Nanoporous Copper–Silver Alloys by Additive-Controlled Electrodeposition for the Selective Electroreduction of CO₂ to Ethylene and Ethanol

Thao T. H. Hoang,†,‡,∥ Sumit Verma,§,∥ Sichao Ma,†,§ Tim T. Fister,† Janis Timoshenko,∥ Anatoly I. Frenkel,∥ Paul J. A. Kenis,∥,§,∥ and Andrew A. Gewirth∥,†,§

†Department of Chemistry, University of Illinois at Urbana–Champaign, Urbana, Illinois 61801, United States
‡Department of Chemical & Biomolecular Engineering, University of Illinois at Urbana–Champaign, Urbana, Illinois 61801, United States
∥International Institute for Carbon Neutral Energy Research (WPI-I2CNER), Kyushu University, Fukuoka 819-0385, Japan
§Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, Illinois 60439, United States
¶Department of Materials Science and Chemical Engineering, Stony Brook University, Stony Brook, New York 11794, United States
#Graduate University of Science and Technology, Vietnam Academy of Science and Technology, Hanoi, Vietnam
©Institute of Chemistry, Vietnam Academy of Science and Technology, Hanoi, Vietnam

Supporting Information

ABSTRACT: Electrodeposition of CuAg alloy films from plating baths containing 3,5-diamino-1,2,4-triazole (DAT) as an inhibitor yields high surface area catalysts for the active and selective electroreduction of CO₂ to multicarbon hydrocarbons and oxygenates. EXAFS shows the co-deposited alloy film to be homogeneously mixed. The alloy film containing 6% Ag exhibits the best CO₂ electroreduction performance, with the Faradaic efficiency for C₂H₄ and C₂H₅OH production reaching nearly 60 and 25%, respectively, at a cathode potential of just −0.7 V vs RHE and a total current density of ~−300 mA/cm². Such high levels of selectivity at high activity and low applied potential are the highest reported to date. In situ Raman and electroanalysis studies suggest the origin of the high selectivity toward C₂ products to be a combined effect of the enhanced stabilization of the Cu₂O overlayer and the optimal availability of the CO intermediate due to the Ag incorporated in the alloy.

1. INTRODUCTION
Carbon dioxide (CO₂) emissions, mostly as the result of human activities involving combustion (burning) of fossil fuels for electricity, heat, and transportation, have increased exponentially.¹ Elevated levels of CO₂ in the atmosphere have been linked to many serious environmental threats, including but not limited to global warming, rising sea levels, and more erratic weather patterns.² Proposed methods for decreasing the levels of CO₂ in the atmosphere involve capturing and sequestering CO₂ underground or underwater,³,⁴ or converting it to value-added chemicals.⁵–⁷ A way to minimize CO₂ emissions could be to utilize clean renewable energy sources such as wind and solar, which are attracting increased attention. However, renewable energy output and energy consumption are intermittent, thus requiring efficient energy conversion and storage systems to be coupled to energy generation. A promising approach to both mitigate CO₂ levels and utilize excess electricity from renewable sources would be to electrochemically reduce CO₂ to value-added chemicals or fuels.⁸–¹⁰

The pioneering work of Hori et al. in the early 1990s showed Cu to be the only transition metal CO₂ electroreduction catalyst that could produce multicarbon hydrocarbons and oxygenates such as ethylene (C₂H₄) and ethanol (C₂H₅OH), albeit at low levels of activity (~5 mA/cm²) and selectivity (i.e., the Faradic efficiency, FE, for C₂H₄ and C₂H₅OH was 25.5% and 5.7%, respectively).¹⁰ Since then, several studies have focused on changing the composition and morphology of Cu-based catalysts to tune and ideally improve the selectivity and activity of CO₂ electroreduction toward multicarbon products.¹³–²⁴ For example, Cu₆O or Cu₆O-derived Cu catalysts have been extensively reported to enhance the electroreduction of CO₂ to C₂ products such as C₂H₄ and C₂H₅OH.¹³–¹⁵,¹⁷ Single-crystal Cu electrodes such as Cu[100]¹⁵ or Cu[100] terraces with Cu[111] or Cu[110] steps have been reported to promote C₂H₄ formation.²⁶ More recently, Cu-based bimetallics have emerged as another class of CO₂ electroreduction catalysts that can enhance the selectivity of CO₂ electroreduction toward different products by modulating the adsorption of key intermediates on the catalyst surface. For instance, enhancements in the activity and selectivity for CO...
have been observed on bimetallic CuAg\textsuperscript{20} and CuAu\textsuperscript{21,22} for formic acid on CuSn and CuPb\textsuperscript{27} and for C\textsubscript{2}H\textsubscript{5}OH on CuZn.\textsuperscript{19} Furthermore, compressively strained CuAg bimetals have been shown to improve the selectivity of CO\textsubscript{2} electroreduction toward multicarbon oxygenates.\textsuperscript{28} However, even after such extensive research efforts, achieving high selectivity (FE \textgreater \textasciitilde 50\%) for C\textsubscript{2} products (C\textsubscript{2}H\textsubscript{4} and C\textsubscript{2}H\textsubscript{5}OH) at high activity (current density \textless \textasciitilde 200 mA/cm\textsuperscript{2}) while requiring low energy input (applied potential \textless \textasciitilde 1.0 V vs RHE), requirements for any industrially interesting process,\textsuperscript{29,30} remains a major challenge in the field.\textsuperscript{31}

In this work, we focus on enhancing the selectivity of CO\textsubscript{2} electroreduction toward C\textsubscript{2} products such as C\textsubscript{2}H\textsubscript{4} and C\textsubscript{2}H\textsubscript{5}OH. A bimetallic CuAg catalyst (prepared using additive-controlled electrodeposition) with a nanoporous structure and low Ag content (\textless 10\%) is reported. The CuAg catalyst exhibits high selectivity toward C\textsubscript{2}H\textsubscript{4} (\textasciitilde 60\%) and C\textsubscript{2}H\textsubscript{5}OH production (\textasciitilde 25\%) at a relatively low applied potential (\textasciitilde 0.7 V vs RHE) and a high current density (\textasciitilde 300 mA/cm\textsuperscript{2}) for the electroreduction of CO\textsubscript{2} in an alkaline flow electrolyzer. These results represent a major improvement in performance over the state-of-the-art Cu-based catalysts for the production of C\textsubscript{2}H\textsubscript{4} (plasma-activated Cu: FE \textasciitilde 60\% at \textasciitilde 0.9 V vs RHE and current density \textasciitilde 20 mA/cm\textsuperscript{2}) evaluated in a two-compartment cell with dissolved CO\textsubscript{2} as the feed and 0.1 M KHCO\textsubscript{3} as the electrolyte under static conditions,\textsuperscript{17} and Cu electrodeposits on both Au and carbon paper. While the results were similar between the two substrates, the error in repeated measurements was higher using the carbon paper relative to the Au substrate, presumably due to the smoother and more reproducible surface presented by the freshly flamed Au.

\textbf{2.3. CO\textsubscript{2} Electroreduction in a Flow Electrolyzer.} Electrochemical measurements and product detection were conducted in a flow electrolyzer setup described previously.\textsuperscript{11} The activity of each catalyst for CO\textsubscript{2} electroreduction was measured by controlling the cell potential (\textasciitilde 1.6, \textasciitilde 1.75, \textasciitilde 1.8, \textasciitilde 1.9, \textasciitilde 2.0, \textasciitilde 2.25, \textasciitilde 2.5, \textasciitilde 2.75, \textasciitilde 3, \textasciitilde 3.5 V) using an Autolab PGSTAT-30, EcoChemie potentiostat. The electrolyte was 1 M KOH. Measurements were obtained with respect to the reversible hydrogen electrode (RHE): E (vs RHE) = E (vs Ag/AgCl) + 0.209 V + 0.0591 V/pH. The gaseous product stream was sampled automatically and diverted and analyzed in a gas chromatograph (Thermo Finnigan Trace GC) equipped with both a thermal conductivity detector (TCD) and a flame ionization detector (FID). The exit electrolyte containing liquid products was collected and analyzed using a \textsuperscript{1}H NMR technique as described previously.\textsuperscript{13} CO\textsubscript{2} reduction experiments, the CO\textsubscript{2} flow rate was set at 7 SCCM. For CO\textsubscript{2} reduction experiments in the presence of CO, the flow rates for CO and CO\textsubscript{2} were 7 SCCM and 1 SCCM, respectively.

\textbf{2.4. In Situ Electrochemical Raman Measurements.} In situ Raman measurements were conducted using a spectroelectrochemical flow cell adapted from the cell described previously.\textsuperscript{34} For Raman experiments, the working electrodes were Cu or CuAg samples electrodeposited on a carbon paper. The counter electrode was a Pt wire and the reference electrode was Ag/AgCl, which was calibrated before each experiment with a normal hydrogen electrode in 1 M HClO\textsubscript{4}. A syringe pump (PHD 2000, Harvard Apparatus) was used to flow the electrolyte through the cell to minimize boundary layer depletion effects and supply fresh electrolyte, thereby helping to maintain constant pH at the electrode surface. The flow rate of the 1 M KOH electrolyte was set at 20 mL/min. The pH of the electrolyte was measured using a calibrated pH meter (Thermo Orion, 9106BNWP). CO\textsubscript{2} gas was introduced into the cell through the back side of the carbon paper working electrode at a flow rate of 4 SCCM. Potentials are reported with respect to the RHE. For each in situ Raman experiment, the potential was held at \textasciitilde 0.7 V, and the Raman spectrum was acquired from 30 1-s acquisitions.

\textbf{3. RESULTS AND DISCUSSION}

\textbf{3.1. Characterization of Cu Films.} Cu and bimetallic CuAg samples with various quantities of Ag dopant were prepared by electrodeposition with and without the presence of
DAT as an electrodeposition additive. Previously, we showed that electrodeposition of Cu in the presence of DAT at pH = 1.5 leads to a wire-like morphology for the Cu deposit, as shown in Figure 1a. We wondered how added Ag might change the deposit morphology. Figure 1b shows a CuAg film (CuAg poly) containing 6% Ag (as measured by ICP-OES) deposited without DAT in solution. The film exhibits large particles, similar to deposits reported previously.35

Addition of DAT to the CuAg plating bath leads to a different morphology. Figure 1c shows the CuAg wire deposit containing 6% Ag (as measured by ICP-OES). The image shows the presence of wire-like deposits exhibiting substantial porosity.32,36 The wires are approximately a factor of 2 smaller in diameter relative to the deposit formed from Cu alone. Deposits made from different amounts of Ag also exhibited structures similar to those found in Figure 1c (see also Figure S1).

Figure 2 shows XRD patterns obtained from CuAg poly (6% Ag) electrodeposited without DAT, Cu wire (0% Ag) electrodeposited with DAT, and CuAg wire (6% Ag) electrodeposited with DAT.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( A_{\text{active}} )</th>
<th>( A_{\text{geometric}} )</th>
<th>Crystalline size (nm)</th>
<th>Loading (mg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuAg poly (6% Ag)</td>
<td>~1.3</td>
<td>~21.1</td>
<td>~0.5</td>
<td></td>
</tr>
<tr>
<td>Cu wire</td>
<td>~7.3</td>
<td>~4.6</td>
<td>~0.3</td>
<td></td>
</tr>
<tr>
<td>CuAg wire (6% Ag)</td>
<td>~8.1</td>
<td>~3.6</td>
<td>~0.3</td>
<td></td>
</tr>
</tbody>
</table>

Figure 1. SEM of (a) Cu wire (0% Ag) electrodeposited with DAT, (b) CuAg poly (6% Ag) electrodeposited without DAT, and (c) CuAg wire (6% Ag) electrodeposited with DAT.

Figure 2. (a) XRD and (b) XPS patterns of CuAg poly (6% Ag) electrodeposited without DAT, Cu wire (0% Ag) electrodeposited with DAT, and CuAg wire (6% Ag) electrodeposited with DAT.

The electroactive surface area of the different Cu and CuAg samples was measured by using Pb UPD to form a conformal Pb coating on the accessible part of the Cu deposit.33,41 The results (Table 1) show that the CuAg sample electrodeposited without DAT exhibits an electroactive surface area similar to the geometric area, as expected due to the large particles seen in the SEM. Alternatively, the Cu wire and CuAg wire (6%) samples exhibit electroactive surface area 7–8 times larger than the geometric area. CuAg wire exhibits ~10% larger surface area than the Cu samples (Figure 1 and Table 1).

Cu and Ag K-edge EXAFS spectra and analysis (Figure 3 and Table 2) were utilized to determine the local bonding environment of Cu and Ag in the samples containing Ag. The data show that both CuAg wire (6%) and CuAg poly (6%) samples appear to be mostly metallic since Fourier transforms (FTs) for experimental and modeled EXAFS data.

Figure 3. Best fit for Ag K-edge and Cu K-edge EXAFS data for CuAg wire and CuAg poly samples and Cu and Ag foils: Fourier transforms (FTs) for experimental and modeled EXAFS data.
Table 2. Values of Structural Parameters for the First Coordination Shell of Cu and Ag Atoms in CuAg Wire and CuAg Poly Samples, Obtained from the Fits of Cu K-Edge and Ag K-Edge EXAFS Data

<table>
<thead>
<tr>
<th></th>
<th>Ag foil</th>
<th>CuAg wire (6%)</th>
<th>CuAg poly (6%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta E_o) (eV), Ag K-edge</td>
<td>−8.6(1)</td>
<td>−10.2(4)</td>
<td>−8.8(1)</td>
</tr>
<tr>
<td>(\Delta E_o) (eV), Cu K-edge</td>
<td>−1.1(4)</td>
<td>0.5(6)</td>
<td>−0.4(5)</td>
</tr>
<tr>
<td>(N_{Ag-Ag})</td>
<td>12</td>
<td>11.0(4)</td>
<td>12</td>
</tr>
<tr>
<td>(N_{Ag-Cu})</td>
<td>2.0(6)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(N_{Cu-Cu})</td>
<td>12</td>
<td>4.6(2)</td>
<td>8.6(4)</td>
</tr>
<tr>
<td>(N_{Cu-O})</td>
<td>0.5(6)</td>
<td>0.4(2)</td>
<td>0.4(2)</td>
</tr>
<tr>
<td>((R)_{Ag-Ag}) (Å)</td>
<td>2.866(1)</td>
<td>2.822(6)</td>
<td>2.858(2)</td>
</tr>
<tr>
<td>((R)_{Ag-Cu}) (Å)</td>
<td>2.641(7)</td>
<td>2.537(2)</td>
<td>2.542(4)</td>
</tr>
<tr>
<td>((R)_{Cu-Cu}) (Å)</td>
<td>1.87(1)</td>
<td>1.85(2)</td>
<td>1.85(2)</td>
</tr>
<tr>
<td>(\sigma^2_{Ag-Ag}) (Å(^2))</td>
<td>0.0104(2)</td>
<td>0.0156(8)</td>
<td>0.0106(1)</td>
</tr>
<tr>
<td>(\sigma^2_{Ag-Cu}) (Å(^2))</td>
<td>0.014(4)</td>
<td>0.0087(5)</td>
<td>0.0086(4)</td>
</tr>
<tr>
<td>(\sigma^2_{Cu-Cu}) (Å(^2))</td>
<td>0.0086(2)</td>
<td>0.003(2)</td>
<td>0.005(5)</td>
</tr>
<tr>
<td>(\sigma^2_{Cu-O}) (Å(^2))</td>
<td>0.003(2)</td>
<td>0.005(5)</td>
<td></td>
</tr>
</tbody>
</table>

For CuAg poly (6%) samples, the contribution of Ag–Cu bonds to the total EXAFS spectra is not significant and cannot be detected within the uncertainties of our analysis (Figure 3). The structure parameters of CuAg poly (6%) (Table 2) that characterize the environment around Ag, as well as the \(\Delta E_o\) parameter that characterizes the electronic state of Ag atoms within error agree with those for bulk Ag material. Similarly, the average interatomic distances of Cu–Cu are the same as in bulk copper metal. These findings indicate that Cu and Ag atoms are completely segregated in the CuAg poly (6%) samples.

CuAg wire (6%), in turn, exhibits Ag–Cu bonds (Figure 3) with distance values between those for pure Cu and pure Ag (Table 2), as expected for alloys. Also, the Ag–Ag distance is slightly reduced in the CuAg wire sample, suggesting at least partial alloying of Ag atoms with smaller Cu atoms. The average interatomic distance for Cu–Cu is close to that in bulk material, which is reasonable considering the large amount of Cu relative to Ag in the CuAg wire (6%) samples.

Figure 3 shows that both CuAg wire (6%) and CuAg poly (6%) appear to be partially oxidized EXAFS fitting results (Figure 3 and Table 2) suggest the presence of Cu(I) oxide. The Cu–O distance of 1.85–1.87 Å is consistent with Cu–O distance in CuO reported previously. Note that CuAg wire (6%) appears to contain more CuO than CuAg poly (6%). These EXAFS data are consistent with the XRD data (Figure 2), in which CuO peak appears in XRD of CuAg wire (6%) but not of CuAg poly (6%).

The presence of CuO in CuAg samples (especially CuAg poly (6%)), which is evidenced in XPS spectra, is not observed in both EXAFS and XRD data. These results suggest that CuO might occur as a thin native oxide layer that forms on top of the CuAg sample in the atmosphere.

It is certainly possible that small amounts of Ag’ are incorporated in the CuO lattice. However, the presence of Ag’ would lead to an exchange reaction producing Ag(0) and Cu(II)O. There is no evidence from either Raman or EXAFS to support or exclude presence of Ag’.

3.2. \(\text{CO}_2\) Electrocatalysis in a Flow Electrolyzer. To evaluate the catalytic activity and the product distribution for the electroreduction of \(\text{CO}_2\) on the Cu and CuAg samples, we tested the materials in a flow electrolyzer. Figures 4 and 5 show the Faradaic efficiency and partial current density for \(\text{CO}_2\) electroreduction as well as all the major products (CO, \(\text{C}_2\text{H}_4\), and \(\text{C}_2\text{H}_5\text{OH}\)) obtained using CuAg poly (6%) electrodeposited without DAT, Cu wire (0% Ag) electrodeposited with DAT, and CuAg wire (6% Ag) electrodeposited with DAT in a 1 M KOH electrolyte as a function of cathode potential.

For CuAg poly (6%) samples, the contribution of Ag–Cu bonds to the total EXAFS spectra is not significant and cannot be detected within the uncertainties of our analysis (Figure 3). The structure parameters of CuAg poly (6%) (Table 2) that characterize the environment around Ag, as well as the \(\Delta E_o\) parameter that characterizes the electronic state of Ag atoms within error agree with those for bulk Ag material. Similarly, the average interatomic distances of Cu–Cu are the same as in bulk copper metal. These findings indicate that Cu and Ag atoms are completely segregated in the CuAg poly (6%) samples.

CuAg wire (6%), in turn, exhibits Ag–Cu bonds (Figure 3) with distance values between those for pure Cu and pure Ag (Table 2), as expected for alloys. Also, the Ag–Ag distance is slightly reduced in the CuAg wire sample, suggesting at least partial alloying of Ag atoms with smaller Cu atoms. The average interatomic distance for Cu–Cu is close to that in bulk material, which is reasonable considering the large amount of Cu relative to Ag in the CuAg wire (6%) samples.

Figure 3 shows that both CuAg wire (6%) and CuAg poly (6%) appear to be partially oxidized EXAFS fitting results (Figure 3 and Table 2) suggest the presence of Cu(I) oxide. The Cu–O distance of 1.85–1.87 Å is consistent with Cu–O distance in CuO reported previously. Note that CuAg wire (6%) appears to contain more CuO than CuAg poly (6%). These EXAFS data are consistent with the XRD data (Figure 2), in which CuO peak appears in XRD of CuAg wire (6%) but not of CuAg poly (6%).

The presence of CuO in CuAg samples (especially CuAg poly (6%)), which is evidenced in XPS spectra, is not observed in both EXAFS and XRD data. These results suggest that CuO might occur as a thin native oxide layer that forms on top of the CuAg sample in the atmosphere.

It is certainly possible that small amounts of Ag’ are incorporated in the CuO lattice. However, the presence of Ag’ would lead to an exchange reaction producing Ag(0) and Cu(II)O. There is no evidence from either Raman or EXAFS to support or exclude presence of Ag’.

3.2. \(\text{CO}_2\) Electrocatalysis in a Flow Electrolyzer. To evaluate the catalytic activity and the product distribution for the electroreduction of \(\text{CO}_2\) on the Cu and CuAg samples, we tested the materials in a flow electrolyzer. Figures 4 and 5 show the Faradaic efficiency and partial current density for \(\text{CO}_2\) electroreduction as well as all the major products (CO, \(\text{C}_2\text{H}_4\), and \(\text{C}_2\text{H}_5\text{OH}\)) obtained using CuAg poly (6%) electrodeposited without DAT, Cu wire (0% Ag) electrodeposited with DAT, and CuAg wire (6% Ag) electrodeposited with DAT in a 1 M KOH electrolyte as a function of cathode potential.

Figure 4a,b shows that the Cu wire and CuAg wire (6%) electrodeposited with DAT exhibit ~5–6 times higher \(\text{CO}_2\) electroreduction current density relative to CuAg poly (6%) electrodeposited without DAT. This enhancement in activity can be explained by the differences in their surface areas (Table 1). In particular, the \(\text{CO}_2\) electroreduction current density values for CuAg poly, Cu wire, and CuAg wire at ~−0.7 V vs RHE are ~−50 mA/cm\(^2\), ~−180 mA/cm\(^2\), and ~−300 mA/
adding CO (1 SCCM) to the CO_2 feed. The graph shows that while the added CO inhibits C_2H_4 production at low potentials, at high potentials added CO promotes the formation of C_2H_4, yielding a Cu wire catalyst only slightly worse than that presented by the CuAg wire electrode.

The Cu wire catalyst reaches 40% FE for C_2H_4 at relatively low potential (∼0.5 V vs. RHE), and the FE is maintained at this level even at more negative potentials (Figure 5). This saturation region of the C_2H_4 FE from the Cu wire catalyst is probably due to the lack of adsorbed CO due to the high turnover rate on the Cu wire electrode surface at more negative potentials. When CO is fed into the system during CO_2 reduction (Figure 6), the saturation region for C_2H_4 production from the Cu wire catalyst disappears.

HER suppression due to compressive strain from incorporation of Ag (∼20%) into the Cu surface, and due to surface mesostructuring, has been suggested to be a possible origin of enhanced selectivity for multicarbon products such as ethylene. However, in our CuAg wire catalyst the Ag content is only 6%. At this low value, compressive strain is likely not present in our alloy, and indeed there is no change in position of the primary reflections in the Cu XRD. Mesostructuring is also not likely to be an origin of the enhancement of ethylene production from CuAg wire. In particular, the mesostructured surfaces of both CuAg wire and Cu wire catalysts are quite similar (similar active surface area and similar morphology), but they exhibit significantly different activity. Also, current density and Faradaic efficiencies for H_2 production from Cu poly, Cu wire, and CuAg wire (Figure S3) are not remarkably different. This result shows that the improved FE for ethylene from CuAg wire is not due to HER suppression.

### 3.3. In Situ Raman Spectroscopy

Figure 7 reports in situ Raman spectra obtained in a flow cell utilizing an electrolyte consisting of 1 M KOH flowing at a rate of 20 mL/min over the Cu or CuAg catalyst supported on carbon paper while CO_2 is flowing at a rate of 4 SCCM and the sample is held at a potential of ∼0.7 V vs. RHE. We measured the pH of the electrolyte before and after flowing through the cell and found no change, showing that the interaction of CO_2 with KOH was minimal in this experimental configuration.

Figure 7a shows the low frequency region. In the case of the Cu wire catalyst, one band is observed at 356 cm⁻¹ (Band B') associated with the Cu–CO stretch. In contrast, Raman spectra obtained from the CuAg wire catalyst exhibit two bands, one at 260 cm⁻¹ (Band A) and another at 369 cm⁻¹ (Band B). Band A is associated with the so-called frustrated rotation (or Cu–C–O bend) of CO bound to the Cu surface. Band B' is similar to band B from the Cu wire catalyst, but shifted by 13 cm⁻¹. Band A has been observed in SERS obtained from Cu surfaces at low temperature. Under these low temperature UV-H conditions, Band A is prominent in samples where the CO concentration on the Cu surface is relatively low. By way of contrast, as the CO concentration is increased, the intensity of band B is found to increase at the expense of band A. This prior work suggests that the appearance of band A in the CuAg wire catalyst is associated with a surface exhibiting a sparser
The catalytic activity of Cu2O decreases quickly due to the presence of Cu2O yields enhancement in CO and C2H4 as the main products at low overpotentials and CH4 or C2H4 at high overpotentials. On the other hand, Cu2O is mostly reported to yield CH3OH with high efficiency. However, the catalytic activity of Cu2O decreases quickly due to the decomposition of Cu2O to Cu, and methanol is formed only during the reduction of these oxide films. After the reaction, both Cu(I) and Cu(II) are present on the electrode, as measured by ex situ Auger. These data are consistent with our in situ Raman data for the Cu wire electrode, which show the presence of both Cu(I) and Cu(II) oxides and is also less effective at producing C2H4 relative to CuAg wire.

The CuAg wire electrode exhibits only Cu2O. The presence of only this oxide is consistent with other reports where the presence of Cu2O yields enhancement in CO and C2H4 production efficiency. It is also reported that the orientation of electrodeposited Cu2O ([110], [111], and [100]) has only a minor effect on product selectivity. However, the initial oxide thickness strongly influences the selectivity of the electrocatalytic process. This behavior was explained by differences in surface roughness and local pH at each sample exhibiting different oxide thickness. Prior work examining the effect of different pH values on ethylene selectivity found that high pH yielded greater C2H4 production.

While the Cu wire electrode exhibits both CuO and Cu2O, no evidence of Cu2O only Cu2O was found on the CuAg wire electrode. This result is consistent with other reports where the presence of Ag significantly improves the resistance to oxidation of CuAg nanoparticles compared to pure Cu nanoparticles; in particular, less CuO was observed in CuAg samples than in Cu samples. The XPS data used to make this conclusion can only distinguish between Cu and CuO, but cannot distinguish between Cu and Cu2O. Thus, no comparison of the relative Cu2O content in Cu and CuAg samples has been reported.

In this work, both Raman and EXAFS suggest that the CuAg wire electrode exhibits enhanced formation of Cu2O and little adsorbed CO. We suggest that the presence of Ag helps promote the formation of Cu2O on the Cu surface. This phenomenon can be explained by using two related thermodynamic arguments. First, the formation enthalpies of Cu2O (−169 kJ/mol) and Ag2O (−31.1 kJ/mol) are substantially different, so any Ag oxide that may form during oxygen exposure will be promptly reduced by the neighboring Cu. Second, Ag has a higher redox potential than Cu and can accept electrons from Cu. Thus, Cu atoms in the CuAg samples will exhibit a slightly more positive charge that promotes formation of Cu2O relative to pure Cu. However, voltammetry associated with Cu oxidation and reduction in alkaline alone, and in CO2 reduction show that there are no explicit oxidation or reduction waves associated with Cu oxidation at the negative potentials considered here.

The GC data show that the presence of Ag in the form of a CuAg alloy in the CuAg wire electrode significantly improves the activity and selectivity of the CO2 electroreduction reaction toward C2H4 production relative to the segregated Ag in the CuAg poly sample and pure Cu. There are two possible reasons for this effect. First, as discussed above, Ag promotes the formation of Cu2O in CuAg electrode, leading to enhancement in CO and C2H4 production efficiency. Second, Ag is an active promoter that forms more CO and could help generate a higher flux of CO, so that neighboring Cu may have more opportunity to participate in coupling. When the Ag content is too small (3% of Ag was tested), the formation of C2H4 decreases especially at high reduction potential where large amount of CO is required to form C2H4 (Figure S2). When Ag content is larger (9% of Ag was tested), the stress inherent in CuAg begins to drive Ag atoms segregate into islands (Figure S2). Thus, when too much Ag is present in CuAg samples, the main product of CO2 reduction reaction will be CO.

4. CONCLUSION

In this work, we have developed a facile method to co-electrodeposit high surface area CuAg alloys, resulting from the inhibition of nucleation through the presence of an additive, DAT. EXAFS data demonstrated that while Cu and Ag atoms in CuAg poly samples that are electrodeposited without DAT are completely segregated, those in CuAg wire samples are more homogeneously mixed. Flow electrolyzer experiments showed that the CuAg wire samples exhibit much higher activity and selectivity for the electroreduction CO2 to C2 products (C2H4 and C2H5OH) in comparison to the CuAg poly and Cu wire samples.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b01868.

SEM images and electrochemical performance data for CuAg wire with 3, 6, and 9% Ag loading, including Figures S1–S5 and Table S1 (PDF)

AUTHOR INFORMATION

Corresponding Author
agewirth@illinois.edu

ORCID

Tim T. Fister: 0000-0001-6537-6170
Anatoly I. Frenkel: 0000-0002-5451-1207
Paul J. A. Kenis: 0000-0001-7348-0381
Andrew A. Gewirth: 0000-0003-4400-9907

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the NSF (Grant CHE-1309731) which is gratefully acknowledged. We also acknowledge the International Institute for Carbon Neutral Energy Research (WPI-I2CNER), which is sponsored by the World Premier International Research Center Initiative (WPI) of MEXT in Japan. A.I.F. and J.T. acknowledge the NSF (Grant CHE-1309731)