



Electrochemical CO₂ reduction to formate on Tin cathode: Influence of anode materials



Hao Jiang^a, Yuemin Zhao^{b,*}, Lizhang Wang^{a,*}, Ying Kong^a, Fei Li^a, Peng Li^c

^a School of Environment Science and Spatial Informatics, China University of Mining and Technology, Xuzhou, Jiangsu 221116, PR China

^b School of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou, Jiangsu 221116, PR China

^c School of Water Resource & Environmental Engineering, East China Institute of Technology, Nanchang, Jiangxi 330013, PR China

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ABSTRACT

In this work, electrochemical CO₂ reduction to formate on Tin cathode coupled with Pt, IrO₂-Ta₂O₅/Ti and β-PbO₂/Ti anodes was investigated by electrochemical tests and lab-scale experiments. The scanning electron microscopy (SEM) and X-ray diffraction (XRD) patterns of the prepared anodes demonstrate the layers doped on Ti plates exist in tetragonal phase of IrO₂ and β-PbO₂ crystals with dendritic and pyramid shapes, respectively, benefiting to increasing anode area in water electrolysis. The electrochemical measurements including cyclic voltammetry (CV), polarization curve and electrochemical impedance spectroscopy (EIS) performed in Na₂SO₄ solution indicate the IrO₂-Ta₂O₅/Ti anode possesses higher oxygen evolution activity compared with those of Pt and β-PbO₂/Ti ones; this is because of its excellent abilities in enlarging electrode area, decreasing oxygen evolution potential (OEP) and increasing oxidation kinetics for water decomposition, which effectively enhances the CO₂ reduction. The faradic and energy efficiencies of IrO₂-Ta₂O₅/Ti anode are 40.2% and 27.4%, raising by ratios of 7.2%, 81.1% and 12.8%, 242.5% to those of Pt and β-PbO₂/Ti, respectively, at applied current of 0.3 A and reaction time of 24 h during formate production. Moreover, the power consumption lowered to 13.0 kW h/kg formate on IrO₂-Ta₂O₅/Ti anode was achieved and it is much less than those on other two anodes, offsetting about 53.8% of the input energy if prices of the formate and electricity are overall taken into account. Therefore, anode materials highly affect the reductive kinetics and employment of anodes with lower OEP is a cost-effective strategy for electrochemical CO₂ reduction.

1. Introduction

During the past decades, many measurements e.g. carbon dioxide (CO₂) geological storage [1], biological electrolysis [2], photo-catalysis [3], hydrogenation [4] and electro-reduction [5–7] have been investigated to relieve the greenhouse effect of atmospheric CO₂. Among these feasible ways, electrochemical CO₂ reduction has attracted much attention because of its high yield, clean and controllable production and environment-friendly properties. Numerous valuable products could be produced from CO₂ electro-reduction, such as formate (HCOO⁻) [8], carbon monoxide (CO) [9], methanol (CH₃OH) [10–12], methane (CH₄) [13,14], ethanol (C₂H₅OH) [15,16], ethylene (C₂H₄) [17,18] and n-propanol (C₃H₇OH) [19], etc. Additionally, it should be pointed out that the kinds of products and faradic efficiency (FE) depend on the electrode materials; for example, formate was obtained on Tin (Sn) cathode with a higher reduction rate (3.21 mmol m⁻² s⁻¹) and FE of 70% [20], while methanol was synthesized on Cu₂O/ZnO gas diffusion electrode at a maximum rate of 4.42 μmol m⁻² s⁻¹ and FE of

25.6% [21]. Although electro-reduction provides an effective route for CO₂ utilization, the out-of-balance between the demanded and generated energy still highly restricts wide spread of such a promising technology [22,23].

As known that CO₂*⁻ (CO₂ + e⁻ → CO₂*⁻) is the necessarily reactive intermediate for generation of the products at different cathodes and its equilibrium potential is higher to -2.141 V (vs. SCE) [24,25] and under such circumstances, it is very difficult to optimize its reductive potentials. It should be noted that cathodic reduction is only a half-reaction in electrolysis and naturally the required potential for anodic oxidation e.g. oxygen evolution determined by anode materials would affect the overall efficiency and voltage in electrochemical CO₂ reduction. In this sense, employment of anode with lower oxygen evolution potential (OEP) maybe can provide another feasible insight for cost-effective strategy in CO₂ conversion to useful chemicals/fuels. However, till then only a few researchers have mentioned the effect of anode materials on CO₂ reduction, e.g. Yadav [26] and Zhang et al. [27] both reported the significant difference of the FE or energy efficiency (EE)

* Corresponding authors at: No. 1, Daxue Road, Quanshan District, Xuzhou City, Jiangsu Province, 221116, PR China.

E-mail addresses: ymzhao.paper@126.com (Y. Zhao), wzlh0731@cumt.edu.cn (L. Wang).

between Co₃O₄, Ir_xSn_yRu_zO₂/Ti and Pt anodes for formate production. Nevertheless, the influence of oxygen evolution ability of anodes on the reduction of CO₂ has not been discussed in detail.

In this work, anodes with lower OEP (IrO₂-Ta₂O₅/Ti and Pt) and higher OEP (β -PbO₂/Ti) were used to investigate the influence of anode materials on electrochemical CO₂ reduction. Numerous measurements including scanning electron microscopy (SEM), X-ray diffraction (XRD), cyclic voltammetry (CV), polarization curve and electrochemical impedance spectroscopy (EIS) were conducted to characterize microstructure, phase composition and oxygen evolution ability of the three anodes. Afterwards, Sn was selected as cathode due to its easy obtainment, cheap price and excellent ability for formate production [28,29], a chemical usually used in pesticides, leather, dyes, pharmaceutical and rubber industries [30,31]. Moreover, the FE, EE, power consumption and output-input ratio were calculated to quantitatively evaluate the influence of anode materials on the CO₂ conversion performance.

2. Experimental

2.1. Materials and electrode preparation

All chemicals used for sample measurement were in analytical pure (Sinopharm Chemical Reagent Corporation, China). Highly pure carbon dioxide ($\geq 99.99\%$) was provided by Xuzhou Luyou Industrial Gas Plant (China) and Pt (99.99%) and Ti plates were purchased from Qixin Company (China).

Prior to the anode preparation, Ti plates were polished with 120-grit sandpaper, then degreased in a boiling 40% NaOH solution for 2 h, etched in a 15% H₂C₂O₄ at 98 °C for 2 h, and washed several times by deionized water. Thermal-decomposition at 500 °C was employed for preparation of IrO₂-Ta₂O₅/Ti electrode and the precursors H₂IrCl₆ and TaCl₅ were dissolved in hydrochloric acid and C₂H₅OH with the molar ratio of Ir/Ta is 7:3, and the total metal concentration was kept at 0.5 M. The β -PbO₂/Ti anode was prepared by electrodeposition conducted in an acid solution composition consisted of 0.5 M Pb(NO₃)₂, 0.2 M Cu(NO₃)₂, 0.1 M HNO₃ and 0.04 M NaF at 65 °C for 1 h and at a current density of 15 mA/cm².

2.2. Physic-chemical characterization

The morphology and phase composition of the IrO₂-Ta₂O₅/Ti and β -PbO₂/Ti were characterized by SEM (Nova Nano SEM 450, FEI, Czech) and XRD (D8 advance, Bruker, Germany). CV, polarization curve and EIS were performed with a CS310 electrochemical workstation (Wuhan CorrTest Instrument Co., Ltd., China) in a three-electrode cell consisted of 0.3 M Na₂SO₄. The cell consists of the IrO₂-Ta₂O₅/Ti, Pt or β -PbO₂/Ti electrode with an area of 4 cm² as the working electrode, Pt as the counter electrode, and a SCE as the reference electrode. CV measurements were conducted between 0 and 1.8 V (vs. SCE) at a scan rate of 50 mV/s. Polarization curve were performed between 0 and 2.5 V (vs. SCE) at scan rate of 1 mV/s. The EIS was obtained over their oxygen evolution potential and the frequency ranged from 100 kHz to 10 mHz. Formate produced in the cathodic zone was directly quantified by ion chromatography (ICS-900, Dionex, USA), using a hybrid of 4.5 mM Na₂CO₃ and 0.8 mM NaHCO₃ as the eluent at a flow-rate of 1 mL/min.

2.3. Electrochemical experiments

Electrochemical CO₂ reduction experiments were performed at 0.3 A using a DC power supply (WYJY-30V10A, Wenkai Company, China). The reactor with size of 50 × 40 × 100 mm was made of polymethyl methacrylate plastics, it consisted of a cathode and an anode chamber separated by a cation exchange membrane (CEM) (CMI-7000, Membranes international Inc., USA). Sn plates (40 × 40 mm) were employed as cathode, and they were etched in aqua regia before electrolysis experiments so as to remove the oxide layer. IrO₂-Ta₂O₅/Ti,

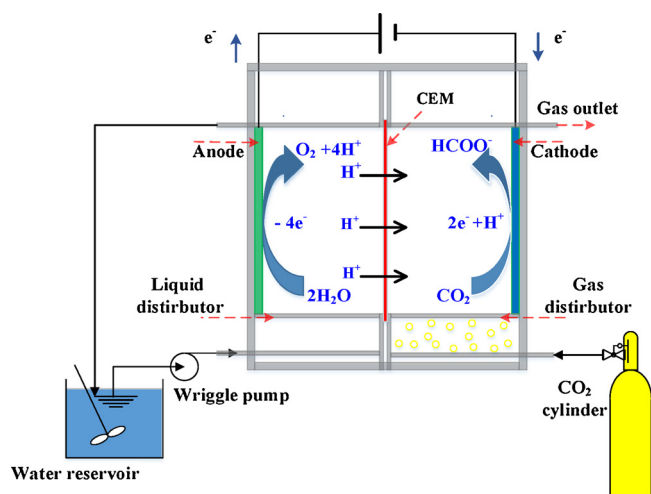


Fig. 1. The schematic for electrochemical CO₂ reduction.

Pt or β -PbO₂/Ti (40 × 40 mm) was selected as anode. An aqueous solution 0.5 M KHCO₃ was used as supporting electrolyte in the cathode chamber. Before the start of each experiment, CO₂ was bubbled into the KHCO₃ solution until saturation, and CO₂ was continuously pumped into the cathode chamber at a flow rate of 250 ml/min during electrolysis. The anolyte used was 0.3 M Na₂SO₄ aqueous solution, which was recirculated between the anolyte storage tank and the anode chamber using peristaltic pump, and the flow rate of 25 mL/min. The schematic of electrochemical reduction of CO₂ was shown in Fig. 1.

2.4. Analytical methods

The faradic efficiency for formation of formate is calculated as follows [32]:

$$FE(\%) = \frac{2mF}{It} \times 100 \quad (1)$$

where the number 2 represents two moles electrons required for formation of 1 mol formate from CO₂; m is the moles of the produced formate, F the Faraday constant (96,485 C/mol), I the applied current (A) and t the electrolysis time (s).

The energy efficiency for electrochemical reduction of CO₂ to formate could be calculated by the following equation:

$$EE(\%) = \frac{U_{\text{theo}} I_{\text{theo}} t_{\text{theo}}}{\bar{U}_{\text{cell}} It} \times 100 \quad (2)$$

where U_{theo} , I_{theo} , t_{theo} are the theoretical cell voltage (V), current density (A) and electrolysis time (s) respectively, \bar{U}_{cell} is the average cell voltage. U_{theo} and \bar{U}_{cell} can be obtained by Eqs. (3) and (4):

$$U_{\text{theo}} = E_a^0 - E_c^0 + IR \quad (3)$$

$$\bar{U}_{\text{cell}} = \int_0^t U(t) dt / t \quad (4)$$

where E_a^0 is 1.23 V (vs. RHE) [33], determined by the standard electrode potential of oxygen evolution reaction (OER); E_c^0 is -0.43 V (vs. RHE at pH 7.0) [34], which denotes the standard electrode potential for CO₂ conversion to formate; R is the overall resistances of the electrolyte, membrane and electrodes, and $U(t)$ the instantaneous voltage at electrolysis time t .

The power consumption (E_{sp} , kWh/kg formate) by using the following equation:

$$E_{\text{sp}} = \frac{\bar{U}_{\text{cell}} It}{Vc} \quad (5)$$

where V is the electrolyte volume in the cathode chamber, and c the formate concentration.

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