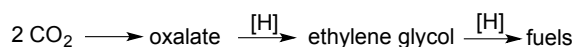


Principal Investigators: Professors T. Daniel P. Stack & Christopher E. D. Chidsey

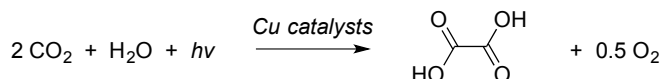
Project Title: Reductive Carbon-Carbon Bond Formation with Carbon Dioxide and Water Oxidation: Immobilized Dinuclear Copper Complexes as Discrete Electrocatalysts.

1. Project Objectives: Developing discrete, polynuclear copper-based electrocatalysts for reductive coupling of CO₂ and the oxidation of water.

2. Project Summary: The production of carbon-based fuels and chemicals from both renewable energy *and* materials is of utmost importance for a sustainable and energy-efficient society. The emerging technologies that directly convert sunlight to energy serve as an important starting point in creating a renewable energy economy, but its intermittent and diffuse availability require that the harvested energy be transformed to high energy density and storable fuels. Developing energy-efficient processes that reductively couple CO₂, an abundant and renewable C₁ source, for the production of value-added chemicals with electrons derived from water oxidation is a goal of great importance. Currently, less than 1% of anthropomorphic CO₂ is used for the production of chemicals. A game-changing strategy would be the synthesis of higher order C_n (n > 1) products and fuels from CO₂, but this practice is limited due to the extreme challenges associated with C-C bond formation and water oxidation under energy-efficient conditions. Developing catalysts capable of efficiently coupling CO₂ to oxalate and subsequently to other C₂ compounds would provide a novel strategy to make value-added chemicals not dependent on fossil fuel reserves.



A long-term vision is the capture and conversions of CO₂ from gas- or coal-fire power plants to large-scale, value-added chemicals or fuels with electron derived from solar-powered water oxidation. The overall transformation resembles photosynthesis, in which nature uses solar power to drive the conversion of CO₂ and water to C_n chemicals and O₂.

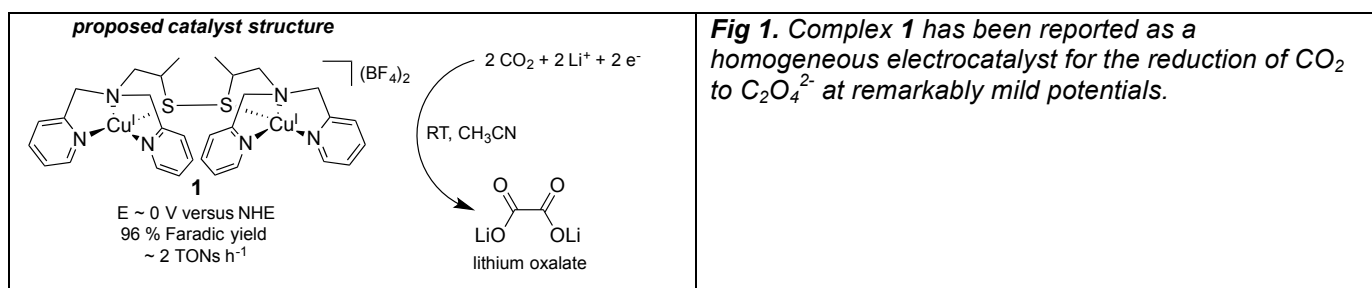


The ongoing research focuses on the development of polynuclear copper catalysts attached to and specifically positioned on inexpensive carbon electrodes for electrocatalytic CO₂ reduction or water oxidation. The proposed research entails ligand synthesis, homogeneous catalyst screening, catalyst imprinting and immobilization, and mechanistic analyses, along with complementary density functional theory (DFT) calculations.

3. Preliminary Results:

3.1 Homogeneous CO₂ Reduction by Cu(I) Complexes:

We are investigating the reductive coupling of CO₂ to oxalate by simple copper complexes. The addition of [Cu^I(MeCN)₄]BF₄ to the disulfide ligand is reported to yield a μ-disulfido Cu(I)Cu(I) complex (**1**) capable of stoichiometrically and electrocatalytically coupling CO₂ to oxalate (**Fig 1**).¹



In our hands, the solid state x-ray structure shows that the disulfide bond is reduced upon the copper coordination to give a μ-thiolato Cu(II)Cu(II) dimeric structure (**2**). Spectroscopic evidence (X-ray Absorption Spectroscopy (XAS), UV-vis spectroscopy, NMR) suggest that a μ-disulfido Cu(I)Cu(I) species (**3**) is in equilibrium with **2** in an acetonitrile solution (**Fig 2**), yet we have not found any evidence of stoichiometric or electrocatalytic CO₂ reductive coupling to oxalate with this complex.¹

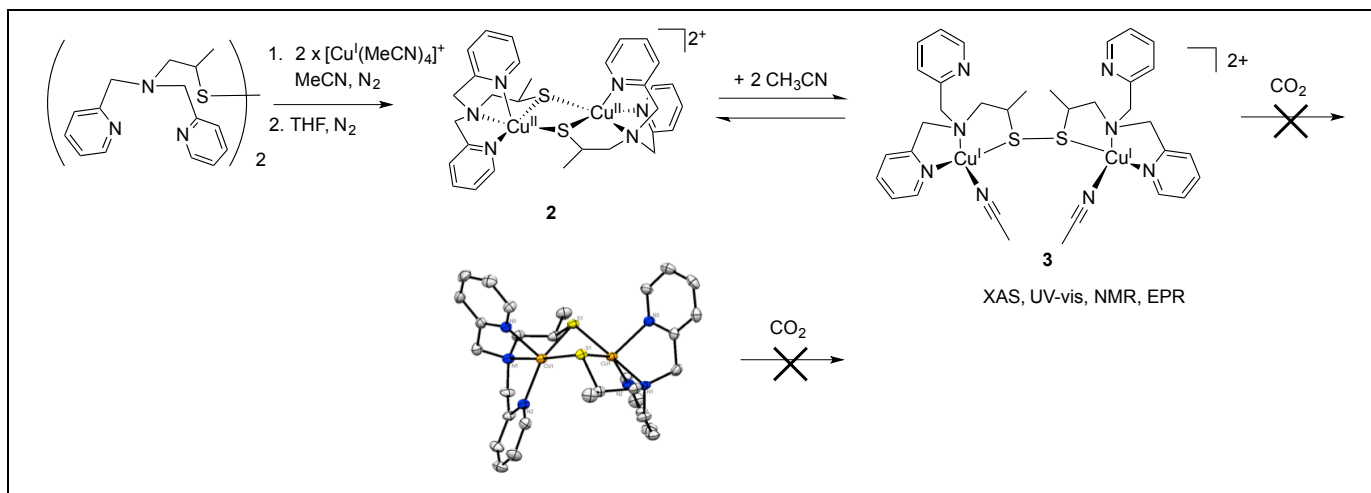
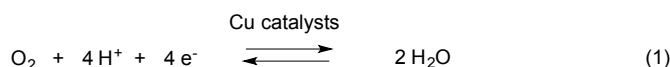


Fig 2. Data show the formation of a Cu^{II} -thiolate (**2** with its x-ray structure). Cu^{I} -disulfide species **3** resemble closely the Cu^{I} -disulfide species **1** proposed by Bouwman *et al.*¹

3.2 Immobilized Discrete Copper Electrocatalysts for O_2 Reduction:



Water oxidation and dioxygen reduction are microscopic reverse processes (eqn 1) that share common reaction mechanisms. The ability of discrete copper complexes to catalyze the electro-oxidation/reduction of water/dioxygen is well documented.²⁻⁴ Studies of dioxygen reduction will inform on how to design electrocatalysts for efficient water oxidation. Using a methodology developed in our labs, $\text{Cu}(1,10\text{-phenanthroline})$ complexes have been covalently attached to a glassy carbon electrode (GCE). The ability to reduce O_2 efficiently is related to the number of dinuclear copper sites on the electrode.² Meyer *et al.* have demonstrated recently that the electrocatalytic rate of water oxidation by copper catalysts have a second-order rate dependence on the copper catalyst.⁴ Although our previous work has focused on O_2 reduction, the principles for creating dinuclear species should be applicable to water oxidation (**Fig 3**).

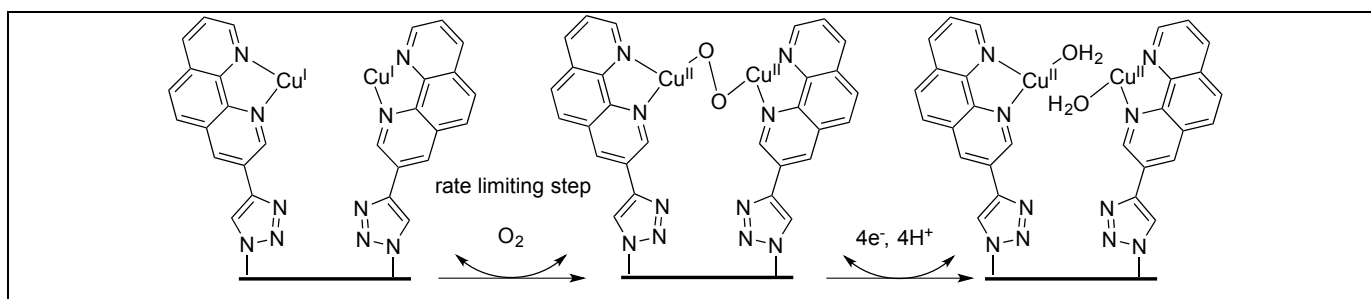
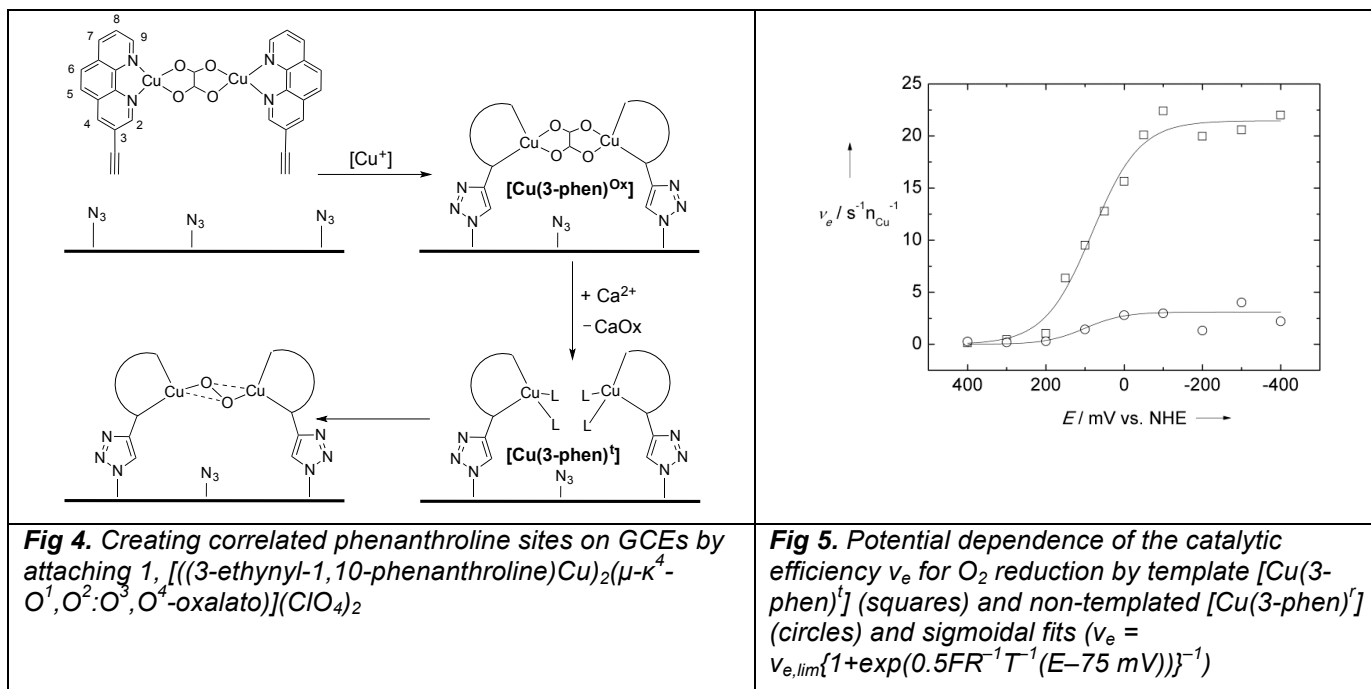


Fig 3. Schematic illustrations of dioxygen reduction and water oxidation, two microscopically reversible processes, catalyzed immobilized dinuclear copper complexes

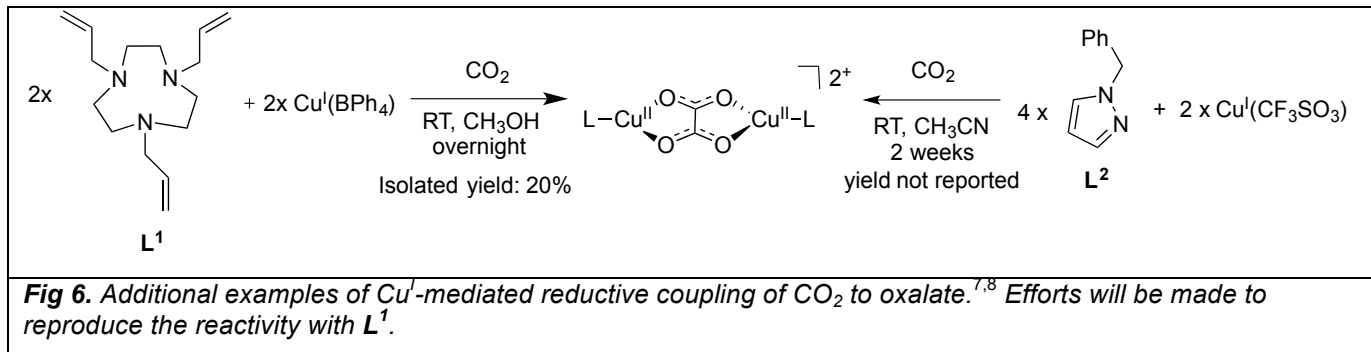
The catalysts are immobilized through a 1,3-dipolar azide-alkyne cycloaddition between a ligand with an ethynyl group and an azide moiety on the GCE surface.⁵ Polynuclear ligand binding sites can be created effectively on a GCE by two methods: (a) controlled azide surface density or (b) templating dinuclear sites by immobilization of complexes with a removable bridging linker, an imprinting technique. The oxalate anion has been successfully used to imprint dinuclear Cu phenanthroline sites (**Fig 4**), even under surface-diluted conditions. A comparison of the kinetic current from O_2 reduction versus copper catalyst surface coverage of both randomly distributed Cu -phenanthroline complexes and imprinted dimeric sites shows significantly more current (~ 10 -fold increase) with the latter with greater faradaic efficiency to water (**Fig 5**), highlighting the importance of a correlated arrangement of the metal centers on the electrode surface for fast and energy efficient conversions.⁶



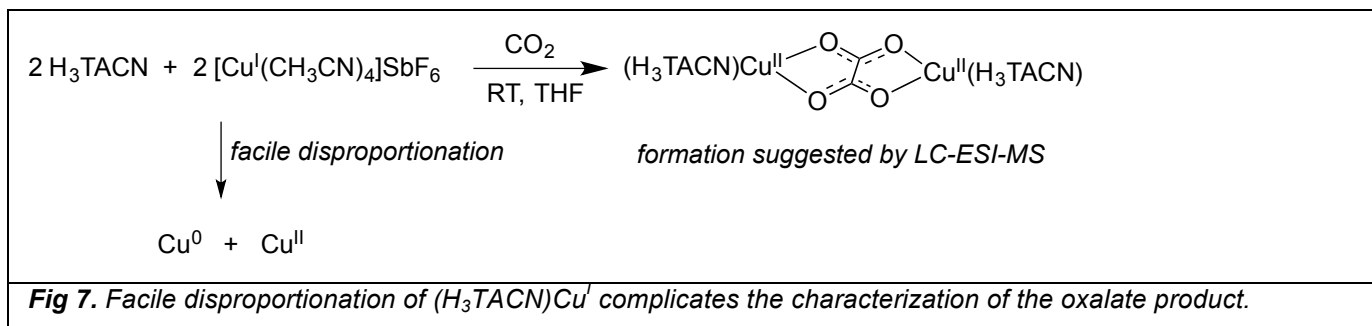
4. Future Plan:

4.1 Homogeneous CO_2 Reduction by Cu(I) Complexes:

Two other Cu complexes with nitrogen-based ligands are reported to promote stoichiometric formation of oxalate products under remarkably mild conditions (Fig 6).^{7,8} The reaction with the more electron-donating triazacyclononane (TACN) ligand (L_1) is much faster than that with the aromatic nitrogen ligand (L_2). Ongoing work involves synthesis of L_1 and efforts to reproduce its reported CO_2 reactivity.⁷ Based on the results of a preliminary screening of a few other mononucleating nitrogen ligands, H_3TACN appears to promote an even faster reductive coupling of CO_2 in a tetrahydrofuran solution at room temperature; the formation of Cu^{II} -oxalate dimer is supported qualitatively by liquid chromatography electrospray ionization mass spectrometry (LC-ESI-MS). Rapid disproportionation to form Cu^0 and Cu^{II} , however, complicates further characterization of the products (Fig 7). The next step is to develop a quantitative analytical method of oxalate based on ion-exchange chromatography, which will allow for quantitative evaluations of the reactions with various ligands and inform on the favorable features of Cu complexes critical for rapid and selective coupling of CO_2 .



Dinucleating the ligands via an appropriate organic linker is a logical approach to promote faster rates of this coupling reaction if the reaction is second order in the concentration of the copper complex. DFT-calculated reaction profiles of mononucleating Cu^{I} -ligand complexes to effect CO_2 reductive coupling will be explored to provide insights into the design of the linker.



3.2 Immobilized Discrete Copper Electrocatalysts:

The template-imprinting method has successfully led to dinuclear sites with immobilized 1,10-phenanthroline ligands for faster and more selective electrocatalytic reduction of O_2 .⁶ We reason that the distance between the two nuclear sites is an important factor affecting the rate and selectivity of the electrocatalysis. Further work will probe initially the effect of various bridging anions on the reduction of O_2 with the same 1,10-phenanthroline ligands, which will establish methodologies to prepare dinuclear sites on GCE surfaces with different dinuclear separations. Water oxidation will also be attempted with these electrodes because efficient electrocatalytic water oxidation has been observed with copper complexes with an analogous ligand, 2,2'-dipyridine, in solutions.³ Promising mononucleating ligands will be used in place of 1,10-phenanthroline to create corresponding dinuclear sites with appropriate dinuclear separations for the electrocatalytic reduction of CO_2 to oxalic acid.

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