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Highly efficient In–Sn alloy catalysts for electrochemical reduction of CO_2 to formate

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ABSTRACT

Gas diffusion electrodes (GDEs), including GDE-$In_{0.90}Sn_{0.10}$, GDE-$In_{0.47}Sn_{0.53}$ and GDE-$In_{0.22}Sn_{0.78}$, were prepared by electrodeposition of In–Sn alloys on carbon fiber paper, and then used to explore the electroreduction of CO_2 to formate in aqueous solution. Compared with commercial indium or Sn foil catalysts, the GDE-$In_{0.90}Sn_{0.10}$ electrode in particular is shown to have excellent catalytic performance towards electroreduction of CO_2 to formate, with a high Faradaic efficiency (~92%). More importantly, the catalytic activity of GDE-$In_{0.90}Sn_{0.10}$ remained reasonably stable over a 22-hour period of electrolysis, and a relatively high electrolytic current density (15 mA cm^{-2}) was obtained in an aqueous medium, demonstrating its potential for electrochemical reduction of CO_2 to formate.

1. Introduction

Carbon dioxide is a non-toxic, abundant and cheap source of carbon. The electrochemical reduction of CO_2 has attracted much attention in recent decades as it can be used to produce valuable chemicals (CO, CH_4, C_2H_4, CH_3OH, HCOOH, $HCOO^-$, etc.) under mild conditions [1]. Among the range of products of CO_2 electroreduction, formate is particularly attractive since formic acid is an important chemical that can be used in pesticides, leather processing, pharmaceuticals and fuel cells [2]. Much research effort has been devoted to the development of efficient electrocatalysts for the conversion of CO_2 to formate. Various metals and alloys, including Bi [3], Pb [4], Pt [5], Sn [6] and In [7], have been shown to be efficient catalysts for the electroreduction of CO_2 to formic acid or formate. Recent investigations have focused on tin- and indium-based catalysts [6–17]. These studies have greatly improved the electrochemical reduction of CO_2. However, it should be noted that some key issues have not yet been solved, such as the deactivation of catalysts, low Faradaic efficiency (FE) and low electrolytic current density. In previous studies [7,8,17,18], the deactivation of catalysts was usually observed after a short period of electrolysis (1–6 h). With indium electrodeposited on a graphite backbone as the catalyst, the FE of formate production decreased almost linearly from 65% to 36% during a 24-hour period of electrolysis [9]. From the viewpoint of industrial applications, it is still a great challenge to develop a stable catalyst system with high activity for the electrochemical reduction of CO_2 to formate. However, it should be noted that claims that fixation of CO_2 could impact its level in the atmosphere would require a scale of technology and the availability of energy on a scale that is beyond reality [19].

In this work, we report a highly efficient and stable In–Sn alloy that catalyses the reduction of CO_2 to formate in aqueous solutions. Our investigations revealed that In–Sn alloys (especially $In_{0.90}Sn_{0.10}$) have excellent catalytic performance, which is superior to that of the single metal electrodes. The activity of the GDE-$In_{0.90}Sn_{0.10}$ electrode catalyst remains almost stable during a 22-hour electrolysis with a high FE (~92%) towards formate formation and a current density of 15 mA cm^{-2} in a CO_2-saturated $KHCO_3$ (0.1 mol L^{-1}) electrolyte solution. To the best of our knowledge, this is one of the best results for catalysing electroreduction of CO_2 to formate to date.

2. Experimental

In–Sn alloy catalysts for use in GDE-In_xSn_{1-x} electrodes were electrodeposited on carbon fiber paper (GDE, Toray, TGP-H090) using a galvanostat at 15 mA cm^{-2} for 5 min at room temperature. The electroplating solution consists of $In_2(SO_4)_3$, Na_2SnO_3 (18 g L^{-1}), methanesulfonic acid and D-gluconic acid (complexing agent). GDE-In_xSn_{1-x} electrode catalysts with different compositions could be obtained by changing the concentration of $In_2(SO_4)_3$ in the electroplating bath (2, 6 and 12 g L^{-1} for the three alloys studied).

An electrochemical workstation (CH Instrument 660 C, Chenhua, China) was used for all the electrochemical experiments. The linear

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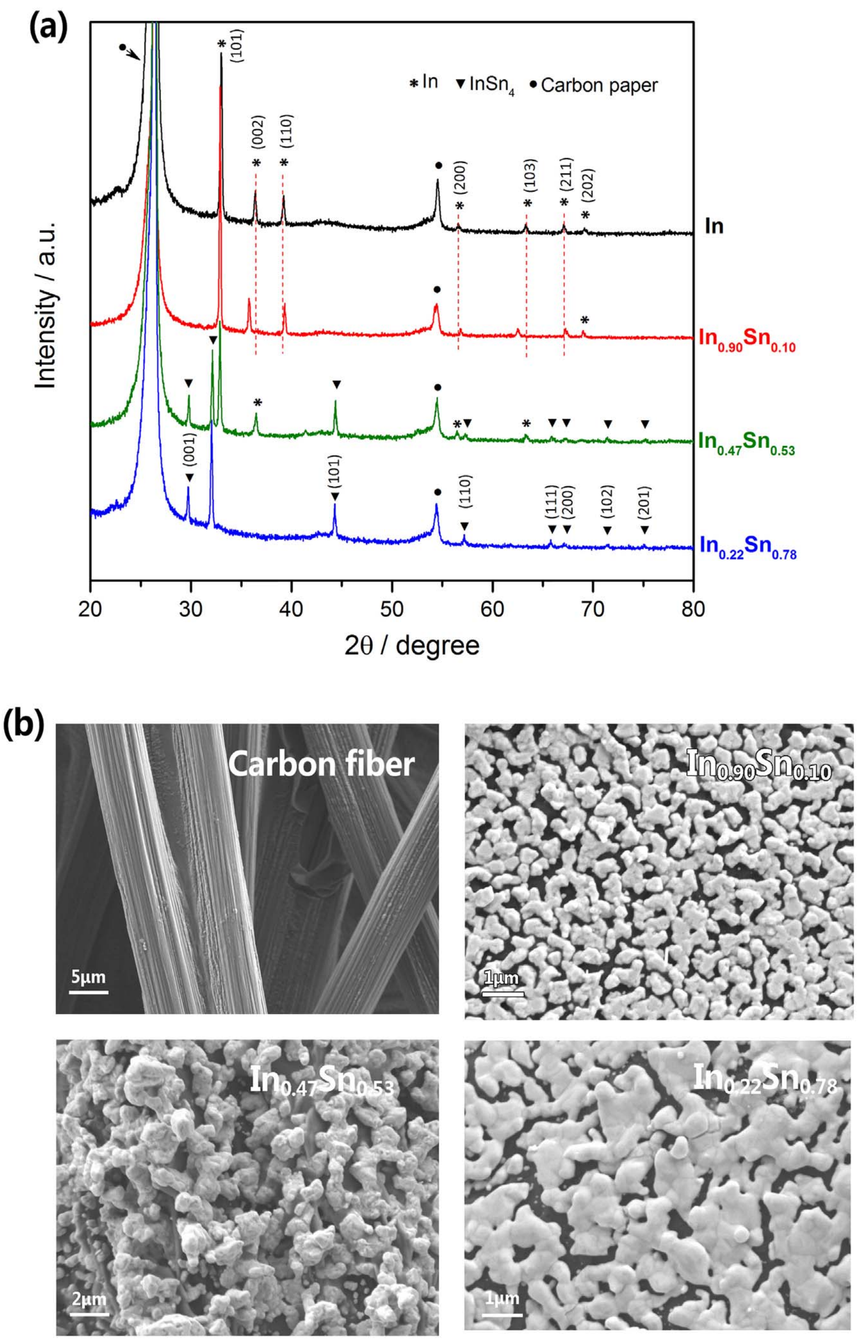

Fig. 1. (a) XRD patterns and (b) SEM images of the GDE-$In_{0.90}Sn_{0.10}$, GDE-$In_{0.47}Sn_{0.53}$ and GDE-$In_{0.22}Sn_{0.78}$ electrodes.

sweep voltammetry (LSV) and electrolysis were performed in a conventional three-electrode H-type cell with cathode and anode chambers separated by a Nafion 117 cation-exchange membrane (Dupont, USA). Leak-free Ag/AgCl (saturated KCl) was used as a reference electrode. The electrochemical reduction of CO_2 at various potentials was performed under a continuous flow of CO_2. For the sake of clarity, the potential reported in this work was transformed to the reversible hydrogen electrode (RHE) scale: E (vs. RHE) = E (vs. Ag/AgCl) + 0.197 V + pH × 0.059 V.

XRD (X-ray diffraction) analysis was performed using a D8 Advance Bruker AXS with a Cu-K_α radiation (λ = 0.15406 nm) source operating at 40 kV and 40 mA. The morphologies and surface components of the as-prepared electrodes were observed using a field-emission scanning electron microscope (FE-SEM, Zeiss Merlin, Germany) equipped with an energy dispersive spectrometer (EDS, Oxford, UK). An inductively coupled plasma-atomic emission spectrometer (ICP-AES, Prodigy, USA) was used to analyse the bulk compositions of the electrodeposits. The formate produced was quantified by ion chromatography (ICS-1000, Dionex, USA).

3. Results and discussion

The compositions of the three electrodeposited GDE-In_xSn_{1-x} alloy electrode catalysts were determined by EDS and ICP-AES and found to be GDE-$In_{0.90}Sn_{0.10}$, GDE-$In_{0.47}Sn_{0.53}$ and GDE-$In_{0.22}Sn_{0.78}$, respectively. The XRD patterns of these GDE-In_xSn_{1-x} electrodes are shown in Fig. 1a. The broad diffraction peaks at 2θ = 26.4° and 54.5° come from the carbon paper [12]. Fig. 1a suggests that the pure indium metal electrodeposited on a GDE electrode has a face-centred tetragonal structure (JCPDS No. 05-0642). For the GDE-$In_{0.90}Sn_{0.10}$ electrode, it can be seen that $In_{0.90}Sn_{0.10}$ consists of an indium crystal phase. However, the diffraction peaks of $In_{0.90}Sn_{0.10}$ alloy are shifted slightly