

Nanostructured Cu Electrodes for Energy-Efficient Conversion of CO₂ to Fuel

Investigator

Matthew W. Kanan, Assistant Professor, Department of Chemistry, Stanford University

Abstract

Converting CO₂ into fuels and chemicals using renewable electricity as the power source requires efficient electrochemical CO₂ reduction catalysts. Copper can reduce CO₂ to multiple products of interest, but it is inefficient because of poor selectivity for CO₂ vs H₂O reduction. Oxide-derived Cu, a nanocrystalline form of Cu prepared by reduction of Cu₂O precursors, has greatly improved selectivity for CO₂ reduction at modest reducing potentials. This GCEP project aims to elucidate the structural origin of the CO₂ reduction properties of oxide-derived Cu and apply these insights to the synthesis of improved catalysts. To test whether the catalytic properties of oxide-derived Cu arise from its microstructural features, alternative nanocrystalline Cu electrodes were prepared by reduction of CuX and Cu₂S precursors (X = halide), electrodeposition from Cu(II) baths, and vapor deposition. A few of these preparations yielded nanocrystalline Cu electrodes significantly improved CO₂ reduction selectivity relative to bulk Cu and an optimized electrodeposited material had selectivity was close to oxide-derived Cu. Thermally annealing active catalysts at 200 °C compromised their CO₂ reduction selectivity without effecting large grain growth, indicating that selectivity is linked to metastable microstructural features. Poisoning studies were used to probe the active sites for CO₂ reduction on oxide-derived Cu. Treatment of oxide-derived Cu with sulfide eliminated its ability to reduce CO₂ to CO but did not eliminate HCO₂⁻ production, suggesting that these products come from different active sites. Ongoing work includes high-resolution TEM studies to determine the microstructural differences between active and thermally deactivated nanocrystalline Cu electrodes and temperature programmed desorption to probe surface structures.

Introduction

The prospect of halting the accumulation of CO₂ in the atmosphere would be greatly improved by the development of scalable CO₂ recycling technologies. Economically feasible production of fuels and chemicals from CO₂ and renewable energy would create a strong incentive to capture CO₂ from point sources or directly from air. A particularly attractive CO₂ recycling strategy is to power a CO₂-fixing electrolytic device with a source of renewable electricity. This strategy enables the use of both wind and solar energy and the electrolytic catalysts (H₂O oxidation and CO₂ reduction) can be optimized independently of renewable energy collection, in contrast to photoelectrochemical approaches. The greatest challenge to electrochemical carbon fuel synthesis is to develop efficient, selective, and robust CO₂ reduction cathodes.

Copper is an attractive material for CO₂ reduction catalysis because it can produce multiple products of interest and it is relatively inexpensive. Unfortunately, like nearly all known CO₂ reduction catalysts, Cu is energetically inefficient and has a strong preference for H₂O reduction, which lowers the yield of CO₂ reduction in aqueous conditions.¹ Modifying Cu to improve its efficiency and control selectivity is essential for developing this material into a viable cathode. Copper nanoparticles synthesized by conventional

methodologies have thus far proven to be comparable to bulk Cu in their catalytic properties. We developed a nanostructured form of Cu called “oxide-derived Cu” that has substantially improved selectivity for CO₂ vs H₂O reduction at modest reducing potentials. The material is prepared by a reductive phase transformation from Cu₂O to metallic Cu. Developing oxide-derived Cu into a practical cathode for fuel-synthesizing devices will require understanding which structural features are essential for catalysis and amplifying these features in improved variants.

Background

Copper is the most heavily studied material for CO₂ reduction catalysis. Polycrystalline and numerous single-crystal Cu electrodes have been evaluated in CO₂-saturated aqueous bicarbonate (HCO₃⁻) solutions at ambient temperature.¹⁻⁵ These studies have revealed a complex, potential-dependent product distribution. At low overpotential, H₂O reduction to H₂ outcompetes CO₂ reduction. At moderate to high overpotentials, CO₂ reduction to CO and HCO₂⁻ become significant products. At very high overpotentials, methane and ethylene are the major products, followed by smaller amounts of oxygenates including ethanol and acetate. In CO-saturated solutions without CO₂, methane, ethylene and oxygenates are also formed but only at similarly negative potentials.⁶⁻⁸ The requirement for large overpotentials to favor CO₂ or CO reduction vs H₂O reduction compromises the energetic efficiency of Cu and promotes electrode deactivation. This problem pertains not only to polycrystalline Cu and low-index surfaces but also to numerous high-index and highly stepped surfaces that have been evaluated as single crystal electrodes.⁵ These results indicate that either the canonical surfaces of Cu are all relatively inactive for CO₂ reduction at low overpotential, or that active surfaces readily rearrange to inactive structures in situ. Computational studies have provided insight into possible reduction pathways on Cu and identified possible potential-determining steps.^{9,10} In addition to bulk Cu surfaces, a recent study observed that Cu nanoparticles ranging in size from 2 nm to 15 nm have comparable or worse selectivity for CO₂ vs H₂O reduction than polycrystalline Cu.¹¹ Very small (< 5 nm) Cu nanoparticles showed a greater propensity for H₂O reduction, suggesting that surface atoms with low coordination numbers promote H₂ formation.

We reported oxide-derived Cu (OD-Cu) and its CO₂ reduction activity in 2012 and very recently reported CO reduction to liquid fuels with this material.^{12,13} OD-Cu is prepared by reducing a relatively thick Cu₂O precursor, either via electroreduction or treatment with H₂ at 130 °C. Compared to Cu foil and Cu nanoparticles, OD-Cu has lower intrinsic (surface area-normalized) H₂O reduction activity and higher intrinsic CO reduction activity. As a result, OD-Cu attains higher selectivity for CO₂ reduction to CO and HCO₂⁻ at low overpotentials and higher selectivity for CO reduction to ethanol and acetate at moderate overpotential. OD-Cu also produces only multi-carbon products from CO₂ reduction at high overpotential, in contrast to the predominant methane formation on other Cu materials. An independent study of CO₂ reduction with OD-Cu observed similar results to our original report and demonstrated that the selectivities were maintained at higher current densities.¹⁴ The intrinsic activities and consequent selectivities of OD-Cu are sensitive to the properties of the Cu₂O precursor and the way in which it is reduced. For example, OD-Cu produced by H₂ reduction has appreciable selectivity for propanol formation in CO reduction whereas the material produced by electroreduction does not.

Transmission electron microscopy (TEM) and grazing incidence X-ray diffraction studies have revealed that OD-Cu materials are nanocrystalline, meaning that they are comprised of continuous networks of nanocrystals linked by grain boundaries (Figure 1).¹³ Our current model is that the grain boundary network is important for the catalytic properties of OD-Cu. In other words, the origin of the catalytic properties of OD-Cu is a microstructural phenomenon. Grain boundary surface terminations may contain active sites that are not otherwise stable¹⁵ and the grain boundaries impose irregular shapes on the nanocrystals that may affect the step density on the particle surfaces that are distal from the grain boundaries.

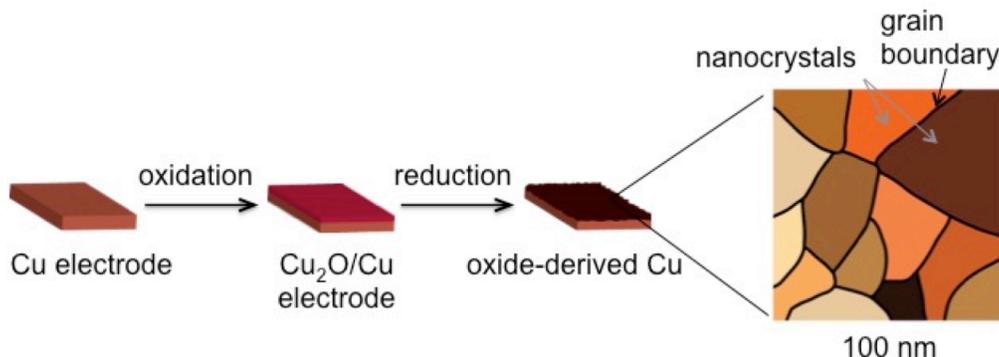


Figure 1: Schematic depiction of the synthesis of oxide-derived Cu and its nanocrystallinity.

Results

The insight from TEM and X-ray diffraction studies that OD-Cu electrodes are nanocrystalline prompted us to examine alternative routes to nanocrystalline Cu. These studies were intended to provide additional evidence for a microstructural origin to the catalytic activity of OD-Cu and assess whether alternative preparations yield more active nanocrystalline material. We have also performed preliminary studies with nanocrystalline forms of other metals to assess the generality of microstructural effects in CO₂ catalysis.

Nanostructured copper electrodes prepared from precursors other than copper oxide

One possible route to nanocrystalline Cu is to perform a reductive phase transformation from a different precursor. We prepared thin films of CuCl, CuBr, CuI, and Cu₂S on Cu foil and reduced these precursors to the corresponding halide-derived or chalcogenide-derived Cu electrodes using similar methods as for OD-Cu. The electrodes were evaluated under standard CO₂ reduction conditions and compared to OD-Cu and polycrystalline Cu foil. Both the chloride-derived and bromide-derived Cu electrodes showed substantially improved selectivity for CO₂ vs H₂O reduction at low overpotential compared to polycrystalline Cu, although neither were as effective as OD-Cu. Iodide-derived and sulfide-derived Cu were essentially completely inactive for CO₂ reduction.

Nanostructured copper electrodes prepared by electrodeposition

Electrodeposition is a well-established method for preparing nanocrystalline metal films.^{16,17} The average crystallite size in electrodeposited films can be systematically varied using different bath conditions and deposition parameters. Under optimized deposition conditions, Cu films deposited from Cu²⁺ baths showed enhanced selectivity for CO₂ reduction at low overpotential and enhanced CO reduction activity relative to bulk. The films were generally less active than oxide-derived Cu. The results provide

additional indirect evidence that nanocrystalline networks are responsible for the catalytic activity of OD-Cu.

Nanostructured electrodes prepared by vapor deposition

Electrodes prepared by reducing Cu(I) precursors or by electrodeposition have high mass loadings and are difficult to configure with practical flow-based or gas diffusion electrolyzers. We are developing methods to remove OD-Cu from the Cu foil substrate and disperse it so that it can be added to carbon supports. Alternatively, it would be advantageous to prepare nanocrystalline Cu directly on carbon supports. The oxide reduction method is not readily adapted for the preparation of thin nanocrystalline Cu on carbon. Vapor deposition methods can be used to prepare nanocrystalline metal films on a variety of substrates.¹⁸ We hypothesized that nanocrystalline metal films deposited prepared by vapor deposition would recapitulate the catalytic properties of oxide-derived metal electrodes. Preliminary studies have achieved some success using this approach with Au, but to date Cu electrodes prepared by vapor deposition have not exhibited enhanced catalytic properties relative to bulk Cu.

Future Plans

Future studies will continue to test the contention that the catalytic properties of OD-Cu are derived from microstructural features that are trapped during the Cu₂O reduction. The surfaces of OD-Cu will be probed using temperature programmed desorption and vibrational spectroscopy. Microstructural features will be probed using high resolution TEM. We will continue to develop alternative routes to nanocrystalline Cu electrodes and evaluate these materials for CO₂ reduction. Vapor deposition of nanocrystalline Cu will be performed at low temperatures to trap metastable grain boundary structures. These studies will be aided by additional experiments with vapor-deposited Au electrodes. Finally, mechanical deformation and compaction techniques will be used to transform Cu foil into a nanograined material and create nanocrystalline Cu from Cu nanoparticles. Comparison of the CO₂ reduction properties of Cu foil before and after deformation and Cu nanoparticles before and after compaction will test the ability to change catalysis by engineering grain boundary networks.

Publications and Patents

None to report

References

1. Hori, Y. in *Modern Aspects of Electrochemistry* Vol. 42 (eds C. G. Vayenas, R. E. White, & M. E. Gamboa-Aldeco) 89–189 (Springer, 2008).
2. Kuhl, K. P., Cave, E. R., Abram, D. N. & Jaramillo, T. F. New insights into the electrochemical reduction of carbon dioxide on metallic copper surfaces. *Energy & Environmental Science* **5**, 7050-7059 (2012).
3. Hori, Y., Kikuchi, K. & Suzuki, S. Production of CO and CH₄ in Electrochemical Reduction of CO₂ at Metal-Electrodes in Aqueous Hydrogencarbonate Solution. *Chemistry Letters*, 1695-1698 (1985).
4. Hori, Y., Murata, A. & Takahashi, R. Formation of Hydrocarbons in the Electrochemical Reduction of Carbon-Dioxide at a Copper Electrode in Aqueous-Solution. *Journal of the Chemical Society-Faraday Transactions I* **85**, 2309-2326 (1989).

5. Hori, Y., Takahashi, I., Koga, O. & Hoshi, N. Selective formation of C₂ compounds from electrochemical reduction of CO₂ at a series of copper single crystal electrodes. *Journal of Physical Chemistry B* **106**, 15-17 (2002).
6. Hori, Y., Murata, A., Takahashi, R. & Suzuki, S. Electroreduction of CO to CH₄ and C₂H₄ at a Copper Electrode in Aqueous-Solutions at Ambient-Temperature and Pressure. *Journal of the American Chemical Society* **109**, 5022-5023 (1987).
7. Hori, Y., Takahashi, R., Yoshinami, Y. & Murata, A. Electrochemical reduction of CO at a copper electrode. *Journal of Physical Chemistry B* **101**, 7075-7081 (1997).
8. Schouten, K. J. P., Qin, Z. S., Gallent, E. P. & Koper, M. T. M. Two Pathways for the Formation of Ethylene in CO Reduction on Single-Crystal Copper Electrodes. *Journal of the American Chemical Society* **134**, 9864-9867 (2012).
9. Peterson, A. A. & Norskov, J. K. Activity Descriptors for CO₂ Electroreduction to Methane on Transition-Metal Catalysts. *Journal of Physical Chemistry Letters* **3**, 251-258 (2012).
10. Montoya, J. H., Peterson, A. A. & Norskov, J. K. Insights into CC Coupling in CO₂ Electroreduction on Copper Electrodes. *Chemcatchem* **5**, 737-742 (2013).
11. Reske, R., Mistry, H., Behafarid, F., Cuenya, B. R. & Strasser, P. Particle Size Effects in the Catalytic Electroreduction of CO₂ on Cu Nanoparticles. *Journal of the American Chemical Society* **136**, 6978–6986 (2014).
12. Li, C. W. & Kanan, M. W. CO₂ Reduction at Low Overpotential on Cu Electrodes Resulting from the Reduction of Thick Cu₂O Films. *Journal of the American Chemical Society* **134**, 7231-7234 (2012).
13. Li, C. W., Ciston, J. & Kanan, M. W. Electroreduction of carbon monoxide to liquid fuel on oxide-derived nanocrystalline copper. *Nature* **508**, 504–507 (2014).
14. Kas, R. *et al.* Electrochemical CO₂ reduction on Cu₂O-derived copper nanoparticles: controlling the catalytic selectivity of hydrocarbons. *Phys Chem Chem Phys* Advance Article (2014).
15. Radetic, T., Lancon, F. & Dahmen, U. Chevron defect at the intersection of grain boundaries with free surfaces in Au. *Phys Rev Lett* **89**, Artn 085502 (2002).
16. Natter, H. & Hempelmann, R. Nanocrystalline copper by pulsed electrodeposition: The effects of organic additives, bath temperature, and pH. *J Phys Chem* **100**, 19525-19532 (1996).
17. Hempelmann, R. & Natter, H. in *Electrodeposition from Ionic Liquids* (eds F. Endres, D. MacFarlane, & A. Abbott) Ch. 9, 213-238 (Wiley-VCH, 2008).
18. Meyers, M. A., Mishra, A. & Benson, D. J. Mechanical properties of nanocrystalline materials. *Prog Mater Sci* **51**, 427-556 (2006).
19. Jiang, K., Li, Q. & Fan, S. Nanotechnology: Spinning continuous carbon nanotube yarns. *Nature* **419**, 801 (2002).
20. Chen, Y. H., Li, C. W. & Kanan, M. W. Aqueous CO₂ Reduction at Very Low Overpotential on Oxide-Derived Au Nanoparticles. *Journal of the American Chemical Society* **134**, 19969-19972 (2012).

Contacts

Matthew Kanan: mkanan@stanford.edu