



Enhancement in carbon dioxide activity and stability on nanostructured silver electrode and the role of oxygen



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ABSTRACT

Current energy production habits deplete fossil fuels and accumulate atmospheric CO₂, which contribute to the global climate change. Electrochemical fuel production via CO₂ reduction reaction is an idealistic yet an achievable process that mitigates CO₂ emissions and simultaneously satisfies energy demands. Here, the enhancement of CO₂ reduction activity and stability on size-controlled particulate Ag electrocatalysts derived from a simple, one-step cyclic voltammetry (CV) process by changing scan rates (1–200 mV/s) was demonstrated. Interestingly, larger nanoparticles prepared by slower scan rates (1–5 mV/s) have exhibited the most degree of enhancement for CO₂ reduction to CO product. Compared to untreated Ag foil, nanostructured Ag electrode has shown an anodic shift of approximately 200 mV in the onset potential of CO partial current density (j_{CO}), 160 mV reduction of overpotential at $j_{CO} = 10 \text{ mA/cm}^2$, and increased Faradaic efficiency (F.E.) for CO production especially at lower biased potentials (–0.89 to –1.19 V vs. RHE). Stability tests have demonstrated a drastic improvement in maintaining CO F.E. X-ray photoelectron spectroscopy suggests that the enhancement is associated with stable oxygen species incorporated on the nanoparticle Ag surfaces during the CV fabrication process.

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1. Introduction

The global dependence on fossil fuel is not only depleting their stock but is contributing the climate change due to CO₂ emission during energy production [1,2]. Electrochemical CO₂ reduction reaction (CO₂RR) is an attractive process that reconverts the greenhouse gas into valuable carbon compounds which decreases their atmospheric concentration and stores energy into chemical bonds at the same time [3]. Essentially being the reverse reaction of combustion, CO₂RR is unfortunately endothermic and requires an external energy source that ultimately should not be from fossil fuels. Coincidentally, since many emerging renewable energies (such as solar and wind energies) have an issues with storing elec-

tricity, integration with CO₂RR may mutually eliminate each other's disadvantages.

Although idealistically convenient, this is a challenging task technically because of the thermodynamically stable conformation of CO₂. Hori et al. extensively studied the electrochemical CO₂ reduction activity on various metal foils but none were found to satisfy the material cost, product selectivity, long term stability, efficiency and safety requirements to be competitive in the economic market [4]. Another difficulty of electrochemical CO₂RR is the prevalence competing hydrogen evolution reaction (HER) and low CO₂ solubility in aqueous solution, while nonaqueous or aprotic solution applications are often environmentally unfriendly and seldom produce high current density due to high solution resistance.

Moreover, density function theory (DFT) calculations estimated that it is difficult for individual bulk metals to selectively reduce CO₂ to CO at low overpotentials since their COOH binding energy and CO binding energy coordinates follow a trend line that lies in tangent to the kinetic volcano for CO evolution [5]. DFT calculations for CO₂ conversion to CH₄ and CH₃OH also follow similar

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volcano plot correlation [6]. To overcome these limitations, another set of DFT calculations also hint that covalent embedment of Ag surfaces with p-block elements like S and Se could enhance the electrochemical CO₂ reduction activity by modulating COOH and CO binding free energies [7]. Additionally, research strategies that apply nanoparticles or nanostructured surfaces have demonstrated enhanced catalytic CO₂RR activities in terms of overpotential and product selectivity; however, exact reason for enhancement effects still remains controversial and requires more studies [8–16].

Among various techniques to fabricate nanostructured metal surfaces, reduction of metal oxides showed promising results in electrochemical CO₂RR application. Representative of these results are modified Au and Cu surfaces through pulsed anodization of the former or thermal oxidation of the latter and subsequent reduction of their oxides, which were found to greatly enhance the intrinsic catalytic activity toward CO₂ reduction by Kanan Group [8,9]. Even most recently, oxide-derived Pb was reported to form HCO₂[−] selectively by suppressing HER [10]. Unfortunately, Au is one of the most expensive noble metal, Cu has poor selectivity among its several hydrocarbon products, and Pb is notoriously toxic. On the other hand, Ag is nontoxic, significantly cheaper than Au, and also has a high selectivity toward CO, a precursor in the Fischer–Tropsch process, despite relatively large overpotential required for CO production compared to Au. For reference, previous works concerning CO₂ reduction on Ag include bare surfaces [17], nanoparticles [11,12], and nanoporous [13] structures which suggest morphology of Ag is important in determining CO₂ reduction activity. As of yet, nanostructured Ag induced from silver oxide have not been studied for CO₂RR electrocatalysts.

Here, we demonstrate that nanostructure formation of Ag is possible when Ag is processed under cyclic voltammetry (CV) in a basic solution and can enhance CO₂RR activity and stability. This facile, one-step process has an added benefit of size-control by simply adjusting the scan rate [18]. This study has reveals an interesting perspective in the CO₂ reduction capability of nanostructured Ag electrodes fabricated at various scan rates. Contrary to our initial expectations, larger nanoparticles around 100–200 nm were found to have mostly enhanced CO₂RR activity toward CO evolution by reducing the required overpotential. In addition, nanostructured Ag samples also showed a remarkable stability in CO Faradaic efficiency (F.E.). Herein, properties and plausible reasons for the unusual CO₂ reduction activity of nanostructured Ag are presented.

2. Experimental

2.1. Preparation of nanostructured Ag

The p-Ag electrocatalyst sample was prepared by first mechanically polishing a Ag foil (25 × 25 × 0.5 mm, Dasom RMS) surface with 1.0 μm and 0.05 μm alumina polishing slurries (Micropolish[®], Buhler) for 15 min each. After each polishing session, the Ag foil was generously washed with and ultrasonicated several times in deionized (DI) water to remove alumina residue and the unpolished reverse side was covered with electrically insulating tape. Then CV was performed in a beaker with 100 mL aqueous 0.1 M NaOH (98.0%, Samchun Chemicals) solution (pH 12.7) with the obverse side facing toward the Pt wire counter electrode and Ag/AgCl reference electrode. Each sample was subjected to five cycles of CV from −0.9 V to 1.0 V vs. Ag/AgCl at varying scan rates (1, 5, 50, and 200 mV/s) and was rinsed with DI water.

2.2. Electrochemical surface area measurement

Electrochemical surface area (ECSA) was measured by adopting an underpotential deposition (UPD) of Pb method [11,12]. CV was

performed in aqueous 5 mM Pb(NO₃)₂ (≥99.0%, Sigma–Aldrich), 10 mM HNO₃, and 10 mM KCl (99.9%, Sigma–Aldrich) solution between −0.05 V and −0.50 V vs. Ag/AgCl at a scan rate of 10 mV/s.

2.3. CO₂ reduction reaction experiment

Electrochemical CO₂RR experiments were conducted in an airtight two-compartment polyether ether ketone (PEEK) cell separated by a proton exchange membrane (Nafion[®], 117). Both compartments held 38 mL aqueous 0.5 M KHCO₃ (≥99.99%, Sigma–Aldrich) solution and were purged with 120 sccm CO₂ until saturated (pH 7.0) for 1 h before the experiment and the CO₂ flow was maintained for its duration. Working electrode (*i.e.*, mechanically polished Ag foil or p-Ag samples) and Ag/AgCl reference electrode were positioned in the catholyte that was stirred at 350 rpm with a magnetic stir bar and the Pt counter electrode was placed in the anolyte. A constant potential was applied with a potentiostat (Ivium, Iviumtechnology) and gaseous products were analyzed by gas chromatography (GC, Yonglin 6500) equipped with a capillary column (Restek, RT[®]-Msieve 5A) and pulsed discharge ionization detector (PDD) using ultra high purity (UHP, 99.9999%) He as the carrier gas. The F.E. of H₂ or CO was calculated according to the following equations,

$$i_{\text{H}_2/\text{CO}} = V_{\text{H}_2/\text{CO}} \times Q \times \frac{2Fp}{RT}$$

$$F.E._{\text{H}_2/\text{CO}} = \frac{i_{\text{H}_2/\text{CO}}}{i} \times 100$$

where $i_{\text{H}_2/\text{CO}}$ is the partial current density of H₂ or CO, $V_{\text{H}_2/\text{CO}}$ is the volume concentration of H₂ or CO measured by GC, Q is the flow rate measured by a universal flow meter (ADM 2000, Agilent Technologies) at the exit of the electrochemical cell, i is the total current density, F is the Faradaic constant, p is the pressure, T is the temperature, and R is the ideal gas constant.

Liquid products were also analyzed by ion chromatography (IC, DIONEX IC25A). The procedure was repeated for various potentials. Solution resistance, R_s , was measured by circle fitting the measurement taken from electrochemical impedance spectroscopy (EIS) and potential values were compensated for iR loss and converted in terms of reversible hydrogen electrode (RHE) by using the following equation:

$$E(\text{vs. RHE}) = E(\text{vs. Ag/AgCl}) + 0.197V + (0.0591 \times \text{pH})$$

2.4. Characterization

The surface morphologies were obtained by field emission gun scanning electron microscopy (FEG-SEM, Inspect F, FEI). The crystal structure was confirmed by measuring X-ray diffraction (XRD-6000, Shimadzu). To analyze the surface element composition, high-resolution X-ray photoelectron spectroscopy (XPS) experiments were performed at the 8A2 beamline at the Pohang Accelerator Laboratory (PAL), which was equipped with an electron analyzer (SES100, Gamma-Data Scienta). The Ag3d and O 1s core level spectra were obtained by using photon energies of 420 and 580 eV respectively to enhance the surface sensitivity. The binding energies of the core level spectra were determined with respect to the binding energies ($E_B = 84.0$ eV) of the clean Au 4f core level for the same photon energy. ¹³CO₂ isotope gas was purchased from Cambridge Isotope Laboratories and was conducted with a gas chromatograph (GC, 6890N network, Agilent Technologies) equipped with a mass-selective detector (MSD, 5973 network, Agilent Technologies).

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