Fabrication of Large Area Ag Gas Diffusion Electrode via Electrodeposition for Electrochemical CO$_2$ Reduction

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Abstract: For the improvement for the commercialization of electrochemical carbon dioxide (CO$_2$) conversion technology, it is important to develop a large area Ag gas diffusion electrode (GDE), that exhibits a high electrochemical CO$_2$ conversion efficiency and high cell performance in a membrane electrode assembly (MEA)-type CO$_2$ electrolyzer. In this study, the electrodeposition of Ag on a carbon-paper gas diffusion layer was performed to fabricate a large area (25.5 and 136 cm$^2$) Ag GDE for application to an MEA-type CO$_2$ electrolyzer. To achieve uniformity throughout this large area, an optimization of the electrodeposition variables, such as the electrodes system, electrodes arrangement, deposition current and deposition time was performed with respect to the total electrolysis current, CO production current, Faradaic efficiency (FE), and deposition morphology. The optimal conditions, that is, galvanostatic deposition at 0.83 mA/cm$^2$ for 50 min in a horizontal, two-electrode system with a working-counter electrode distance of 4 cm, did ensure a uniform performance throughout the electrode. The position-averaged CO current densities of 2.72 and 2.76 mA/cm$^2$ and FEs of 83.78% (with a variation of 3.25%) and 82.78% (with a variation of 8.68%) were obtained for 25.5 and 136 cm$^2$ Ag GDEs, respectively. The fabricated 136 cm$^2$ Ag GDE was further used in MEA-type CO$_2$ electrolyzers having an active geometric area of 107.44 cm$^2$, giving potential-dependent CO conversion efficiencies of 41.99%–57.75% at $V_{cell} = 2.2–2.6$ V.

Keywords: carbon dioxide; Ag catalyst; gas diffusion electrode; electrodeposition

1. Introduction

Carbon dioxide (CO$_2$) is one of the representative greenhouse gases generated during the combustion and chemical processes of fossil fuels. Studies have been performed on the conversion of CO$_2$ into value-added chemicals via thermochemical, electrochemical and photochemical methods [1–6]. Among them, the electrochemical conversion of CO$_2$ is an effective way to generate various organic materials from CO$_2$ under atmospheric temperature and pressure conditions [7] by using product-selective catalysts and a liquid-dissolved/direct gaseous CO$_2$ feed. However, because CO$_2$ is thermodynamically stable, having a linear molecular structure, the use of a suitable catalyst is necessary to reduce CO$_2$. Depending on the selectivity of the catalyst, the products of electrochemical CO$_2$ conversion can vary, e.g., CO [8,9], CH$_4$ [10,11], C$_2$H$_6$ [12,13], HCOOH [14,15], and many other low-C products. Among the products, CO has the following benefits: a small amount of electrical energy required for production [16,17], a simple reaction path [18], and a high market price as a feed material for the Fischer–Tropsch process [19].
Thus, numerous studies have been performed on the electrochemical reduction of CO\(_2\) to CO. Metal catalysts such as Au and Ag have high CO selectivity [7], since Au and Ag are known to have weak metal-CO binding [20] which is beneficial to CO production [21]. Although Ag has benefits over Au with regard to cost, it requires a higher overpotential than Au, owing to its moderate activity [22]. To overcome this, the fabrication of nanoparticles with unique shapes, such as nano-corals or triangular nanoplates, which maximize the amounts of active sites for CO production, has been attempted in many studies [23–25]. For example, Ag nano-coral catalysts fabricated by Hsieh et al. [23] had a CO production current density of 6.62 mA/cm\(^2\), which was approximately 16.55 times higher than that of Ag nanoparticles.

However, most previous studies focused on the development of new catalysts having the advantageous physicochemical properties and high selectivity/activity for CO production at the laboratory level using half-cells and H-type cells [24,26–29], which cannot yet be scaled for commercialization. For the large-scale conversion of CO\(_2\), systems using an aqueous solution-based electrolyte with dissolved CO\(_2\) should be avoided, owing to the limited solubility of CO\(_2\) in water (~0.03 mol kg\(^{-1}\) at ~300 K and 1 atm) [30]. In contrast, flow cell systems such as proton-exchange membrane (PEM)-based membrane electrode assembly (MEA)-type CO\(_2\) electrolyzers [31–35], are capable of converting large amounts of CO\(_2\). Some of them have achieved very high efficiencies of 80%–85%, with high CO partial current densities of 50–290 mA/cm\(^2\) [31,33], and there are still items to consider, such as using commercial electrodes [31,32], a small electrode area [33,34], and high operating cell voltage [31]. In our previous study, we examined the performance of an Ag gas diffusion electrode (GDE), having a geometric area of 2.8 × 2.8 cm\(^2\), and fabricated via electrodeposition to control hydrophilicity using acid-treated carbon paper for a PEM-based MEA-type CO\(_2\) electrolyzer [36]. The PEM-based MEA-type CO\(_2\) electrolyzer using Ag GDE is commercially advantageous, but in order to manufacture a high-capacity system for the large-scale conversion of CO\(_2\), a fabrication method for large area electrodes must be developed.

In the present study, we present the studies of a large area (25.5 and 136 cm\(^2\)) Ag GDE, having a uniformly high electrochemical CO\(_2\) conversion efficiency and high cell performance throughout the geometric area, which is suitable for scaling the MEA-type CO\(_2\) electrolyzer. The main objective was to achieve the uniformity of the electrodeposited Ag catalyst over a large area for maintaining high activity, even with a large electrode. To achieve the effective production of large area electrodes using electrodeposition, the process variables that can affect the current distribution [37–39], such as the electrodes system, electrodes placement, deposition current density and deposition time, were optimized with regard to uniformity and performance.

2. Materials and Methods

2.1. Materials and Equipments

Ag catalysts were prepared via electrodeposition using a potentiostat (CS310, Wuhan CorrTest Instruments Corp., Ltd., Wuhan, China). The substrate for Ag electrodeposition was a carbon paper (AvCarb Material Solutions, Lowell, MA, USA; AvCarb MGL 280, 1594009)-based gas diffusion layer. The substrate was employed after pretreatment in a sulfuric acid (H\(_2\)SO\(_4\); 95%, Junsei, 8301051250) solution using a sonicator for 15 min [36]. A mixture of 0.6 M ammonium sulfate ((NH\(_4\))\(_2\)SO\(_4\), 99%, 11566; Alfa Aesar, Haverhill, MA, USA) as the supporting electrolyte, 0.01 M silver nitrate (AgNO\(_3\), 99.9%, Alfa Aesar, 11414) as the Ag precursor, and 0.04 M ethylenediamine (C\(_2\)H\(_8\)N\(_2\), 99%, E1521; Aldrich, St. Louis, MO, USA) [40] was used as the electrolyte (pH of 8.6). The geometric area of the carbon paper used for electrodeposition was 25.5 and 136 cm\(^2\), respectively, and the lead wires were connected either at the top or at the sides of the carbon paper according to the arrangement of the electrodes (Figure 1).
2.2. Fabrication of Ag GDE

The Ag catalyst was fabricated in both three-electrode and two-electrode systems to examine the differences in the morphology and CO₂ conversion efficiency, at room temperature and ambient pressure. For the three-electrode system, an electrodeposition of the Ag catalyst was performed using acid-treated carbon paper, a Pt plate, and a saturated calomel electrode (SCE) saturated KCl as the working, counter, and reference electrodes, respectively, at −0.49 V (vs. SCE) for 50 min. The effect of the deposition time on the characteristics of the Ag catalysts can be found in our previous work, particularly on the adhesion problem at the longer deposition time [41]. For the two-electrode system, electrodeposition of the Ag catalyst was performed via galvanostatic methods for the same duration. The same working and counter electrodes were used: acid-treated carbon paper and a Pt plate, respectively. The galvanostatic deposition conditions were varied, such as the deposition current (0.63, 0.83 and 1.03 mA/cm²), the distance between the working and counter electrodes (1, 2, 4 and 5 cm), and the deposition time (5 and 50 min). The morphology and uniformity of the Ag deposits were analyzed using field-emission scanning electron microscopy (FE-SEM, SIGMA, Carl Zeiss) at different positions on the large area Ag GDE (denoted as A–E). The loading amounts of Ag by electrodeposition were analyzed with inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 8300, Perkin Elmer, Waltham, MA, USA).

2.3. Electrochemical CO₂ Reduction to CO in Half-Cell

For testing the CO₂ reduction to confirm the uniform activity throughout the large area Ag GDE, the electrodeposited Ag GDEs were cut into three pieces (for the 25.5 cm² GDE) or five pieces (for the 136 cm² GDE), each having a geometric area of 2.56 cm². The positions of the cut pieces are shown in Figure 1a,b and Figure 9a. Using the cut pieces as working electrodes, the electrochemical CO₂ reduction was conducted using a potentiostat (WaveNow, Pine Instrument, Grove City, PA, USA) in a laboratory-made H-type cell, where the cathodic and anodic parts were divided by a PEM (Nafion 212, DuPont™), and Pt gauze and an SCE were used as the counter and reference electrodes, respectively. The electrolyte and operating conditions for the CO₂ reduction were based on our previous experimental method [42]. In detail, 0.5 M potassium hydrogen carbonate (KHCO₃, 99.5%, 6580-4400, Daefung, Siheung-si, South Korea) was used for both the anolyte and the catholyte. The catholyte was saturated with CO₂ gas for at least 30 min, and the anolyte was saturated with Ar gas for at least 30 min. During the operation, CO₂ gas was continuously injected into the catholyte at a flow rate of 10 mL/min using a flow controller to maintain the CO₂ saturation state. The CO₂ reduction was performed for 30 min under a constant voltage of −1.5 V (vs. SCE), and the generated gas (CO, H₂) was injected into a gas chromatograph (GC, 7890A, off-line mode, Agilent, Santa Clara, CA, USA). The produced H₂ and CO were detected using a thermal-conductivity detector and a flame ionization detector, respectively. The average electrolysis current density measured during the last 1 min of the reduction was denoted as the total current density. The electrochemical Faradaic efficiency (FE) and the CO production partial current [22] were calculated using the detected concentrations of CO and H₂, and the amounts of charge supplied during the same period of the last 1 min.
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Figure 1. Schematic diagrams of the (a) vertical three-electrode system and (b) horizontal two-electrode system for fabricating the 25.5 cm² Ag gas diffusion electrode (GDE). The sectioned positions used in the subsequent analysis were denoted as A, B and C. (c) Total electrolysis current density and CO production current density of the Ag GDE fabricated in each electrode system according to the position and (d) the corresponding FE for CO and H2. The Ag deposition conditions were –0.49 V (vs. the saturated calomel electrode (SCE)) for 50 min in the three-electrode system, and 0.83 mA/cm² for 50 min in the two-electrode system. The CO2 reduction was performed at a constant voltage of –1.5 V (vs. SCE) in a laboratory-made H-type cell. 0.5 M KHCO3 was used for both the anolyte and the catholyte.

2.4. Electrochemical CO2 Reduction to CO in MEA-Type Electrolyzer

For the MEA-type CO2 electrolyzer, the fabricated 136 cm² Ag GDE (actual geometric area of 107.44 cm²) with the optimized electrodeposition condition was used as the working electrode. The counter electrode for oxygen evolution was fabricated by the spray coating of IrO2 stock solution composed of IrO2 (99.99%, Alfa Aesar), Nafion-perfluorinated resin binder (5 wt%, Sigma-Aldrich), isopropyl alcohol (70%, Honeywell Research Chemicals) and de-ionized water onto the oxalic-acid-pretreated Ti paper, giving 1 mg/cm² of IrO2 loading. Once the electrodes were prepared, the MEA was fabricated by assembling the two electrodes with the PEM (Nafion 117, DuPontTM). A thicker membrane of Nafion 117 (183 µm) was used in making MEA instead of Nafion 212 (50.8 µm) to ensure the mechanical stability under the condition of massive CO2 feed and pressurized system explained in the forthcoming section.

10 mL/min of KHCO3 solution (1.0 M; 99.7%, Sigma-Aldrich) and 100 mL/min of KOH solution (1.0 M; 90%, Sigma-Aldrich) were fed and circulated as the catholyte and anolyte, respectively, using flow fields at both electrodes. Gaseous CO2 at a rate of 150 mL/min (the ratio of the volumetric gaseous flow rate to the cross-sectional area for the gas flow channel was 83.3 cm/sec) were also fed to the cathode using a separated flow field. The electrolysis performance was evaluated at a different cell potential ($V_{cell}$) range (1.8 to 3.4 V), using a potentiostat (HCP-803, Bio-Logic Science Instruments, Seyssinet-Pariset, France) under pressurized conditions at 4 bar. The amounts of produced CO and H2 during the electrolysis were measured by a GC (7890B, Agilent, off-line mode).

3. Results and Discussion

Large area (25.5 cm²) Ag GDEs were manufactured using three- and two-electrode systems to examine the effects of the electrode system on the uniformity of the catalyst formation and the
electrochemical CO₂ reduction efficiency. Figure 1a shows a schematic of the three-electrode system consisting of working, counter and reference electrodes. The reference electrode was between the working and counter electrodes, and the distance between the electrodes was maintained at 1.5 cm (Note that the placement of the reference electrode at the side of the working electrode was not adopted here, since it may cause severe non-uniform distribution in the solution resistances between the closest and the farthest parts of the working electrode, particularly in the case of the large area working electrode). Figure 1b shows a schematic of the two-electrode system consisting of working and counter electrodes, where the distance between the electrodes was fixed as 4 cm. Because there was no reference electrode in the two-electrode system, the reduced restriction on placing the electrodes allowed for a horizontal arrangement of the electrodes. In both figures, A, B and C represent the pieces cut to evaluate the uniformity within the electrode. The electrochemical CO₂ reduction using each piece in Figure 1a,b was measured. Both the total reduction current and the CO production partial current are presented in Figure 1c. As shown, the Ag GDE deposited via the two-electrode system exhibited higher total current density and CO current density values than the Ag GDE deposited via the three-electrode system. In particular, the Ag GDE fabricated via the two-electrode system exhibited similar total current density values (3.09–3.33 mA/cm²) and CO current density values (2.61–2.83 mA/cm²), regardless of the position within the large electrode. However, for the three-electrode system, the total current density was in the range of 1.65–2.58 mA/cm² according to the position, exhibiting non-uniformity. The non-uniformity was also severe in the case of the CO current density, which ranged from 0.55 to 2.01 mA/cm². The variation in the performance according to the position within the electrode was confirmed by examining the FE, as shown in Figure 1d. The Ag GDE fabricated via the two-electrode system exhibited a highly uniform and high CO FE of 81.95%–85.2%, regardless of the position. In contrast, the Ag catalyst fabricated via the three-electrode system exhibited a CO FE ranging from 33.5% to 93.88%, depending on the position, exhibiting severe non-uniformity. The non-uniform characteristics of the Ag GDE fabricated with the three-electrode system are attributed to the uneven mass transport caused by the insertion of the reference electrode between the working and counter electrodes. Moreover, the differences in the length from the reference electrode to each position of the large working electrode might have caused differences in the ohmic voltage drop.

This is supported by the morphologies of the deposited Ag, which are shown in Figure 2 for both electrode systems. Figure 2a shows the FE-SEM results for the Ag GDE deposited in the three-electrode system, and Figure 2b shows those for the two-electrode system, according to the position. In Figure 2a, a decrease in the deposition amount of the Ag catalyst from bottom to top (A → C) is observed. However, in Figure 2b, the deposition amount and morphology do not exhibit any significant differences with respect to the position. Therefore, with the two-electrode system, the electrodeposition of Ag exhibited higher uniformity throughout the electrode, which is important for the scale-up of the electrode. Therefore, electrodeposition using the two-electrode system was studied for the optimization of the deposition variables for fabrication of a 25.5 cm² large area GDE.

Figure 3 shows the total and CO partial current densities and the calculated FE, according to the position on the 25.5 cm² Ag GDE fabricated at different deposition currents of 0.63, 0.83 and 1.03 mA/cm² for the two-electrode system. The distance between the electrodes and the deposition time were fixed at 4 cm and 50 min, respectively. Regardless of the deposition current density, the Ag catalyst fabricated via the two-electrode system maintained uniformity in both the total and CO currents. The CO current densities at different positions were 2.25–2.51 mA/cm² for the deposition current density of 0.63 mA/cm², 2.61–2.83 mA/cm² for the deposition current density of 0.83 mA/cm², and 2.41–2.79 mA/cm² for the deposition current density of 1.03 mA/cm². Generally, the CO current density was highest when the Ag catalyst was deposited at 0.83 mA/cm². Figure 3b shows the FE of CO and H₂ according to the deposition current and position. For the deposition currents of 0.63, 0.83 and 1.03 mA/cm², the CO FE at different positions was 82.15%–85.5% (3.35% difference), 81.95%–85.2% (3.2% difference), and 77.65%–86.95% (9.3% difference), respectively. The 25.5 cm² large area Ag GDE fabricated via the two-electrode system with a deposition current of 0.83 mA/cm² had a high
CO current density and uniform CO FE of >80%. The morphologies of the Ag GDE according to the deposition current and position are presented in Figure 4. As shown, there was no significant difference in the morphologies of the Ag deposits, and Ag catalysts with a dendrite morphology were uniformly formed for all samples regardless of the deposition current density and the position.

![Field emission scanning electron microscope (FE-SEM) images of the fabricated 25.5 cm² Ag GDE (Figure 1) according to the position on the electrode: (a) three-electrode system; (b) two-electrode system.](image)

**Figure 2.** Field emission scanning electron microscope (FE-SEM) images of the fabricated 25.5 cm² Ag GDE (Figure 1) according to the position on the electrode: (a) three-electrode system; (b) two-electrode system.

![Total electrolysis current density and CO production current density of the 25.5 cm² Ag GDE according to the position and (b) the corresponding FE for CO and H₂. Ag deposition was performed with different deposition current densities (0.63, 0.83 and 1.03 mA/cm²) for 50 min with a fixed working-counter electrode distance of 4 cm. The CO₂ reduction was performed at a constant voltage of −1.5 V (vs. SCE) in a laboratory-made H-type cell. 0.5 M KHCO₃ was used for both the anolyte and the catholyte.](image)

**Figure 3.** (a) Total electrolysis current density and CO production current density of the 25.5 cm² Ag GDE according to the position and (b) the corresponding FE for CO and H₂. Ag deposition was performed with different deposition current densities (0.63, 0.83 and 1.03 mA/cm²) for 50 min with a fixed working-counter electrode distance of 4 cm. The CO₂ reduction was performed at a constant voltage of −1.5 V (vs. SCE) in a laboratory-made H-type cell. 0.5 M KHCO₃ was used for both the anolyte and the catholyte.
Figure 4. FE-SEM images of the fabricated 25.5 cm² Ag GDE (Figure 3) according to the position on the electrode. Ag deposition was performed with different deposition current densities: (a) 0.63 mA/cm², (b) 0.83 mA/cm² and (c) 1.03 mA/cm².

Figure 5 shows the effect of the distance between the electrodes (1, 2, 4 and 5 cm) on the uniformity of the activity of the 25.5 cm² large area Ag GDE according to the position. The deposition current density and deposition time were fixed at 0.83 mA/cm² and 50 min, respectively. The total current density and CO current density for each case according to the position are shown in Figure 5a. The total current density and CO current density exhibited good uniformity, with slight differences of 0.61, 0.29, 0.24 and 0.43 mA/cm² in the total current density and 0.36, 0.3, 0.22 and 0.16 mA/cm² in the CO current density for distance between working and counter electrodes of 1, 2, 4 and 5 cm, respectively. In general, a shorter distance between the electrodes yielded a larger variation in the CO current density. Figure 5b presents the H₂ and CO FE according to the electrode distance. As shown, the CO FE at different positions was 73.15%–83.37% (10.22% difference), 80.36%–86.67% (6.31% difference), 81.95%–85.2% (3.25% difference), and 71.17%–81.43% (10.26% difference) for the distances of 1, 2, 4 and 5 cm, respectively. The highest average CO FE of 83.78% and the smallest CO FE variation of 3.25% were observed for the 4 cm distance. The drop of CO FE in the case of 5 cm is probably due to the voltage loss during the deposition resulting from the increased solution resistance between the electrodes. This implies that there might be a counterbalance between the uniformity in the distribution of the deposition current and the ohmic drops as the electrode distance changes, giving that 4 cm as the most desirable distance under this system.

Figure 6 shows the morphologies of the Ag GDE according to the distance between the electrodes and the position. Likely to the small variation in the total/CO current densities and FE (Figure 5), the morphology and uniformity were similar among the Ag deposits, and all the samples exhibited dendrite morphologies with slight deviation in the dendrite densities.
Figure 5. (a) Total electrolysis current density and CO production current density of the 25.5 cm² Ag GDE according to the position and (b) the corresponding FE for CO and H₂. Ag deposition was performed at 0.83 mA/cm² for 50 min with different working-counter electrode distances: 1, 2, 4 and 5 cm. The CO₂ reduction was performed at a constant voltage of −1.5 V (vs. SCE) in a laboratory-made H-type cell. 0.5 M KHCO₃ was used for both the anolyte and the catholyte.

Figure 6. Cont.
Figure 6. FE-SEM images of the fabricated 25.5 cm² Ag GDE (Figure 5) according to the position on the electrode. Ag deposition was performed with different working–counter electrode distances: (a) 1 cm, (b) 2 cm, (c) 4 cm, and (d) 5 cm.

As a final variable, the deposition time was reduced to 5 min with simultaneous variation of the distance between the electrodes, at a fixed deposition current of 0.83 mA/cm². Figure 7 shows the total and CO current density, as well as the FE of H₂ and CO. In general, the reduction in the deposition time to 5 min severely degraded the activity and uniformity of the Ag GDE. For example, low CO current densities of 0.54–0.75 mA/cm² at a 1 cm distance, 0.49–0.64 mA/cm² at a 2 cm distance, and 0.62–0.83 mA/cm² at a 4 cm distance were observed. Additionally, the calculated CO FE in Figure 7b was relatively low, and exhibited non-uniform behavior with the decrease in the deposition time compared with the 50 min deposition cases in Figure 5, regardless of the electrode distance. The deteriorated activity and uniformity were closely related to the morphology of the Ag GDE, as shown in Figure 8. In contrast to the fully covered deposits in Figure 6 obtained with a longer deposition time of 50 min, the Ag deposits shown in Figure 8 exhibited relatively low coverage, with less-developed short dendrites at the main branches of the carbon paper. These relatively less-developed catalysts are believed to be the cause of the low CO current and non-uniformity. Position A had more dense Ag deposits than the other two positions when the distance between the electrodes was 1 and 2 cm.

Figure 7. (a) Total electrolysis current density and CO production current density of the 25.5 cm² Ag GDE according to the position and (b) the corresponding FE for CO and H₂. Ag deposition was performed at 0.83 mA/cm² for 5 min with different working–counter electrode distances: 1, 2 and 4 cm. The CO₂ reduction was performed at a constant voltage of −1.5 V (vs. SCE) in a laboratory-made H-type cell. 0.5 M KHCO₃ was used for both the anolyte and the catholyte.
At lower or higher \(V\) as the previous results [36,41], the CO ratio according to the positions was 2.76 mA/cm\(^2\). The average CO current density among the positions was slightly enhanced with the increased area of 136 cm\(^2\). The average CO current density among the positions was very close to 0, implying that almost no reduction reaction was happening. 

Using the optimized deposition variables that yielded the highest CO current density, CO FE, and uniformity in the fabrication of the 25.5 cm\(^2\) Ag GDE (two-electrode system, 0.83 mA/cm\(^2\) deposition current, 4 cm working–counter electrode distance, and 50 min deposition time), we fabricated a larger GDE with an area of 136 cm\(^2\). For this larger Ag GDE, five different positions were selected to evaluate the uniformity (Figure 9a). First, the uniformity of the deposit was confirmed using FE-SEM, and the results are shown in Figure 9a. The coverage and morphology of the Ag deposit were not significantly different for the different positions (A–E), and were very similar to those of the 25.5 cm\(^2\) GDE. The total current density, CO current density, and FE of CO/H\(_2\) were also evaluated according to the position, and the results are presented in Figure 9b,c. Although the variation of the CO current density among the positions was slightly enhanced with the increased area of 136 cm\(^2\), excellent uniformity in both the total current density and CO FE was observed. The average CO current density among the positions was 2.76 mA/cm\(^2\). The average CO FE was as high as 82.78%. This implies that the optimized deposition variables were successfully employed for the fabrication of a very-large-area Ag GDE with highly uniform CO production activity within the electrode.

Figure 10 shows the performance of MEA-type CO\(_2\) electrolyzer with 136 cm\(^2\) Ag GDE (actual geometric area of 107.44 cm\(^2\)) according to the cell potential \((V_{cell})\) ranging from 1.8 to 3.4 V. The loading amounts of Ag were measured by ICP-OS to be 1.32 mg/cm\(^2\). Figure 10a exhibits the total reduction current density, giving an increasing trend of the total current density with \(V_{cell}\). At a \(V_{cell}\) of 1.8 V, the total current density was very close to 0, implying that almost no reduction reaction was happening. As the \(V_{cell}\) was gradually increased, the total current density was substantially increased, giving 151.66 mA/cm\(^2\) at 3.4 V. The produced CO ratio over the other gaseous products (mostly H\(_2\), no other gaseous products were detected with GC) was calculated and shown in Figure 10b. Likewise our previous results [36,41], the CO ratio according to the \(V_{cell}\) exhibited a peak value of 57.75% at 2.2 V. At lower or higher \(V_{cell}\) than 2.2 V, the CO ratio rapidly decreased showing a volcano-like behavior. Particularly at high \(V_{cell}\) over 3 V, most of the electrolysis currents came from vigorous hydrogen evolution giving a very low CO ratio. Therefore, the large area (>100 cm\(^2\)) Ag-GDE was effectively fabricated by the optimized electrodeposition method, and the MEA-type electrolyzer using it was

![Figure 8. FE-SEM images of the fabricated 25.5 cm\(^2\) Ag GDE (Figure 7) according to the position on the electrode. Ag deposition was performed at 0.83 mA/cm\(^2\) for 5 min with different working-counter electrode distances: (a) 1 cm, (b) 2 cm, and (c) 4 cm.](image-url)
Coatings successfully used in the CO$_2$ electroreduction to produce CO at the operation cell potential between 2.2 to 2.6 V.

![Image](image-url)

**Figure 9.** (a) FE-SEM images of the fabricated 136 cm$^2$ Ag GDE according to the position on the electrode. Ag deposition was performed at 0.83 mA/cm$^2$ for 50 min with a working-counter electrode distance of 4 cm. (b) Total electrolysis current density and CO production current density of the 136 cm$^2$ Ag GDE according to the position and (c) the corresponding FE for CO and H$_2$. The CO$_2$ reduction was performed at a constant voltage of $\sim$1.5 V (vs. SCE) in a laboratory-made H-type cell. 0.5 M KHCO$_3$ was used for both the anolyte and the catholyte.

![Image](image-url)

**Figure 10.** Performance of large area (107.44 cm$^2$) MEA-type CO$_2$ electrolyzer according to the applied cell potential (1.8 to 3.4 V) under pressurized condition at 4 bar; (a) total reduction current density and (b) CO ratio over other gaseous products. The 136 cm$^2$ large area Ag GDE fabricated by the optimized electrodeposition method (Figure 9) was cut to make 107.44 cm$^2$ Ag GDE. 10 mL/min of 1.0 M KHCO$_3$ solution and 100 mL/min of 1.0 M KOH solution were fed and circulated as the catholyte and anolyte, respectively, using flow fields at both electrodes. Gaseous CO$_2$ at a rate of 150 mL/min were also fed to the cathode using a separated flow field.
4. Conclusions

The electrodeposition variables were optimized for fabricating large area (25.5 and 136 cm$^2$) Ag GDEs for application to an MEA-type CO$_2$ electrolyzer. In the fabrication of a large electrode via electrodeposition, it is essential to achieve uniformity among different positions on the electrode, which requires optimization of the electrode system, electrode arrangement, deposition current, and deposition time. By comparing the total electrolysis current, CO production current, FE and deposition morphology, it was confirmed that galvanostatic deposition at 0.83 mA/cm$^2$ for 50 min in a horizontal two-electrode system with a working-counter electrode distance of 4 cm was the best condition for fabricating the large area Ag GDE with uniform performance throughout the electrode. Position-averaged CO current densities of 2.72 and 2.76 mA/cm$^2$ and FEs of 83.78% and 82.78% were obtained for 25.5 and 136 cm$^2$ Ag GDEs, respectively. The fabricated large area Ag GDE (actual geometric area of 107.44 cm$^2$) was be used in MEA-type CO$_2$ electrolyzers, giving potential-dependent CO conversion efficiencies of 41.99%–57.75% at $V_{cell} = 2.2–2.6$ V.

**Author Contributions:** Conceptualization, S.-K.K.; Formal analysis, S.-K.K. and J.H.J.; Funding acquisition, S.-K.K.; Investigation, S.O., H.P., H.K., Y.S.P. and M.G.H.; Methodology, S.O. and S.-K.K.; Supervision, S.-K.K.; Validation, S.-K.K. and J.H.J.; Writing—original draft, S.O. and H.P.; Writing—review and editing, S.-K.K. All authors have read and agreed to the published version of the manuscript.

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