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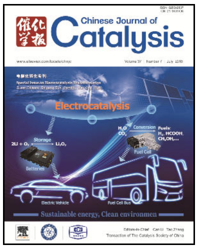

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Electrochemical CO_2 reduction to formic acid on crystalline SnO_2 nanosphere catalyst with high selectivity and stability

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ABSTRACT

A novel catalyst for CO_2 electroreduction based on nanostructured SnO_2 was synthesized using a facile hydrothermal self-assembly method. The electrochemical activity showed that the catalyst gave outstanding catalytic activity and selectivity in CO_2 electroreduction. The catalytic activity and formate selectivity depended strongly on the electrolyte conditions. A high faradaic efficiency, i.e., 56%, was achieved for formate formation in $KHCO_3$ (0.5 mol/L). This is attributed to control of formate production by mass and charge transfer processes. Electrolysis experiments using SnO_2-50/GDE (an SnO_2-based gas-diffusion electrode, where 50 indicates the 50% ethanol content of the electrolyte) as the catalyst, showed that the electrolyte pH also affected CO_2 reduction. The optimum electrolyte pH for obtaining a high faradaic efficiency for formate production was 8.3. This is mainly because a neutral or mildly alkaline environment maintains the oxide stability. The faradaic efficiency for formate production declined with time. X-ray photoelectron spectroscopy showed that this is the result of deposition of trace amounts of fluoride ions on the SnO_2-50/GDE surface, which hinders reduction of CO_2 to formate.

1. Introduction

The increased amount of CO_2 in the atmosphere is claimed to be one of the major contributors to the greenhouse effect, and will result in serious global warming issues [1]. Among various conversion methods, the electrochemical synthesis of high-value chemicals from CO_2 offers several advantages such as process simplicity and flexibility, and production of various organic chemicals, depending on the type of catalyst used [2,3]. CO_2 is a stable molecule and generally produced by fossil fuel combustion and respiration. Converting CO_2 to useful chemicals at the same rate as its present production is beyond our current scientific and technological abilities [4]. The reduction of CO_2 involves the use of specific metal catalysts, to achieve product selectivity, and because of the sluggish kinetics of CO_2 electroreduction [5].

The study of CO_2 electroreduction in aqueous solutions at ambient temperature has focused on metal electrodes [3,6].

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The catalytic reduction of CO_2 to methanol was achieved over Cu under hydrothermal conditions with a methanol yield of 11.4% [7]. The product distributions and faradaic efficiencies obtained in the electrochemical reduction of CO_2 with Cu foams differ significantly from those obtained at smooth electropolished Cu electrodes. This is attributed to the high surface roughness, hierarchical porosity, and confinement of reactive species in the case of Cu foams. The faradaic efficiency for formic acid production at Cu foam electrodes was higher at all tested potentials, with a maximum efficiency of 37% at −1.5 V, which is the highest value obtained for the electroreduction of CO_2 to formic acid at a Cu electrode under ambient pressure [8]. The use of gas-diffusion electrodes (GDEs) for electrochemical reduction of CO_2 on Pb, In, and Sn under acidic conditions gave high efficiencies for formic acid (pH ≈ 2) production [9]. An Sn-based GDE (SGDE) showed good stability during CO_2 reduction; the faradaic efficiency for conversion of CO_2 to formate reached 18% during the initial 5 min and remained at about 12% until the end of the reduction time, i.e., 1 h [10]. Recently, SGDEs have attracted much attention for CO_2 reduction. Wang et al. [11,12] reported that an SGDE with polytetrafluoroethylene as an additive gave a good electrochemical performance, because of the increased active catalyst surface area and CO_2 diffusion, and high catalyst loading, i.e., 5 mg/cm^2.

The deactivation of Sn-metal-based electrodes during CO_2 reduction is fast, and the reduction reaction on these electrodes requires an overpotential of at least ~860 mV at a current density of 4–5 mA/cm^2 in an aqueous solution saturated with CO_2 at 0.1 kPa [13]. It is vital to explore the use of metal oxides in CO_2 reduction to overcome this problem, but there have been few reports of such studies. The role of metal oxides, whether as catalysts for the formation of formic acid or as precursors for the fabrication of well-structured catalysts, remains unclear. Kanan's group [14] published several reports on the metal oxide effect in CO_2 reduction. The faradaic efficiency for CO_2 reduction depended greatly on the presence of SnO_x; Sn/SnO_x thin-film electrodes catalyzed the formation of CO and formic acid as the main reaction products. The faradaic efficiency for formic acid reached 30% at −0.7 V vs the normal hydrogen electrode. An important result of this study is the observation that controlling the size of tin oxide nanoparticles (NPs) on carbon supports enables overpotentials as low as ~340 mV to be achieved for CO_2 reduction to formate, with significant enhancements in current density to over 10 mA/cm^2 on high-surface-area graphene supports. Reduced nanoscale tin oxide catalysts are highly stable during controlled-potential electrolysis [15].

The most important and valuable products of CO_2 reduction are formate and formic acid. SnO_2 shows good catalytic activity in formate production, but the electrolyte conditions greatly affect the formation of formic acid [16–19]. The pH value of the electrolyte significantly affects the electrode potentials for the reduction of H_2O and CO_2 [20]:

$$H^+ + 2e^- \leftrightarrow H_2$$

$$CO_2 + H^+ + 2e^- \leftrightarrow HCOO^-$$

An environment that is too acidic promotes hydrogen formation, and one that is too alkaline does not favor formation of formic acid. CO_2 electrolysis in a neutral or mildly alkaline environment stabilizes the oxide. The electrolyte concentration also greatly influences the formation of formic acid [21]. The faradaic efficiency for formic acid production in $KHCO_3$ (0.5 mol/L) was greater than that in K_2CO_3 (0.1 mol/L) with an Sn granule electrode in a fixed-bed reactor [16]. The highest achieved faradaic efficiency for formate production was 88.4% in 0.1 mol/L $KHCO_3$ at −1.72 V vs the saturated calomel electrode (SCE) [17], and the faradaic efficiency was between 65.0% and 79.9% in $KHCO_3$ (0.5 mol/L) [22].

In this work, we developed a novel SnO_2 NP catalyst with a high catalytic efficiency for CO_2 electroreduction, based on a GDE. Unlike that used in Wang's group [11], the catalyst was a nanostructured tin oxide consisting of SnO_2 NPs with highly porous structures, and was synthesized using a facile hydrothermal self-assembly process. SnO_2-50/GDE (an SnO_2-based gas-diffusion electrode, where 50 indicates the 50% ethanol content of the electrolyte) was prepared by coating SnO_2 catalyst ink on a gas-diffusion carbon paper sheet. The SnO_2 catalyst ink was prepared by homogeneously mixing SnO_2 catalyst particles, 5 wt% Nafion solution, and isopropyl alcohol. The electrolyte conditions, i.e., the pH and concentration, were controlled, to enable a better understanding of the mechanisms of the effects of the electrolyte on formic acid formation and the faradaic efficiency. The SnO_2 NP catalyst morphology was examined using scanning electron microscopy (SEM). The electrochemical properties of the modified electrode, i.e., SnO_2-50/GDE, in CO_2 reduction were investigated thoroughly using cyclic voltammetry (CV), linear sweep voltammetry (LSV), CO_2 electrolysis, and ion chromatography. The production rate and faradaic efficiency for formate, which can be used as a liquid fuel during CO_2 reduction, were also investigated.

2. Experimental

2.1. *Catalyst synthesis*

An SnO_2 NP catalyst was synthesized from $SnCl_4$ and D-glucose monohydrate using a facile hydrothermal self-assembly process. $SnCl_4$ (4 mmol) was mixed with D-glucose monohydrate (10 mmol) and the mixture was dissolved in distilled water and ethanol (totally 35 mL) with stirring until a transparent solution was obtained. The mixture solution was transferred to a 100 mL Teflon-lined stainless-steel autoclave, which was sealed and kept at 180 °C for 24 h. The formed black powder was collected, washed several times with ethanol/water, and dried in a vacuum oven at 60 °C for 5 h. The obtained powder was calcined in air at 550 °C for 5 h, during which the black sediment gradually turned white, indicating the successful removal of carbon by oxidation in air, to give the SnO_2 NP catalyst. The catalyst is denoted by SnO_2-50, where 50 indicates that the percentage of ethanol content in the mixture solution is 50%.

2.2. *Electrode preparation and electrochemical tests*

For all electrochemical measurements, the SnO_2-50 NP cat-