Effects of Ag Nanoparticle Coated Metal Electrodes on Electrochemical CO₂ Reduction in Aqueous KHCO₃

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ABSTRACT

Electrochemical CO₂ reduction is crucial for developing a sustainable closed-carbon-cycle society; however, the factors determining product selectivity have not been fully established, especially when the reaction is carried out over metal cathodes. The selectivity of the CO₂ reduction pathway can be improved by modifying the cathode's catalyst surface. This can be achieved by using specific surface of single crystal or by alloying through the addition of an impurity. In this study, the products of electrochemical CO₂ reduction were evaluated in an aqueous KHCO₃ system at various applied currents and with various metal cathodes. The metal cathodes were coated by Ag nanoparticles, as the Ag cathode was determined to yield the best Faradaic efficiency for CO production in an aqueous KHCO₃ system. Our results suggest that some Ag coated cathodes enhance CO₂ reduction, and thus the reduction products are tunable through surface modification.

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Keywords : Electrochemical CO₂ Reduction, Cathode Metal, Product Selectivity, Ag Nanoparticle Coating

1. Introduction

Like hydrogen storage and water electrolysis, electrochemical CO₂ reduction is an attractive technique for storing renewable energy in chemical form. By exploiting the CO₂ reduction reaction, a carbon-recycling society could be developed.¹ Initial studies of the electrochemical reduction of CO₂ started with the so-called “H-type cell”, as shown in Fig. 1. Recently, the cell configuration has changed to gas-diffusion electrodes (GDEs), membrane electrode assemblies (MEAs), and zero-gap electrodes to improve the partial current density of CO₂ reduction.^{2–13} However, the GDE- and MEA-type CO₂ reduction cells continue to suffer from problems, including local pH differences and the poor or excessive wettability of the GDE.^{8,14–20}

Aside from the poor partial current density arising from limited CO₂ supply, there are additional problems with electrochemical CO₂ reduction systems, for example, the product selectivity, time dependence, and stability of the applied bias. This is in distinct contrast to the simplicity of water electrolysis. In particular, the products of the CO₂ reduction reaction change as the cathode material and current density changes.^{21,22} In addition, the reduction of CO₂ is also affected by H₂ formation via water electrolysis because the H₂ formation process is simpler than that of CO₂ reduction.

Only Cu cathodes reduce CO₂ to a range of products, including CH₄ and C₂H₄. However, the product selectivity of the electrochemical CO₂ reduction reaction by the Cu cathode has not been established, even though product selectivity control has been studied for a long time. The control of product selectivity requires good

knowledge of the CO₂ reduction reaction pathway, which is currently poorly understood.^{2,21–23} Electrode modification can improve this selectivity. Specifically, the modification of Cu cathode electrodes has focused on the Cu surface orientation and facet control.^{6,21,22,24} The use of a partially oxidized Cu cathode alloyed with small amounts of impurity metals has also been investigated.^{3,22,25,26}

In this study, we report the use of cathodes with a catalytic nanoparticle coating, the preparation of which is much simpler than the previously reported electrode modifications. The CO₂ reduction ability of various metal cathodes was first evaluated to find a suitable nanoparticle coating material. The results indicated that the Ag cathode showed the most stable and highest CO₂ reduction ability, and was thus used as the cathode coating material. Then, the effect of the Ag nanoparticle coating on the ability of various metal electrode surfaces to reduce CO₂ was evaluated.

2. Experimental Procedure

Electrochemical CO₂ reduction using an H-type cell (Fig. 1) with various metal plates (Ag, Au, Cu, Sn, Ti, and Zn) as the cathode materials was used to evaluate the product selectivity, efficiency, and stability.

The H-type cell for the CO₂ reduction reaction was prepared in our laboratory. The metal plates used as the working electrodes (WE) are summarized in Table 1, and the plate shapes are shown in Fig. 2. The connecting wire was a polytetrafluoroethylene (PTFE)-coated Cu wire connected to the top of the narrow region by spot welding. A Pt wire (diameter 0.5 × 35 mm, 99.98 %, Nilaco) was used as the counter electrode (CE). Ag/AgCl (3 mol/dm³ NaCl aqueous solution) was used as the reference electrode (RE). The WE and RE were placed in the same cell chamber as the cathode and separated from the CE using a Nafion membrane (DuPont: NRE-211). The electrolyte was aqueous 0.1 mol/dm³ (M) KHCO₃ (45 mL in each compartment), and the compartments were fitted with CO₂ bubblers. The water used here was ultra-pure water. The tools and materials were not subjected to further purification.²⁷

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Figure 1. Schematic of the H-type cell (GC: gas chromatograph).

Table 1. Summary of metal plates uses as cathodes. The areas of the electrodes dipped into the electrolyte are also listed.

Material	Product	Purity [%]	Electrode area [cm ²]
Ag	Nilaco AG-403518	99.98	5.18
Au	Nilaco AU-173388	99.95	4.51
Cu	Nilaco CU-113511	99.99	5.18
Sn	Nilaco SN-443518	99.999	5.18
Ti	Nilaco TI-453512	99.95	5.18
Zn	Standard test Piece	99.99	5.18

Table 2. Summary of the loading of Ag nanoparticles spray-coated on the metal plates used as cathodes. The amounts are the total of the Ag nanoparticles, Nafion dispersion, and water. The used electrode materials and the areas of the electrodes dipped into electrolyte were the same as shown in Table 1.

Material	Electrode Area [cm ²]	Ag dispersion [mg/cm ²]
Ag	5.18	0.66
Cu	5.18	0.60
Sn	5.18	0.52
Ti	5.18	0.48

Figure 2. Cathode shape.

the analysis for the evaluation of organic acids.²⁸ The liquid products were evaluated using a gas chromatograph (Agilent 7890 B) equipped with a flame ionization detector (FID).

Plate cathodes (Ag, Cu, Sn, and Ti) modified by spray-coating with Ag nanoparticles (1.0 wt% aqueous dispersion of 15-nm Ag nanoparticles, US Research Nanomaterials) were also used for comparison with the pure metal cathodes. The metal plates used and their shapes were the same as those of the pure metal electrodes. The ink for the spray-coating was a mixture of 0.30 mL of the Ag nanoparticle dispersion, 3.0 mL of 5.0 % Nafion ionomer solution dispersed in water, and 15.0 mL of pure water. The sample holder for the spray-coater was kept at 70 °C. The total amounts of spray-coated Ag nanoparticles, water, and Nafion dispersion are summarized in Table 2. The experimental setups were the same as those used for the pure metal cathode evaluation, and the measurements were also chronopotentiometric, but the current was selected to achieve a starting voltage of around -1.65 to -1.70 V vs. Ag/AgCl (3 mol/dm³ NaCl aqueous solution) because the currents differed from those for the pure metal cathodes.

3. Results and Discussion

3.1 Evaluation of CO₂ reduction over the pure metal cathodes

The CO₂ reduction ability of several metal electrodes was evaluated to find a suitable nanoparticle coating material. The dependences of the CO₂ reduction reaction on the cathode metal are discussed in the subsequent sections. The applied currents were -3 , -6 , -9 , -12 , and -20 mA in all experiments. The detailed time dependencies are shown in the Supporting Information.

Figure 3. Potentials (vs. Ag/AgCl (3 mol/dm³ NaCl aqueous solution)) and faradaic efficiencies (FE) of the gas products for the Ag electrode at applied currents (from left to right) of -3, -6, -9, -12, and -20 mA after 60 min reaction.

Figure 4. Potentials (vs. Ag/AgCl (3 mol/dm³ NaCl aqueous solution)) and faradaic efficiencies (FE) of the gas products for the Au electrode at applied currents (from left to right) of -3, -6, -9, -12, and -20 mA after 60 min reaction. The data at 180 min at -12 mA (and -20 mA) may include large errors.

3.1.1 Ag electrode

The potentials and faradaic efficiencies (FEs) of the gas products produced with the Ag electrode at different applied currents are shown in Fig. 3. The FE for conversion to CO changed with change in the applied bias, and over 90% FE was observed at approximately -9 and -12 mA. Further, the FE increased with increase in the applied bias in the low-current region and decreased with increase in the applied bias at the high-current region. The FEs were mainly stable over the experimental run.

3.1.2 Au electrode

The potentials and FEs of the gas products produced with the Au electrode at different applied currents are shown in Fig. 4. The CO products had FEs of below 60%, even though Au is a well-known catalyst for the production of CO by CO₂ reduction. The bias of the Au electrode tended to be more positive than that of the Ag electrode by approximately 0.1 V at each current value.

Figure 5. Potentials (vs. Ag/AgCl (3 mol/dm³ NaCl aqueous solution)) and faradaic efficiencies (FE) of the gas products for the Cu electrode at applied currents (from left to right) of -3, -6, -9, -12, and -20 mA after 60 min reaction.

3.1.3 Cu electrode

The potentials and FEs of the gas products produced with the Cu electrode with change in applied current are shown in Fig. 5. In particular, the amount of CO₂ reduction products increased and the amount of the H₂ byproduct decreased as the potential became increasingly negative. In addition, the bias of the Cu electrode was more negative than that of the Ag electrode, about -0.1 V at -20 mA, and this increased with increase in the applied current. The gas and liquid products evaluated after 180 min of reaction are shown in Fig. 6. The trends in the gas products are similar to those obtained after 60 min. A larger range of gas products was produced at -20 mA after 180 min than at 60 min, and the main liquid product in the electrolyte after the reaction was HCOOH.

3.1.4 Sn electrode

The potentials and FEs of the gas products produced with the Sn electrode with change in applied current are shown in Fig. 7. CO was observed as the main gas product, and the FEs decreased as the applied current increased. Based on the evaluation of the electrolyte after the reaction, the main liquid product was found to be HCOOH. The bias of the Sn electrode tended to be more positive than that of the Ag electrode by approximately 0.05 V at each current value.

3.1.5 Ti electrode

The potentials and FEs of the gas products produced with the Ti electrode at different applied currents are shown in Fig. 8. The bias of the Ti electrode tended to be more negative than that of the Ag electrode by about -0.1 V at each current value. In addition, no gas products reduced from CO₂, except for H₂, were produced.

3.1.6 Zn electrode

The potentials and FEs of the gas products produced with the Zn electrode at different applied currents are shown in Fig. 9. The bias of the Zn electrode tended to be more negative than that of the Ag electrode by about -0.1 V at each current value. CO production was relatively stable during the experiment, but the FEs changed with the change in the current. In particular, the FEs for CO reduction tended to be higher at -9 and -12 mA than those at the other current values.

3.1.7 Selection of nanoparticle and electrode materials

Based on the above results, Ag is the best cathode material when the target product of CO₂ reduction is CO. Specifically, the FE for CO production was relatively high and stable throughout the experiments. In contrast, the FE of reduction product produced over

Figure 6. Potentials (vs. Ag/AgCl (3 mol/dm³ NaCl aqueous solution)) and faradaic efficiencies (FE) of the gas products for the Cu electrode at applied currents (from left to right) of -3 , -6 , -9 , -12 , and -20 mA after 180 min reaction. The FEs of the liquid products were also evaluated after 180 min reaction. “Total with Liq” indicates the sum of gas and liquid products.

Figure 7. Potentials (vs. Ag/AgCl (3 mol/dm³ NaCl aqueous solution)) and faradaic efficiencies (FE) of the gas products for the Sn electrode at applied currents (from left to right) of -3 , -6 , -9 , -12 , and -20 mA after 60 min reaction. The other main product was liquid HCOOH.

Figure 8. Potentials (vs. Ag/AgCl (3 mol/dm³ NaCl aqueous solution)) and faradaic efficiencies (FE) of the gas products for the Ti electrode at applied currents (from left to right) of -3 , -6 , -9 , -12 , and -20 mA after 60 min reaction.

the Au electrode, which is a well-known electrode for the production of CO by CO₂ reduction, was relatively low compared with the Ag electrode. It was found that the Ti electrode cannot reduce CO₂, and, instead, water electrolysis occurs. However, the Cu electrode can produce CH₄ and C₂H₄ gas products in addition to CO.

From these results, Ag was selected as the nanoparticle materials used to coat metal electrodes, thus modifying their CO₂ reducing abilities. Electrodes to be coated were Ag, Cu, Sn, and Ti, and were selected because of the variation in their CO₂ reduction ability.

3.2 Evaluation of Ag-nanoparticle-coated metal cathodes for CO₂ reduction

Ag nanoparticles were dispersed in Nafion and spray-coated on Ag, Cu, Sn, and Ti electrodes, and the CO₂ reduction ability of the modified metal electrodes was evaluated.

Because the currents differed from those of the pure metal electrodes, the chronopotentiometry currents were selected to

achieve similar biases (around -1.65 to -1.70 V vs. Ag/AgCl (3 mol/dm³ NaCl aqueous solution)) at the point of initial measurement. The selection of an appropriate applied bias for the cathode is important because it most likely determines the products of CO₂ reduction.

3.2.1 Cyclic voltammetry comparison with pure metal cathodes

The cyclic voltammograms of the pure metal electrodes and Ag-nanoparticle spray-coated electrodes are compared in Fig. 10. The voltammograms were obtained before CO₂ reduction and after the reduction reaction once CO₂ had been bubbled through the solution for 60 min. The currents obtained for the Ag-nanoparticle-coated metal electrodes at the same bias for the Ag and Sn electrodes were lower than those of the pure metal electrodes. The currents for the Cu electrode increased, and those for the Ti electrode did not show a significant change. The changes in the current–voltage characteristics show that the reaction path or the activation energy of CO₂ reduction can be easily modified by changing the surface conditions.

Figure 9. Potentials (vs. Ag/AgCl (3 mol/dm³ NaCl aqueous solution)) and faradaic efficiencies (FE) of the gas products for the Zn electrode at applied currents (from left to right) of -3 , -6 , -9 , -12 , and -20 mA after 60 min reaction.

reaction started. In contrast, only some of the Ag-nanoparticles on the Sn and Ti electrodes peeled off.

The applied bias for the Ag-nanoparticle-coated Ag electrode was more negative than that of the pure Ag electrode. This means that more energy is required for CO₂ reduction over the Ag-nanoparticle-coated Ag electrode, and this is probably a result of the Ag nanoparticle coating, which prevented CO₂ reduction on the Ag electrode surface. In particular, Ag surface oxides between the Ag-nanoparticles and Ag electrode or Nafion ionomer would increase the potential applied to the cathodes. In contrast, the applied bias for the Ag-nanoparticle-coated Cu electrode was more positive than that of the pure Cu electrode. Further, the applied bias of the Ag-nanoparticle-coated Sn electrode changed drastically after the CO₂ reduction reaction started, but the potential was slightly more positive than that of the pure Sn electrode. The applied bias for the Ag-nanoparticle-coated Ti electrode was similar to or more positive than that of the pure Ti electrode.

The products of CO₂ reduction for the Ag-nanoparticle-coated Ag and Sn electrodes were similar to those of the pure metal electrodes, but the ratio of H₂ produced over the Sn electrode was slightly higher than that of the pure Sn electrode. The C₂H₄ product of the CO₂ reduction for the Ag-nanoparticle-coated Cu electrode increased compared to that of the pure Cu electrode, but the amount of H₂ byproduct remained similar. Interestingly, a small amount of CO was produced over the Ag-nanoparticle-coated Ti electrode, even though the Ti electrode showed no CO₂ reduction.

These results show the possibility of controlling the products of electrochemical CO₂ reduction by modifying the cathode surface using coatings of additional materials. These product changes are a result of changes in the reaction pathway considering the shifts in bias observed on surface modification.

4. Summary

Electrode surface modification by nanoparticle coating on metal cathode for CO₂ reduction was performed. To select the nanoparticle material and metal electrodes to be coated, CO₂ reductions of pure metal cathode (Ag, Au, Cu, Sn, Ti, and Zn) were evaluated. It was found that the products of CO₂ reduction depend on the electrode

Figure 10. Cyclic voltammograms of pure metals (Ag, Cu, Sn, and Ti) and Ag-nanoparticle spray-coated metals before CO₂ reduction but after CO₂ bubbling. Four cycles were carried out for each measurement.

with Ag nanoparticles

Ag
Potential

-15 mA

Cu

-35 mA

Sn

-20 mA

Ti

-10 mA

Products (Liquid product evaluations were performed for Cu, Sn, Ti samples)

Figure 11. Time-dependent potentials (vs. Ag/AgCl (3 mol/dm³ NaCl aqueous solution)) and faradaic efficiencies (FEs) of the gas products for Ag-nanoparticle spray-coated Ag (at -15 mA), Cu (at -35 mA), Sn (at -20 mA), and Ti (at -10 mA). The liquid products in the electrolytes, except for those of the Ag electrode, were evaluated after reaction. The currents were selected so that the biases for CO₂ reduction were similar.

material. Since the Ag cathode showed good CO₂ reduction selectivity for CO production and stability, Ag was selected as the nanoparticle material to coat several metal electrodes.

Cyclic voltammetry and chronopotentiometry measurements were also carried out on Ag-nanoparticle-coated metal electrodes (Ag, Cu, Sn, and Ti). Compared to the pure metal cathodes, the absolute current at the same voltage decreased for the coated Ag and Sn electrodes but increased for the coated Cu electrode; the reduction products were similar for the coated Ag and Sn electrodes, but the amount of C₂H₄ increased for the Cu electrode; and CO was observed as a product for the coated Ti electrode, even though CO₂ reduction is not usually observed over Ti electrodes. These results show that the products of CO₂ reduction can easily be controlled by cathode surface modification.

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Data Availability Statement

The data that support the findings of this study are openly available under the terms of the designated Creative Commons License in J-STAGE Data listed in D1 of References.

Conflicts of Interest

There are no conflicts of interest to declare.

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