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System Integration of Rationally Designed Dilute Alloy Catalysts for Energy-Efficient Electrochemical CO2-To-Fuel Conversion

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Disclaimer

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Final Technical Report

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List of Acronyms

CO: Carbon monoxide
CO_2: Carbon dioxide
C_1: Products that contain one carbon atom like carbon monoxide and methanol
C_2: products that contain two carbon atoms like ethylene and ethanol
C_{2+}: Multi-carbon molecules like ethylene, ethanol, and propanol
EB: Electron beam
EE: Energy efficiency
eCO_2R: electrochemical CO_2 reduction
FY: Faradaic yield
GDE: Gas diffusion electrode
GDL: Gas diffusion layer
HER: Hydrogen evolution reaction
MS: Magnetron sputtering
npAu: Nanoporous gold
SEM: Scanning electron microscopy
TEM: Transmission electron microscopy
TEM-EELS: TEM based electron energy loss spectroscopy

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Executive Summary

Energy effiecient electrochemical conversion of CO_2 to high-demand chemicals and transportation fuels using renewable solar and wind energy is a key technology needed for a high-productivity, low-carbon future. However, the development of scalable, low-cost, active, selective, and stable electrocatalysts remains a key challenge that needs to be overcome to enable high-volume conversion of CO_2 to feedstock chemicals for the chemical industry. In previous work, Lawrence Livermore National Laboratory (LLNL) has developed a rational design platform for dilute alloy transition metal electrocatalysts that promise to make electrochemical CO_2 conversion more energy-efficient and selective.

In this project, we worked with our industrial partners, Twelve and TotalEnergies, to improve scale-up, integration, and stability of LLNL's dilute alloy catalyst technology into an industry-relevant zero-gap electrolyzer platform. Through virtual experiments and data analysis, we designed efficient and cost-effective copper-based catalysts. The catalyst was specifically designed to streamline the slowest and most energy-intensive step of the electrochemical chemical transformation of CO_2 to multi-carbon products – that is making the carbon-carbon bond by dimerization of the reaction intermediate carbon monoxide - resulting in up to 10% improvement in energy efficiency for C_2 products while simultaneously increasing the selectivity towards C_2 products. We tested two different scalable catalyst coating technologies and down-selected magnetron sputtering as the technique that provided the best control over catalyst loading, composition, and morphology. Using this technology, we successfully demonstrated integration of our dilute alloy catalysts into a 100 cm^2 electrolyzer platform with Faradaic efficiencies for ethylene production reaching 40% at a current density of 200 mA/cm^2. We also developed the technology to integrate a well-defined nanoscale porosity by depositing alloy compositions that were compatible with dealloying, that is, selective leaching of an alloy component to generate nanoscale porosity. We observed that integration of the dealloying-derived nanoporosity improved catalyst performance and stability by leading to a more hydrophobic catalyst/anion exchange membrane interface. Unsolved problems that still need to be addressed are corrosion of the Cu catalyst -specifically if the used catalyst is exposed to air - as well as long term stability do to salt formation/deposition and flooding of the catalyst/electrolyzer flow channels, especially at higher current densities. As we only worked on optimization of catalyst composition, coating thickness, and morphology, further performance optimization will require a system level approach that includes optimization of electrolyzer design and membrane technology.

Introduction

Electrochemical conversion of CO_2 from an industrial waste product to high-demand chemicals and transportation fuels promises to reduce the energy intensity of key chemicals and prepare us for a high-productivity, low-carbon future. Targeted chemicals include ethylene, ethanol and methane that are needed to feed industrial chemical process lines and power vehicles. Electrochemical CO_2 reduction (eCO_2R) also provides a pathway for high-volume, seasonal storage of renewable energy by transforming intermittent renewable electric energy, such as solar and wind, into chemical energy. The development of scalable, low-cost, active, selective, and stable electrocatalysts remains one of the key challenges of electrochemical conversion of CO_2. In previous work LLNL has developed a rational design platform for dilute alloy transition metal electrocatalysts that promise to make electrochemical CO_2 conversion more energy-efficient and selective. The catalysts were specifically designed 1) to be thermodynamically stable with respect to composition under eCO_2R conditions and 2) to streamline the slowest and most energy-intensive step of the electrochemical chemical transformation of CO_2 to multi-carbon products. The slowest step of eCO2R towards multi-carbon products the dimerization of the reaction intermediate carbon monoxide resulting in the formation of carbon-carbon bonds, and testing of our dilute alloy catalysts revealed energy efficiency improvements for C_2 products of up to 10% while simultaneously increasing the selectivity towards C_2 products. In this project we demonstrated the scalability and integration of LLNL's dilute alloy catalyst technology using an industry-relevant zero-gap electrolyzer platform for energy efficient large-scale CO_2-to-fuel conversion.

Implementing electrochemical CO_2 reduction at the gigaton scale will enable us to supplement and ultimately replace fossil fuels as the source of gas and feedstock chemicals. This forms the basis of the fifth industrial revolution, which will transform energy storage as well as fuel and feedstock chemical production. LLNL's dilute alloy catalyst technology provides an enabling component for this revolutionary technology as it opens the door to large-scale fabrication of highly reactive non-precious metal catalysts, where the reactivity is linked to thermodynamically stable dilute surface alloys rather than to thermodynamically unstable low coordination reaction sites or other transient surface configurations.

Background

Current catalyst technologies are mostly based on generating active reaction sites through realization of certain catalyst morphologies that are thermodynamically unstable, and thus prone to deactivation. In contrast, our theory-guided dilute alloy catalyst technology is based on generating active sites through identifying thermodynamically stable dilute alloy surface configurations that, by definition, are stable. In these dilute alloy configurations, the promoting dilute alloy component boosts activity by lowering the activation barriers of the rate-limiting step, while the majority alloy component, Cu, provides selectivity towards the desired multi-carbon product molecules.

So far, copper and its alloys remain the only catalysts that have been demonstrated to efficiently convert CO_2 into multi-carbon (C_{2+}) products, such as ethylene, ethanol, acetate, and propanol. Previous studies focused primarily on understanding the effect of the copper catalyst morphology and composition on the eCO_2R performance [1-11]. Compared to catalyst and electrolyzer design, far fewer studies have addressed catalyst integration despite its critical importance on overall device performance and electrolyzer size upscaling. Hand, screen, spray, and inkjet painting are frequently used methods for applying the catalyst coating on the GDL or the electrolyzer membrane [12-14]. While all these methods are scalable towards larger electrodes and generally can provide good thickness and uniformity control (with exception of hand brush painting), they require development of suitable and stable particle-based ink systems. Furthermore, the particle character of the resulting catalyst coatings can cause poor electrical connectivity and mechanical properties. But despite critical importance for industrial applications, few studies have systematically addressed the effect of catalyst deposition method and coating thickness on eCO_2R performance, especially for scalable electrolyzer designs.

Results and Discussion

To identify catalyst synthesis and integration techniques that best fit commercialization requirements for eCO2R, we worked on the following tasks: 1) Scale up catalyst production and fabrication of uniform large area catalyst coatings with precisely controlled thickness, composition and morphology; 2) Optimization of catalyst composition in terms of eCO2R performance as measured by energy efficiency and selectivity towards C_{2+} products; and 3) Addressing catalyst stability related to morphology.

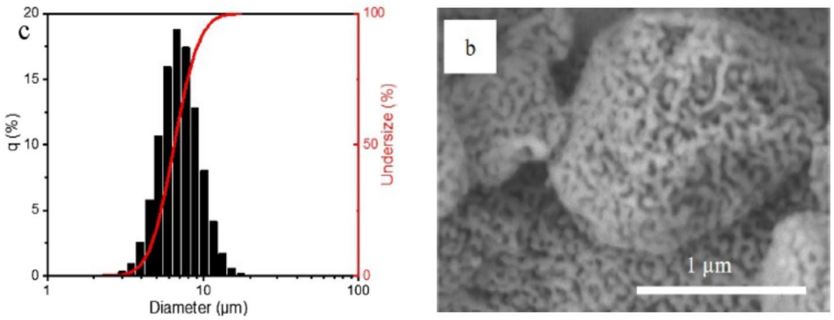


Figure 1: Particle size distribution of ball-milled aluminium-based Cu alloy, and b) SEM image showing the microstructure of the npCu powders obtained by dealloying aluminium-based Cu alloy powder in 6 M KOH.

We first used ball-milling as a scalable approach to fabricate 10+ g quantities of catalyst particles, enough to coat ten 1000 cm^2 gas diffusion layer (GDL) substartes even at relatively high catalyst loadings of 1 mg/cm^2. Specifically, we fabricated nanoporous dilute Cu alloy particles with a narrow sub-one-micron size distribution by first ball milling an aluminum-based precursor alloy followed by selective leaching of the aluminum component (Figure 1). The resulting nanoporous copper powders were integrated onto a 25 cm^2 gas diffusion electrolyzer for electrochemical CO_2 reduction and tested at current densities ranging from 50 to 150 mA/cm^2. Faradaic yields (FY) for ethylene production of up to 34 % were achieved at 75 mA/cm^2. While this approach is universal and can applied to other alloy systems, and allows fabrication of nanoporous metal powder catalysts at large scales, we found that integration in the electrolyzer resulted in relatively high cell voltages of up to 5.4 V for 150 mA/cm^2 current density [15] which limits the energy efficiency that can be achieved.

We then focused on physical vapor deposition techniques that promised easier integration of LLNL's dilute alloy catalyst technology. We selected magnetron sputtering (MS) over electron-beam (EB) deposition as it provided better compositional control, a requisite for reproducible and accurate catalyst composition. The thickness of the catalyst coatings was kept constant at either 400 nm or 800 nm as previous work on pure Cu catalysts showed that these thicknesses result in the highest energy efficiency (i.e., sum over the Faradaic efficiency times theoretical cell potential divided by the applied potential for all eCO_2R products). Testing pure Cu catalyst coatings in a large electrode area zero-gap electrolyzer yielded a Faradaic efficiency for ethylene production of up to 39% demonstrating performance scalability for eCO_2R.

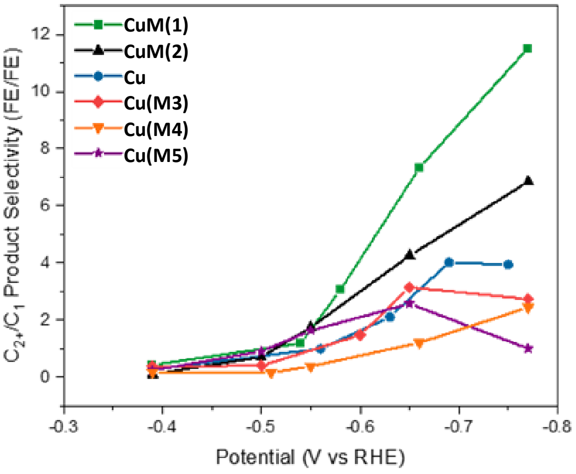


Figure 2: C_2/C_1 product ratio as a function of applied electrochemical potential for various Cu based dilute alloys. Note the shift towards C_2 products for the CuM(1) and CuM(2) alloy catalysts compared to pure Cu (blue).

Using this experimental platform allowed us to measure the effect of the dilute alloy component (M) on eCO2R activity and selectivity without interference from changes of the catalyst morphology. Guided by theory, we selected representative Cu based dilute alloy systems which were predicted to either increase or decrease the C_2/C_1 selectivity compared to pure Cu catalysts coatings, and that were thermodynamically stable under eCO2R conditions [16]. The morphology of these MS dilute alloy catalyst coatings was assessed by scanning electron microscopy (SEM), and the distribution and chemical state of the dilute alloy metal component was measured by transmission electron microscopy (TEM) and TEM based electron energy loss spectroscopy (TEM-EELS). To assess the effect of the CO2R electrolyzer environment on activity and selectivity, we tested all catalyst coatings in two different electrolyzer designs – a large-area (25/100 cm^2) zero-gap electrolyzer design and a smaller scale three-compartment microfluidic electrolyzer. We observed excellent agreement of the measured C_2-product selectivity with the theory predicted CO dimerization enthalpy which is the rate limiting step of the CO_2R towards C_2 products. Specifically, the C_2/C_1 product selectivity in the microfluidic electolyzer increased from about 4 to 10 as the calculated CO dimerization reaction enthalpy decreased by serval hundred meV (Figure 2). In general, the zero-gap electrolyzer environment resulted in a higher C_2/C_1 selectivity (C_2/C_1~10-30) than the microfluidic electrolyzer (C_2/C_1~4-10). Liquid multicarbon products (such as ethanol) were responsible for most of the C_2/C_1 selectivity increase of dilute alloy catalysts. The theory also predicted that the dilute alloy activity is sensitive to the surface termination of the dilute alloy catalyst with the activity boosting effect being more pronounced on 111 facets compared to 100 facets, a trend that also was observed experimentally. The highest device level energy efficiencies for C_{2+} products in the zero-gap electrolyzer at 200 mA/cm^2 were 33% (57% for CO_2RR and HER combined) compared to 22% for the pure Cu catalyst.

To assess catalyst stability, we tested 100/400 nm MS Cu catalyst coatings in the large electrode area zero-gap electrolyze setup for 6.5 hours at 200 mA/cm^2. No difference between 100 and 400 nm coatings in terms of stability and Faradaic yield towards ethylene was observed. For the specific test conditions, the FY towards ethylene decreased from 35% to about 20%. The MS Cu coatings still looked metallic after opening and rinsing the Cu coated GDL, but when turned black within minutes. These experiments rule out that the loss of selectivity towards ethylene is due to corrosion of the Cu catalyst during eCO_2R but seems to be flooding related due to salt accumulation in the catalyst-GDE layer and flow channels which also seems to accelerate Cu corrosion once exposed back to air.

To tune surface area and wetting behavior of MS catalyst coatings, we studied controlled integration of dealloying derived nanoporosity, that is, nanoporosity created by selective leaching of one or more alloy components. To establish this technology, we first used the Au-Ag system depositing 400/800 nm thick MS $Au_{0.3}Ag_{0.7}$ coatings which were then dealloyed in nitric acid to obtain 400/800 nm thick nanoporous Au (npAu) catalyst coatings [17]. We observed that, compared to dense MS Au films without integrated nanoporosity, the npAu catalyst coatings enabled higher Faradaic yields and improved catalyst stability for CO_2-to-CO reduction with Faradaic yields of up to 88% at 100 mA/cm^2. For a 800 nm npAu coating, the device level energy efficiency for CO_2 to CO conversion reached 45% (52% for CO + H_2) at 100 mA/cm^2 with a single pass CO_2 conversion efficiency of ~12%. Contact angle measurements revealed that npAu coatings provide a more hydrophobic electrode interface compared to MS Au coatings, suggesting that the more hydrophobic interfacial environment of npAu coatings helps mitigating electrode flooding which is associated with performance deterioration over time. We when developed a process to generate nanoporous Cu (npCu) coatings from MS Cu-Al coatings. The eCO2R tests of these npCu catalyst coatings showed no significant performance improvements over dense MS Cu alloy catalyst coatings demonstrating once more that the environment created by eCO2R is an important component controlling the performance at the device level.

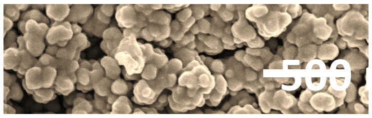
Benefits Assessment

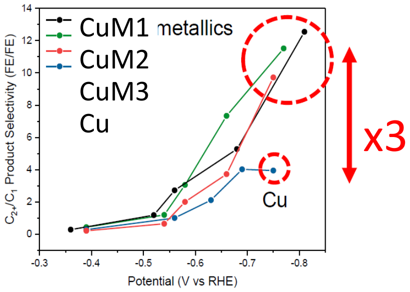
This project established catalyst coating technologies that enable scalable integration of dilute alloy catalyst coatings with controlled nanoporosity. Specifically, MS is scalable to very large electrode areas (~10^4 cm^2),[18, 19] produces less waste and is less labor-intensive than traditional electrodeposition methods, thus making them cost competitive, despite higher capital costs.[20] We tested serval dilute alloy compositions that were predicted to improve the CO_2 to C_{2+} product selectivity and energy efficiency by lowering the energetic barrier of the rate limiting CO coupling reaction and found excellent agreement between predicted and experimentally C_2/C_1 product selectivity.

Commercialization

Commercialization will require further de-risking of the technology with respect of system level performance and lifetime

Accomplishments





- Developed a scalable dilute alloy catalyst technology for electrochemical CO_2 reduction that increase the product selectivity towards C_{2+} products at high current densities (400 mA/cm^2) to more than 90% (3x that of the standard Cu catalyst in the same environment)
- Demonstrated half-cell eCO_2R energetic efficiencies of 51% (56.5% for eCO_2RR and HER combined) with C_{2+} FE of 70% at 400 mA/cm^2 (microfluidic GDE)
- Demonstrated device level eCO_2R energetic efficiencies of 32% for C_{2+} eCO_2R (57% for eCO_2R and HER combined) in zero-gap gas diffusion electrolyzer @ 200 mA/cm^2
- Performed tests at the 100 cm^2 electrode scale reaching ethylene FYs of up to 40% @ 200 mA/cm^2
- Developed predictive theory allowing evaluation of stability and activity of dilute Cu-based alloys for electrochemical CO_2 reduction (*J. Chem. Phys.* 2021, **155**, 114702)
- Developed scalable dilute-alloy catalyst coating technology using physical vapor deposition methods (*ACS Appl. Mater. Interfaces* **2022**, 14, 7731−7740)
- Developed scalable technology for integration of nanoporous catalyst coatings with controlled porosity by either spray coating ball-mill derived nanoporous Cu catalyst particles (*J. CO_2 Utilization* **2021,** 45, 101454) or by dealloying MS alloy coatings (*The J. Phys. Chem. C* **2022,** 126, 19637-19646).

Conclusions

This project established the technology to predict, fabricate, and integrate stable and active dilute alloy eCO_2R catalysts that allow one to tailor product selectivity and optimize energy efficiency.

Recommendations

Further improvements in terms of energy efficiency, selectivity, and stability will require a system level approach where all electrolyzer components are optimized at the same time.

References

1. Hori, Y., et al., *Electrocatalytic Process of CO Selectivity in Electrochemical Reduction of CO_2 at Metal Electrodes in Aqueous Media.* 1994 Electrochim. Acta 39: p. 1833-1839
2. Hori, Y., et al., *Electrochemical Reduction of Carbon Dioxide at Various Series of Copper Single Crystal Electrodes.* 2003 J. Mol. Catal. A Chem. 199: p. 39-47
3. Kuhl, K.P., et al., *New Insights into the Electrochemical Reduction of Carbon Dioxide on Metallic Copper Surfaces.* 2012 Energ. Environ. Sci. 5: p. 7050-7059
4. Li, C.W. and M.W. Kanan, *CO_2 Reduction at Low Overpotential on Cu Electrodes Resulting from the Reduction of Thick Cu_2O Films.* 2012 J. Am. Chem. Soc. 134: p. 7231-7234
5. Reske, R., et al., *Particle Size Effects in the Catalytic Electroreduction of CO_2 on Cu Nanoparticles.* 2014 J. Am. Chem. Soc. 136: p. 6978-6986
6. Lu, Q., J. Rosen, and F. Jiao, *Nanostructured Metallic Electrocatalysts for Carbon Dioxide Reduction.* 2015 Chemcatchem 7: p. 38-47
7. Loiudice, A., et al., *Tailoring Copper Nanocrystals towards C-2 Products in Electrochemical CO_2 Reduction.* 2016 Angew. Chem. 55: p. 5789-5792
8. Hahn, C., et al., *Engineering Cu Surfaces for the Electrocatalytic Conversion of CO_2: Controlling Selectivity Toward Oxygenates and Hydrocarbons.* 2017 Proc. Natl. Acad. Sci. USA 114: p. 5918-5923
9. Ma, S., et al., *Electroreduction of Carbon Dioxide to Hydrocarbons Using Bimetallic Cu-Pd Catalysts with Different Mixing Patterns.* 2017 J. Am. Chem. Soc. 139: p. 47-50
10. Jiang, K., et al., *Metal Ion Cycling of Cu Foil for Selective C-C Coupling in Electrochemical CO_2 Reduction.* 2018 Nat. Catal. 1: p. 111-119
11. Nitopi, S., et al., *Progress and Perspectives of Electrochemical CO_2 Reduction on Copper in Aqueous Electrolyte.* 2019 Chem. Rev. 119: p. 7610-7672
12. Taylor, A.D., et al., *Inkjet Printing of Carbon Supported Platinum 3-D Catalyst Layers for Use in Fuel Cells.* 2007 J. Power Sources 171: p. 101-106
13. Jhong, H.R., F.R. Brushett, and P.J.A. Kenis, *The Effects of Catalyst Layer Deposition Methodology on Electrode Performance.* 2013 Adv. Energy Mater. 3: p. 589-599
14. Wang, Z.Q. and Y. Nagao, *Effects of Nafion Impregnation using Inkjet Printing for Membrane Electrode Assemblies in Polymer Electrolyte Membrane Fuel Cells.* 2014 Electrochim. Acta 129: p. 343-347
15. Qi, Z., et al., *Scalable fabrication of high activity nanoporous copper powders for electrochemical CO2 reduction via ball milling and dealloying.* 2021 Journal of CO2 Utilization 45: p. 101454
16. Weitzner, S.E., et al., *Evaluating the stability and activity of dilute Cu-based alloys for electrochemical CO2 reduction.* 2021 Journal of Chemical Physics 155
17. Qi, Z., et al., *Effect of Gold Catalyst Surface Morphology on Wetting Behavior and*

Electrochemical CO2 Reduction Performance in a Large-Area Zero-Gap Gas Diffusion Electrolyzer. 2022 The Journal of Physical Chemistry C 126: p. 19637-19646

18. Kukla, R., *Magnetron Sputtering on Large Scale Substrates: An Overview on the State of the Art.* 1997 Surf. Coat. Tech.
93: p. 1-6
19. Jankowski, A., M. McKernan, and J. Chesser, *The Use of Magnetron Arrays for Depositing Large-Area Oxide Coatings.* 2000 Surf. Coat. Tech. 133-134: p. 602-605
20. Merlo, A. and G. Leonard, *Magnetron Sputtering vs. Electrodeposition for Hard Chrome Coatings: A Comparison of Environmental and Economic Performances.* 2021 Materials 14