Sequential Cascade Electrocatalytic Conversion of Carbon Dioxide to C-C Coupled Products

Joel W. Ager

Joint Center for Artificial Photosynthesis, Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, 94720, CA (USA)

Abstract:

Cascade catalytic processes perform multi-step chemical transformations without isolating the intermediates. Here, we demonstrate a sequential cascade pathway to convert CO_2 to C_{2+} hydrocarbons and oxygenates in a two-step electrocatalytic process using CO as the intermediate. CO_2 to CO conversion is performed by using Ag and further conversion of CO to C-C coupled products is performed with Cu. Two approaches are shown here:

1. Cascade conversion of CO to C2+ oxygenates on microfabricated interdigitated Au and Cu electrodes
2. Cascade reactor with convective transport of the reaction intermediate.

Introduction

In cascade catalysis, two or more catalyzed reactions are coupled together in a single pot, without isolation of the reaction intermediates. Natural photosynthesis provides a prototypical example of an enzymatic cascade, and there has been intense interest in the prospects of coupling enzymes with synthetic homogeneous and heterogeneous catalysts to increase the reactivity, selectivity, and sustainability of chemical syntheses. Electrochemical CO2 reduction (CO2R), which can be performed under mild conditions of ambient pressure and room temperature, is an excellent platform for exploring cascade approaches for selective chemical synthesis. Notably, catalysts (e.g. Ag, Au) which produce CO and which convert CO to C-C coupled products (e.g. Cu) are attractive for this purpose

Results, Highlights, and Accomplishments

Cascade Electrocatalysis for CO_2 Conversion

Scientific Achievement

Bimetallic cascade catalysis system for electrochemical CO_2 reduction using CO as an intermediate species

Significance and Impact

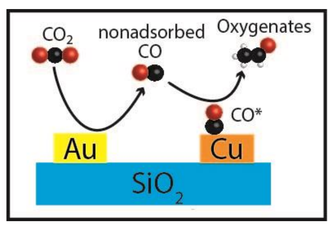
Inspired by the multi-step enzymatic pathways found in the Calvin cycle, first demonstration of sequential cascade electrocatalysis for chemical synthesis

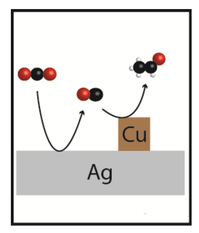
Research Details

–Micropatterned bimetallic catalysts: Ag/Au produce the CO intermediate, which undergoes further conversion to C_{2+} products on Cu

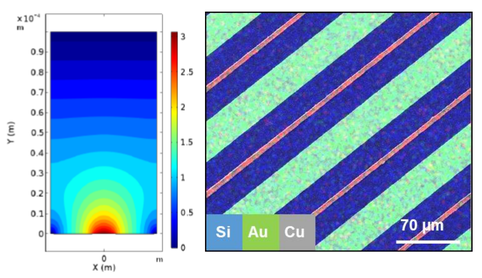
–Modeling and experiment confirm diffusional transport of CO intermediate over 10's of microns

–Ratio of Ag/Au to Cu controls activity of intermediate CO; higher CO activities favor oxygenate (ethanol, acetate, acetaldehyde) over ethylene formation

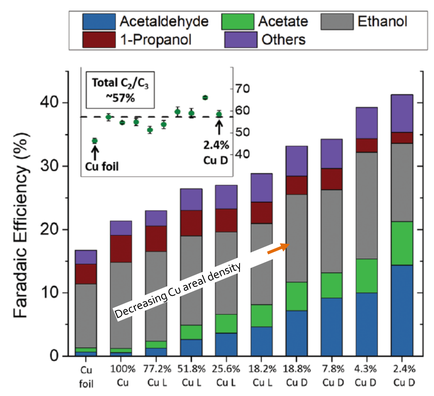




Independently addressable (left) and coupled (right) bimetallic arrays used for two-step cascade conversion of CO_2



Simulations and experiment confirm transport and conversion of CO intermediate



While maintaining 50-70% FE to C_{2+} products, selective oxygenate production is achieved at small relative coverages of Cu (high local concentration of CO intermediate)

Team

Yanwei Lum (JCAP), Gurudayal (JCAP), David Perone (LBNL and EPFL), Saurabh Malini (UCB), and Sophia Haussener (EPFL)

Cascade Electrocatalysis for CO_2 Conversion with Convective Transport

Scientific Achievement

Efficient transport of intermediate species in a cascade CO_2 reduction reactor

Significance and Impact

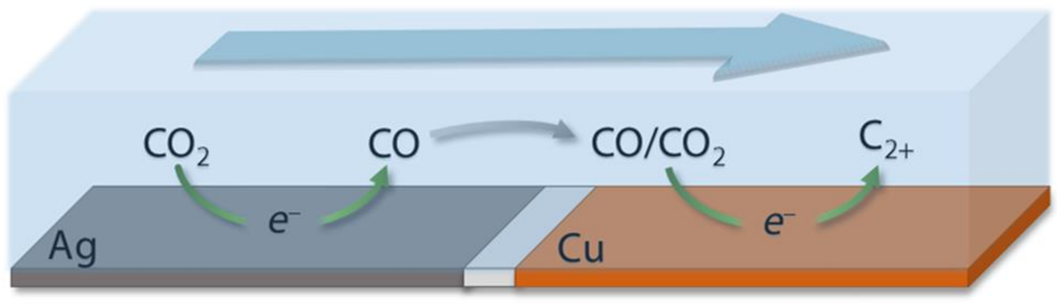
Modular concept will allow selective and efficient CO2R

Research Details

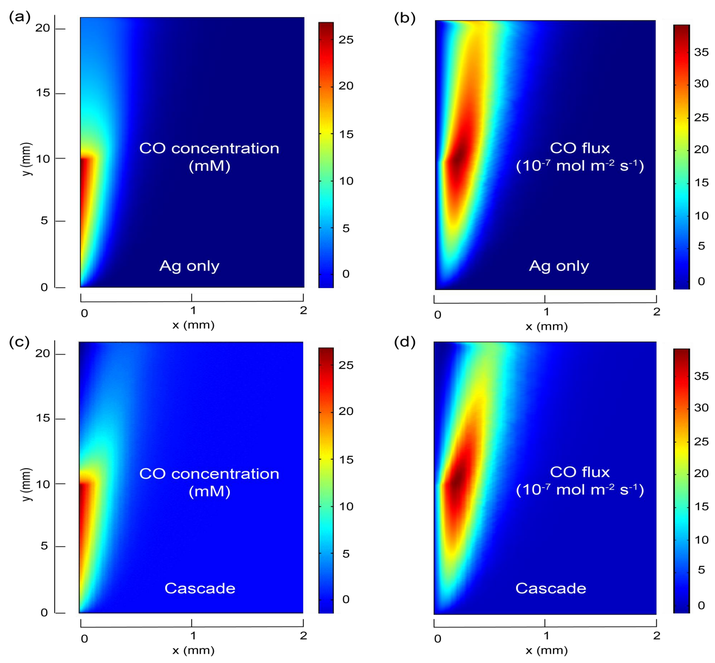
–Ag produces the CO intermediate, which undergoes further conversion to C_{2+} products on Cu located downstream in the reactor

–Modeling and experiment confirm efficient conversion of the CO mediated by convective transport

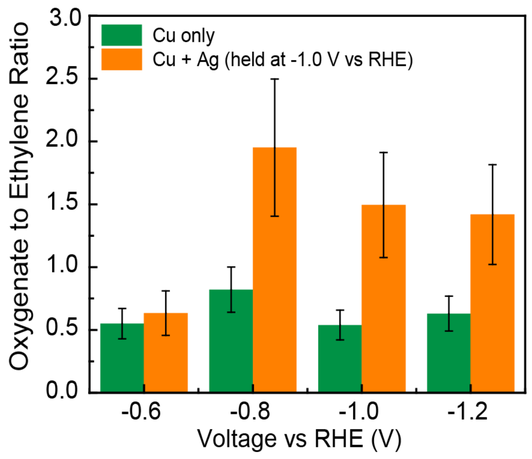
–Operation in cascade mode, as compared to control experiments performed with only the Cu electrode activated, leads to an increase in the oxygenate to hydrocarbon ratio.



Schematic of cascade electrochemical CO2 reduction reaction.



(a, c) Contour plot of CO concentrations for a flow rate of 2 ml/min, a, and diffusion-limited conversion at the Cu electrode and in cascade mode. (b, d) CO flux (concentration * flow velocity) for the conditions used in (b) at the Ag electrode and in cascade mode.



Oxygenate to ethylene ratio as a function of voltage in cascade mode. Error bars are standard deviations from repeat experiments, typically 3

Outlook

This type of cascade cell concept could potentially be coupled electrochemical CO_2 reduction with enzymes for high energy density product formation. It is also conceptually possible to scale the approach to more electrodes and different geometries to drive CO_2R with high intermediate conversion efficiency and high yield to C-C coupled products.

Acknowledgment

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References

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Gurudayal; Perone, D.; Malani, S.; Lum, Y.; Haussener, S.; Ager, J. W. Sequential Cascade Electrocatalytic Conversion of Carbon Dioxide to C–C Coupled Products. *ACS Appl. Energy Mater.* **2019**, *2*, 4551–4559.