Electrochemical Reduction of Carbon Dioxide to Formate on Palladium-Copper Alloy Nanoparticulate Electrode

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ABSTRACT

The bimetallic alloy nanoparticle catalysts composed of Pd and Cu were synthesized for electrochemical reduction of CO\textsubscript{2}. The effect of the catalyst composition on the CO\textsubscript{2} reduction activity and the selectivity was investigated, and at the high Pd/Cu ratio CO\textsubscript{2} reduction to formate rather than hydrogen evolution proceeded predominantly. The combination of Pd with Cu also changed the stability of the catalyst. By using the bimetallic catalyst, stable reduction current was obtained in the long-term electrolysis while a monometallic Pd catalyst suffered from deactivation due to poisoning by CO\textsubscript{2}. These improvements are attributable to the electrical interaction between Pd and Cu. The resultant lowering shift of a d-band center reduced binding strength of CO, leading to the achievement of stable reduction of CO\textsubscript{2} with a small overpotential.

Keywords : Carbon Dioxide, Electrocatalyst, Nanoparticle, Alloy

1. Introduction

An attractive method for solving the issue of global warming caused by the increase in greenhouse gas emissions involves electrochemical reduction of CO\textsubscript{2} into valuable chemicals such as CO, formate, methanol, methane and other hydrocarbon compounds.\textsuperscript{1–5} This process can be carbon-free when the electrochemical system is operated using electricity obtained from renewable energy sources. However, since CO\textsubscript{2} is thermodynamically and chemically stable, it is less reactive, suggesting that a large overpotential is required to reduce it electrochemically. Therefore, considerable efforts have been made to develop a variety of electrocatalyst that can be operated at small overpotential.\textsuperscript{6–8}

Recently, it has been reported that Pd nanoparticles show remarkable activity toward reduction of CO\textsubscript{2} to formate,\textsuperscript{9–15} which can be used as a hydrogen carrier, a fuel in direct formic acid fuel cells and a chemical feedstock for the synthesis of formic acid.\textsuperscript{16–21} Formate production by Pd nanoparticles can proceed close to the thermodynamic potential, and their selectivity for the reduction of CO\textsubscript{2} to formate is quite high. In addition, the large surface area owing to the small particle size allows a high current density, indicating that Pd nanoparticles are a promising CO\textsubscript{2} reduction catalyst. However, one of the key drawbacks in using Pd nanoparticles is their deactivation during the electrocatalysis. This deactivation has been considered to be due to surface poisoning by CO, which is formed as an intermediate species of CO\textsubscript{2} reduction and occupies active sites by strong adsorption.\textsuperscript{12–14}

To overcome this drawback, alloying is one of the most attractive candidate approaches. It is believed that by alloying with a second component, due to electronic and geometric effects, binding strength of the intermediate species could be effectively tuned to accelerate the reaction rate on the catalyst surface.\textsuperscript{22–25} Therefore, considerable experimental and theoretical studies have been conducted on Pd-based alloy catalysts.\textsuperscript{26–31} Among them, Pd-Cu alloy catalyst has been demonstrated to be effective for electrochemical oxidation of small organic molecules without deactivation by CO poisoning,\textsuperscript{32–35} and the weakening of CO adsorption by Cu introduction has been reported.\textsuperscript{36–39} Additionally, in the previous study, we examined CO\textsubscript{2} reduction activity of a Pd catalyst modified with a Cu layer by underpotential deposition and confirmed that the Cu modification is effective for preventing CO poisoning.\textsuperscript{40}

In this study, we synthesized Pd-Cu alloy nanoparticles that catalyze electrochemical reduction of CO\textsubscript{2} to formate and examined the effect of the alloy composition on activity, selectivity, and stability of the catalysts. The addition of Cu brought much better stability than the monometallic Pd catalyst, and the reason for the improvement was discussed based on the consideration of their electronic structures.

2. Experimental Section

2.1 Preparation of catalysts

Pd-Cu catalysts supported on carbon black with 20 wt% Pd loading and with different compositions of Cu were synthesized by the metal salt reduction method.\textsuperscript{42} In a typical synthesis of the Pd\textsubscript{x}Cu\textsubscript{1–x} catalyst, 60 mg of Vulcan XC-72 carbon, 3.3 mL of 45 mM PdCl\textsubscript{2} and 1.2 mL of 24 mM CuCl\textsubscript{2} were added into 10 mL of water. Subsequently, the solution was sonicated for 30 min and stirred for 4 h. After pH of the solution was adjusted to 8.5 with 0.1 M Na\textsubscript{2}CO\textsubscript{3}, 10 mL of 50 mM NaBH\textsubscript{4} was slowly added to the solution and stirred for an additional 1 h. Finally, the mixture was washed, filtered and dried at 50°C for 12 h. Other catalysts with different atomic ratios of Pd and Cu were prepared in the similar manner except that the components of the initial solution were different.

2.2 Characterization of electrocatalysts

The crystal structures of the prepared electrocatalysts were analyzed by X-ray diffraction (XRD) using a PW-1700 X-ray diffractometer (PANalytical). X-ray photoelectron spectroscopy (XPS) measurements were performed with an AXIS ULTRA spectrometer (KRATOS). The binding energies were calibrated with reference to the C 1s peak at 284.6 eV. Transmission electron microscopy (TEM) inspection was performed using a Tecnai Osiris microscope (FEI). For the inspection, catalyst powder was deposited...
on nickel microgrids. The histograms of particle size distribution were obtained from randomly selected 100 particles.

2.3 Electrochemical measurements

Electrochemical measurements were carried out using a commercial potentiostat and potential programmer (HZ-5000, Hokuto Denko). An FTO-coated glass substrate (surface area: 2.0 cm²) deposited with thin film of the prepared catalysts served as the working electrode. 18.6 mg of the catalyst was dispersed in a 0.5 M H₂SO₄ solution containing 1.6 mL of isopropanol and 89.6 µL of 5 wt% Nafion solution by using sonication for 30 min. 86.4 µL of the resultant catalyst-coated substrate was heated at 130°C for 30 min. A platinum wire and a silver/silver chloride electrode (Ag/AgCl/KCl(sat.)|AgCl) were used as a counter and a reference electrode, respectively. All the potentials measured with respect to the reference electrode was converted to the reversible hydrogen electrode (RHE) reference scale using the equation U(RHE) = U(versus Ag/AgCl/KCl(sat.)) + 0.197 + 0.0591 × pH. The electrolyte solution used for CO₂ reduction experiments was 0.5 M NaHCO₃ aqueous solution and was purged with CO₂ for 20 min before electrolysis. The pH of the CO₂-saturated electrolyte was 7.2. Electrolyses were performed in a gas-tight two-compartment electrochemical cell and the two compartments were separated by a piece of anion exchange membrane (SELEMION AMV, AGC Engineering). In control experiments, 0.5 M Na₂SO₄ aqueous solution whose pH was adjusted to 7.2 with 1 M NaOH was used as an electrolyte after bubbling with Ar for 20 min.

For CO stripping voltammetry, an electrode was held at 0.25 V in 0.5 M H₂SO₄ and the preadsorption of CO was performed by bubbling CO gas into the electrolyte for 20 min to ensure that the Pd sites were sufficiently covered by CO. Then, the dissolved CO was removed from the electrolyte by bubbling Ar for 30 min while maintaining the potential at 0.25 V. Finally, the CO stripping voltammogram was recorded by scanning the potential up to 1.2 V at 50 mV s⁻¹. All the potentials described in this paragraph are also in the RHE scale.

2.4 Product analysis

Gas phase products, CO and hydrogen, were collected from the cathodic compartment of the electrochemical cell and analyzed by using a gas chromatograph (GC-8A, Ar carrier, SHIMADZU) equipped with a thermal conductivity detector (TCD) and a packed column (SHINCARBON ST 50/80, 6.0 m × 3.0 mm, Shinwa Chemical Industries). For the analysis of liquid phase products, formate, a gas chromatograph (Trucera, He carrier, SHIMADZU) equipped with a barrier discharge ionization detector (BID) and a capillary column (Rtx-WAX, 60 m × 0.53 mm, Restek) was used. Prior to the measurement, sodium ions in the electrolyte was removed by using a proton exchange resin (IC-H plus, Alltech). Specifically, 7 mL of sample was filtered through the resin over 7 min, and then 0.1 µL of the filtered sample was injected into the gas chromatograph.

3. Results and Discussion

Figure 1 shows XRD patterns of the synthesized Pd-Cu alloy catalysts with monometallic Pd and Cu catalysts. In addition to the diffraction peak at 24.8° assigned to the (0 0 2) plane of carbon support, four peaks appeared around 40°, 45°, 68° and 81° which are characteristic of face-centered cubic Pd-Cu alloy, corresponding to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes, respectively. No peaks assigned to discrete Pd or Cu particle were identified for the Pd₁Cu₁ and Pd₃Cu₁ catalysts, which indicate that the nanoparticles were bimetallic alloys. With an increase in Cu content, the peaks progressively shifted to higher angles, which can be ascribed to the decreased lattice constant due to the replacement of Pd atom with smaller Cu atoms.

Figure 2 shows TEM images of the Pd, Pd₅Cu₁ and Pd₃Cu₁ catalysts and their histograms of particle size distribution. In all cases, the spherical particles were uniformly deposited on the carbon support. According to the histograms, the average particle size of the Pd, Pd₅Cu₁ and Pd₃Cu₁ catalysts were 4.2, 3.8 and 3.5 nm, respectively, indicating that the synthesized particles had almost the same size.

XPS spectra of Pd 3d peak region for the Pd, Pd₅Cu₁ and Pd₃Cu₁ catalysts are shown in Fig. 3. Two peaks (Pd 3d₅/₂ and Pd 3d₃/₂) of the Pd 3d spectrum can be deconvoluted into two pairs of doublets associated with the Pd³⁺ and Pd²⁺ valence states,

![Figure 1. XRD patterns of the (a) Pd, (b) Pd₅Cu₁, (c) Pd₃Cu₁ and (d) Cu catalysts. * indicates the peak of Cu₂O.](image)

![Figure 2. TEM images and corresponding particle size distribution histograms of the (a) Pd, (b) Pd₅Cu₁, and (c) Pd₃Cu₁ catalysts.](image)
higher binding energies compared to those of the Pd catalyst. These positive shifts can be ascribed to electron transfer of Pd valance electrons to Cu, corresponding to the lowering of the d-band center of the catalysts. Such a d-band center shift can greatly affect their catalytic performance by weakening the chemisorption energy of reactant molecules on the surface of Pd atoms. The CO stripping curves of the Pd, Pd$_5$Cu$_1$, and Pd$_1$Cu$_1$ catalysts are shown in Figs. 4(a) and 4(b), respectively. Obviously, with increasing Cu content in the catalysts, the d-band center gradually shifted away from the Fermi level, and the onset potential of CO oxidation appeared at more negative potential, indicating that the removal of CO out of the catalyst surface was facilitated. Thus, as deduced from the XPS Pd 3d spectra, alloying with Cu led to the lowering of the d-band center and the weakening of CO adsorption to the Pd catalysts, which is expected to offer higher stability for electrocatalysis.

To examine the CO$_2$ reduction activity of the catalysts with different compositions, linear sweep voltammetry was carried out in CO$_2$ saturated solution. As shown in Fig. 5(a), the monometallic Pd catalyst exhibited the highest current density in the whole potential range compared with other catalysts. Meanwhile, this overall current density does not mean the catalytic activity for CO$_2$ reduction, because hydrogen evolution reaction often proceeds as a competition reaction. In fact, reduction current was also observed in the absence of CO$_2$, although the current density was smaller than that observed in the presence of CO$_2$ (Fig. 5(b)). In order to investigate the selectivity of the Pd-Cu catalysts, the Faradaic efficiency was determined based on the product analysis. Figure 5(c) shows the Faradaic efficiencies measured at $-0.15$ V using the catalysts with the different Pd/Cu molar ratios, and the amount of each product is summarized at Table 1. For the Pd-containing catalysts, formate generated as the sole product of CO$_2$ reduction with the small overpotential of $0.15$ V. Notably, formate was not detected in the absence of CO$_2$ (only hydrogen evolution was observed), indicating that formate is a product of CO$_2$ reduction. The Faradaic efficiency of formate production was the highest for the monometalic Pd catalyst, and the value decreased with increasing the Cu content. In contrast, hydrogen evolution dominantly proceeded on the mono-

![Figure 3](image-url) XPS spectra of Pd 3d peak regions for the (a) Pd, (b) Pd$_5$Cu$_1$, and (c) Pd$_1$Cu$_1$ catalysts.

![Figure 4](image-url) (a) CO stripping voltammograms and (b) XPS spectra of valence band for the Pd, Pd$_5$Cu$_1$, and Pd$_1$Cu$_1$ catalysts. The dashed lines indicate the positions of the d-band centers.

![Figure 5](image-url) (a, b) Linear sweep voltammograms measured under (a) CO$_2$ and (b) Ar atmospheres and (c) Faradaic efficiencies of CO$_2$ reduction using the Pd, Pd$_5$Cu$_1$, Pd$_1$Cu$_1$ and Cu catalysts. The red, blue and black plots in (c) indicate Faradaic efficiencies for the production of formate, CO and hydrogen, respectively.

|                | formate/µmol | CO/µmol | H$_2$/µmol |
|----------------|--------------|---------|------------|
| Pd             | 49           | 0       | 18         |
| Pd$_5$Cu$_1$   | 64           | 0       | 28         |
| Pd$_1$Cu$_1$   | 28           | 0       | 18         |
| Cu             | 0.25         | 0.17    | 3.7        |

Table 1. Amount of products generated during the electrolysis at $-0.15$ V for 90 min.
metallic Cu catalyst while CO and formate also slightly generate. These results agree with the previous report that Pd is active for CO2 reduction at the range of small overpotential while CO2 reduction on Cu initiates from around ~0.6 V.2,4,6 The long-term stability of the catalysts for CO2 reduction was investigated by chronoamperometry with CO2 bubbling at −0.15 V (Fig. 6). At the beginning of the electrolysis, the highest current density was observed with the monometallic Pd catalyst; however, it gradually decreased during the electrolysis for 5 h. According to the literature, this deactivation is considered to be due to poisoning of the catalyst by CO which generates as an intermediate species of CO2 reduction.5,12-14 Since the adsorption strength of CO to Pd is too strong, CO once formed occupies the active sites and prevents the formation of CO on the catalyst during CO2 reduction. In the formate pathway, CO2 to CO can be a competitive reaction. Recently, CO2 reduction using the Pd, Pd5Cu1, Pd1Cu1 and Cu catalysts.  

Figure 6. Comparison of chronoamperograms for CO2 reduction using the Pd, Pd5Cu1, Pd1Cu1 and Cu catalysts.

In summary, we have synthesized bimetallic Pd-Cu catalysts with different compositions and investigated their electrocatalytic activities for CO2 reduction. The catalysts with a higher Pd/Cu ratio generated larger reduction current and formate was produced as the main product. The combination with Cu significantly improved the stability of the Pd catalyst and enabled stable electrolysis by suppressing CO poisoning. XPS and CO stripping studies indicated that the downward shift of the d-band center due to electron transfer from Pd to Cu is responsible for the weakening of the adsorption of CO. Thus, the bimetallic Pd-Cu alloy nanoparticle catalysts could convert CO2 to formate with low overpotential without causing the deactivation by CO poisoning. This study demonstrates the potential of Pd-Cu alloy nanoparticles as an active and robust electrocatalyst and its combination with photocatalysts or photoelectrodes would offer the possibility for the efficient solar-driven conversion of CO2. Such a study is underway in our laboratory.

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