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Short communication

Electrochemical reduction of carbon dioxide: *IV* dependence of the Faradaic efficiency and current density on the microstructure and thickness of tin electrode

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HIGHLIGHTS

- Sn gas diffusion electrode with 20 wt.% Nafion was optimal for the conversion of CO_2 to formate.
- The optimized Nafion fraction was found to be independent of Sn particle size (100 nm–2 μm).
- The optimized thickness of GDE was ~9 μm when 100-nm Sn particles were used with 20 wt.% Nafion.

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ABSTRACT

Central to the conversion of CO_2 in a full electrochemical cell is its cathode microstructure, which governs gas diffusion, charge exchange and transfer, and subsequently carbon dioxide reduction reaction. In this article, we report the effects of microstructure of Sn catalyst layer on the Faradaic efficiency towards formate formation as a function of Nafion loading, thickness of the catalyst layer, and catalyst particle size. Electrode with 17–20 wt.% Nafion was found to exhibit the highest partial current density towards the formation of formate when the average particle size of Sn catalysts ranged from 100 nm to 1.5 μm. This Nafion fraction is lower than what was reported, 30–36 wt.%, in the cathode of proton exchange membrane fuel cells. Moreover, the partial current density for formate formation was observed to increase with the thickness of catalyst layer, but eventually saturated because the reaction zone was limited by mass transfer. The Faradaic efficiency towards the formation of formate exhibited nearly thickness-independence due to the counteractive effects caused by increasing local proton concentration and decreasing electrical field when catalyst layer thickness was increased.

1. Introduction

The cathode microstructure of proton exchange membrane fuel cells (PEMFCs) plays a critical role in gas diffusion, charge exchange and transfer, and subsequently oxygen reduction reaction (ORR) as well as the overall fuel cell performance. [1,2] A generic catalyst layer in the gas diffusion electrode (GDE) consists of electrocatalyst and Nafion, [1,3,4] where Nafion allows the integration of porous catalyst layer with the electrolyte, thus increasing the three-dimensional reaction zone. The role of Nafion fraction in the catalyst layer on PEMFC performance has been reported in literature [1,4–6], which showed that the optimized Nafion fraction was in the range of 30–36 wt.%, regardless of platinum loading in the electrodes. Recently, the configuration of PEMFCs was adopted for the electrochemical reduction of CO_2 to produce fuels [7–9]. Similar to ORR, the addition of Nafion in the catalyst layer improved the electrocatalytic activity towards CO_2 reduction by increasing the triple-phase boundary among reactant gases, electrolyte and catalyst particles. The electroreduction of CO_2, however, is expected to be more sensitive to the local proton concentration than ORR because CO_2 reduction reaction competes with hydrogen evolution reaction. As a consequence, even though this technology offers a promising approach to mitigate CO_2 in the atmosphere, it is often limited by its low Faradaic efficiency and current density, particularly towards the formation of liquid fuels [10]. Hence, it is necessary to investigate the role of cathode microstructure on the activity and selectivity of an electrochemical cell to convert CO_2 to fuels. In this article, we report our work on the effects of Nafion loading, the thickness of catalyst layer, and Sn particle size on the Faradaic efficiency and current density for the conversion of CO_2 to

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formate. The electrode design was a pivotal part in our recently published research [8,11,12].

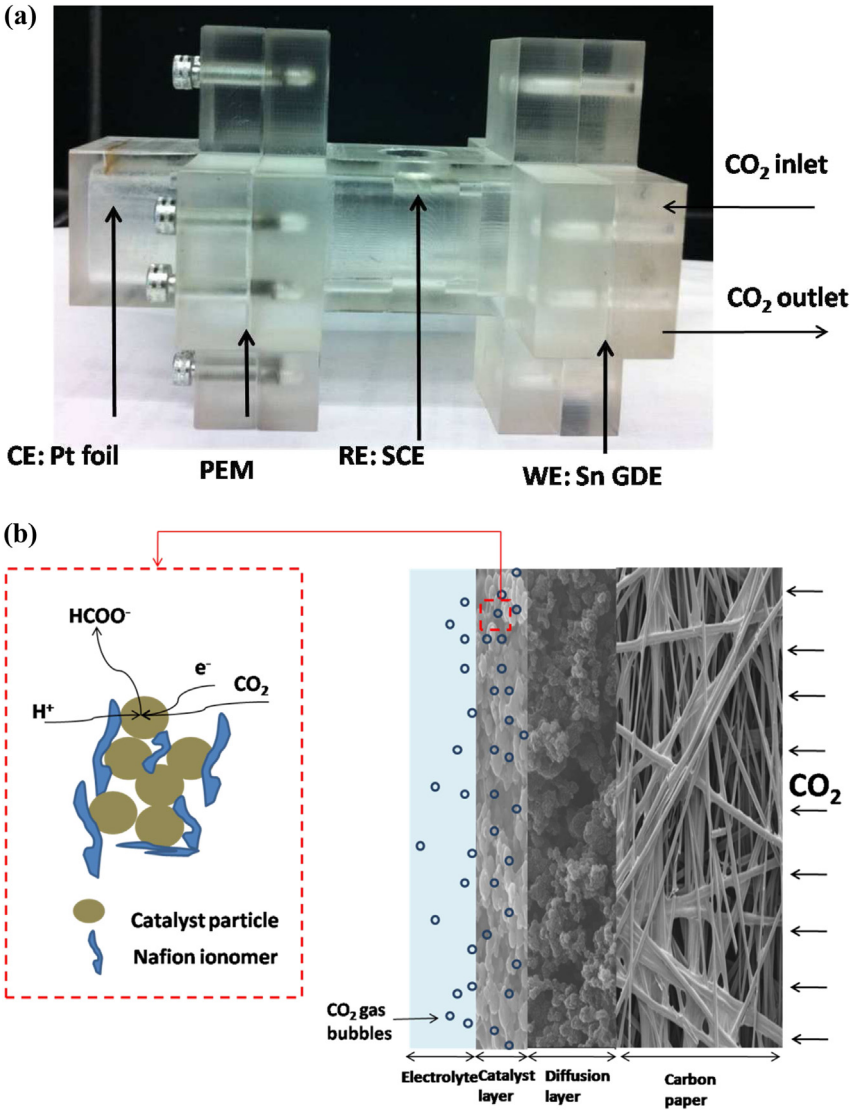
2. Experimental

2.1. Preparation of Sn GDEs

The Sn GDE was prepared by spraying Sn catalyst ink onto a gas diffusion layer (Sigracet® GDL 10BC). The Sn catalyst ink was made by mixing Sn powders (Alfa Aesar, APS 100 nm), Nafion ionomer (DuPont), deionized water (Resistivity $\geq$ 18.2 MΩ cm^{-2}), and isopropanol (Sigma Aldrich), followed by ultrasonicating the mixture for an hour. In order to optimize Nafion fraction, the weight ratio of Sn:Nafion was varied from 1:1 to 20:1. In order to study the effects of Sn loading on the activity and selectivity, different Sn GDEs with loadings varying from 0.67 mg cm^{-2} to 6.55 mg cm^{-2} were also prepared with the same Nafion fraction of 20 wt.% (weight ratio Sn:Nafion of 4:1). In addition, Sn powders (Sigma Aldrich) with a size ~1–2 μm were chosen to study the effect of particle size on percolation threshold and consequently electrochemical performance of the electrode. The geometric area of Sn GDE used was 4 cm^2.

2.2. Electrolysis

The performance of Sn GDE was evaluated in a home-made electrochemical cell (see Scheme 1a), in which an aqueous electrolyte, GDE, and gas CO_2 channels were assembled in series. This cell configuration enables the electrochemical reduction of CO_2 at the triple-phase interfaces as shown in Scheme 1b. The compartment for the working electrode was separated from that hosting the counter electrode by a proton exchange membrane (Nafion®, DuPont). The working electrode, Sn GDE, was supplied with gaseous CO_2 at 45 ml min^{-1} at 25 °C and 1 atm. CO_2 flew along a serpentine channel over Sn GDEs and diffused through gas diffusion layer to Sn catalyst layer. A platinum foil (3 × 3 cm^2) and a saturated calomel electrode (SCE) were used as the counter and reference electrode, respectively. A stationary aqueous solution of 0.5 M $KHCO_3$ was used as the electrolyte. All the electrochemical measurements were conducted by employing Solartron 1470



Scheme 1. (a) A photo of half cell setup for measuring the electrocatalytic activity of Sn GDEs towards CO_2 reduction, and (b) schematic of CO_2 reduction at the triple-phase interfaces.