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Electrochemical CO₂ reduction to formic acid on crystalline SnO₂ nanosphere catalyst with high selectivity and stability

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ABSTRACT

A novel catalyst for CO₂ electroreduction based on nanostructured SnO₂ was synthesized using a facile hydrothermal self-assembly method. The electrochemical activity showed that the catalyst gave outstanding catalytic activity and selectivity in CO₂ 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 KHCO₃ (0.5 mol/L). This is attributed to control of formate production by mass and charge transfer processes. Electrolysis experiments using SnO₂-50/GDE (an SnO₂-based gas-diffusion electrode, where 50 indicates the 50% ethanol content of the electrolyte) as the catalyst, showed that the electrolyte pH also affected CO₂ 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 SnO₂-50/GDE surface, which hinders reduction of CO₂ to formate.

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1. Introduction

The increased amount of CO₂ 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 CO₂ offers several advantages such as process simplicity and flexibility, and production of various organic chemicals, depending on the type of catalyst used [2,3].

CO₂ is a stable molecule and generally produced by fossil fuel combustion and respiration. Converting CO₂ to useful chemicals at the same rate as its present production is beyond our current scientific and technological abilities [4]. The reduction of CO₂ involves the use of specific metal catalysts, to achieve product selectivity, and because of the sluggish kinetics of CO₂ electroreduction [5].

The study of CO₂ electroreduction in aqueous solutions at ambient temperature has focused on metal electrodes [3,6].

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The catalytic reduction of CO₂ 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 CO₂ 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 CO₂ to formic acid at a Cu electrode under ambient pressure [8]. The use of gas-diffusion electrodes (GDEs) for electrochemical reduction of CO₂ 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 CO₂ reduction; the faradaic efficiency for conversion of CO₂ 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 CO₂ 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 CO₂ diffusion, and high catalyst loading, i.e., 5 mg/cm².

The deactivation of Sn-metal-based electrodes during CO₂ 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/cm² in an aqueous solution saturated with CO₂ at 0.1 kPa [13]. It is vital to explore the use of metal oxides in CO₂ 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 CO₂ reduction. The faradaic efficiency for CO₂ 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 CO₂ reduction to formate, with significant enhancements in current density to over 10 mA/cm² 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 CO₂ reduction are formate and formic acid. SnO₂ 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 H₂O and CO₂ [20]:

An environment that is too acidic promotes hydrogen formation, and one that is too alkaline does not favor formation of

formic acid. CO₂ 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 KHCO₃ (0.5 mol/L) was greater than that in K₂CO₃ (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 KHCO₃ at −1.72 V vs the saturated calomel electrode (SCE) [17], and the faradaic efficiency was between 65.0% and 79.9% in KHCO₃ (0.5 mol/L) [22].

In this work, we developed a novel SnO₂ NP catalyst with a high catalytic efficiency for CO₂ electroreduction, based on a GDE. Unlike that used in Wang's group [11], the catalyst was a nanostructured tin oxide consisting of SnO₂ NPs with highly porous structures, and was synthesized using a facile hydrothermal self-assembly process. SnO₂-50/GDE (an SnO₂-based gas-diffusion electrode, where 50 indicates the 50% ethanol content of the electrolyte) was prepared by coating SnO₂ catalyst ink on a gas-diffusion carbon paper sheet. The SnO₂ catalyst ink was prepared by homogeneously mixing SnO₂ 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 SnO₂ NP catalyst morphology was examined using scanning electron microscopy (SEM). The electrochemical properties of the modified electrode, i.e., SnO₂-50/GDE, in CO₂ reduction were investigated thoroughly using cyclic voltammetry (CV), linear sweep voltammetry (LSV), CO₂ electrolysis, and ion chromatography. The production rate and faradaic efficiency for formate, which can be used as a liquid fuel during CO₂ reduction, were also investigated.

2. Experimental

2.1. Catalyst synthesis

An SnO₂ NP catalyst was synthesized from SnCl₄ and D-glucose monohydrate using a facile hydrothermal self-assembly process. SnCl₄ (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 SnO₂ NP catalyst. The catalyst is denoted by SnO₂-50, 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 SnO₂-50 NP cat-

alyst was coated on a gas-diffusion carbon paper sheet (Toray, TGP-H-090) to form a working electrode. The catalyst ink was prepared by suspending the SnO_2 -50 NP catalyst (15 mg) in a mixture of 5 wt% Nafion solution (100 mg) and 99.7 wt% isopropyl alcohol (1.4 mL; Sinopharm Chemical Reagent Co.). A catalyst-coated gas-diffusion layer on 4 cm^2 Toray carbon paper (TGP-H-090), denoted by SnO_2 -50/GDE, was used as the working electrode. It was tested using a conventional three-electrode electrochemical H-type cell.

Electrochemical characterization was performed using a standard H-type cell (Aldrich Nafion®117) equipped with a gas inlet and outlet, which allowed the passage of either N_2 (99.99%) or CO_2 (99.99%) through the solution, to investigate the catalyst properties and CO_2 reduction performance. A standard H-type cell, with a piece of Nafion®117 cation-exchange membrane (H^+ form) as a separator, SnO_2 -50/GDE as the working electrode, a Pt foil electrode as the counter electrode, and an SCE as the reference electrode were used. All electrochemical measurements were performed using a CHI 660E instrument. For the CO_2 reduction measurements, aqueous electrolytes of KHCO_3 concentration from 0.1 to 1.0 mol/L were used as the functional electrolyte to obtain the desired solution concentration; CO_2 gas (99.99%) at 1 atm was bubbled through the solution for 30 min before all measurements.

The electrocatalytic activity of the SnO_2 -50/GDE working electrode was tested using CV and LSV at potential scan rates of 50 and 5 mV/s, respectively, in the potential range 1.0 to -1.6 V vs the SCE. Controlled-potential electrolysis was performed using a CHI 660E electrochemical analyzer, with the same standard H-type cell. An aqueous KHCO_3 (0.5 mol/L) electrolyte was used for the CO_2 reduction measurements; CO_2 gas (99.99%) at 0.1 kPa was bubble through the solution for at least 30 min before each measurement. For long-term electrolysis measurements, a constant potential of -1.70 V vs the standard hydrogen electrode (SHE) was imposed for 28 h. For soluble product measurements, a constant potential of -1.70 V vs the SHE was imposed for 1 h, and the electrolysis currents were recorded continuously. All tests were performed at ambient temperature and pressure.

2.3. Physical characterization and reduction product determination

The crystal-phase X-ray diffraction (XRD) pattern of the SnO_2 -50 NP catalyst synthesized at 180°C for 24 h was obtained using a Philips PW3830 X-ray diffractometer equipped with a $\text{Cu } K_\alpha$ radiation ($\lambda = 0.15406$ nm) source. The intensity data were collected at 25°C in the 2θ range from 0° to 90° , at a scanning rate of $1.20^\circ/\text{min}$. The morphology of the SnO_2 -50 catalyst was examined using SEM (Ultra plus thermal field-emission instrument, Carl Zeiss SMT AG, Germany). The chemical composition of SnO_2 -50/GDE after long-term electrolysis was determined using X-ray photoelectron spectroscopy (XPS; Kratos AXIS Ultra DLD electron spectrometer with $\text{Al } K_\alpha$ X-ray anode source, $h\nu = 1486.6$ eV, at 250 W and 14.0 kV). The solution after CO_2 reduction was diluted 50 times or 100 times (which is convenient for formate detection in the mobile phase)

before determination of the soluble reduction products. The product solution was filtered using a filtration membrane ($0.22\ \mu\text{m}$) and the formate concentrations in the electrolyte were determined directly by ion chromatography (ICS-90, Dionex, USA), using an AS144 mm $\times$ 250 mm separation column and a flow rate of 1 mL/min. The mobile phase used in instrument preparation was a mixed aqueous solution of Na_2CO_3 (3.5 mmol/L) and NaHCO_3 (1.0 mmol/L), and aqueous H_2SO_4 (20 mmol/L) was used as the regenerating liquid.

3. Results and discussion

3.1. Physical characterization of SnO_2 NP catalyst

The morphology and crystal structure (phase composition) of SnO_2 were examined using SEM and XRD, respectively. Fig. 1 shows SEM images at two magnifications of the SnO_2 -50 NP catalyst, which was prepared using a solvent of ethanol : distilled water = 1 : 1. Fig. 1(a) shows that the sample consisted of a mixture of NP and nanosphere aggregates of diameter 500 nm to 1 μm with a highly porous structure. The high-resolution SEM image (Fig. 1(b)) shows that these large NPs and nanospheres have a clear three-dimensional hierarchical structure, consisting entirely of secondary structures composed of aggregated small primary SnO_2 NPs of diameter 20–25 nm. This special morphology provides catalysts with large surface areas, and greatly affects the catalytic activity in CO_2 electroreduction [23,24].

The crystalline structure of as-prepared SnO_2 was confirmed using XRD. The XRD pattern in Fig. 2 shows that the hierarchical structure consisted of small SnO_2 NPs with good phase purity. The increased intensity of the (110), (101), (200),

Fig. 1. SEM images of SnO_2 -50 aggregates at different magnifications. (a) $\times 10000$; (b) $\times 100000$.

Fig. 2. XRD pattern of SnO₂-50 prepared from the solvothermal reaction.

and (211) diffraction peaks, from tetragonal SnO₂, show that the SnO₂ NPs had pronounced crystallinities. The main diffraction peaks from (110), (101), (200), and (211) were broad, which indicated that the SnO₂ NPs were nanocrystalline. The crystallinity was calculated to be 72% and the crystalline grain sizes of these four crystal surfaces were 14.8, 17.1, 15.4, and 15.7 nm, respectively.

3.2. Effects of electrolyte concentration on electrochemical activity in catalytic CO₂ reduction

The CO₂ reduction activity at an SnO₂ electrode prepared from SnO₂-50/GDE was investigated using LSV in N₂- and CO₂-saturated KHCO₃ solution (0.5 mol/L), as shown in Fig. 3(a). The SnO₂-50/GDE showed good catalytic activity in CO₂ reduction, with a negative onset potential at −0.56 V vs the SHE, which is 130 mV more positive than that under N₂. The significant increase in the current in the high potential range under N₂ can be attributed to the reduction of hydrogen ions. However, the higher current in the presence of CO₂ can be ascribed to the reduction of CO₂ and H₂O; the enhanced current indicated reduction to formate. The maximum current density at −1.36 V vs the SHE under CO₂ was about 1.5 times that under N₂.

The effects of electrolyte concentration on the electrochemical catalytic activity in CO₂ reduction using KHCO₃ solutions of various concentrations with CO₂ bubbling and the SnO₂-50/GDE were studied using LSV. The scans (Fig. 3(b)) show that the SnO₂-50/GDE gave a positive onset potential (about −0.56 V vs the SHE) in all the tested electrolytes. Fig. 3(b) shows that when the KHCO₃ solution concentration was 0.1 mol/L, the current density was 15.5 mA/cm². The catalytic activity increased with increasing KHCO₃ solution concentration from 0.1 to 0.5 mol/L, as can be seen from the more positive onset potential and higher current density. The KHCO₃ solution (0.5 mol/L) gave the best catalytic activity for CO₂ reduction, with a maximum current density of 25.0 mA/cm², and the most positive onset potential, i.e., −0.56 V vs the SHE. When the electrolyte concentration was further increased to 1.0 mol/L, the current density decreased sharply to 20 mA/cm², and the CO₂ reduction catalytic activity declined compared to that in KHCO₃ solution (0.5 mol/L).

Fig. 3. Linear sweep voltammetric (LSV) curves of SnO₂/GDE-50. (a) In N₂- and CO₂-saturated KHCO₃ (0.5 mol/L) electrolytes; (b) In CO₂-saturated KHCO₃ electrolyte at different concentrations.

Controlled-potential electrolysis was performed to investigate the effects of electrolyte concentration on the formate yield and faradaic efficiency using the SnO₂-50/GDE. The experiments were performed using CO₂-saturated KHCO₃ solution. The results (Fig. 4) show that formate production depended strongly on the electrolyte concentration. The faradaic efficiency for formate production first increased, reached a maximum value, and then decreased with increasing electrolyte concentration. The highest faradaic efficiency obtained in this research was 56%, in KHCO₃ solution (0.5 mol/L), which is significantly better at a low overpotential (−0.56 V vs the SHE) than the values reported elsewhere [15,22,25,26]. High faradaic efficiencies achieved with Sn-based electrodes have previously been reported [10,15,20]. Formate production began when the electrolyte concentration was 0.1 mol/L; the faradaic efficiency for formate formation was 29% and the amount of formate produced was 82 mg/L. On further increasing the solution concentration from 0.1 to 0.5 mol/L, the faradaic efficiency and formate production increased; the highest faradaic efficiency was obtained using 0.5 mol/L KHCO₃; the corresponding formate production was 292 mg/L. This is consistent with the superior catalytic activity in KHCO₃ (0.5 mol/L) described above. The maximum formate production was 428 mg/L in KHCO₃ (0.7 mol/L). However, the faradaic efficiency decreased sharply with further increases in the electrolyte concentration. HCO₃[−] is directly involved in the reduction of CO₂ to formate;

Fig. 4. Effects of the electrolyte concentration on formate yield and faradaic efficiency for formate production at the SnO₂-50/GDE electrode in CO₂-saturated KHCO₃ solution.

when the HCO₃⁻ concentration is low, CO₂ reduction is controlled by mass transfer. The faradaic efficiency for formate production therefore increased with increasing KHCO₃ concentration. When the concentration increased sufficiently, the formate synthesis was controlled by charge transfer, therefore further increasing the KHCO₃ solution concentration did not increase the faradaic efficiency. In addition, the pH of the system increased with increasing HCO₃⁻ concentration, leading to an improved formate synthesis potential; therefore, the faradaic efficiency at a high formate concentration decreased sharply.

3.3. Effects of electrolyte pH values on catalytic CO₂ reduction

The effects of the electrolyte pH were investigated at pH = 6, 7, 8.3, and 9, because high acidity promotes hydrogen formation and high alkalinity is not conducive to the formation of formic acid. A KHCO₃ solution of concentration 0.5 mol/L, which gives the optimum catalytic activity, was selected as the target electrolyte. The initial pH of the KHCO₃ solution (0.5 mol/L) was 8.3. Fig. 5(a) shows that the onset potential was more positive at pH = 8.3 than at the other pH values tested. At the most negative potential, the cathodic current density was much larger at pH = 8.3 than at other pH values, and almost twice that at pH = 6. These results suggest that the optimum electrolyte pH for electroreduction of CO₂ was 8.3; CO₂ reduction in this mildly alkaline environment maintains the oxide stability. Fig. 5(b) shows that the highest formate production obtained was 259 mg/L, at an electrolyte pH = 8.3; this agrees well with the catalytic activity determined from the LSV curves (Fig. 5(a)). For electrolytes of pH = 6 and 7, formate production, about 180 mg/L, was clearly lower than that achieved at pH = 8.3. However, further increasing the electrolyte from pH = 8.3 to 9.0 caused formate production to decrease slightly. Fig. 5(c) shows the faradaic efficiencies and the total charge *Q* during electrolysis for formate production as a function of electrolyte pH. The trends shown in Fig. 5(c) for the faradaic efficiency are similar to those for formate production shown in Fig. 5(b). The faradaic efficiency for formate production increased with increasing from pH = 6 to 8.3, at which it reached a maximum of

Fig. 5. The effect of the electrolyte pH value on the CO₂ reduction: (a) LSV curves; (b) Formate production; (c) Faradaic efficiencies of formate and total charge *Q* on the SnO₂-50/GDE electrode in CO₂-saturated KHCO₃ solution (0.5 mol/L).

56%, and the total charge reached 126 C. As the pH value increased further, the faradaic efficiency began to drop. This may be because the alkaline environment did not benefit formate production.

3.4. Faradaic efficiency for long-term CO₂ electrolysis to formate

Fig. 6(a) shows the degradation rates of the faradaic efficiency for formate production on SnO₂-50/GDE for 28 h. It was previously reported [3,16,17] that a high faradaic efficiency was observed during initial electrolysis, but the efficiency then decreased significantly. In the first hour, the formate faradaic efficiency reached 56%, which was the highest value during the first 5 h, and the corresponding formate production was 419

Fig. 6. (a) Variations of the faradaic efficiency and formate production for 28 h long time electrolysis; (b) High-resolution F 1s XPS spectrum of SnO₂-50/GDE electrode after electrolysis in CO₂-saturated KHCO₃ solution (0.5 mol/L); (c) Full spectrum scanning.

mg/L. When CO₂ reduction was performed for 5 h, the formate faradaic efficiency sharply decreased to 44%, and formate production increased sharply and almost linearly to 1779 mg/L. After CO₂ electrolysis for 17 h, the faradaic efficiency decreased significantly, and was almost half that in the first hour. As the electrolysis time increased from 17 to 28 h, the faradaic efficiency and formate production both decreased steadily; the faradaic efficiency decreased to 24% after 28 h. As previously reported, the faradaic efficiency for formate production changes with electrolysis time. This can be explained by formate oxidation on the anode or contamination of the SnO₂-50/GDE cathode with impurities [3,16,17]. We determined the cathode composition before and after electrolysis using XPS. The results suggest that the decrease in the faradaic efficiency was caused by deposition of trace amounts of contaminant ions on the SnO₂-50/GDE surface, mainly fluoride as

shown in Fig. 6(b). The presence of fluoride hindered CO₂ reduction to formate on the SnO₂-50/GDE surface. The full spectrum scan (Fig. 6(c)) showed that a large amount of fluoride, present as an impurity in the KHCO₃ electrolyte, was deposited on the electrode. The high-resolution F 1s XPS had a peak at 688.8 eV, which is consistent with F 1s bound to carbon in a straight chain.

4. Conclusions

Nanostructured SnO₂ particles were synthesized using a facile hydrothermal self-assembly method, and their use as a catalyst in CO₂ electroreduction was investigated. SEM showed that the SnO₂ NPs had a three-dimensional hierarchical structure, and consisted of a mixture of NP and nanosphere aggregates of diameter 500 nm to 1 μm, with a highly porous structure. The catalytic activity and formate selectivity depended strongly on the electrolyte concentration. The results showed that the catalytic activity increased with increasing electrolyte concentration from 0.1 to 0.5 mol/L, at which the best catalytic activity was obtained. The highest faradaic efficiency obtained was 56% in KHCO₃ (0.5 mol/L). This was attributed to direct involvement of HCO₃[−] in the reaction; formate formation was controlled by mass transfer and charge transfer at low and high HCO₃[−] concentrations, respectively. The electrolyte pH affected formate production during CO₂ reduction. Our results suggest that pH = 8.3 was the optimum electrolyte pH for electroreduction of CO₂; CO₂ reduction in a mildly alkaline environment maintained oxide stability. A catalyst stability test for 28 h showed degradation of the faradaic efficiency for formate production on SnO₂-50/GDE. The decreased faradaic efficiency was caused by deposition of fluoride ions on the SnO₂-50/GDE surface, as shown by XPS. The presence of fluoride hindered the reduction of CO₂ to formate on the SnO₂-50/GDE surface.

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Graphical Abstract

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Electrochemical CO₂ reduction to formic acid on crystalline SnO₂ nanosphere catalyst with high selectivity and stability

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The influence of electrolyte conditions on selectivity and activity were studied by electrochemical characterization. A faradaic efficiency of 56% HCOOH was achieved at -1.7 V vs SHE. The deposition of the trace fluoride ions has some influences on formate information.

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高选择性和稳定性SnO₂纳米催化剂上CO₂电化学还原为甲酸付奕舒^a, 李亚楠^a, 张霞^a, 刘予宇^{b,c,#}, 周晓东^d, 乔锦丽^{a,*}^a东华大学环境科学与工程学院, 上海201620, 中国^b太原理工大学环境科学与工程学院, 山西太原030024, 中国^c东北大学大学院环境科学研究科, 仙台980-8579, 日本^d南卡罗来纳大学化学工程系, 哥伦比亚, 南卡罗来纳州29208, 美国

摘要: 作为最重要的还原产品, 甲酸是CO₂还原中非常有价值的液体燃料. 已有研究报道, Sn类金属电极对甲酸生成有很好的催化活性, 所用电解液均为KHCO₃溶液(0.5 mol/L), 但多数研究没有对其电解液条件的影响给出清晰解释. 一般而言, 电解液pH值会影响H₂O和CO₂还原的电极电势, 酸性环境有利于氢析出, 碱性环境则不利于甲酸形成. 在中性偏碱性环境, CO₂电解可以提供维持氧化物稳定性的可能性. 同时, 电解质浓度也极大地影响甲酸形成. 研究表明, 当在固定床反应器中使用Sn颗粒电极, 在KHCO₃溶液(0.5 mol/L)中甲酸的法拉第效率比K₂CO₃溶液(0.1 mol/L)的法拉第效率更大. 我们研究组通过简单的水热自组装法成功制备了一种纳米结构SnO₂催化剂. 其中SnO₂-50纳米催化剂由三维多级结构组成, 为纳米颗粒和微米球的聚集体, 其中含有直径为500 nm–1 μm的高度多孔结构. 该催化剂负载气体扩散电极用于CO₂电化学还原, 表现出优异的CO₂还原催化活性和甲酸选择性. 与其他文献报道相比, 该电极具有明显的低过电位(–0.56 V vs. SHE). 经研究发现, 这与甲酸形成由传质和电荷传递过程控制有关, 同时CO₂还原强烈依赖于电解液条件. 此外, 催化剂的电化学性能和甲酸选择性强烈依赖于电解液浓度. 在0.5 mol/L KHCO₃电解液中, 当电解液浓度为0.1–0.5 mol/L时, 催化性能随电解液浓度增加而提高, 同时在电解液浓度为0.5 mol/L时催化性能达到最佳, 获得56%的甲酸法拉第效率, 这主要是由于HCO₃[–]直接参与反应的结果. 在电解液浓度较低时, 甲酸的形成为传质控制, 而在电解液浓度较高时, 甲酸的形成为电荷传递控制.

同时我们发现在形成甲酸过程中, 电解液pH值对CO₂电化学还原过程有很大影响. 为了研究电解液pH值影响, 重点

考察了 pH 值分别为 6, 7, 8.3 和 9 时的电位值, 其原因是酸性过高有利于氢气形成, 碱度过高不利于甲酸形成. 结果表明, pH = 8.3 的电解液为 CO₂ 还原的最佳电解液条件. 此外, 在最负的电势下, 电解液 pH=8.3 时, 阴极电流密度比其他电解液都大, 几乎是 pH=6 的电解液的 2 倍. 此时在中性偏碱性环境下, CO₂ 还原可以提供维持氧化物稳定性的可能性. 当电解液 pH 增加到 9.0 时, 甲酸产量及法拉第效率略有下降, 可能是碱性环境不利于甲酸形成.

同时, 对 SnO₂-50 纳米催化剂经 28 h 电解后的甲酸法拉第效率的衰减机制进行了深入研究. 结果表明, 随着电解时间延长, 甲酸法拉第效率衰减. 电解时间为 1–28 h 时, 法拉第效率和甲酸产量均保持平稳下降趋势, 28 h 后法拉第效率由初始的 56% 降至 24%. 有文献报道, 甲酸法拉第效率随电解时间的改变主要是由于阳极上甲酸的氧化或阴极上杂质的污染. 为了证明阴极电解后的状态, 我们对 SnO₂-50/GDL 阴极电解前后的 XPS 谱进行了分析. 结果发现, 法拉第效率的下降是由于痕量氟离子沉积到 SnO₂-50/GDL 电极表面, 这些痕量氟离子可能来自反应槽, 阻碍电极表面 CO₂ 电化学还原为甲酸.

关键词: 二氧化碳还原; 二氧化锡; 甲酸; 法拉第效率

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