



Studies on the faradaic efficiency for electrochemical reduction of carbon dioxide to formate on tin electrode



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HIGHLIGHTS

- pH value in CO₂-saturated KHCO₃ solution has an effect on CO₂ reduction.
- Oxidation of formate is main reason for efficiency decreasing with time lasted.
- Formate oxidization accelerates as formate concentration in electrolyte increases.
- Faradaic efficiency is >91% when formate concentration is <0.01 mol L⁻¹.

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ABSTRACT

The electrochemical reduction of carbon dioxide (CO₂) on Sn electrode has been investigated in aqueous KHCO₃ solution by cyclic voltammetry and controlled potential electrolysis. The results show that the faradaic efficiency for producing formate is affected by the electrolysis potential, the concentration and pH value of KHCO₃ solution; the reason for the decrease of faradaic efficiency as the electrolysis time lasts is the oxidation of formate on the Pt anode. When the concentration of the formate in the electrolyte is less than 0.01 mol L⁻¹, the faradaic efficiency can reach above 91%.

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1. Introduction

The transformation of CO₂ into value-added chemicals and fuels has attracted much attention in recent years. Up to now, many chemical, photochemical, electrochemical and photoelectrochemical methods have been investigated for the purpose [1–5]. Among these routes, electrochemical reduction of CO₂ is a promising process because the product can be selectively controlled by changing the electrolysis condition, such as electrode [6–10] and electrolyte [11,12]. To date, formic acid [13], carbon monoxide [14], methanol [15], and oxalic acid [16] have been prepared by this way. Electrochemical reduction of CO₂ also supplies a route that makes full use of the renewable photovoltaic, wind and marine energies that depend seriously on weather [17,18].

The electrode materials include various pure metals, coordination compounds or alloys, which play very important roles in

determination of the products [19–26]. For example, Sn, Pb, Hg and In electrodes tend to produce formate in aqueous solution with high faradaic efficiency [27,28]. It is very interesting that faradaic efficiency for formic acid production in electrochemical reduction of CO₂ in aqueous KHCO₃ solution in a fixed-bed reactor was 90% at 30 min, but it decreased to 30% after 2 h. The reason for this decrease was suggested to be the oxidation of formic acid [29]. However, another report revealed that the decrease should be resulted from the deposition of Zn on the surface of Sn electrode during electrolysis [30]. These two reports have provided different explanations for the decrease of faradaic efficiency.

Agarwal et al. discussed the engineering and economic feasibility of large-scale electrochemical reduction of CO₂ to formate, and suggested that this process can be operationally profitable [31]. Therefore, it is important to find out what exactly determines the faradaic efficiency of the electrochemical reduction of CO₂.

In this paper, Sn was chosen from the metals with high faradaic efficiency for producing formate because of its low cost and relatively low toxicity. The influences of key variables like the electrolysis

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potential, the concentration and pH value of the KHCO_3 solution on the faradaic efficiency for producing formate were studied to obtain the optimal electrolysis condition. The most importantly, it is to find out the reason why the faradaic efficiency decreases.

2. Experimental

All the materials were purchased ($\geq 99.5\%$) from commercial companies, and used without further treatments.

Scanning electron microscope (SEM) images were taken with a Hitachi S-4800 microscope at an acceleration voltage of 15 kV. The pH values of all the electrolytes were determined by a pen-like pH meter (CT-6022, Shanghai Rentong Meter Co., Ltd., China).

The products in the electrolyte were directly analyzed by ion chromatography (ICS-900 Dionex). The column was an IonPac AS11-HC anionic column using 0.02 mol L^{-1} KOH as the mobile phase at the rate of 1 mL min^{-1} . $10 \mu\text{L}$ of the electrolyte were used for each time. The amount of formate in the electrolyte was also determined by titration (see Supporting information for details).

The cell used here is an airtight and undivided glass cell equipped with a gas inlet and outlet which is able to pass the either N_2 (99.99%) or CO_2 (99.99%) through the solution. A conventional three-electrode system was used during the measurements. The working electrode was always a Sn plate with a geometric surface area of 1 cm^2 . To obtain repeatable results, each Sn plate electrode is used only once. A Pt plate ($1 \times 1 \text{ cm}^2$) and an Ag/AgCl electrode (sat. KCl) were used as counter and reference electrodes, respectively. The electrolyte used was 40 mL of KHCO_3 aqueous solution. All experiments were performed under room temperature and ambient pressure.

Cyclic voltammetry (CV) experiments were carried out using a CS350 electrochemical workstation (Wuhan CorrTest Instrument Co., Ltd., China) after purging the solution with either N_2 or CO_2 for 30 min for the actual determinations. The current density (j) is determined on the geometrical area of the electrode.

Controlled potential electrolysis was carried out using a LAND CT2001C cell performance-testing instrument (Wuhan Electronics Co., Ltd., China) in the same three-electrode electrochemical cell. The electrolyte was saturated with CO_2 before each electrolysis process, and CO_2 gas was continuously aerated at a flow rate of 10 mL min^{-1} during the electrolysis process. The electrolysis experiments were terminated when the total charge passed reached a certain value. The average current density (j_a) is expressed as the total current divided by the geometric surface area of the Sn electrode (1 cm^2) for all cells.

The faradaic efficiency for the formation of formate (f) is determined by Equation (1):

$$f = n_{\text{formate}} nF/Q \quad (1)$$

where n_{formate} is the moles of the formate produced; n represents the number of electrons required for the formation of one molecule of formate from CO_2 ($n = 2$ here); F is Faraday's constant (96485 C mol^{-1} of electrons); and Q is the total charge in Coulomb passed across the electrode during the electrolysis.

3. Results and discussion

3.1. CV measurements

Fig. 1 depicts the voltammograms of the Sn electrode in 0.1 mol L^{-1} KHCO_3 solution after being bubbled with N_2 or CO_2 for 30 min. The anodic peaks between -0.3 and -0.6 V and the cathodic peak between -0.8 and -1.1 V in CV curves can be attributed to the formation and the reduction of tin oxides in basic

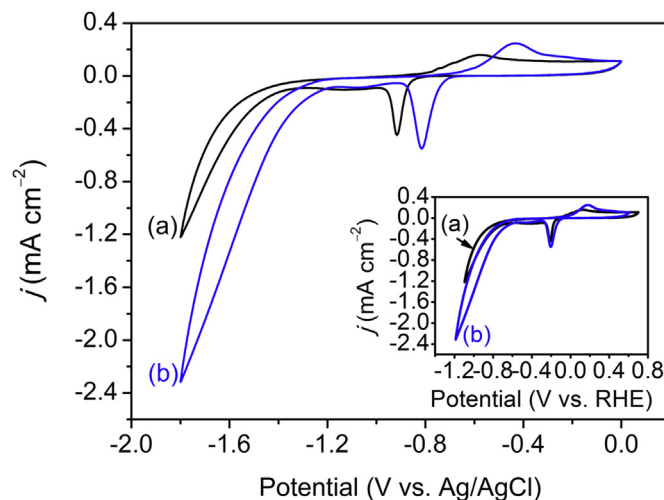


Fig. 1. Cyclic voltammograms on the Sn electrode in 0.1 mol L^{-1} KHCO_3 solution after being bubbled with N_2 (a) and CO_2 (b) for 30 min. The inset is the same cyclic voltammograms based on the RHE reference scale. The scan rate was 0.05 V s^{-1} .

media respectively [32]. On the cathodic end of the voltammograms, sharp increases of the current densities can be observed under both N_2 and CO_2 (curves a and b in Fig. 1), which should be most probably caused by the reduction of water (under N_2) and CO_2 (under CO_2).

Theoretically, it can be predicted that the pH value of the KHCO_3 solution will be lowered if the solution is saturated with CO_2 because of the reaction (2):



Experiments did show that the pH value of the KHCO_3 solution increases continuously if it is bubbled with N_2 because of the dissipation of CO_2 , but it decreases if it is saturated with CO_2 (see Tables S1 and S2 in Supporting information for details). If the KHCO_3 solution has been bubbled with N_2 and CO_2 for 30 min, the pH values are 8.69 and 6.98 respectively.

As the pH value seriously affects the electrode potentials for the reduction of H_2O and CO_2 :



the CV curves should be adjusted to exclude the effect of pH. By converting the reference scale from Ag/AgCl to RHE using $E(\text{vs. RHE}) = E(\text{vs. Ag/AgCl}) + 0.1988 \text{ V} + 0.0591 \text{ V} \times \text{pH}$, the cyclic voltammograms is re-plotted in the inset of Fig. 1. It can be seen that peaks related to the formation and the reduction of tin oxides almost overlapped [32]; and in the left end, the potential at the same current under CO_2 is 0.1 V higher than that under N_2 , and the current density at the same potential for the latter is about twice of that for the former. The increase of cathodic current can only be caused by the reduction of water under N_2 , but the enhanced current can be caused by both the reduction of CO_2 and H_2O under CO_2 . We tried to find out if there is any substance that can reduce KMnO_4 in strong alkaline solution, and found that the solution after 5 circles of the CV scan under CO_2 contained the substance that made the color change from purple, characteristic of KMnO_4 , to the green color of K_2MnO_4 in a few minutes; however, that under N_2 did not. Therefore, a small amount of formate formed.

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