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Porous tin-based film deposited on copper foil for electrochemical reduction of carbon dioxide to formate

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ABSTRACT

Electrochemical reduction of carbon dioxide (CO_2) has been studied using a Sn/Cu electrode as the cathode in aqueous KHCO_3 solution. The Sn/Cu electrode has been prepared by electrodeposition a Sn-based film on a Cu foil from a sodium citrate aqueous electrolyte containing SnCl_2 . Here, we have explored the effects of the deposition time, the thickness of the Sn-based film and the electrolysis potential on the faradaic efficiency for producing formate. The results demonstrate that maximum faradaic efficiency of 91.5% is obtained at -1.8 V vs. Ag/AgCl on the Sn/Cu electrode possessing a ~ 325 nm thick Sn-based film which is prepared by electrodeposition for 15 min. The Sn/Cu electrode has big current density and excellent catalytic activity for CO_2 reduction compared with the Sn electrode.

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Introduction

In recent years, more and more CO_2 has been released into the atmosphere due to the industrial combustion of fossil fuels. To alleviate both the environmental and energy stresses, CO_2 must be recycled and reused to synthesize useful chemicals or fuels. Converting CO_2 and H_2O into commodity chemicals using renewable energy could significantly reduce CO_2 emissions by replacing existing fossil fuel-based syntheses [1–3]. To date, carbon monoxide, methanol, oxalic acid, and formate or formic acid (depending on pH) have been prepared by electrochemical reduction of CO_2 [4–8]. Among them, formic acid and formate are relatively high-value commodity chemicals that are currently synthesized from CO that is produced by steam reforming natural gas.

Up to now, various electrode materials (including metals, metal oxides, metal complex, polymers, alloys or composite materials) have been used for electrochemical reduction of CO_2 to formate [9–14]. Metal electrodes were the traditional electrodes due to their excellent performance for electrochemical reduction of CO_2 which has been studied extensively. Among them, Cu electrode is a commonly used electrode for electrochemical reduction of CO_2 . For improve the catalytic performance of the Cu electrode, researchers have developed many novel construction of electrodes, including Cu nanofoams [15], Cu nanoparticles [16], Cu alloys [17], nanoporous Cu [18] or Cu oxides [19]. These reports have greatly enriched the types of the electrodes used for electrochemical reduction of CO_2 . And the novel electrodes have higher specific surface areas which can provide more active sites to accelerate the

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electrochemical reaction, whereas, these Cu-based electrodes have low product selectivity to formate in aqueous electrolytes. Qiao et al. had reported that an effective fibrous Cu electrode surface, created using a procedure combining high-temperature annealing and electro-reduction, is explored for CO₂ reduction to produce HCOO⁻, and the highest faradaic efficiency obtained was ~43% [20]. Sen et al. had reported that the highest faradaic efficiency for electrochemical reduction of CO₂ to formate on copper foams with hierarchical porosity was 29% [15]. Unlike Cu, Sn is an excellent catalyst for electrochemical reduction of CO₂ to formate, and the faradaic efficiency can easily achieve above 80% at the appropriate electrolysis conditions [14]. It is necessary to develop an electrode that can integrate the properties of Sn with high catalytic activity and special structured Cu substrate with big specific surface area, and the target electrode will possess high selectivity and high production rate of formate.

There are two reported methods to effectively fabricate Sn films on some substrates: sputtering and electrochemical plating [21,22]. Compared with the method of sputtering, the electrochemical plating is easier to implement because it does not need expensive equipment. For now, an effective electrochemical plating technology is needed for preparing Sn deposited Cu electrode. In this paper, a Sn-based film was decorated on a Cu substrate by electrochemical deposition in aqueous solution, which was used as a cathode for electrochemical reduction of CO₂. The Cu substrate used in this experiment is the polished Cu foil. The influences of key variables like the deposition voltage, the thickness of the Sn-based film and the electrolysis potential on the faradaic efficiency for producing formate were studied to obtain the optimal electrolysis conditions.

Experimental

Preparation of Sn/Cu electrode

A Cu foil with a thickness of 0.1 mm was cleaned with ethanol and deionized water ultrasonically, dried with flowing air and electropolished in 85% H₃PO₄ at 4 V vs. a Pt counter electrode for 5 min, successively. Then the obtained Cu foil was used as the substrate for electrochemical deposition. The electrochemical deposition was performed on the Cu substrate in aqueous electrolytic solution. Sodium citrate was first dissolved in deionized water to form a 0.05 mol L⁻¹ solution, and the resulting pH was adjusted to 6 with H₂SO₄. Then SnCl₂ was added to the above solution and its concentration was 0.018 mol L⁻¹. The solution was moderately stirred at least 10 h before electroplating process commencement. Agitation was kept on within the process. Sn-based film was deposited on the Cu substrate by galvanostatic electroplating at 2.4 mA for different times, and the obtained sample was marked as Sn/Cu.

Electrochemical experiments

The cell used here is an airtight and undivided glass cell equipped with a gas inlet and outlet which is able to pass

either N₂ (99.99%) or CO₂ (99.99%) through the solution. A conventional three-electrode system was used during the electrochemical measurements. The working electrode was a Sn/Cu electrode with the geometric surface area of 1 cm². A Pt plate (2 cm²) was chosen as the counter electrode and an Ag/AgCl electrode (sat. KCl) was chosen as the reference electrode. All potential values were in reference to Ag/AgCl electrode. The electrolyte used was 40 mL of 0.1 mol L⁻¹ KHCO₃ aqueous solution. All experiments were performed under room temperature (20 ± 3 °C) and ambient pressure.

The electrochemical measurements were performed with a CHI 660D electrochemical workstation (Shanghai Chenhua Instruments Co., Ltd., China). Linear sweep voltammetry (LSV) was performed in 0.1 mol L⁻¹ KHCO₃ aqueous solution after being bubbled with N₂ or CO₂ for 30 min at a scan rate of 0.05 V s⁻¹. The current density (*j*) is determined on the geometrical area of the electrode. Electrochemical impedance spectroscopy (EIS) was performed in 0.1 mol L⁻¹ KHCO₃ aqueous solution after being bubbled with CO₂ for 30 min, which was recorded at the frequency range from 4 × 10⁴ to 0.01 Hz with amplitude of 0.01 V.

Controlled potential electrolysis was carried out using a LAND CT2001C cell performance-testing instrument (Wuhan Electronics Co., Ltd., China). The electrolyte was saturated with CO₂ before each electrolysis process, and CO₂ gas was continuously aerated at a flow rate of 20 mL min⁻¹ during the electrolysis process. The electrolysis experiments were terminated when the amount of charge passed reached to 40C. The average current density (*j_a*) is expressed as the total current divided by the geometric surface area of the Sn electrode (1 cm²) for all cells.

Analysis and calculations

Scanning electron microscope (SEM) images and energy dispersion spectroscopy (EDS) were taken with a Hitachi S-4800 microscope at an acceleration voltage of 15 kV. X-ray diffraction pattern (XRD) was recorded on a Bruker D8 Advance powder X-ray diffractometer using Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$), scan range from 25 to 85°.

The products in the electrolyte were directly analyzed by an ion chromatography instrument (Dionex ICS-900) equipped with IonPac AS11-HC (250 mm × 4 mm) and AG11-HC (50 mm × 4 mm) columns. 0.03 mol L⁻¹ KOH solution was used for isocratic elution, and leaching rate was 1 mL min⁻¹. 10 μ L of the sample were used for each time.

The thickness of Sn-based film (δ) on the Sn/Cu electrode can be roughly calculated by equation (1):

$$\delta = (m_2 - m_1) \times 10^7 / (\rho S) \quad (1)$$

where δ is the thickness of electrodeposited Sn-based film and its unit is nanometer; m_1 and m_2 are the weights of the Cu foils before and after electrodeposition of Sn, respectively, and the units of which are gram; ρ is the density of Sn (7.298 g cm⁻³); S is the geometric surface area of the Cu foil ($S = 10 \text{ cm}^2$ here).

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