Suppression of Competing Reaction Channels by Pb Adatom Decoration of Catalytically Active Cu Surfaces During CO₂ Electroreduction

Cheonghee Kim,† Tim Möller,‡ Johannes Schmidt,† Arne Thomas,‡ and Peter Strasser*‡

Department of Chemistry, Chemical Engineering Division, Technical University Berlin, 10623 Berlin, Germany
Department of Chemistry, Functional Materials, Technical University Berlin, 10623 Berlin, Germany

Supporting Information

ABSTRACT: The direct electrochemical conversion of carbon dioxide to chemicals and fuels is of fundamental scientific and technological interest. The control of the product selectivity, expressed in terms of the Faradaic efficiency, has remained a great challenge. Herein, we describe a surface-electrochemical synthetic strategy to tune the electrochemical CO₂ reduction selectivity and yield by controlled suppression of the hydrogen evolution reaction (HER) reaction channel, resulting in increased Faradaic efficiencies for fuels and chemicals. We demonstrate that bimetallic catalysts consisting of only minute submonolayer amounts of Pb adatoms deposited on Cu surfaces exhibit and maintain unusually high selectivities for formate (HCOO⁻) over a large range of overpotentials. The bimetallic adatom electrodes were prepared using under-potential electrodeposition (UPD), which is able to precisely control the adatom coverage. While as little as 0.16 ML Pb surface adatoms on a polycrystalline Cu surface boosted the observed Faradaic HCOO⁻ product selectivity 15 times, the 0.78 ML Pb/Cu catalyst showed the most favorable ratio of HCOO⁻/H₂ production rate thanks to the effective suppression of the HER combined with a partial (−1.0 to −1.1 V vs RHE) enhancement of the HCOO⁻ production. We argue that the favorable product efficiency is caused by selective adatom poisoning on the strongest binding hydrogen adsorption sites; in addition, electronic effects of Pb adatoms change the chemisorption of reactive intermediates. Our study reveals synthetic access to tailored selective bimetallic copper catalysts for the electrochemical CO₂ reduction and demonstrates the enormous effect of even minute amounts of surface adatoms on the product spectrum.

KEYWORDS: lead, copper, bimetallic catalyst, CO₂ reduction reaction, selectivity

INTRODUCTION

Carbon dioxide is a key greenhouse gas leading to global climate changes, so conversion of anthropogenic atmospheric CO₂ to fuels and chemicals could be an important contribution toward a sustainable global carbon cycle.¹⁻⁴ Electrochemical CO₂ reduction reaction to higher-value hydrocarbon molecules is an attractive process since it can be coupled with renewable energy resources such as solar and wind.⁵⁻⁷ However, to date highly energy- and Faraday-efficient (chemically selective) electrocatalysts for CO₂ reduction have been largely elusive, especially at high current densities, because of large kinetic overpotentials and the competitive kinetically facile hydrogen evolution reaction (HER) in aqueous environments.⁶ Therefore, developing efficient CO₂ reduction catalysts with suppressed HER and reduced overpotential has remained a scientific challenge of great urgency.

A large number of metal catalysts most prominently copper (Cu), gold (Au), silver (Ag), tin (Sn), and others have been investigated for the electrocatalytic CO₂ reduction.⁸⁻¹⁴ Among them, Cu has been identified as promising catalyst to produce hydrocarbons such as methane (CH₄), ethylene (C₂H₄), and alcohols. More recently, for Cu metal catalysts, most studies focused on investigating recently emerged reactivity-controlling factors and hypotheses such as grain boundaries, Cu⁺ species, subsurface oxygen atoms, local pH effects, size effects, and shape effects and their influence on the electrocatalytic CO₂ reduction activity and selectivity.¹⁵⁻²⁵ For example, Mistry et al. reported that the presence of Cu⁺ species in preoxidized Cu catalysts are key factor for high activity and enhanced ethylene selectivity in electrocatalytic CO₂ reduction.²³ Although they developed new plasma-treated Cu catalysts with improved activity and selectivity, they still produced large amounts of hydrogen gas.

This is why strategies to tune CO₂ reduction activity and selectivity by suppressed HER are so important. Metals known to have a naturally low HER efficiency are tin (Sn), indium (In), and lead (Pb). As main group metals, they have been known to mechanistically favor formic acid, while hydrogen
production is largely suppressed.\textsuperscript{5,25,26} The reason for that has been uncovered: Density functional theory (DFT) calculations compared and classified metal catalysts according to their major product during electrochemical CO\textsubscript{2} reduction. That way it became possible to understand the origin of their reactivity in terms of correlated binding energies of intermediates, explaining their mechanistic reactivity.\textsuperscript{27} That study demonstrated that formic-acid-producing metals have none or only negligible amounts of atomic hydrogen adsorbed at the relevant potentials. In particular, oxide-derived lead (OD-Pb) has exhibited 700-fold lower H\textsuperscript{+} reduction activity.\textsuperscript{28}

Having said that, a plausible strategy toward Cu-based catalyst with suppressed HER involves the combination of main group metal properties and Cu catalysts in form of bimetallic surface catalyst systems. These differ from bulk Cu alloy systems (ordered or disordered) in that they are not subject to preferential surface segregation effects and allow the evaluation of intrinsic bimetallic synergies. Some scattered Cu-based surface bimetallic approaches have been reported.\textsuperscript{29-34} Cu–In and Cu–Sn bimetallic catalysts prepared by electrochemical reduction on oxide-derived copper (OD-Cu) showed unusually high CO Faradaic efficiency. These studies demonstrated that use of a second metal like core–shell structure has the capacity to control the entire set of CO\textsubscript{2} reaction pathways in favor of one single product. Still, beyond these two examples, few to none studies have considered bifunctional and electronic structure effects between Cu and submonolayer adatoms of a second metal for CO\textsubscript{2} reduction. This study changes this.

Here, we demonstrated that submonolayer adatoms of a dissimilar metal electrodeposited on a polycrystalline Cu surface strongly enhances the catalytic selectivity (Faradaic efficiency) of the electrochemical CO\textsubscript{2} reduction reaction due to the coverage-controlled suppression of the HER. As a model system, we considered the Pb/Cu system and deposited Pb adatoms in the form of sub- to one-single monolayer on Cu foils using an underpotential deposition method (UPD). While as little as 0.16 ML Pb surface adatoms on a polycrystalline Cu surface boosted the observed Faradic HCOO\textsuperscript{−} product selectivity 15 times, the 0.78 ML Pb/Cu catalyst exhibited unusually high selectivity for electrochemical CO\textsubscript{2} reduction to HCOO\textsuperscript{−}, and showed previously unachieved HCOO\textsuperscript{−}/H\textsubscript{2} production ratios. We propose that neighboring Pb adatoms were decorated on the HER active site to weaken the adsorption of atomic hydrogen, and at the same time served as active sites for the CO\textsubscript{2} reduction, thereby stabilizing reactive intermediates of the formic acid molecule.

**Experimental Section**

**Preparation and characterization of Pb electrodeposited Cu foil.** The Cu foil (Alfa Aesar, 1.0 mm thickness, 99.9999%\textsuperscript{5}) was cut to the desired electrode size (1 \times 2.5 cm) and electropolished in 85% phosphoric acid (Sigma-Aldrich, \geq 85%) at 4 V versus titanium wire (Ti; Alfa Aesar, 1.0 mm dia, 99.99%) for 5 min. The Cu electrode was rinsed with ultrapure water and dried with nitrogen. Pb was electrodeposited on Cu electrodes in an aqueous solution of 0.01 M Pb(ClO\textsubscript{4})\textsubscript{2}-xH\textsubscript{2}O (Aldrich, \geq 99.995%) with 0.1 M HClO\textsubscript{4} (Aldrich, 70%) by adjusting the applied potential to control the extent of layer deposition. The Pb foil (Alfa Aesar, 1.0 mm thickness, 99.9999\%) was cut to the desired electrode size (1 \times 2.5 cm) and mechanically polished with alumina slurries, and then thoroughly rinsed with ultrapure water and dried with nitrogen.

The prepared electrodes were analyzed by X-ray photoelectron spectroscopy (XPS; Thermo Scientific K-Alpha) and atomic force microscopy (AFM; Cypher S).

**Electrochemical measurements.** Platinum mesh 100 (Sigma-Aldrich 99.99%) and Ag/AgCl (3 M NaCl) were used as a counter electrode and a reference electrode, respectively. Electrochemical measurements were performed by using EC-Lab SP-300 potentiostat in a custom-made two-compartment electrochemical cell, and Nafion 212, a proton exchange membrane, was used to separate the catholyte and the anolyte. The electrolyte solution (0.1 M KHCO\textsubscript{3}; Sigma-Aldrich, \geq 99.95%) was purged with high purity CO\textsubscript{2} (99.999%) gas which average flow rate (Q) was 30 cc/min, and the pH of the electrolyte was 6.8 after saturation. The CO\textsubscript{2} reduction reaction was measured by using chronoamperometry at each fixed potential and gaseous products were quantified by a gas chromatograph (GC; Shimadzu GC 2014) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). Argon (air liquid 5.0) was used as the carrier gas. To quantify formic acid concentration, the electrolyte was analyzed by high-performance liquid chromatograph (Agilent 1200 series) equipped with an organic acid resin from Ziemer chromatographie column, a reflection index detector (RID) and a UV detector.

Solution resistance was measured with Potential Electrochemical Impedance Spectroscopy (PEIS) to correct iR loss. The measured potentials for CO\textsubscript{2} reduction reaction were compensated for iR loss and were reported versus the reversible hydrogen electrode (RHE) by using the following equation. The potential of the reference electrode for Ag/AgCl (3 M NaCl) is 0.21 V.

\[
E \text{(vs RHE)} = E \text{(vs Ag/AgCl)} + 0.21 \text{V} + 0.0591 \text{V} \times \text{pH}
\]

**Calculations of the production rate and Faradaic efficiency of products.** The production rate and Faradaic efficiency were calculated from GC chromatogram peak areas. The production rate \(n\) \text{mol}\text{·g}^{-1}\text{·h}^{-1} is the electrolysis time, \(i_{\text{total}}\) is a measured current by the potentiostat, \(F\) is Faradaic constant, \(P_0\) is pressure, \(T\) is temperature, and \(R\) is ideal gas constant, 83.144 mL·bar·mol\textsuperscript{-1}·K\textsuperscript{-1}.

The production rate is calculated as:

\[
\text{production rate} = V \times Q \times \frac{P_0}{RT}
\]

The overall Faradaic efficiency is:

\[
F.\ E. = \frac{i_{\text{partial}}}{i_{\text{total}}} \times 100 = \frac{nF \times \text{production rate}}{i_{\text{total}}} \times 100
\]

For liquid product, the production rate and Faradaic efficiency were calculated from HPLC chromatogram peak areas where \(C_{\text{liquid}}\) is the concentration of liquid products based on calibration of the HPLC, \(v\) is the volume of the electrolyte, \(t\) is the electrolysis time, \(Q_{\text{total}}\) is a measured total charge.

The production rate is calculated as:

\[
\text{production rate} = \frac{C_{\text{liquid}} \times v}{t}
\]

The overall Faradaic efficiency is:

\[
F.\ E. = \frac{Q_{\text{partial}}}{Q_{\text{total}}} \times 100 = \frac{nF \times C_{\text{liquid}} \times v}{Q_{\text{total}}} \times 100
\]
RESULTS AND DISCUSSION

Pb adatom-modified polycrystalline Cu surfaces were prepared using an underpotential deposition method (UPD)\(^{35,36}\) that was performed in the solution of 0.1 M HClO\(_4\) and 0.01 M Pb(ClO\(_4\))\(_2\)·\(x\)H\(_2\)O with electropolished Cu foil as substrates. The coverage of Pb on the Cu foil was precisely controlled from 1 monolayer (ML) down to submonolayer adatoms by adjusting the applied electrode potential as shown in Figure 1a. The peak at \(-0.26\) V (vs Ag/AgCl) indicates that a Pb monolayer is formed on the Cu foil surface. Through the UPD charge, it can be estimated the amount of charge required to form the monolayer on the exposed Cu surface. Furthermore, by comparing the ratio of the applied charge to the total lead UPD charge, the deposited amounts were controlled to 0.16, 0.54, 0.78, and 1 ML Pb/Cu. The number, shown as Figure 1a inset, indicates four distinct applied potentials (vertical yellow lines numbered one to four) and their related Pb adatom coverage of 0.16, 0.54, 0.78, and 1 ML Pb, respectively. The samples are henceforth referred to as xML Pb/Cu.

To confirm the Pb deposition, X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) were conducted on reference electropolished Cu foils and xML Pb/Cu bimetallic samples. Figure S1a shows the Cu 2p peaks for both 0.78 ML Pb/Cu and Cu foil samples. Furthermore, only the 0.78 ML Pb/Cu displayed Pb 4f peaks (Figure S1b) which indicate Pb was well-deposited on the Cu surface. In addition, the amount of Pb on the Cu foil was estimated by using Cu 2p and Pb 4f peaks in XPS. The atomic ratio of Pb was 1.09, 1.37, 3.12, and 1.31% (Figure 1b), which was in good agreement with the charge-based coverage evaluations, given the difficulties to accurately detect and quantify individual adatom coverages by methods with multinanometer probing depth. Even though 1 ML Pb/Cu amount seemed like an outlier, it was in accordance with expectations as addressed below. Atomic force microscopy (AFM) topographical images in Figure 1c, 1d, and Figure S2 evidence that Pb adatoms were deposited two-dimensionally in a single-layer morphology on the Cu substrates and did not result in 3D Pb clusters or nanoparticles under the chosen underpotential conditions. We found that, from AFM images, the surface roughness was decreased during the Pb deposition. It is noteworthy that the 1 ML Pb/Cu electrode was not uniform due to 37% of Pb–Cu lattice mismatch and the resulting thermodynamic instability.\(^{37}\) This is why the 1 ML Pb/Cu XPS result deviated from the
atomic ratio trend. Figure 1e shows a schematic illustration of where the Pb adatoms are located on the copper surface. Next, the electrochemical CO$_2$ reduction reaction of the prepared Pb/Cu electrodes was explored. It is noteworthy that regardless of the Pb coverage, the Pb adatom modified Cu electrodes mainly produced formic acid (Figure S3 and Figure S4). Figure 2 shows the $iR$-corrected potential dependent production rate and Faradaic efficiency profiles of H$_2$ and HCOO$^-$ measured at the steady-state current density in CO$_2$-saturated 0.1 M KHCO$_3$ for Cu foil, 0.78 ML Pb/Cu and Pb foil. The 0.78 ML Pb/Cu showed an exceptionally low H$_2$ Faradaic efficiency given the high overpotential compared to both pure Cu and pure Pb foils (Figure 2a), while it had comparable HCOO$^-$ Faradaic efficiency with a solid pure Pb foil (Figure 2b). This is important and underlines the massive effect of adatom decoration. The maximum HCOO$^-$ Faradaic efficiency was 74.2 ± 2.3% at −1.14 V, 25.3 ± 4.9% at −1.04 V, and 81.4 ± 5.2% at −1.17 V for 0.78 ML Pb/Cu, Cu foil, and Pb foil, respectively. Although Pb foil showed higher maximum HCOO$^-$ Faradaic efficiency, it required a more anodic onset overpotential than the 0.78 ML Pb/Cu (Figure S5a) in the lower cathodic potential region (−1.0 to −1.1 V vs RHE).

In order to investigate the variations in the Faradic competition between hydrogen evolution and CO$_2$ reduction, we compared absolute product yields for HER (Figure 2c), and HCOO$^-$ production by CO$_2$ reduction reaction (Figure 2d), respectively. We emphasize that the competitive H$_2$ production rate at 0.78 ML Pb surface coverage was extremely suppressed, in particular as much as 652 times lower, compared with a pure Cu foil. Even pure Pb, commonly known as the most efficient material to suppress HER, showed a larger H$_2$ evolution rate (Figure S5b) than the bimetallic 0.78 ML Pb/Cu catalysts. Thus, 0.78 ML Pb/Cu not only displayed increased absolute HCOO$^-$ production rates compared to Pb at overpotentials in the range of −1.0 to −1.1 V vs RHE but also significantly decreased H$_2$ production rates over a broad overpotential range of −1.1 to −1.3 V. Clearly, the 0.78 ML Pb/Cu has a somewhat lower rate of HCOO$^-$ formation than Cu foil due to the blocking effect of Pb adatoms of sites (Figure S5c) that previously served for the formation of H$_2$ and HCOO$^-$.

To demonstrate the exceptional product selectivity of the 0.78 ML Pb/Cu surface, we then considered the ratio of the HCOO$^-$/H$_2$ production rates in Figure 3. For the Faraday
amounts of Pb adatoms caused the emergence of new catalytic properties of a metal surface.38 Comparing HCOO− to the Cu surface, suppression of H2 production was observed such that the 0.78 ML significantly outperformed Cu and Pb metals individually by having greater HCOO−/H2 ratios over the entire applied potential range up to high current densities. The Pb/Cu system represents an impressive example of the dramatic effect of an incomplete adatom overlayer of a dissimilar metal on the electronic and structural properties, and ultimately catalytic properties of a metal surface.38−40 Minute amounts of Pb adatoms caused the emergence of new beneficial catalytic properties for the electrochemical CO2 reduction reaction.

In order to gain insight in the effects of Pb adatoms over the entire coverage range, the production rate and Faradaic efficiency of all samples were compared at fixed potentials of −1.05 and −1.25 V vs RHE (Figure 4). All of Pb/Cu electrodes showed lower H2 production rate than Cu foil, and the 0.78 ML Pb/Cu showed the lowest H2 and CH4 production rate compared with 0.16, 0.54, and 1 ML Pb/Cu (Figure 4a). On the other hand, all Pb modified Cu electrodes displayed similar HCOO− and CO production rates. These trends remained similar even at −1.25 V vs RHE (Figure 4b) suggesting that absolute HCOO−, CO, and CH4 production rates were quite independent of the detailed Pb amount. More specifically, the 1 ML Pb/Cu sample ceased to produce CH4 just like Pb foils at −1.25 V vs RHE. Pb foil exhibited lower overall activity at −1.05 V vs RHE, yet higher H2 production rate at −1.25 V vs RHE compared to the bimetallic electrodes. Comparing HCOO− Faradaic efficiencies of all samples at a fixed applied potential of −1.05 V vs RHE (Figure 4c), Faradaic efficiency of 0.78 ML Pb/Cu revealed the highest selectivity thanks to suppressed HER. The Faradaic efficiency of HCOO− was 44.0 ± 1.5%, 50.9 ± 11.8%, 70.5 ± 0.7%, 52.2 ± 5.6%, 14.9 ± 4.9%, 50.3 ± 17.3% for 0.16 ML, 0.54 ML, 0.78 ML, 1 ML Pb/Cu, Cu foil and Pb foil, respectively. At more negative potentials (−1.25 V vs RHE), the favorable differences between HCOO− and H2 Faradaic efficiencies widened for the bimetallic Pb adatom Cu electrodes. Figure 4d shows a comparative synopsis of products and their Faradaic efficiency at −1.25 V vs RHE. The Faradaic efficiency of Cu foil exhibited 4.0 ± 3.0%, 30.7 ± 1.3%, and 51.6 ± 2.2% for HCOO−, H2, and CH4, respectively. Noteworthy, the HCOO− Faradaic efficiencies for 0.16, 0.54, and 0.78 ML Pb/Cu were about 10 times higher than those of H2 Faradaic efficiency. In contrast, the HCOO− Faradaic efficiencies of 1 ML Pb/Cu and Pb foil ranged only about 6 times and 3 times higher than the H2 Faradaic efficiency, respectively. In brief, the Pb/Cu system showed an efficient selectivity (ratio of desired product/H2 product) over the entire potential.

Considering the electrocatalytic properties of Pb-deposited Cu catalysts and density functional theory (DFT) calculation of Cu and Pb metals reported in literature,37,41−44 we propose a plausible mechanism for the selective formation of formic acid: Cu mainly produces methane, ethylene, hydrogen, and alcohols depending on the applied potential during CO2 reduction. Pb, in contrast, primarily generates formic acid and hydrogen. The product selectivity of the CO2 reduction reaction is controlled by the chemisorption of reactive intermediates such as *CHO or *COOH. HCOO− is thought to form by a one proton-one electron transfer to *CHO. While *COOH leads to the formation of *CO, which subsequently desorbs to form gaseous CO(g) if and only if the CO chemisorption is sufficiently weak, *CO can be further protonated and reduced to CH4 or undergo C−C coupling with another *CO to form C2H4 and C2H5OH if the *CO chemisorption is strong enough.27,46,47 Cu was shown to...
support both pathways, while Pb is thought to stabilize only the \( \text{OCHO} \) intermediate. In addition, it has also been reported that the formation of selective products in electrochemical \( \text{CO}_2 \) reduction is affected by the morphology and roughness of Cu. The high index surfaces of copper such as \( \text{Cu}(110) \) or \( \text{Cu}(211) \) are known as the active sites for producing \( \text{C}_1 \) hydrocarbons, while the selectivity of \( \text{CH}_4 \) and \( \text{CH}_2 \) is controlled by the ratio of \( \text{Cu}(100) \) to \( \text{Cu}(111) \) facets. Given that, even at small coverages, Pb adatoms is able to strongly enhance the HCOO\(^-\) formation, we conclude that Pb adatoms must be decorated preferentially on shared active sites for the HER and the \( \text{CO}_2 \) reduction on Cu surface (Figure 1e), resulting in substantial suppression of HER and drastic change in the carbonous product spectrum, mainly producing HCOO\(^-\). Any other sites on the residual Cu surface must be related to the formation of products other than HCOO\(^-\). Following Taylor’s concept of a small fraction of catalytically active surface sites within a large total population of surface sites, the primary reaction product HCOO\(^-\) is likely produced on that minute amount of under potentially deposited Pb adatoms or Pb adatom pairs, where only the \( \text{OCHO} \) intermediate is stabilized. We concluded that Pb/Cu system has both geometry and electronic structure effect due to its highly suppressed \( \text{H}_2 \) production and comparatively accelerated HCOO\(^-\) production relative to Pb.

\section*{CONCLUSIONS}
We have prepared (sub) monolayer Pb modified Cu catalysts using electrochemical underpotential deposition (UPD). Minute coverages of Pb demonstrated massive effects on the catalytic activity and selectivity of the electrochemical \( \text{CO}_2 \) reduction reaction. Pb adatom modified Cu electrodes are exceptionally effective HCOO\(^-\) producers and display unprecedented sustained suppression of the competitive hydrogen evolution resulting in high product efficiencies. Especially, the 0.78 ML Pb/Cu showed a high ratio of HCOO\(^-\)/\( \text{H}_2 \) production rate due to effective suppression of HER which was suppressed as much as 652 times compared with Cu foil. We found that the Pb adatom, regardless of the amount, could be placed on the active site of \( \text{CO}_2 \) reduction and the active site of HER, thereby stabilizing the \( \text{OCHO} \) intermediate and weakening the \( \text{H} \) adsorption to strongly affect the Cu electrode activity. It is expected that the high selectivity and activity in electrochemical \( \text{CO}_2 \) reduction can be tuned with a second metal, which may have effects in changing the binding energy strength and selective affinity for determining intermediates. If it can maintain efficient selectivity, especially at high overpotential, this will be one of the key factors in the development of future flow cells.

\section*{ASSOCIATED CONTENT}

* Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.catal.8b02846.

AFM topographical images and further electrochemical \( \text{CO}_2 \) reduction data (PDF)

\section*{AUTHOR INFORMATION}

**Corresponding Author**
*E-mail: pstrasser@tu-berlin.de.*

**ORCID**
Cheonghee Kim: 0000-0002-9502-3429

Tim Möller: 0000-0002-4353-0197
Arne Thomas: 0000-0002-2130-4930
Peter Strasser: 0000-0002-3884-436X

**Notes**
The authors declare no competing financial interest.

\section*{ACKNOWLEDGMENTS}
This work was supported German Federal Ministry of Education and Research (Bundesministerium für Bildung und Forschung, BMBF) under Grant #03SF0523 “CO2E-KAT”. We thank Jana Lutzki in the Technische Universität Berlin for her support with AFM measurements and Taeho Yoon for his great help with the 3D figure.

\section*{REFERENCES}