CO$_2$ electroreduction at Au$_x$Cu$_{1-x}$ obtained by pulsed laser deposition in O$_2$ atmosphere

C. Roy[a], J. Galipaud[a], L. Fréchette-Viens[a], S. Garbarino[a], J. Qiao[b,*], D. Guay[a,*]

[a] Institut National de la Recherche Scientifique INRS-Énergie, Matériaux et Télécommunications, 1650, Lionel-Boulet Boulevard, Varennes, J3X1S2, Canada
[b] College of Environmental Science and Engineering, Donghua University, 2999 Ren'min North Road, Shanghai 201620, China

ABSTRACT

Au$_x$Cu$_{1-x}$ thin films were synthesized by pulsed laser deposition (PLD) and their electrocatalytic properties towards CO$_2$ reduction in aqueous solution were assessed. The presence of an O$_2$ atmosphere during the PLD process modified the chemical nature of the resulting Au$_x$Cu$_{1-x}$ films, with different oxide types identified by X-ray photoelectron spectroscopy. The impact of these oxides, and of the Cu/Au stoichiometry, on the partial current density and conversion efficiency were assessed. The formation of Au$_x$Cu$_{1-x}$ alloy thin films and/or the introduction of an O$_2$ atmosphere during deposition does not yield to any marked increase of the formation of carbonaceous compounds, and CO and H$_2$ were the only two products formed, along with formate detected in trace amounts ($< 1\%$). Oxide-derived Au catalysts obtained by PLD under O$_2$ atmosphere do not alter CO$_2$ selectivity towards CO formation. High copper content catalysts deposited in vacuum exhibit the lowest overall CO FE%, while increasing the Au content enhances it. The same trend is observed for Au$_x$Cu$_{1-x}$ catalysts deposited under 2 and 220 mTorr O$_2$, aside from the fact that increasing Cu content under high O$_2$ pressure has a less negative influence on CO FE%.

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1. Introduction

Environmental remediation is a major concern in our modern society and the fate of CO$_2$ in the environment is at the heart of this problematic. An alternative approach to underground storage is to consider the CO$_2$ molecule as a chemical reagent rather than a noxious product [1–3]. A wide range of CO$_2$ conversion techniques, including chemical, photochemical, electrochemical, and biological, were investigated and are in different stages of development [4]. Among them, CO$_2$ electrochemical reduction is attractive, as it allows the direct and selective synthesis of high-value products [5]. It is also attractive because the reaction usually takes place at ambient conditions.

According to Bandi et al. [6] and based on the correlation between d-character and CO$_2$ adsorption properties, Au was identified as the most efficient cathode material for CO$_2$ conversion to CO, and reportedly represents the catalyst of choice to benchmark CO evolution performances [7]. In agreement with the low activation energy reported for CO desorption (E$_a$ = 38 kJ mol^{-1}) from Au(110) surfaces [8], Au exhibits the highest activity at

low overpotentials towards CO formation [9–12] due to its optimal binding strength for COOH and CO intermediate species [13]. For high coverage of CO adsorbates, CO desorption is also promoted through the occurrence of dipole-dipole repulsion interactions at Au surfaces [14]. While CO release is easily achieved on Au surfaces at low overpotentials, further conversion to other value-added hydrocarbons and/or alcohols is impeded.

On the other hand, Cu is known to produce complex carbon products such as formate, hydrocarbons (CH$_4$, C$_2$H$_4$) and alcohols [15]. According to Jaramillo et al. [16], as many as 16 different products (from C$_1$ to C$_5$, hydrocarbon unsaturated species, etc.) were detected on polycrystalline Cu. The catalytic activity and selectivity of Cu are highly sensitive to electrolysis conditions such as pH, buffer species, presence of impurities, applied potential, surface structure and morphology [5,17,18,19–21]. The mechanism of the reaction is not clearly understood but CO appears to be an important intermediate for most reaction pathways [22]. While Cu exhibits a stronger ability to perform CO protonation than other metals [23], high overpotentials are required to form any of these products with acceptable CO$_2$ conversion rates.

In recent years, bimetallic catalysts have been extensively studied for CO$_2$ electroreduction [24]. Among others, CuAu was proposed for CO$_2$ electroreduction [25,26]. The activation energy for CO desorption from stepped Cu (111) is higher (E$_a$ = 67 kJ mol^{-1})

* Corresponding author. Tel.: +15142286941; fax: +14509298102.
E-mail addresses: qiaojinli2014@126.com (J. Qiao), guay@emt.inrs.ca (D. Guay).

[26] than from Au (110) surfaces ($E_a = 38 \, kJ \, mol^{-1}$) [14] and therefore CO desorption from Au should be kinetically favored. At the same time, the presence of an oxophilic element (in this case, Cu) close to Au atoms may potentially stabilize active $COOH_{ads}$ intermediates by forming an additional bond at the oxygen end [13,23], thus increasing the bonding strength of COOH to the surface without increasing CO adsorption energy. The use of AuCu bimetallic catalyst is expected to modify the product distribution during the CO_2RR since it is expected that CO_2 molecules will first be selectively reduced to CO on Au atoms before being further reduced to hydrocarbons on adjacent Cu atoms if the CO_2RR can be favored versus HER. Indeed, the formation of CH_4, C_2H_4 and $HCOO^-$ on intermetallic Au_3Cu alloy nanocrystals has indeed been reported, while these compounds were not observed on pure Au nanoparticles [27]. Elsewhere, enhanced selectivity (28%) for methanol and ethanol formation was observed on nanostructured $Au_{0.36}Cu_{0.64}$ catalyst [28]. However, the current efficiency for the formation of hydrocarbons remain low and the presence of Cu atoms does not prevent the formation of H_2 and CO. For example, 65% Faradic Efficiency (%FE) towards CO evolution at E = −0.73 V vs RHE was also reported on $CuAu_3$ nanoparticles [29], while a factor of x2 increase of the %FE towards CO evolution was reported at CuAu alloyed thin films compared to Au [14]. For this approach to succeed, the CO and H_2 faradic efficiencies should be lowered.

Aside from the nature of the catalysts, other material properties such as surface crystallographic orientation [30] and morphology [31,32] were recently shown to strongly influence CO_2 electro-reduction properties. Oxide formation followed by oxide reduction was recently shown to also enhance the CO_2 reduction properties of metals. The materials treated in this way were called "oxide-derived (OD-) materials" [33], and this approach was shown to enhance CO_2 reduction properties when applied to Sn [34], Cu [33,35], In [36] and Au [9]. The OD-materials was postulated to be more active by virtue of the formation of more active sites as a result of the OD-treatment. Accordingly, it is hypothesized that OD-AuCu alloys will show improved CO_2RR characteristics by virtue of combining a bifunctional catalyst with the formation of more active sites. To the best of our knowledge, CO_2 reduction activity at alloys derived from oxidized precursors has not yet been investigated.

In this study, different types of AuCu thin films were prepared by pulsed laser deposition (PLD). PLD is interesting as it allows the preparation of films with similar morphological features but different stoichiometry. Oxide-derived Au_xCu_{1-x} films were obtained under different O_2 partial pressures in the PLD chamber to form complex oxide materials with controlled, well-defined stoichiometry and structure. In the following, CO_2 electroreduction in the low overpotential region on oxide-derived Au_xCu_{1-x} films enables the determination of (i) any synergetic effect between Au and Cu, and (ii) the impact of oxide-derived CuAu bimetallic films on faradaic efficiency and activity.

2. Experimental

2.1. Electrode preparation

Samples were deposited by pulsed laser deposition (PLD) on carbon paper (Toray Industries, inc., TGP-H-090) held 6 cm in front of the target in a custom-made stainless-steel vacuum chamber (base pressure: 2×10^{-5} mbar). Carbon paper was used as substrates due to the low background activity generated in electrochemical experiments. A KrF laser beam (248 nm, 17 ns pulse width, 30 Hz repetition rate, 6 J cm^{-2}) was focused on a rotating gold target (99.99%, Kurt J. Lesker, mirror-polished) partially covered by a copper foil (99.9999%, 0.1 mm, Alfa Aesar).

Different stoichiometries of Cu:Au were obtained by modifying the area covered by the copper foil on the gold target, and were further measured by energy-dispersive x-ray spectroscopy (EDX). In each case, 70,000 pulses were performed, which correspond to a thickness of *ca.* 150 nm (Fig. S1). To modify the resulting oxidation states, experiments were conducted at room temperature and under different O_2 pressures.

2.2. Electrochemical characterization and electrolyses

A three-compartment glass cell connected to a potentiostat/galvanostat (Biologic SP300) was used for CO_2 electrolysis experiments. A Nafion® membrane (membrane N117, 7 mm thick, Ion Paul Inc.) was used to separate the working and counter electrode (platinum mesh, Alfa Aesar) compartments to prevent the re-oxidation of reduced CO_2 products. All electrochemical data was collected vs. Hg/HgSO$_4$ and converted to a reversible hydrogen electrode (RHE) scale, using the following equation: $V_{vsRHE} = V_{vsHg/HgSO4} + 0.656 + 0.059*6.8$. All potential values noted below refer to the RHE scale. Ohmic resistance was measured prior to CO_2 electrolysis through a current interrupt technique and used to correct the working potential value. Typical resistances of 30 Ω were measured.

All Au_xCu_{1-x} samples were tested as working electrodes for CO_2 electroreduction at ambient temperature and pressure. Electrochemical surface characterization was achieved in Ar-saturated 0.1 M KOH (99.999%, Air Liquide) electrolyte while CO_2-saturated 0.1 M KHCO$_3$ (99.99%, Praxair) electrolyte was used to evaluate the films' catalytic properties for CO_2 reduction. This later electrolyte was obtained from bubbling CO_2 into 0.1 M KOH (99.99% KOH pellets, Sigma-Aldrich) until the measured pH remained stable (i.e. pH = 6.8). All solutions were prepared with deionized water (resistivity >18.2MΩ cm^{-1}, Millipore, Milli-Q gradient). Chrono-potentiometric measurements (CP) at $-1 \, mA \, cm^{-2}_{geo}$ in Ar-saturated 0.1 M KOH were performed prior to any CO_2 electrolysis to fully reduce the oxide species. Following CO_2 electrolyses in CO_2-saturated 0.1 M KHCO$_3$, CVs were recorded in Ar-saturated 0.1 M KOH.

2.3. Product quantification

Gas chromatography (GC, Agilent Technologies 490 Micro GC) was used at the end of each electrolysis (*ca.* 30 min) for the quantification of CO and H_2, the only major gas-phase products. Longer electrolysis (*ca.* 120 min) was also performed to ease the detection of liquid products. Only traces (<1%) of formate were detected using ^{1}H NMR (600 MHz, Varian Inova) (results not shown). The product distribution was not changed as compared to shorter (30 minutes) electrolysis period. Using the charge passed during the overall reduction process, the total faradaic efficiency was calculated by determining the number of coulombs associated with the measured amount of each product, then dividing by the total charge passed. Faradic efficiencies of 100 ± 7% were obtained.

2.4. Physical characterization

Energy-dispersive X-ray spectroscopy (EDX) analyses were performed using a JEOL JSM 6300F microscope. Three measurements were recorded on each film and the average values taken as the bulk concentration. In the following discussion, all Au and Cu films are denoted as Au_xCu_{1-x}, with x corresponding to the Au atomic content obtained by EDX analysis.

X-ray photoelectron spectroscopy (XPS) was performed using a VG Escalab 220I-XL apparatus. A polychromatic Mg K$_\alpha$ source (1253.6 eV) with a pass energy of 100 eV for wide-scan survey spectra, and 20 eV for high resolution spectra, was used. XPS