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Direct formation of dendritic Ag catalyst on a gas diffusion layer for electrochemical CO₂ reduction to CO and H₂

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ABSTRACT

Dendritic Ag (a CO₂-to-CO reduction catalyst) has been synthesized on carbon paper (CP) using pulse electrodeposition to fabricate a gas diffusion electrode. A combination of sonication and pulse deposition facilitated mass transfer of Ag ions to the CP, enlarging the catalyst active surface area without significantly changing the Ag crystalline structure. The current density of CO₂ reduction was proportional to the surface area of dendritic Ag. Further improvements in performance were achieved by adding polyethylene glycol to the CO₂ reduction cell catholyte that removed the CO gas bubbles produced at the electrode surface. The fabrication methods presented herein suggest an effective gas diffusion electrode for application in the membrane-electrode-assembly-type single cell for electrochemical CO₂ reduction.

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Introduction

Electrochemical conversion of waste CO₂ into valuable products, such as renewable fuels and industrially relevant chemicals, is a promising carbon management method for minimizing CO₂ emissions [1–6]. Representative products from electrochemical CO₂ conversion are CO, HCOOH, C₂H₅OH, and CH₄ whose production is determined by the electrochemical parameters of the reaction cells and the types

of catalysts used [7–10]. Among these products, CO is one of the most attractive products because it can be used as a reactant for the industrial production of various value-added chemicals. Besides CO production, H₂ evolution simultaneously occurs during electrolysis using an aqueous electrolyte. Both the CO production and H₂ evolution compete against each other, and direct syngas production with controlled compositions of H₂ and CO is possible, which can further be converted to hydrocarbon fuels via the Fischer-Tropsch process [11,12]. Particularly, the price of CO is

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relatively high compared to other C1 chemicals [5]. In addition, during electrochemical production of CO the separation of the produced CO from the liquid electrolyte is relatively easy and there are a number of electrocatalysts that show relatively high selectivity for CO production [5]. For example, Ag is known to be a suitable electrode material for the electrochemical conversion of CO₂ to CO, owing to its high selectivity and moderate price. To improve the electrocatalytic performance of Ag electrodes, strategies to modulate the crystal structure and increase the active surface area have been extensively investigated [2,3,13–15].

A popular approach for improving the performance of a catalyst without changing the nature of the material is tuning its morphological structure to give a larger surface area and higher selectivity towards CO production. Representative examples of possible morphologies include three-dimensional hierarchical nanoporous, inverse opal, and dendrite structures [2,3,15–17]. Furthermore, the formation of these hierarchical catalysts with large surface areas and excellent catalytic activities when incorporated into gas diffusion electrodes (i.e., carbon paper, CP) is necessary for large scale CO₂ electrolysis. These devices would be similar to the proton exchange membrane (PEM) water electrolyzers or PEM fuel cells based on the membrane-electrode assembly [18–23]. The incorporation of a catalyst into CP usually consists of two steps: the synthesis of the catalyst and subsequent coating onto the CP using spray coating, brushing, decal, or other methods [24–26]. Although the coating method results in rigid and durable structure, it results in limited catalyst utilization, as the deficient ionic and/or electronic contacts between the catalyst layer and CP prevent the full utilization of the catalyst. Furthermore, chemical synthesis of the catalysts is often a complex process composed of multiple steps requiring extreme conditions. For these reasons, direct electrodeposition of the catalyst onto a CP substrate offers a promising alternative for the fabrication of an electrode for use in a water electrolyzer [27–34]. Furthermore, the morphology and crystalline structure of an electrodeposited catalyst can be easily controlled by adding organic chemicals or by varying the deposition technique, for example multi-step or pulse/pulse-reverse deposition could be utilized [15,22,29,35]. These techniques can modulate the influence of mass transfer, nucleation density, and crystalline structure, which are important factors that directly affect the formation of the catalyst. However, electrodeposition on CP often suffers from limited penetration of the electrolyte (in other words poor wetting of the electrolyte) into the hydrophobic pore structure of CP, resulting in surface-limited deposition of the catalysts. In addition, for the gas-evolving electrolysis such as in water and CO₂ electrolyzers, the produced gases (H₂, O₂ and CO) must immediately be removed from the electrode surface to minimize the so-called bubble overpotential [36,37]. Therefore, mass transfer issues in terms of enhanced transport of the deposition electrolyte and removal of the electrolytically produced gases are particularly important.

In this study, a dendritic Ag catalyst was directly formed on CP for the electrochemical reduction of CO₂ to CO and H₂ using pulse electrodeposition and sonication. Simple galvanostatic electrodeposition was not able to form Ag catalysts with large surface areas because of the mass transfer limitations of Ag

ions. Therefore, we adopted a pulse electrodeposition and sonication strategy because it has been previously reported that the application of sonication and pulse (or pulse-reverse) electrodeposition can enhance the mass transfer of electrochemical species from the bulk to electrode surface [38–40]. The deposition characteristics of the Ag catalysts were strongly dependent on the pulse parameters and sonication, which affect the mass transfer of the Ag ions to be deposited. For subsequent CO₂ reduction, polyethylene glycol (PEG) was added as a surfactant to reduce the extent of bubble overpotential. The resulting CO₂ reduction performances were measured under varying process variables to optimize the conditions for electrocatalytic reduction.

Materials and methods

Ag electrodeposition was performed with a potentiostat (EG&G 2273, Princeton Applied Research). CP (Ballard, Avcarb MGL370, geometric area = 5 cm²), Pt mesh, and Ag/AgCl (saturated with KCl) were used as the working, counter, and reference electrodes, respectively. The Ag electrodeposition was conducted in an electrolyte composed of 0.01 M AgNO₃ (silver nitrate, Sigma-Aldrich, 99%), 0.6 M (NH₄)₂SO₄ (ammonium sulfate, Daejung, 99%), and 0.04 M ethylenediamine (Sigma-Aldrich, 99%), using a method described in detail in our previous study [15]. A galvanostatic deposition method was used and the current density for Ag electrodeposition was optimized based on the nucleation density of Ag on CP. The optimum current density that resulted in the highest nucleation density was used for subsequent experiments. Linear sweep voltammetry (LSV) was performed by sweeping the potential from the open circuit potential to –2.0 V (vs. Ag/AgCl) at a 100 mV/s scan rate to investigate the effect of sonication on the mass transfer of Ag ions. Galvanostatic pulse electrodeposition was also used to enhance the mass transfer of Ag ions. The pulse electrodeposition consisted of on-time (T_{on}) and off-time (T_{off}), and T_{off} is the most important variable contributing to the maintenance of high Ag ion concentration near the electrode surface. During the T_{off}, the replenishment of Ag ions occurs near the electrode surface by diffusion, which may improve the properties of the resulting Ag deposits, such as nucleation density and eventual morphology [41–43]. Thus, we focused on the effects of T_{off}. The peak current density applied during the T_{on} was 15 mA/cm² and T_{on} was fixed at 0.25 s while the T_{off} was varied from 0.5 to 3 s. The sonication was applied by a sonicator (LK-U065D, Mujigae; 40 kHz, 150 W) during the electrodeposition process.

The surface morphologies of the fabricated Ag catalysts on the CP were characterized using field emission scanning electron microscopy (FE-SEM, S-4800, Hitachi). The cross-sectional images of the deposited Ag on the CP were further analyzed by energy-dispersive X-ray spectroscopy (EDS, Merlin Compact, Zeiss). The crystalline structure of the deposited Ag catalysts was examined by X-ray diffraction (XRD, D8-Advance, Bruker).

The surface area of the prepared Ag catalysts were measured using the electrochemical oxidation reaction of Ag in a N₂-purged 0.1 M KOH (potassium hydroxide, Sigma-Aldrich)

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