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Analysis on the effect of operating conditions on electrochemical conversion of carbon dioxide to formic acid

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ABSTRACT

Electrochemical reduction of CO₂ to HCOOH was performed on a Sn electrode using a proton exchange membrane-embedded electrolysis cell. The effects of reaction conditions such as catholyte and anolyte types, reduction potential, catholyte pH, and reaction temperature on the amount of HCOOH and its faradaic efficiency were investigated. Four different electrolytes (KOH, KHCO₃, KCl, KHSO₄) were chosen as the candidate catholyte and anolyte; the most suitable electrolyte was chosen by monitoring the amount of HCOOH and faradaic efficiency. The effect of the pH of the selected catholyte on the conversion of CO₂ to HCOOH was also investigated. In addition, the reaction temperature was varied and its effect was studied. From the observations made, we determined the optimal reaction conditions for the production of HCOOH via the electrochemical reduction of CO₂ by a systematic approach.

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Introduction

Over the decades, tremendous environmental challenges have emerged owing to global warming caused by the emission of greenhouse gases such as CO₂, N₂O, and CH₄. Various efforts have been undertaken for decreasing the atmospheric concentration of such gases, especially CO₂, which is

massively produced by power plants [1–11]. A substantial reduction of CO₂ can be achieved by capturing CO₂, and then either storing it or transforming it to other forms of compounds. This entire process is known as carbon capture and storage, or sequestration (CCS) [2,3], and is essential to prevent the release of a large quantity of CO₂ into the atmosphere. The CO₂-capture systems are classified into three categories: precombustion, postcombustion, and oxygen

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combustion [8]. For the sequestration of captured CO₂, underground and underwater storage methods have been proposed [8]. Recently, it was acknowledged that the conversion of the captured CO₂ into hydrocarbon fuels was also promising and feasible.

CO₂ can be converted by photochemical [11–13], biochemical [14], and electrochemical [1,3–10,13] conversion, and stored as various forms of hydrocarbon compounds. Among the different conversion technique mentioned hereinabove, the electrochemical conversion (reduction) of CO₂ has notable advantages because it is not affected by geology, amount of sunlight, or weather, and only requires electricity [8]. Moreover, the method, when combined with the renewable energy sources such as sun and wind, can be utilized as an energy storage system through the reductive fixation of CO₂.

Researches have shown that various hydrocarbon compounds could be produced via the electrochemical reduction of CO₂, depending on the operating conditions [15–17] and the type of catalyst used [1,18–24]. The resulting liquid products such as formic acid (HCOOH) and methanol (CH₃OH) could be stored and handled more easily compared to the gaseous products. HCOOH is relatively less toxic and fetches a high price compared to the other liquid products obtained from the reduction of CO₂. Furthermore, HCOOH can be utilized for producing paper pulp and pretreating leather products. It can also act as feedstock for chemical synthesis, especially in C1 chemistry. To this end, research pertaining to the conversion of CO₂ into HCOOH using Pb, Hg, In, and Sn catalysts has been drawing enormous attention recently [1,4,22–26]. CH₃OH is produced when either Mo [27] or titanium oxide [28] is used for the conversion of CO₂. As gas-phase products, methane (CH₄) can be produced on Cu catalysts [1,10,16,29], while carbon monoxide (CO) is formed on Au, Ag, and Zn catalysts [1,19,29,30].

Depending on the modes of ion-exchange through the electrolyte, the electrochemical conversion of CO₂ can be classified as follows: proton exchange membrane (PEM) [4,9,10,14], anion exchange membrane (AEM) [5], and solid oxide electrolyte [15]. The schematic of the electrochemical reduction of CO₂ by the PEM-based method is depicted in Fig. 1. The water-splitting reaction takes place at the anode generating oxygen, electron, and proton. Then, utilizing protons transferred through the PEM to the cathode, CO₂ are

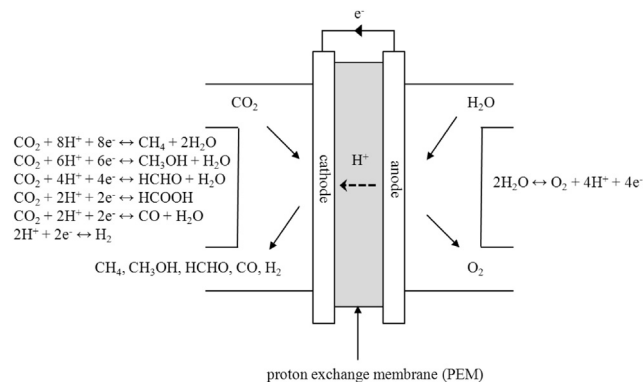


Fig. 1 – Schematic of electrochemical reduction of CO₂ in proton exchange membrane (PEM)-based reactor.

electrochemically reduced to hydrocarbon compounds along with the formation of gaseous hydrogen [16].

In this study, the production of HCOOH was attempted via the reduction of CO₂ on Sn. Compared to In and Hg, Sn is more advantageous in terms of the price per ton (London Metal Exchange in Nov. 2013: Sn 23,025 USD/ton, In 650,000 USD/ton) and safety [31]. In the past, the electrochemical conversion of CO₂ using Sn has been performed and reported with a wide range of reaction conditions such as reduction potential [9,23,26], catholyte type [23,26], temperature [32], and pH [33]. Recently, Wu et al. [26] has investigated the effects of electrolyte and reduction potential on the selectivity and the activity of Sn in the reduction of CO₂ to formic acid in a single chamber cell. The cation effect (K⁺, Na⁺, Cs⁺) and the anion effect (HCO₃⁻, SO₄²⁻, Cl⁻) of the electrolyte were presented and compared.

In this respect, a systematic approach on the variation, and hence, the optimization of these reaction conditions including types of both catholyte/anolyte, pH, and temperature is still needed. Therefore, we attempted to electrochemically reduce CO₂ into HCOOH and maximize the production efficiency by varying the reaction conditions. First, we determined the optimum reduction potential and appropriate catholyte. Second, an optimum pH, which favored the reduction of CO₂ over the hydrogen evolution reaction (HER), was determined. Third, four different anolytes were tested to find the most appropriate anolyte. Finally, the temperature at which the reaction occurred most efficiently was determined.

Experimental

A lab-made PEM-embedded electrolysis cell, made of polycarbonate, was used for the electrochemical reduction of CO₂ (Fig. 2). The cathodic and anodic parts, both having the same volume of 260 mL, were separated using Nafion™ 211 (Dupont). The cell temperature was controlled by an outside water jacket connected to a thermostat. A Sn foil (Alfa Aesar, 99.9%) with an area of 10 cm² was used as the cathode, while Pt-sputtered Ti mesh (Pt thickness = 1 μm) with an area of 40 cm² and Ag/AgCl were used as the counter and reference electrodes, respectively. A potentiostat (Autolab,

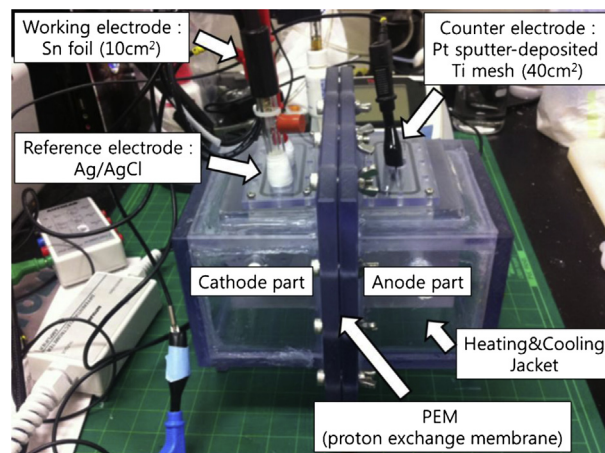


Fig. 2 – Electrochemical cell used in CO₂ reduction.

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