Catalyst development

1 Introduction

Electrochemical reduction of CO₂ is a viable alternative to tackle both the issues of energy crises and global warming. The reduction products such as formate ion (formic acid), CO and methanol can be further utilized as fuels or feed-stock for chemicals. Furthermore, formic acid is among the most favorable products as it is environmentally friendly and has several commercial uses as well. It is widely used as a preservative and an antibacterial agent. It is also used in leather industries for tanning and dyeing as well as in production of rubber as a coagulant. Recently, it has also found its usage in fuel cells as direct formic acid fuel cells (DFAFC). However, product of CO₂ electroreduction

depends largely on the catalyst employed. It has been well established that metals such as Pb, Sn, Bi, Hg, In etc. reduces CO₂ exclusively to formate ions in alkaline medium. Recently we have demonstrated the use of a gas diffusion layer electrode wherein the nanoparticles of Pb, Bi and Sn reduced CO₂ to produce formate ions in alkaline medium [1]. It was observed that nanoparticles of Pb outperformed Bi and Sn, both in terms of formation rates of formate ions and Faradaic efficiencies. Moreover, in concurrence with existing literature, all the three metals catalysts reduced CO₂ electrochemically exclusively to formate ions. Interestingly, although the crystal structures at room temperature are different for Pb, Bi and Sn (viz. face centered cubic (FCC), rhombohedral and body centered

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tetragonal (BCT) respectively) but the metals have similar characteristics of producing formate ions except variation in the rates of production. An interesting question is then if a combination of these metals promote/synergise the electroreduction of CO_2 to formate ions.

Alloying has already been investigated in various forms with respect to catalysis and improvements in activities have been reported. Alloys have been reported by a significant number of researchers to perform better than constituting individual metals. Numerous instances of alloying for increase in catalytic activity for electro-oxidation of alcohols and CO as well as electrochemical reduction of O_2 and CO_2 have been reported. Electro-oxidation of alcohols as methanol and ethanol has been improved by binary alloys as Pt–Ru [2], Pt_2In_3 [3] and ternary alloys such as Pt–Rh– SnO_2/C [4, 5]. An improved oxidation rate of CO was obtained by adding Sn and Ge to Rh and Ir electrodes [6]. Alloyed electrodes such as Pt–Ir have also been utilized in polymer electrolyte fuel cells for better catalytic activities [7]. Oxygen reduction activity was found to be better for ternary alloy catalysts such as $\text{Pt}_{50}\text{Pd}_{30}\text{Co}_{20}$ [8], Pt–Pd–Au alloy [9] and binary alloys as Pd–Mo [10], Pd–W [11], Pd–Co [12], Pd–Ni [13] and alloys of Pt with Ni, Fe and Co [4] in comparison to constituting metals. Specifically, improvements in efficiency of CO_2 electroreduction by utilizing alloys have been reported by few researchers. Though the majority of the work is on coinage metals such as alloys of Cu with Au [14, 15], Ag [16, 17], Ni, Sn and Pb [18], Ag–In [19], W–Au [20] and Pd–Pt [21]. Relatively, alloys of Pb, Sn, and Bi have received less attention for example Pb–Sn [22–25], Sn–In [26]. Therefore, it can be considered well established that alloying of metals enhances catalytic activity in several cases. At the same time, alloying of Pb is not extensively studied in regard to CO_2 electroreduction. Therefore, investigation of effect of alloying Pb with metals as Bi and Sn on catalytic activity towards CO_2 electroreduction is undertaken in this work. Accordingly Pb, Bi and Sn metals were targeted to be mixed in different compositions to form binary or ternary alloys. Subsequently these alloys could be investigated for extents of CO_2 electroreduction to realize the effect of alloying. However, before such an attempt at alloying three metals is undertaken, it might be instructive to study the ternary phase diagram starting with the binary ones from existing literature.

W. Herold studied the Pb–Bi phase diagram in detail and reported a miscibility of about 22 wt% of Bi in Pb to about 1 wt% of Pb in Bi. The Pb-lattice expands on addition of Bi till about 20 wt% Bi. Phase transformation occurs from fcc (pure Pb) to hexagonal (pure β -phase) on further addition of Bi in Pb. Additionally, based on the discrepancy in the value of specific heat of alloys with those calculated from simple mixtures, they speculated formation of a new phase having stoichiometry as $\text{Pb}_{75}\text{Bi}_{25}$ (β -phase). This was

corroborated later by X-Ray Diffractometry (XRD) studies where existence of a phase having a close-packed hexagonal structure over the range of 25–33% by weight of bismuth in lead was observed [27]. In contrast to the Pb–Bi phase diagram, the Sn–Bi phase diagram revealed only a limited solubility of Sn in Bi and almost zero solubility of Bi in Sn. Correspondingly, XRD analysis for different compositions of Sn–Bi metals revealed peaks corresponding to either that of tetragonal tin or rhombohedral bismuth [27]. Likewise for the Sn–Bi system, Pb and Sn also have limited solubilities at 300 K, i.e. about 0.05 at% Sn solubility in Pb and negligible solubility of Pb in Sn. XRD analysis of Pb–Sn mixtures reveals too an aggregation of individual peaks of Pb and Sn. Many of the results obtained are consistent with the incongruous crystal structure of Pb (FCC), Bi (Rhombohedral), and Sn (BCT).

One of the earliest investigations on the Pb–Bi–Sn ternary alloy system was performed by Rudberg according to Osamura [28]. The cooling curves of binary alloys showed four inflection points at low and high temperature corresponding to multiple phases. Interestingly, the two inflections points at lower temperature remained invariant with respect to composition of the starting mixture. It was speculated that the composition at the lower temperature corresponds to the eutectic composition. The eutectics of the binary alloys of the three metals were found out as: (1) Pb–Bi at 57 at% Bi (129 °C); (2) Bi–Sn at 56 at% Bi (143 °C); and, (3) Pb–Sn at 74.2 at% Sn (188 °C). The invariant temperature of the ternary alloy eutectic composition ($\text{Pb}_{29}\text{Bi}_{46}\text{Sn}_{25}$) was found to be 98 °C. A very comprehensive study on Pb–Bi–Sn system was provided by Osamura [28]. In addition to the eutectics observed for the binary alloy systems, a ternary eutectic and an eutectoid was also observed. Furthermore, a ternary metastable phase (referred as X; X = Pb, Bi and Sn in 40.2, 54.7 and 5.1 at % respectively) was reported that stayed stable only at high temperatures. The ternary eutectic ($\text{L} \leftrightarrow \text{X} + (\text{Bi}) + (\text{Sn})$) is reported to occur at 96 °C for Pb, Bi and Sn in 28.6, 46.3 and 25.1 at %, respectively. At the temperature of 78 °C another ternary eutectoid reaction occurs ($\text{X} \leftrightarrow \beta + (\text{Sn}) + (\text{Bi})$; $\beta = \text{Pb}_{75}\text{Bi}_{25}$) was observed. However, below the temperature of 78 °C, the phase X does not exist and hence the phases remaining in the phase diagram are (Pb), (Bi), (Sn) and (β) [28]. Evidently, literature suggests that at room temperature, Pb–Bi–Sn system consists of 3 binary eutectics and a single ternary eutectic. The binary and ternary mixtures of the metals investigated i.e. Pb, Bi and Sn are reported to form eutectic alloys at compositions viz. $\text{Pb}_{25.8}\text{Sn}_{74.2}$, $\text{Pb}_{44}\text{Bi}_{56}$, $\text{Bi}_{43}\text{Sn}_{57}$ and $\text{Pb}_{29}\text{Bi}_{46}\text{Sn}_{25}$ [29].

In the above context, the present work is undertaken with the aim of establishing the effect of addition of similar (formate ion producing) metals i.e. Bi and Sn to Pb in various extents on their activity for CO_2 electroreduction.

It may be reiterated here that all the three metals exhibit different crystal structures. An attempt was made by the authors of this work to synthesize metal alloy nanoparticles (Pb, Bi and Sn) by a method similar to that of preparing monolithic/mono metallic metal nanoparticles by sodium borohydride reduction mentioned elsewhere [1]. The supported catalyst particles were then heat treated under Argon atmosphere at temperatures of 200 and 400 °C in two independent experiments. At both the temperatures, alloy formation could not be observed as per the XRD investigations. This could be due to following reasons: (1) insufficient temperature for metal diffusion to form alloys and (2) presence of oxide layers at the surface of metals which prevents melting and alloying. Moreover, the melting temperatures of the metals Pb, Bi and Sn are 327, 271 and 232 °C respectively. Thus, nanoparticles of alloys could not be prepared and authors of this work had to shift their focus towards synthesis of bulk alloyed catalysts.

For this purpose, bulk electrodes were fashioned by melting pure Pb–Bi–Sn and mixing to form different ternary and binary mixtures and alloys. All the bulk electrodes were prepared in similar manner and were evaluated for electrochemical reduction of CO₂ identically. The formation rates of formate ions were compared and the improvement in catalytic properties was found to be linked to certain extent with the hydrogen evolution current on each catalyst material under identical conditions.

2 Experimental

2.1 Chemicals

All the chemical reagents used for synthesis and electrochemical studies were of analytical grade and were used without any further purification. Sodium hydroxide pellets (NaOH, Emplura grade, 97%), sodium hydrogen carbonate powder (NaHCO₃, Emplura grade, 99%), formic acid (HCOOH, Emparta grade, 98%), nitric acid (HNO₃, Emplura grade, 68%) and sulphuric acid (H₂SO₄, Emsure grade, 98%) were all acquired from Merck, India. The stock solutions of 1.0 M concentration were prepared for both HNO₃ and H₂SO₄. A high purity Pb foil (99.9%) was obtained from Molychem, India and high purity (99.999%) lead was obtained from Vedanta Hindustan Zinc Limited, Udaipur, India). High purity tin foil (99.5%) and bismuth pellets (99.5%) were acquired from Loba Chemie, India. All the solutions were prepared in de-ionized water (18.2 MΩ-cm). High purity argon (Ar) and H₂ gases (99.999%) were obtained from Mars Gas (Mumbai, India) and CO₂ gas (99.999%) was procured from Inox India (Vadodara, India).

2.2 Preparation of catalysts

The catalysts to be evaluated were decided in such a manner such that the compositions of the alloys methodically divide the Pb–Bi–Sn ternary (composition) graph. To observe the effect of alloying, Sn was added in Pb so as to systematically divide the compositions of Pb and Sn on a 5–point scale by atomic percentage (Pb, Pb₇₅Sn₂₅, Pb₅₀Sn₅₀, Pb₂₅Sn₇₅, Sn). Pb₂₅Sn₇₅ provides a near-eutectic composition for Pb–Sn alloys. Similar to that for Pb–Sn system, Pb–Bi system was also divided to prepare alloys of different compositions (Pb, Pb₇₅Bi₂₅, Pb₅₀Bi₅₀, Pb₂₅Bi₇₅, Bi). As mentioned in earlier section, β-phase exists for Pb–Bi alloys as a homogeneous phase. Thus, apart from earlier mentioned compositions, 3 more compositions viz. eutectic (Pb₄₄Bi₅₆), β-phase (Pb₇₀Bi₃₀) and a near β-phase (Pb₆₅Bi₃₅) were also prepared. Similar to Pb–Sn system, 5 compositions for addition of Bi in Sn were also decided to be prepared. Other than addition of Sn and Bi individually in Pb, the effect of addition of both Bi and Sn was also investigated by preparing 3 compositions for ternary alloys of Pb–Bi–Sn (Pb₅₀Bi₂₅Sn₂₅, Pb₂₅Bi₅₀Sn₂₅, Pb₂₅Bi₂₅Sn₅₀). Accompanying the 3 mentioned compositions, one eutectic composition of Pb–Bi–Sn ternary alloy (Pb₂₉Bi₄₆Sn₂₅) was also prepared. All the compositions written as subscripts refer to the atomic percentage of that corresponding element, unless stated otherwise. All the compositions prepared are indicated in the Fig. 1 that shows depiction of the ternary phase diagram of Pb–Bi–Sn at 300 K obtained from Thermo-Calc software [30] (Original diagram is provided in Section S1–supporting information).

The binary and ternary catalysts were prepared by melting the predetermined weight of the metals (viz. Pb, Sn and Bi) and allowing them to cool at room temperature and pressure conditions. The metals were either cut into small pieces using scissors (Pb and Sn) or crushed into powdered form using an agate mortar (Bi) for the ease of weighing into appropriate quantity. The metal/mixture catalysts were prepared in two forms, a stub of dia. 5 mm and a sheet of thickness about 300 μm. The stubs were prepared for the electrochemical characterization of catalysts and the sheets were used to assess CO₂ electroreduction capabilities of the catalyst material. The stubs were prepared in a glass tube of internal dia. 5 mm with one end closed. The glass tube was saturated with Ar by purging for 15 min by sealing it with Parafilm and then the open end was closed using a small piece of rubber cork of size punched suitably. The glass tube was then heated on a Bunsen burner to melt the metal pieces and the tube was shaken well to mix the molten metals. A cleaned copper wire was used for electrical connection by dipping it in molten metal mixture till about quarter length of the stub. The glass tube was finally broken to obtain the catalyst

Fig. 1 Ternary phase diagram of Pb–Bi–Sn. The numbers in octagon represent the nominal compositions and numbers in square represent XPS compositions as per the provided legend in the figure. The green coloured lines indicate boundaries of single phase region and the red colored lines signify boundaries for mixed phase region. The figure obtained from Thermo-Calc software could be found in the supporting information

stub arrangement fixed with wire. The obtained stub was then polished on emery paper (400 and 1200 mesh successively) in such a manner that face of the catalyst stub turned to a flattened circular shape. It was done to ensure that only 5 mm diameter geometrical area of catalyst surface would be available for electrochemical reactions after insulating the cylindrical face of catalyst stub using enamel paint.

For electroreduction of CO_2 , sheet form of catalysts was employed. The preparation of catalyst sheets was done by taking the predetermined weights of the metals in a 20 ml glass vial. The glass vial was then saturated with Ar for 15 min by sealing it with Parafilm and then closed with a rubber cork for heating as explained in the previous paragraph. The glass vial was heated on a Bunsen burner till the metals melted and was shaken well while heating to obtain a homogeneous mixture of molten metals. The well-shaken molten metal mixture was then allowed to cool naturally and solidify. The cooled metal mixture was then rolled in a cold roller to a thickness of about $300 \pm 30 \mu m$. Due to work hardening of $Sn_{75}Bi_{25}$ during rolling, sheet could not be rolled thinner beyond $450 \mu m$. Subsequently, alloys with higher Bi content in Sn were omitted from investigation. Additionally, similar difficulty of work-hardening was encountered for $Pb_{44}Bi_{56}$ among Pb–Bi alloys for addition of Bi to Pb. Thus, all Pb–Bi catalysts with bismuth composition greater than 56 atomic% could not be prepared as sheets and hence were not evaluated in this work. The metal sheets were then cut

in a 1 cm square face as the electrode with a thin tail as a connector. The width of the tail was about 3 mm and a length was about 3 cm. The electrical connection was made through the tail and electrode was positioned such that the only the square face was submerged completely into the electrolyte. The portion of the tail just above the square face was coated with a glitter-free nail polish to make it insulated from the electrolyte. The connecting clip attached to the catalyst tail was also insulated by wrapping Teflon around it to avoid contact with electrolyte. The schematic of catalyst stub and sheet is provided in supporting information. A set of minimum 4 numbers of sheet catalysts were prepared for each compositions. Each experiment involving sheet catalysts was conducted on a fresh catalyst of the corresponding composition.

2.3 Material characterization of alloys

The XRD technique was used for phase identification of the synthesized alloy sheets. The sheets were firstly cleaned with DI water, then cleaned with phosphate free liquid detergent (Labdet 05, Loba Chemie, India) to remove excess oil residing on surface of the catalyst and subsequently followed by DI water to remove detergent as well. Further, the sheets were cleaned with acetone solution under sonication for 30 s and dried. X-ray diffraction patterns were recorded in a Panalytical Empyrean diffractometer using Cu-K α radiation ($\lambda = 1.54060 \text{ \AA}$). The X-ray generator operating conditions were 40 mA and 45 kV.

The XRD graphs were recorded for 2θ values from 20° to 70° with a step size of 0.0260° and a dwell time of 22.23 s. Peak positions were obtained from XRD data by fitting Gaussian profile using FITYK software [31]. The peak positions were compared with ICDD database reference cards (JCPDS). The ICDD reference numbers of the phases utilized for comparison are Pb: 00-004-0686; Sn: 00-004-0673; $\text{Pb}_{70}\text{Bi}_{30}$: 00-039-1087; Bi: 00-044-1246; PbO : 01-076-1796; Bi_2O_3 : 00-041-1449 and SnO_2 : 00-046-1088.

X-ray photoelectron spectroscopy (XPS) was utilized to determine surface composition of the synthesized catalyst sheets. The sheets were cleaned in a manner similar to that of the sample preparation for XRD analysis. The XPS investigations were carried out on a Kratos analytical axis supra instrument with Al anode using ESCAPE software. The X-ray source was operating at 75 W (0.32 A filament current and a dwell time of 314 ms). The high resolution spectrum was obtained with a step size of 0.1 eV. The obtained peak positions were compared with standard database provided by NIST, United States. The XPS spectra were obtained for all of the catalysts in the as-synthesized state. The data points obtained from XPS analysis were deconvoluted and a mixed Gaussian–Lorentzian function (30% Gaussian) was employed for fitting of the deconvoluted peaks. Furthermore, obtained fitted peak positions were corrected for charging and others effects by taking C 1s (284.7 eV) as the reference. Inductively coupled plasma–atomic emission spectroscopy (ICP–AES) was conducted to determine the bulk elemental composition of the synthesized catalysts. The catalyst sheets were first cleaned in a manner similar to that used in XRD analysis then was dissolved in hot nitric acid and stored overnight. The dissolved solution was then filtered in a glass filtration assembly using a $0.22\ \mu\text{m}$ nylon filter paper. ICP–AES analysis was done on ARCOS, Simultaneous ICP Spectrometer model of SPECTRO Analytical Instruments GmbH, Germany.

2.4 Electrochemical characterization of alloys

A Biologic potentiostat (VSP-300) was employed for electrochemical experiments. Electrochemical characterization of catalysts using cyclic voltammetry (CV) and linear sweep voltammetry (LSV) was performed on a 3-electrode configuration in a conventional 5-neck cell. The electrochemical experiments for CO_2 electroreduction to formate ions were carried out in a 2-compartment cell separated by a glass frit. It might be worthwhile to mention here that all the electrochemical experiments were conducted in high compliance mode of potentiostat using a 48 V booster due to high impedance conditions prevailing for the experiments. A Hg/HgO reference electrode (0.3 M KOH) was used as the reference

electrode. The potentials of Hg/HgO reference electrode utilized were determined against a suitable RHE (reversible hydrogen electrode) in Ar saturated 0.5 M NaOH ($\text{pH} = 13.42$), Ar saturated 0.5 M NaHCO_3 ($\text{pH} = 8.72$) and CO_2 saturated 0.5 M NaHCO_3 ($\text{pH} = 7.39$) that were found to be 0.913, 0.627 and 0.560 V (vs RHE). A cleaned and rolled platinum mesh was used as a counter electrode in both the cell configurations. The Pt mesh counter was placed in the frit-separated compartment of electrochemical cell employed for CO_2 electroreduction experiments. The square face of metal sheet working electrode was dipped in such a way that square face was parallel to glass frit separation of the electrochemical cell.

It could be relevant to mention here that cleaning of catalyst surface by polishing on emery paper was performed only for catalyst stubs as the sheet form of catalysts was quite thin and fragile to be cleaned in this manner. Additionally, a potential of $-1.5\ \text{V}$ (vs Hg/HgO) was applied to electrodes (both stubs and sheets) for 300 s in a separate electrochemical cell containing Ar saturated 0.5 M NaOH. This was repeated before all experiments in order to reduce the metal oxides that might have been formed at the surface of the metal electrodes. Cyclic voltammetry (CV) experiments were recorded on prepared stubs in Ar saturated 0.5 M NaOH solutions for all the catalysts. The CVs were recorded at a scan rate of 50 mV/s from -1.9 to 0 V vs Hg/HgO to investigate the oxidation and reduction behavior of catalysts during application of potential. The lower limit of the CVs were kept slightly above the hydrogen evolution potential and the higher turn around potential was kept immediately before the region of oxygen evolution for all catalysts [32–34]. The voltammograms presented here represent the first cycle on a freshly polished and electrochemically reduced electrodes.

Current–potential behavior of catalysts were also observed by performing linear sweep voltammetry (LSV) experiments carried out in Ar and CO_2 saturated 0.5 M NaHCO_3 . The electrodes were cleaned, polished and the surface oxides were reduced before the LSV experiments as described in the previous section. The LSV experiments were conducted for potential range of -0.7 to $-2.5\ \text{V}$ (vs Hg/HgO) at a scan rate of 5 mV/s. The starting potential for LSV viz. $-0.7\ \text{V}$ vs Hg/HgO, was chosen such that to avoid any anodic reactions. In another set of experiments, current densities for hydrogen evolution were measured on the prepared catalysts at $-2.0\ \text{V}$ (vs Hg/HgO) from the linear sweep voltammetry experiments performed in H_2 saturated 0.5 M NaHCO_3 at 5 mV/s from -0.7 to $-2.5\ \text{V}$ (vs Hg/HgO). The pretreatment of catalysts was performed in a manner similar as described previously.

2.5 Electrocatalytic reduction of CO₂

In an independent set of experiments, CO₂ electroreduction in 0.5 M NaHCO₃ was performed on pure Pb foil sheet electrodes of similar dimensions as in this work. The electroreduction was carried out at various potentials of −1.6, −1.8, −2.0 and −2.2 V (vs Hg/HgO) under identical conditions. It was observed that the rate of formate production ($\dot{R}_{\text{HCOO}^-}$) was maximum for −2.0 V. Subsequently, it was decided to compare the catalysts on the basis of their $\dot{R}_{\text{HCOO}^-}$ at −2.0 V (vs Hg/HgO).

The investigation of CO₂ electroreduction was carried on catalyst sheets cut in square shape in an arrangement made as described in the previous Sect. 2.2. Further, surface oxides of the electrodes were reduced before carrying out chronoamperometry (CA) experiments for investigation of CO₂ electroreduction as described in the previous section. The CA experiments for electroreduction of CO₂ were carried in a CO₂ saturated 0.5 M NaHCO₃ solution at −2.0 V (vs Hg/HgO) for 3 h. CO₂ was continuously purged into electrolyte at a rate of about 100 ml/min in the compartment with working electrode. 500 µl (1% of the total volume) of electrolyte solution was withdrawn at a regular interval of 0.5 h from the start of the experiment for product analysis by HPLC. Additionally, same volume of fresh 0.5 M NaHCO₃ solution was injected into the cell to maintain a constant volume of electrolyte. CA experiments were done primarily to investigate the products and their rates of formation. Faradaic efficiencies were calculated for all experiments to observe effectiveness of the process. The expression utilized for calculation of Faradaic efficiency is provided in Eq. 1:

$$\text{Faradaic Efficiency (\%)} = \frac{\eta_{\text{FA}}}{\eta_{\text{q}}} \times 100 = \frac{\eta_{\text{FA}}}{q/(\eta_{\text{e}} \times F)} \\ \times 100 = \frac{\eta_{\text{e}} \times F \times \eta_{\text{FA}}}{i \times t} \times 100$$

η_{FA} = number of moles of formate ions produced during the process (mmol); η_{q} = number of moles of charge consumed during the process (mmol); η_{e} = 2, number of electrons required for electroreduction of CO₂ to formate ion; F = 96,485, Faraday constant (C/mol); $q = i \times t$, charge consumed during the process (mC); i = current obtained during the process (mA); t = time of process run (s).

The obtained samples of CO₂ electrolytic reduction process were subjected to an Agilent 1260 Infinity Quaternary Liquid Chromatography HPLC instrument. A Bio-Rad Aminex HPX-87H column with a mobile phase of 13 mM H₂SO₄ was used to separate the products. A UV-visible range of variable wavelength detector was employed for detection and quantification of products was performed at a wavelength of 210 nm. The preparation of samples

suitable for HPLC analysis was done by mixing 300 µl of 1 M H₂SO₄ to 500 µl of the electrolyte collected from reaction vessel. The acidified mixture was then subjected to pass through 0.22 µm Nylon syringe filter so as to remove solid particles or precipitates. Consistently, only formate ions were detected as product of CO₂ electroreduction on all the catalysts employed and quantification was done from a calibration graph obtained for various known concentrations (0.01–10 mM) of formic acid under similar conditions of HPLC instrument.

Literature suggests that the only product for electroreduction of CO₂ on these metals is formate ions. To confirm this, we have carried the process of CO₂ electroreduction in the gas leak-proof conditions in the same electrochemical cell by sealing the cell openings using rubber corks and Teflon tape. The electrolyte was purged with CO₂ for about half an hour before the process. The gas samples were collected after process completion and were analyzed in Nucon Gas Chromatograph instrument (Mumbai, India). Exclusively Pb and Pb₂₉Bi₄₆Sn₂₅ were utilized for this investigation as all the pure phases of Pb–Bi–Sn ternary phase diagram are included in the chosen catalysts. It was found out from the gas analysis that only H₂ was present as the product gas along with trace amount of N₂ and O₂ and bulk of CO₂ was present in the reaction cell. Hence, it could be reasonable to state that no gaseous products were formed due to the CO₂ electroreduction process on Pb–Bi–Sn catalysts. Consequently, only liquid product analysis was carried on further.

3 Results and discussions

3.1 Material and electrochemical characterization of alloys

(1)

The synthesized catalysts were prepared by melting predetermined weights as described previously in Sect. 2.2. In order to obtain the bulk and surface composition of the synthesized catalysts, ICP-AES and XPS were conducted respectively. The results of both the ICP-AES and XPS analysis compared with nominal compositions are provided in Section S4 (supporting information). It could be observed that the bulk compositions obtained from ICP-AES analysis are in a fair agreement with the nominal compositions. Further, it was noted from XPS analysis that the surface of all catalysts consisted of oxides of the constituent metals. This observation is also in conjugation with the fact that metals utilized in this work (Pb, Bi, Sn) are non-noble metals and hence have a tendency to oxidize in ambient conditions. The relative composition of metals present at the surface of each catalyst was also determined and is presented in Fig. 1. Further, it has been observed from XPS

analysis that the surface compositions of the synthesized catalysts are close to the nominal compositions. A representation of both nominal and XPS compositions have been provided in Fig. 1.

The X-ray diffractograms obtained for the as-synthesized catalysts are provided in Section S3(a),(b),(c) (supporting information). The materials were characterized according to phases expected to be present in the composition of the metals mixed. The expected phases were decided as per the equilibrium ternary phase diagram of Pb, Bi and Sn metals obtained at 300 K through the Thermo-Calc software (Section S1 (supporting information)). The phases detected were matched with the corresponding compound with ICDD reference datacards. The Table 1 provides the phases detected in the corresponding XRD graphs of the catalyst.

The phases observed from the XRD analysis confirm to the expected phases as per the ternary phase diagram (Fig. 1). The results of the phases detected are provided in Table 1. It can also be observed from XRD graphs that Pb, Sn and $\text{Pb}_{70}\text{Bi}_{30}$ are the only single phase catalysts and this observation is also in agreement to the theoretical ternary phase diagram (Section S1 (supporting information)). For both Pb and Sn pure metal catalysts along with binary compositions of Pb–Sn, XRD reflections indicates presence of only metal phases of Pb and Sn at the bulk of catalyst. For the Pb–Bi binary catalysts, $\text{Pb}_{70}\text{Bi}_{30}$ is detected

as the major phase present in all catalysts along with bismuth metal oxide as minor phase or impurity. Impurities detected in the catalyst XRD have been marked as (1) in Table 1. Other than the pure β phase ($\text{Pb}_{70}\text{Bi}_{30}$), oxides of bismuth and lead are detected in minute quantities as impurities in Pb–Bi binary catalysts. $\text{Pb}_{70}\text{Bi}_{30}$ (β phase) is the major phase present in the synthesized ternary catalysts as well. Along with $\text{Pb}_{70}\text{Bi}_{30}$ (β phase), single metal phases of Pb, Bi and Sn were also found as the minor phases in the XRD graphs of ternary catalysts. Therefore, it could be established from the XRD analysis that all catalysts are composed of single phases Pb, Bi, Sn and $\text{Pb}_{70}\text{Bi}_{30}$; mixed in different compositions. This indicates that one of the factors of variation in catalytic activities of different catalysts could be variation in the amount of single phases present in each catalyst. Thus the catalysts were synthesized for various compositions of the constituent metals (single phases) and evaluated.

The potential window selected for CVs on the catalysts stubs show the characteristic anodic peaks for metals (Pb, Bi and Sn) converting to their respective oxides/hydroxides. The peaks corresponding to metal oxides/hydroxides converting back to their metallic state has been shown in the reverse scan of the CVs. All the metals chosen for this work (Pb, Bi and Sn) undergo reactions that also form ions in the selected potential window. However, due to possible dissolution reaction, the electrochemically active surface area of catalyst gets modified during every cycle of CV and hence subsequent cycles of CV do not retrace the current–potential behavior as previous cycle of CV. Subsequently, only the first cycle of the CVs have been compared. Figures for comparison of CVs could be found in supporting information. The CVs recorded on all the alloys exhibited individual characteristics of the constituent metals. The CVs obtained for pure metals Pb and Sn matched with that obtained in our previous work [1]. The detailed explanation of the CVs could be found in the supporting information. The obtained CVs confirm the presence of constituting metals at the surface of the catalyst electrodes.

3.2 Electrocatalytic reduction of CO_2

Other than the CVs, electrochemical characterization of all catalyst stubs was also done by recording LSVs in both Ar and CO_2 environments. It could be observed from obtained LSV graphs for all the catalysts (Section S6(a),(b),(c) (supporting information)) that currents obtained in presence of CO_2 for almost all the values of potentials were higher than those obtained in presence of Ar. The Fig. 2a, b, c, d provides LSVs for single phase catalysts including ternary eutectic alloy. In presence of Ar, the plausible reaction is evolution of hydrogen on the catalyst whereas, in presence

Table 1 XRD analysis of prepared catalysts and their constituents phases

Catalyst	Phases detected by XRD peak matching analysis			
Pb	Pb			
$\text{Pb}_{75}\text{Sn}_{25}$	Pb	Sn		
$\text{Pb}_{50}\text{Sn}_{50}$	Pb	Sn		
$\text{Pb}_{38}\text{Sn}_{62}$	Pb	Sn		
$\text{Pb}_{25}\text{Sn}_{75}$	Pb	Sn		
Sn	Sn			
$\text{Pb}_{75}\text{Bi}_{25}$	$\text{Pb}_{70}\text{Bi}_{30}$	Pb(1)	$\text{Bi}_2\text{O}_3(1)$	
$\text{Pb}_{70}\text{Bi}_{30}$	$\text{Pb}_{70}\text{Bi}_{30}$	PbO(1)		
$\text{Pb}_{65}\text{Bi}_{35}$	$\text{Pb}_{70}\text{Bi}_{30}$	Bi		
$\text{Pb}_{50}\text{Bi}_{50}$	$\text{Pb}_{70}\text{Bi}_{30}$	Bi	$\text{Bi}_2\text{O}_3(1)$	
$\text{Pb}_{44}\text{Bi}_{56}$	$\text{Pb}_{70}\text{Bi}_{30}$	Bi	$\text{Bi}_2\text{O}_3(1)$	Pb(1)
$\text{Sn}_{75}\text{Bi}_{25}$	Sn	Bi	$\text{Bi}_2\text{O}_3(1)$	
$\text{Pb}_{50}\text{Bi}_{25}\text{Sn}_{25}$	$\text{Pb}_{70}\text{Bi}_{30}$	Sn		
$\text{Pb}_{29}\text{Bi}_{46}\text{Sn}_{25}$	$\text{Pb}_{70}\text{Bi}_{30}$	Bi	Pb(1)	
$\text{Pb}_{25}\text{Bi}_{50}\text{Sn}_{25}$	$\text{Pb}_{70}\text{Bi}_{30}$	Bi		
$\text{Pb}_{25}\text{Bi}_{25}\text{Sn}_{50}$	$\text{Pb}_{70}\text{Bi}_{30}$	Sn	Bi	

(1) Represents that there is only one reflection of that phase

Pb: 00-004-0686; Sn: 00-004-0673; $\text{Pb}_{70}\text{Bi}_{30}$: 00-039-1087; Bi: 00-044-1246; PbO: 01-076-1796; Bi_2O_3 : 00-041-1449 and SnO_2 : 00-046-1088

Fig. 2 Linear Sweep Voltammetry of catalysts recorded in Ar (Black) and CO₂ (Red) saturated 0.5 M NaHCO₃. LSV obtained for single phase catalyst (**a** Pb; **b** Sn; **c** Pb₇₀Bi₃₀) and ternary eutectic catalyst (**d** Pb₂₉Bi₄₆Sn₂₅) are shown

of CO₂, electrocatalytic reduction of CO₂ is also probable along with evolution of hydrogen. The difference of currents obtained in Ar and CO₂ is observed to be higher in ternary eutectic alloy in comparison to current difference obtained at other catalysts. Whilst the currents obtained in CO₂ atmosphere are greater than that in Ar atmosphere, this could not be considered as certainty of CO₂ electroreduction though it could be indicative of the same.

It can also be observed from the obtained LSVs for both Pb and Sn catalysts that the difference in the LSV recorded in Ar and CO₂ increases gradually as potential applied becomes more negative. This might also indicate that the rate of CO₂ electroreduction increases gradually as more negative potential is applied. It could be interesting to note that currents obtained at Pb for both Ar and CO₂ environments are relatively higher than that obtained at Sn catalyst. The higher value of current in Ar environment is indicative of Pb having higher hydrogen evolution current than Sn for the potentials applied. For Pb₇₀Bi₃₀ (β -phase), the current difference is quite low which suggests that activity of Pb₇₀Bi₃₀ could be relatively lower for CO₂ electroreduction. The difference in the current obtained on Pb₂₉Bi₄₆Sn₂₅ was observed to be highest among all catalysts. This indicates that production of formate ions could be maximum for Pb₂₉Bi₄₆Sn₂₅.

Electrochemical activity of all the synthesized catalysts towards CO₂ electroreduction was compared basically on the amount of formate ions produced and the Faradaic

(or coulombic) efficiency of the reduction process. The process of CO₂ electroreduction was carried at -2.0 V (vs Hg/HgO) for reaction run time of 3 h and liquid product of the process was collected in a systematic manner as described in previous Sect. 2.5. It was also observed that the amount of formate produced increased linearly with respect to time for all the catalysts. Hence, the formation rate of formate ions was obtained for each experiments as mmol/h (i.e. total millimoles of formate produced in the process run divided by 3 h). Formate ion production rate ($\dot{R}_{\text{HCOO}^-}$) has been observed for each catalyst with experiments performed a minimum of 4 times and the averaged value is provided in Fig. 3.

For Pb–Sn alloy catalysts, it could be observed that formate ions production rate (indicated within parenthesis as mmol/h) is higher for catalysts that contain both Pb and Sn than for pure Pb (0.1835 ± 0.036 mmol/h) and Sn (0.2883 ± 0.049 mmol/h) catalysts. Indeed for increasing amount of Sn in Pb, the rate for formate ions production keeps on increasing till the composition reaches that of Pb–Sn eutectic (Pb₂₅Sn₇₅: 0.3176 ± 0.05 mmol/h). Further addition of Sn in Pb exhibits deterioration in formation rate of formate ions produced on the catalyst. This suggests that addition of Sn in Pb enhances the activity for CO₂ electroreduction. This observation is similar to work by Choi et al. in which $\dot{R}_{\text{HCOO}^-}$ was observed to be highest for a near eutectic composition Pb_{43.7}Sn_{56.3}. Among all the compositions investigated, the highest Faradaic

efficiencies for CO₂ electroreduction were observed for Pb_{22.7}Sn_{77.3} and Pb_{43.7}Sn_{56.1} and it is interesting to note that the eutectic composition of Pb–Sn (Pb_{74.2}Sn_{26.8} (at%)) lies in between them. Hence, it could be possible that the maxima for Faradaic efficiency of CO₂ electroreduction lies in between the two observed compositions i.e. at or near Pb–Sn eutectic composition [24].

For addition of Bi in Pb, the $\dot{R}_{\text{HCOO}^-}$ increased for 25 at% Bi addition but then decreases till the composition becomes that of β -phase. Here also, the $\dot{R}_{\text{HCOO}^-}$ and Faradaic efficiency is observed to be highest for eutectic and near eutectic compositions for Pb–Bi system. These results suggest that addition of Bi in Pb also enhances the electroreduction of CO_2 on catalysts and the highest rate ($\dot{R}_{\text{HCOO}^-}$) is obtained for the eutectic and near-eutectic compositions of Pb–Bi alloys. Unlike addition of Bi or Sn in Pb, addition of Bi in Sn resulted in a decrease in $\dot{R}_{\text{HCOO}^-}$. This implies that addition of Bi in Sn did not have a positive effect towards CO_2 electroreduction. Similar observations have been made for ternary alloys of Pb–Bi–Sn prepared in different compositions. The production of formate ions increases as both Bi and Sn are added to Pb till eutectic composition ($\text{Pb}_{29}\text{Bi}_{46}\text{Sn}_{25}$: 0.3405 ± 0.058 mmol/h), which is similar to that obtained for the Pb–Sn and Pb–Bi systems. The highest Faradaic efficiency was observed for ternary eutectic of Pb–Bi–Sn. Besides the eutectic composition ($\text{Pb}_{44}\text{Bi}_{56}$: 0.2774 ± 0.034 mmol/h), catalyst with composition of pure single phase of $\text{Pb}_{70}\text{Bi}_{30}$ ($\text{Pb}_{70}\text{Bi}_{30}$: 0.2429 ± 0.065 mmol/h) and another catalyst ($\text{Pb}_{65}\text{Bi}_{35}$:

0.18 ± 0.02 mmol/h) with Pb₇₀Bi₃₀ as major component and Pb as minor component provided effect of addition of Bi in Pb. It was observed that though the rate of formate ions production ($\dot{R}_{\text{HCOO}^-}$) by CO₂ electroreduction increases on addition of Bi in Pb but the rate falls as composition reaches near Pb₇₀Bi₃₀ phase. Interestingly, minimum rate was observed for Pb₆₅Bi₃₅ that has Pb₇₀Bi₃₀ phase as major component and Pb as minor component. This suggests that presence of β-phase does not enhance CO₂ electroreduction to a greater extent in comparison to pure Pb or Bi metal catalysts. Moreover, $\dot{R}_{\text{HCOO}^-}$ increases on further addition of Bi in Pb for Pb₅₀Bi₅₀ (Pb₅₀Bi₅₀: 0.3058 ± 0.079 mmol/h) and displays a slight decrease for Pb₄₄Bi₅₆ (Pb₄₄Bi₅₆: 0.2774 ± 0.034 mmol/h; eutectic composition of Pb–Bi). Similar to other systems evaluated, rate was observed to be higher at composition near to eutectic composition in Pb–Bi system. Further, it was found that the rate of CO₂ electroreduction decreased on addition of Bi in Sn (Sn₇₅Bi₂₅: 0.174 ± 0.068 mmol/h). As mentioned earlier, due to work hardening of alloys during preparation, catalysts with higher amount of Bi in either Pb or Sn could not be prepared and evaluated.

The data from the experiments performed suggests that formation rates of formate ions ($\dot{R}_{\text{HCOO}^-}$) by electroreduction of CO_2 are higher for eutectics than for other compositions of addition of Bi, Sn or both Bi–Sn in Pb metal. Additionally, the ternary eutectic of Pb–Bi–Sn alloy exhibits a higher $\dot{R}_{\text{HCOO}^-}$ than both Pb–Sn and Pb–Bi eutectic catalysts. This suggests that the rate of formate ions production by CO_2 electroreduction is maximum for Pb–Bi–Sn eutectic composition among all binary and ternary compositions prepared.

The Faradaic efficiencies for all the catalysts employed were calculated as provided in the experimental Sect. 2.5. The values of the Faradaic efficiencies were observed to be almost constant and to lie within a bracket of 14–30% for the overall process run of 3 h. The maximum values of the Faradaic efficiencies were observed to be about 27–32% for $\text{Pb}_{75}\text{Bi}_{25}$, $\text{Pb}_{50}\text{Bi}_{50}$ and all the ternary alloys including ternary eutectic catalyst. The Faradaic efficiencies for CO_2 electroreduction were observed to follow similar pattern to that of formate ions production rate. For all the ternary alloys investigated, Faradaic efficiency was highest for $\text{Pb}_{29}\text{Bi}_{46}\text{Sn}_{25}$ (ternary eutectic) alloy in harmony to the variation in values of formate ions production rate on ternary alloys. A minimum value of the Faradaic efficiency was observed for pure Pb and $\text{Pb}_{65}\text{Bi}_{35}$ catalysts. This is in harmony to the values of formate ions production rates that are minimum also for Pb and $\text{Pb}_{65}\text{Bi}_{35}$ catalysts. It could be interesting to note that the values of Faradaic efficiencies observed for ternary compositions were among the

highest observed values in comparison to all binary and ternary alloys investigated.

Besides composition, the extent of hydrogen evolution reaction taking place on respective catalyst could also affect the performance of catalyst during CO_2 electroreduction. Due to negative potential applied at catalyst for electroreduction of CO_2 , occurrence of hydrogen evolution can take place as well. Though presently, we are not certain of the reasons regarding better performance of eutectics against other compositions, we suspect that the increase in production rates of formate ions ($\dot{R}_{\text{HCOO}^-}$) on catalysts could be due to suppression of hydrogen evolution at the surface. To check the same we embarked upon evaluating j_{H_2} at -2.0 V (vs Hg/HgO) in a solution saturated with H_2 and devoid of CO_2 . A comparison of formate ions production rate ($\dot{R}_{\text{HCOO}^-}$) with current of hydrogen evolution (H_2 sat. 0.5 M NaHCO_3) has been made in Fig. 4. Hydrogen evolution is a competitive reaction to CO_2 electroreduction that can block the active sites. Interestingly, it was observed that the current densities obtained in above conditions (j_{H_2}) were decreasing in a manner similar to the increment of formation rates of formate ions. For Pb–Sn alloy system, obtained hydrogen evolution currents were higher for Pb in comparison to the Sn catalyst which is in agreement with the observations of LSV experiments comparing Ar and CO_2 saturations (Section S6(a),(b),(c) (supporting information)). Furthermore, j_{H_2} for $\text{Pb}_{25}\text{Sn}_{75}$ is lower than other compositions except for pure Sn. This could imply that hydrogen evolution is suppressed to

higher extent on $\text{Pb}_{25}\text{Sn}_{75}$ (Pb–Sn eutectic) in comparison to other alloys of Pb–Sn evaluated. Similar results have been observed by Choi et al. where for $\text{Pb}_{22.7}\text{Sn}_{77.3}$ and $\text{Pb}_{43.7}\text{Sn}_{56.1}$, lowest Faradaic efficiencies for hydrogen evolution were observed [24]. Hence, as explained in previous section, it could be possible that the minima of Faradaic efficiency of hydrogen evolution lie at the Pb–Sn eutectic composition. Indeed, corresponding pattern of j_{H_2} was observed for Pb–Bi–Sn ternary alloys and Pb–Bi binary alloys and the minimum values of j_{H_2} were observed for the eutectic compositions of the corresponding system. Identical to addition of Bi or Sn or both in Pb, addition of Bi in Sn ($\text{Sn}_{75}\text{Bi}_{25}$) causes a decrease in hydrogen evolution current as compared to Sn. Hence, it could be implied that addition of Bi in Sn suppresses evolution of hydrogen. Furthermore, j_{H_2} values of Pb–Bi–Sn eutectic catalyst has been observed to be lowest among all the catalysts evaluated except for $\text{Pb}_{75}\text{Bi}_{25}$ and $\text{Sn}_{75}\text{Bi}_{25}$ which suggests that rate of production of formate ions ($\dot{R}_{\text{HCOO}^-}$) is also highest for the same catalyst as well. Thus, it could be stated that greater suppression of hydrogen evolution was observed on the eutectic compositions as compared to other compositions.

Consequently, careful perusal of the data from the performed experiments suggested that both the rates of formate ions formation ($\dot{R}_{\text{HCOO}^-}$) by electroreduction of CO_2 and Faradaic efficiencies are higher for eutectic or near eutectic compositions than for other compositions consisting of addition of Bi, Sn, and both Bi–Sn in Pb metal. Additionally, the ternary eutectic of Pb–Bi–Sn alloy exhibits a higher formation rate of formate ions than both Pb–Sn and Pb–Bi eutectic catalysts. This suggests that the rate of formate ions production by CO_2 electroreduction ($\dot{R}_{\text{HCOO}^-}$) is maximum for Pb–Bi–Sn eutectic composition among all binary and ternary compositions evaluated here. It could be interesting to note that the values of Faradaic efficiencies observed for ternary compositions were among the highest observed values in comparison to all binary and ternary alloys investigated. Also, relatively lower values of j_{H_2} on eutectics in comparison to other compositions of the alloy system suggests that suppression of hydrogen evolution could be one of the factors that contribute to the improvisation in the activity of catalysts towards CO_2 electroreduction.

Fig. 4 The current densities at each catalyst obtained at -2.0 V (vs Hg/HgO) in H_2 saturated 0.5 M NaHCO_3 solution. The formate ion production rate (black square) for each prepared catalyst is shown at -2.0 V (vs Hg/HgO) in CO_2 saturated 0.5 M NaHCO_3 solution. The Faradaic efficiencies of the corresponding catalysts are also displayed (blue circle). The catalysts consisting of single phase are displayed in green colored symbols and catalysts corresponding to eutectic compositions are shown in red colored symbols

4 Conclusions

In summary, we have evaluated effect on CO_2 electroreduction at -2.0 V (vs Hg/HgO) for addition of Bi, Sn metals as individually and in combinations to Pb metal for synthesizing catalysts. It has been observed in this work that addition of both Bi and Sn individually to Pb metal by preparing Pb–Bi and Pb–Sn alloys causes increase in the

rate of CO₂ electroreduction. Further, the rate of electroreduction of CO₂ could be increased by preparing ternary alloys of Pb–Bi–Sn. It was also observed that the eutectic composition of the corresponding metal alloy system provided the highest rate of formate ions production. Faradaic efficiencies for all catalysts were observed in the range of 14–30%. Current corresponding to hydrogen evolution were observed to be lower for the catalysts having higher formate ions production rate. This suggests that one of the factors contributing towards enhanced CO₂ electroreduction on eutectics could be the suppression of hydrogen evolution at the surface of catalyst. Thus, the Pb alloy catalysts used in this study to produce formate ions by CO₂ electroreduction performs best for eutectic compositions. Based on a comparative analysis of the eutectics, the rate of formate ion production by electrochemical reduction of CO₂ follows an order of:

Pb–Bi–Sn eutectic (Pb₂₉Bi₄₆Sn₂₅)
 > Pb–Sn eutectic (Pb₂₅Sn₇₅)
 > Pb–Bi eutectic (Pb₄₄Bi₅₆).

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Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests.

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