

Effect of the surface roughness of copper substrate on three-dimensional tin electrode for electrochemical reduction of CO₂ into HCOOH



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ABSTRACT

The tin electrode with three-dimensional (3D) porous structure was prepared using copper foil as the substrate by electrochemical deposition method for the electrochemical reduction of CO₂ into HCOOH. The results indicate that the faradaic efficiency (FE) and the energy conversion efficiency (EE) of CO₂ to HCOOH are dependent on the surface roughness of copper foil that can be controlled by the electropolishing time. The prepared 3D tin electrode on the smoothest Cu foil exhibits the highest FE (90%) and EE (50%) at -1.2 V (vs. RHE), which were 1.6 times those on the original copper foil. Meanwhile, the Sn loss ratio of this electrode in the electrochemical process is the lowest, showing good stability.

1. Introduction

The ever-increasing concentration of atmospheric carbon dioxide is the main cause of greenhouse gas effect [1]. Electrochemical reduction of carbon dioxide into energy-rich fuels and useful chemicals has received considerable attention in recent years as a potential strategy for mitigating excessive emissions of carbon dioxide and effectively storing intermittent renewable energy simultaneously [2,3]. Among the products (e.g., syngas, acids, alcohols, hydrocarbon) [4] from carbon dioxide reduction reaction (CO₂RR), formic acid (HCOOH) is a promising chemical as a fuel and a hydrogen storage material [5,6]. However, many metal electrodes reported (e.g., plumbum, mercury, indium, cadmium) for CO₂ to HCOOH are poisonous, costly, or both [5]. Nevertheless, tin and its correlative catalysts, as nontoxic and inexpensive materials, are a kind of ideal cathode materials for CO₂RR to HCOOH [5–8]. The faradaic efficiencies and final production rates of formic acid were reported from 23% to 93.6% and from 3 to 797 $\mu\text{mol h}^{-1} \text{cm}^{-2}$ with different tin based cathodes, and the stability of the tin based cathode was reported more than 15 h [6]. To enhance the electroactive area and the current density, tin electrode with three dimensional (3D) porous structure has been made by electrochemical deposition with hydrogen bubbles evolution [9,10], which is a very simple and fast method. In addition, such obtained self-supported cellular structure as monolithic electrode is cheap but effective for CO₂RR without a binder such as nafion solution [11] or poly-tetrafluoroethylene [7,12].

So far, the effect of experimental conditions on the performance of CO₂RR to HCOOH at Sn based electrodes has been widely investigated.

It has been shown that the HCOOH formation rate depends strongly on various parameters, such as pH [13], supporting electrolyte [14], the potential and the CO₂ partial pressure [15]. Recently, many researchers have devoted to study the influence of structure and morphology [5–8] of the tin electrode on the performance of CO₂RR. In order to enhance the faradaic efficiency and the production rate of HCOOH, tin was deposited on different substrates. Wang et al. [16] prepared Sn/f-Cu electrode by electrodepositing Sn on a Cu foam substrate in aqueous plating solution for the electrochemical reduction of carbon dioxide in aqueous KHCO₃ solution. The results demonstrate that the maximum faradaic efficiency of 83.5% can be obtained at -1.8 V vs. Ag/AgCl, the average current density and the production rate of formate with the Sn/f-Cu electrode are twice higher than those with the Sn plate electrode. However, the effect of surface roughness of the substrate on the efficiency and the stability of the electrode for CO₂RR is still unclear at present. Herein, a series of 3D tin electrodes on copper foils with different surface roughness were controllably prepared by electrochemical method and the important dependence of the energy efficiency and the stability of the electrode for CO₂RR on the surface roughness of the substrate was investigated and revealed for the first time.

2. Experimental

2.1. Preparation of Cu foil supported tin electrodes

Copper foil as a rectangular substrate (1 cm \times 2 cm) was annealed at 500 °C for two hours in the tube furnace with argon, and then cleaned under ultrasonication with ethanol, acetone and 2 M HCl for

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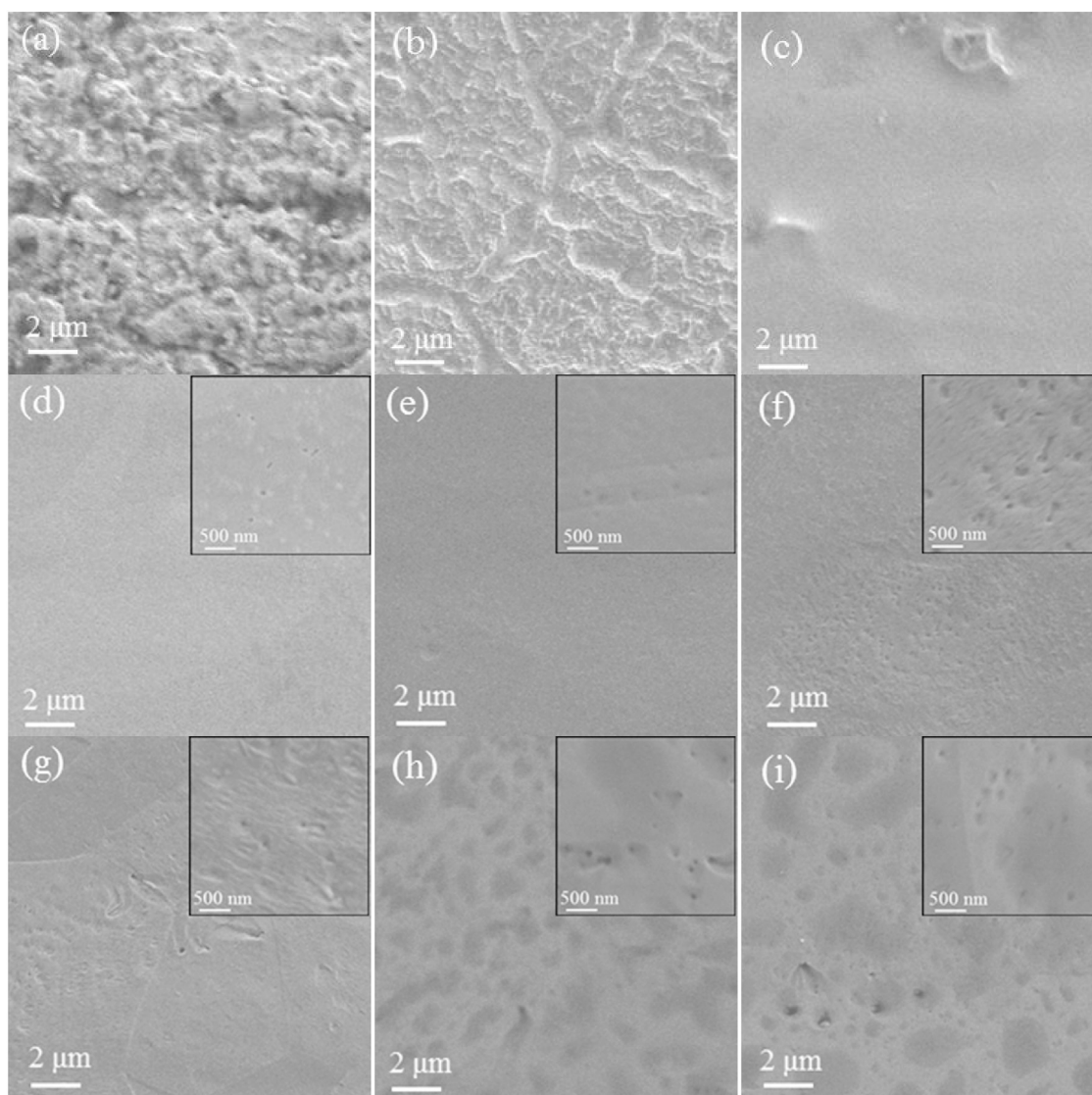


Fig. 1. SEM images of the electropolished copper foils. Polishing time: (a) 0 s, (b) 10 s, (c) 20 s, (d) 25 s, (e) 30 s, (f) 60 s, (g) 120 s, (h) 240 s and (i) 480 s.

15 min, sequentially. The foil was cleaned under ultrasonication with 2 M HCl for 15 min again, and then curdled in drying oven at 60 °C. To ensure the working area of 1 cm² and the reserved area of about 0.2 cm² for electrode holder, the rest and the other side of the foil were sealed with epoxy resin. In a three-electrode system, the Cu foil, Ag/AgCl electrode (KCl saturated) and platinum plate electrode was used as the working electrode, reference electrode, and counter electrode, respectively. All the potentials in the work were converted into the reversible hydrogen electrode (RHE). Cu foil was electro-polished in 60 wt% phosphoric acid at 0.73 V (vs. RHE) with a potentiostat (CHI 630E, Shanghai). The polished Cu foils with different roughness were obtained by controlling the polishing time from 0 s to 480 s. Tin electrodes with 3D porous structure on these polished copper foils were prepared by electrochemical deposition method with the polished copper foil as cathode and tin foil as anode and the distance of 2 cm between these two electrodes. Then direct current with high current density of 2 A cm⁻² was applied for 2 min in 1.2 M HCl solution containing 0.1 M SnCl₂ and 0.1 M trisodium citratedihydrate (Na₃C₆H₅O₇) in ice-water bath. The as-prepared tin electrode with Cu foil substrate was cleaned with deionized water (Milli-Q[®], ~18MΩ cm) and dried in nitrogen at room temperature.

2.2. Electrochemical CO₂RR

Electrochemical CO₂RR was performed with a CHI 630E electrochemical workstation in an H-type cell, which has good gas and liquid tightness and even agitation (400 r min⁻¹). The H-type cell was separated by Nafion 117 (DuPont). The prepared tin electrode as the working electrode and Ag/AgCl electrode as the reference electrode were placed in one side of H-type cell, and platinum plate electrode as the counter electrode was placed in the other side with 0.1 M KHCO₃ aqueous solution used as the electrolyte (each side 40 mL). The electrolyte was bubbled with CO₂ or N₂ at the flow rate of 7.37 mL min⁻¹ to construct CO₂-saturated or CO₂-free electrolyte at 0 °C. The electroreduction time was 1 h at preset potential (-1.0 V, -1.1 V, -1.2 V and -1.3 V vs. RHE). It is noteworthy that the electrode holder should avoid being contacted with the electrolyte in the electrochemical process (See schematic illustration Fig. S1).

2.3. Quantitative analyses and electrode characterizations

CO and H₂ evolved from CO₂ and water as associated reactions during the electrochemical reduction of CO₂ were quantified using gas chromatograph with a packed column, a flame ionization detector and a thermal conductivity detector every 30 min. The main reduced

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