



Development of rolling tin gas diffusion electrode for carbon dioxide electrochemical reduction to produce formate in aqueous electrolyte



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HIGHLIGHTS

- A rolling gas diffusion electrode is developed for CO₂ electrochemical reduction.
- CO₂ electrochemical reduction is dominated by the electron transfer rate.
- Excellent Faraday efficiency towards formate formation is obtained.
- Formate is released into the electrolyte easily and the catalyst is stable.

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ABSTRACT

Carbon dioxide electrochemical reduction to produce formate (CERPF) basing on gas diffusion electrode (GDE) is a promising carbon cycle technology. However, its performance is still restrained by formate accumulation and catalyst loss in the catalyst layer (CL). In this study, a novel rolling Sn-loading GDE (SGDE) without porous hydrophilic CL is developed. The electrochemical behavior of CERPF on the SGDE is investigated by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The electrochemical performance of the SGDE for CERPF is assessed by constant potential electrolysis. The results show that the CERPF process basing on the SGDE performs a double charge transfer and is dominated by the electron transfer rate. The highest partial current density for CERPF ($17.43 \pm 2.60 \text{ mA cm}^{-2}$) and corresponding Faraday efficiency ($78.60 \pm 0.11\%$) are obtained under the applied potential of $-1.8 \text{ V vs Ag/AgCl}$ in 0.5 M KHCO_3 solution. The produced formate is allowed to be released into the electrolyte easily and the catalyst holds steady during the CERPF process. Since its excellent electrochemical performance and low fabrication cost (ca. $30 \text{ \$ m}^{-2}$), bright prospect for SGDE application in CERPF can be convinced.

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1. Introduction

Carbon dioxide (CO₂) concentration in the atmosphere now increases each year by about 2 ppm, continuing the inexorable rise toward 400 ppm and beyond [1,2]. It definitely leads to an ascent of the temperatures at the troposphere (particularly on the earth's surface), an increase in the precipitation, and a raise of the sea level [3]. Reducing CO₂ atmospheric concentration has therefore become a critical issue [4]. Many attempts have been made, such as carbon capture and sequestration [5], chemical usage [6], photochemical reduction [7], and electrochemical reduction [8]. Of those methods,

electrochemical reduction can not only reduce CO₂ emission, but also produce a variety of valuable materials such as formic acid/formate, carbon monoxide, methane, ethylene, methanol, and ethanol [9] under mild conditions involving moderate temperature and atmospheric pressure [8]. Formic acid is an additive widely used in the field of medicine, chemical industries, as well as the leather industry [8]. For CO₂ electrochemical reduction to produce formate (CERPF) with aqueous electrolyte, solid electrodes are widely used while CO₂ is provided by the continuous sparging in the electrolyte. Owing to the relatively low solubility of CO₂ in water under ambient conditions (ca. 0.033 M), the current density is severely limited by the mass transfer of CO₂ from the bulk to the electrode surface. It is estimated that the mass transfer limiting current density for CERPF is 6 mA cm^{-2} [10]. In order to break through the mass transfer limitation and increase the current density for CERPF, gas diffusion electrode (GDE) has been

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introduced [4,11]. The typical GDE is a porous composite electrode, usually assembled by a gas diffusion layer (GDL), a current collector and a catalyst layer (CL) [11]. CERPF occurs in the gas–liquid–solid three phase interface (TPI), being located in the CL [11]. In the CERPF system where GDE is used as the cathode, CO₂ in the atmosphere typically diffuses through the hydrophobic region of the GDL to the reaction site (i.e. TPI) in the porous hydrophilic region of the CL [12,13]. To date, two types of GDEs have been widely used for CERPF. In the first one, the CL is composed of catalyst, carbon black and polytetrafluoroethylene (PTFE) binder, where PTFE allows forming the TPI. While the GDL consists of carbon black and PTFE binder [14]. In the second one, the CL consists of catalyst and Nafion binder, where Nafion allows forming the hydrophilic TPI. The GDL is typically made of carbon paper which is wet-proofed with PTFE [15,16]. It has been reported that the current density for CERPF can be increased by one to two orders of magnitude with GDE [10,11,14].

Although these results are exciting, several problems still need to be solved. For example, the two types of GDEs noted above are all suffering from the accumulation of liquid-phase reaction products in the reaction sites of the CL due to its porosity and hydrophilicity [10,16]. Moreover, the second GDE noted above is also suffering from catalyst loss in the CL possibly because of poor adhesion of Nafion binder [17,18]. Thus, it is necessary to develop a new GDE to solve these problems as well as achieve excellent electrochemical performance for CERPF. In addition, it is also necessary to investigate the electrochemical behavior of CERPF basing on GDE, which can give us abundant information to improve the CERPF process and electrode performance [19]. So far, the electrochemical behavior of CERPF basing on GDE is less studied [15,20–24].

In the present work, a novel rolling Sn-loading GDE (SGDE) was developed. In order to avoid the accumulation of liquid-phase reaction products, the porous hydrophilic CL is abandoned. It only consists of a GDL and a copper mesh plated with Sn, where Sn plays a role of catalysis for CERPF and the copper mesh acts as the current collector. The morphology of the SGDE was examined by scanning electron microscope (SEM). The electrochemical behavior of CERPF on the SGDE was investigated by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The assessment for the electrochemical performance of the SGDE for CERPF was carried out under constant potential electrolysis. The optimal current density and Faraday efficiency for formate production via the CERPF process on the SGDE were achieved by regulating the electrolysis potential and electrolyte concentration. In addition, the morphology and crystal structure of Sn catalyst in the SGDE before and after the constant potential electrolysis were examined by SEM and X-ray diffraction (XRD), respectively.

2. Experimental

2.1. SGDE fabrication

The SGDE consisted of a GDL and a Sn-loading copper mesh. The GDL was prepared firstly by distributing conductive carbon black (Jinqiushi Chemical Co. Ltd., Tianjin, China) into an appropriate amount of ethanol in a beaker and ultrasonic agitated for 20 min. It was followed by dripping PTFE suspensions (60 wt%, Hesen, Shanghai, China) into a blend slowly still with ultrasonic agitation. The mass ratio of conductive carbon black and PTFE was 3:7. After another 20 min, the blend was stirred at 353 K bath to give a dough-like paste. The paste was then rolled to a gas diffusion film of 0.15 mm thickness by a rolling-press device which demarcates the space of the two rolls by two pressure gages. The Sn-loading copper mesh was made as follows: the copper mesh (60 mesh, 70 μm wire diameter) was first immersed in acetone for 24 h and then etched in hydrochloric acid (10%). After washed by the distilled water, it was immersed in an

electroless acidic tin plating bath consisting of 0.02 M stannous sulfate, 0.22 M sulfuric acid and 0.6 M thiourea at 319 K. Finally, the Sn-loading copper mesh was rolled on the GDL and sintered for 20 min at 613 K to obtain the final electrode of 0.2 mm thickness. More details of the SGDE (fabrication method and morphology) were described in the Supporting information (Figs. S1 and S2).

2.2. Electrochemical measurements

The electrochemical measurements containing CV and EIS were tested by an electrochemical workstation (CHI600D, Shanghai Chenhua Instruments Co., China) at ~298 K in a conventional three-compartment electrochemical cell (Fig. S3). The anodic chamber and the cathodic chamber were separated by a proton exchange membrane (PEM, Nafion117, 4 cm diameter, Dupont, USA). Specially, a gas chamber was designed. The SGDE (7 cm²) and Pt sheet (1 cm², Tianjin Aidahengsheng Technology Co. Ltd., China) were chosen as the working electrode and counter electrode, respectively. The reference electrode was Ag/AgCl electrode (sat. KCl, Tianjin Aidahengsheng Technology Co. Ltd., China), being extended to the surface of the working electrode by using a Luggin capillary. All of the potential values were in reference to Ag/AgCl unless otherwise noted. The electrolyte was 0.1 M KHCO₃ solution. CV was conducted from -1.8 V to 0 V under different scan rates from 0.1 V s⁻¹ to 1.2 V s⁻¹. EIS was performed over a frequency range of 100 kHz–0.1 Hz with the AC signal amplitude of 0.005 V superimposed on different dc potentials in the range from -1.1 V to -1.3 V. Before each measurement, the electrolyte was degassed with N₂ (99.99%, Tianjin Sizhi gas Co. Ltd., China) for 30 min for a baseline. After that N₂ or CO₂ (99.99%, Tianjin Sizhi gas Co. Ltd., China) was continuously sparged in the gas chamber through the measurement.

2.3. CERPF tests

CERPF tests were done at ~298 K under a constant potential mode in the same three-compartment electrochemical cell as described in Fig. S3, where the electrochemical reactions at both anode and cathode sides are also presented. Electrolyte was circulated by using a peristaltic pump (BT-yz1515, Tianjin Sabo Instruments Co., China) with a flow rate of 25 mL min⁻¹. The flow rate of CO₂ was 30 mL min⁻¹. An electrolytic time of 30 min was applied for each batch. The catholyte was sampled after each batch of electrolysis for analysis.

2.4. Analysis and calculation

The morphology of the SGDE was observed by using SEM (S-3500N, Hitachi Limited, Japan and SUPRA 55/55VP, ZEISS Co., Germany). The crystal structure of Sn catalyst in the SGDE was characterized by XRD (Rigaku D/MAX-2500, Cu Kα, Japan) with a scan rate of 4° min⁻¹ in a 2θ range from 20° to 90°.

The Nyquist plot of impedance was simulated by Zsimpwin software (ver. 3.10).

The production of formate was analyzed by a high performance liquid chromatography (L6-P6, Beijing Puxitongyong Instruments Co., China) equipped with a C18 reversed phase column (250 mm × 4.6 mm × 5 μm) with UV detection at 210 nm. The mobile phase was 10% methanol aqueous solution at 0.6 mL min⁻¹. The pH of the liquid sample was adjusted to pH = 2 in advance. The Faraday efficiency of formate (FE) was calculated according to Equation (1) as follows:

$$FE = \frac{n_{\text{formate}} \times n \times F}{\int_0^t Idt} \times 100\% \quad (1)$$

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