

# Immobilization of Discrete Electrocatalysts on Carbon Surfaces

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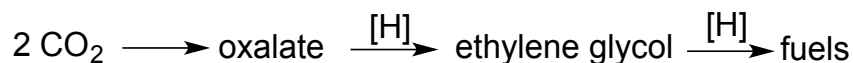
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## Abstract:

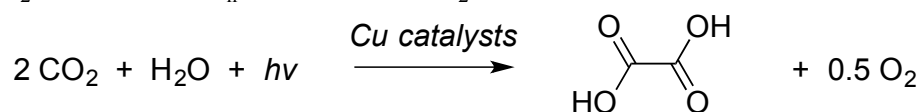
Our research focus has been on the development of discrete metal catalysts on carbon surfaces to achieve electrocatalytic oxidation of fuels or reduction of CO<sub>2</sub> or O<sub>2</sub>. Developing reproducible synthetic coupling strategies of discrete metal complexes to carbon surfaces is one step toward realizing electrocatalytic conversion with such catalysts; a more robust and reproducible chemical attachment strategy to high surface carbon materials has been developed using an alternative synthetic pathway that includes a copper catalyzed cyclization pathway. Using this attachment strategy, a discrete ruthenium complex is now capable of electrocatalytic oxidation of methanol to formaldehyde for the first time. Yet, using copper catalysts, we find no evidence that CO<sub>2</sub> can be reduced at modest potentials under ambient conditions to oxalate as described in the literature, though DFT calculations suggest modest CO<sub>2</sub> coupling barriers using simple macrocyclic amine copper complexes. A 10-fold enhanced reduction reactivity of O<sub>2</sub> to water from an imprinting dimeric copper catalyst as compared to its randomly distributed monomeric counterpart highlights a new synthetic strategy for creating multinuclear metal catalyst sites for surface-immobilized electrocatalysis.

## Introduction:

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 the intermittent and diffuse availability of sunlight requires that the harvested energy be transformed to high energy density and storable fuels. Developing energy-efficient processes that reductively couple CO<sub>2</sub>, an abundant and renewable C<sub>1</sub> 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 anthropogenic CO<sub>2</sub> is used for the production of chemicals. A game-changing strategy would be the synthesis of higher order C<sub>n</sub> (n > 1) products and fuels from CO<sub>2</sub>, 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 CO<sub>2</sub> to oxalate and subsequently to other C<sub>2</sub> 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 conversion of CO<sub>2</sub> from gas- or coal-fired power plants to large-scale, value-added chemicals or fuels with electrons derived from solar-powered water oxidation. The overall transformation resembles photosynthesis, in which nature uses solar power to drive the conversion of CO<sub>2</sub> and water to C<sub>n</sub> chemicals and O<sub>2</sub>.



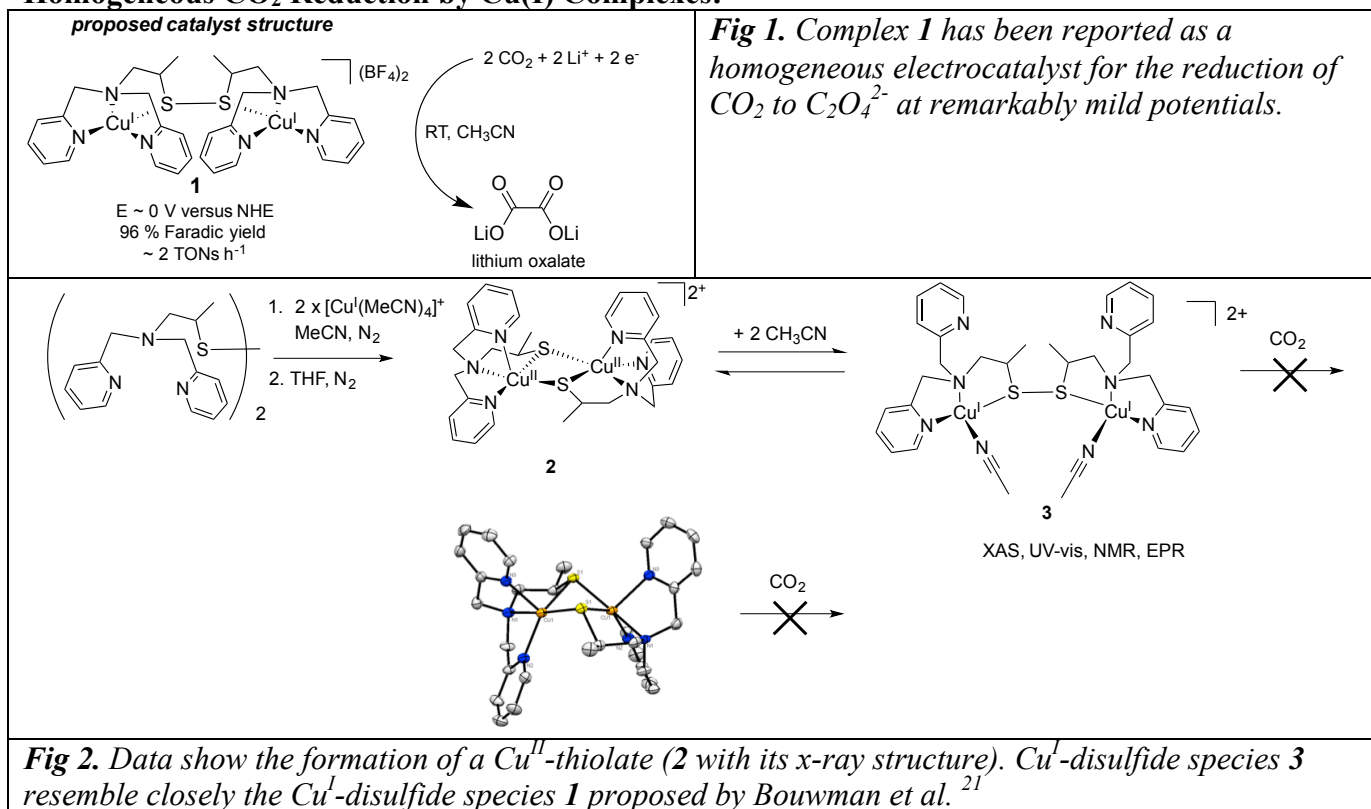
Developing kinetically rapid, durable catalysts for new transformations is one of our research major goals. Molecular catalysts have been particularly important in this endeavor because of their synthetic variability, which provides structure-reactivity information. Immobilizing molecular catalysts on electroactive heterogeneous scaffolds makes catalyst separation from products facile, and is an alternative to catalysis with noble metal surfaces.

A variety of methods exist for covalent attachment of molecular species to heterogeneous surfaces. Molecular complexes have been immobilized covalently on numerous surfaces (carbon,<sup>1,2,3</sup> metal,<sup>4</sup> metal oxide,<sup>5,6</sup> silicon,<sup>7</sup> and metal organic frameworks<sup>8</sup>) via a variety of techniques (copper catalyzed azide-alkyne cycloaddition,<sup>3,9</sup> silane deposition,<sup>10</sup> electrochemical grafting,<sup>1</sup> thiol-Au binding,<sup>4</sup> phosphonate<sup>11</sup> and carboxylate<sup>12</sup> binding). Covalently attached, surface-immobilized molecular complexes have demonstrated water oxidation,<sup>13,14</sup> carbon dioxide reduction,<sup>15,16</sup> and alcohol oxidation,<sup>5,17,18</sup> reactions, which is related to their homogeneous catalyst counterparts.<sup>14,19</sup> The potential advantage of immobilized variants is the elimination of deactivation pathways possible or probable with solution species, thereby highlighting new active species of interest.<sup>20</sup>

Our ongoing research focuses on the development of metal-based catalysts attached to inexpensive carbon electrodes for electrocatalytic oxidative or reductive processes. The proposed research entails ligand synthesis, homogeneous catalyst screening, catalyst immobilization on carbon surfaces, and mechanistic analysis, along with complementary density functional theory (DFT) calculations to probe potential reaction mechanisms. Significant effort is directed into the systematic derivatization of carbon surfaces to assure reproducible attachment strategies.

## Results:

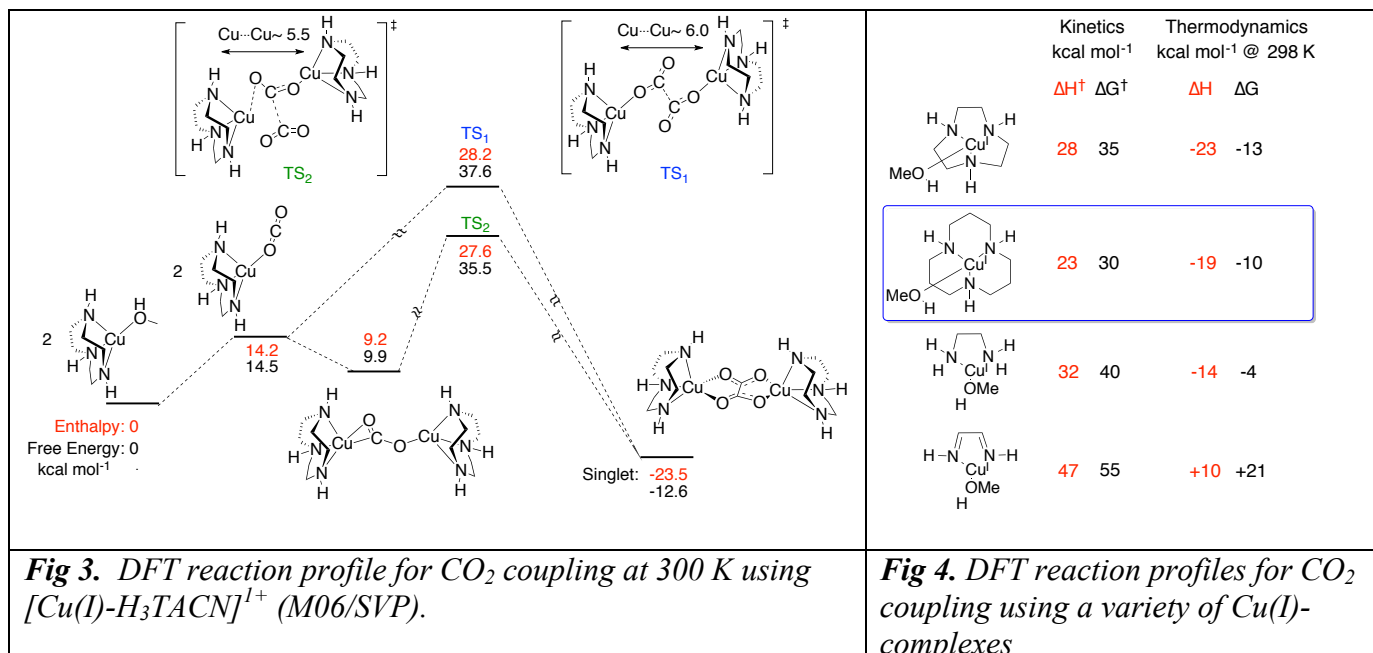
### Homogeneous CO<sub>2</sub> Reduction by Cu(I) Complexes:



We have investigated the reductive coupling of CO<sub>2</sub> to oxalate by simple copper complexes. The addition of [Cu<sup>I</sup>(MeCN)<sub>4</sub>]BF<sub>4</sub> to the disulfide ligand is reported in the literature to yield a μ-disulfido Cu(I)Cu(I) complex (**1**) capable of stoichiometrically and electrocatalytically coupling CO<sub>2</sub> to oxalate (**Fig 1**) at remarkably mild potentials.<sup>21</sup>

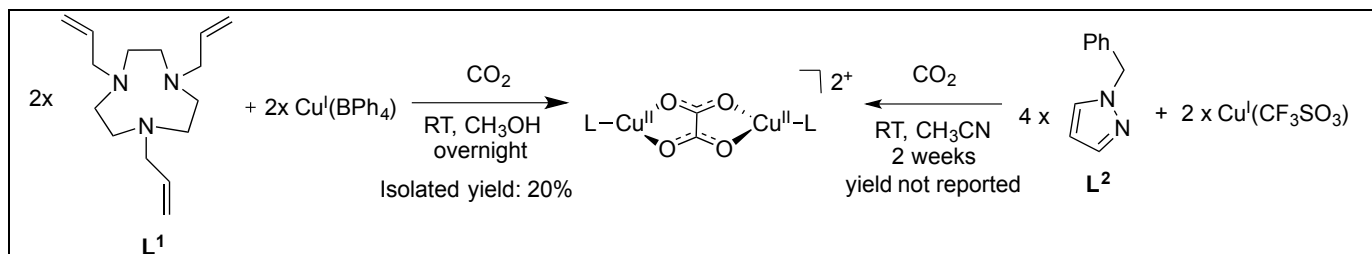
In our hands, the solid state x-ray structure shows that the disulfide bond is reduced upon the copper coordination to give a μ-thiolato Cu(II)Cu(II) dimeric structure (**2**). Spectroscopic evidence (X-ray Absorption Spectroscopy, UV-vis spectroscopy, NMR) suggest that a μ-disulfido Cu(I)Cu(I) species (**3**) is in equilibrium with **2** in an acetonitrile solution (**Fig 2**), yet we have found no evidence of stoichiometric or electrocatalytic CO<sub>2</sub> reductive coupling to oxalate with this complex.<sup>21</sup> A paper detailing redox behavior of the ligand has been published.<sup>22</sup>

DFT calculations suggest that the coupling free energy barriers of CO<sub>2</sub> to oxalate with Cu(I)-aza macrocyclic complexes are reasonable, as low as 30 kcal mol<sup>-1</sup> (**Fig 4**). Such barriers would lead to very slow reaction rates under ambient conditions, but higher temperatures might be viable (**Fig 3 & 4**). The potential energy surfaces of an entire family of Cu(I)-aza macrocyclic complexes were calculated to determine the lowest coupling barrier. In each case, an asymmetric transition state is correlated with the lowest free energy barrier. The Cu(I) complexes with the lowest barriers possess the attribute that their Cu(I) forms are highly stabilized and the steric demands of the ligand are minimized. In all cases, the reaction is calculated to be exergonic. With this information, we screened a variety of Cu(I) aza-macrocycles for CO<sub>2</sub> coupling both at ambient and elevated temperature, but under no conditions could we detect oxalate formation.



Two other Cu complexes with nitrogen-based ligands are reported in the literature to promote stoichiometric formation of oxalate products under remarkably mild conditions (**Fig 5**).<sup>23,24</sup> By literature precedent, the CO<sub>2</sub> reaction of the Cu(I) complexes with the more electron-donating triazacyclononane (TACN) ligand (**L**<sub>1</sub>) is faster than that with the aromatic nitrogen ligand (**L**<sub>2</sub>), but in both cases the

oxalate yield is low and characterization has relied solely on x-ray crystallography. As above, we have explored the coupling capacity of these two complexes with  $\text{CO}_2$ ,<sup>23</sup> and do not find any significant oxalate formation under all conditions attempted. We must conclude from our investigations that coupling of  $\text{CO}_2$  using cationic aza-macrocylic Cu(I) complexes is not a viable strategy to oxalate formation at temperatures below  $100^\circ\text{C}$ .

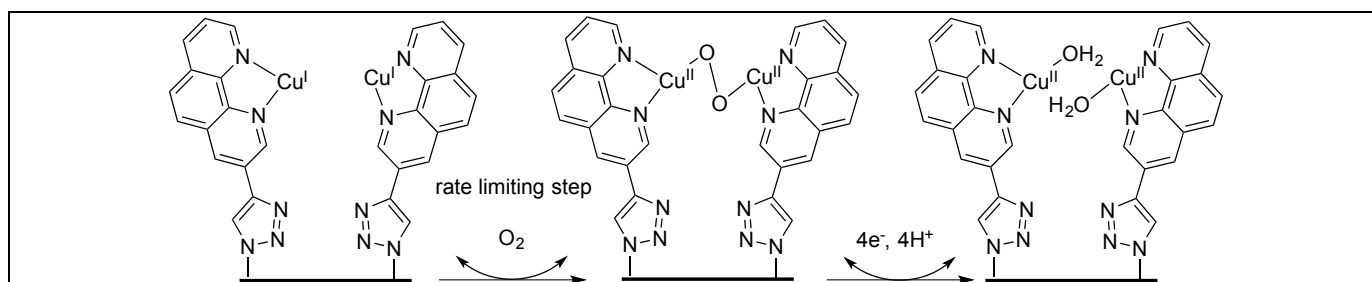


**Fig 5.** Literature examples of  $\text{Cu}^{\text{I}}$ -mediated reductive coupling of  $\text{CO}_2$  to oxalate.<sup>23,24</sup>

### Immobilized Discrete Copper Electrocatalysts for $\text{O}_2$ Reduction: Cu catalysts



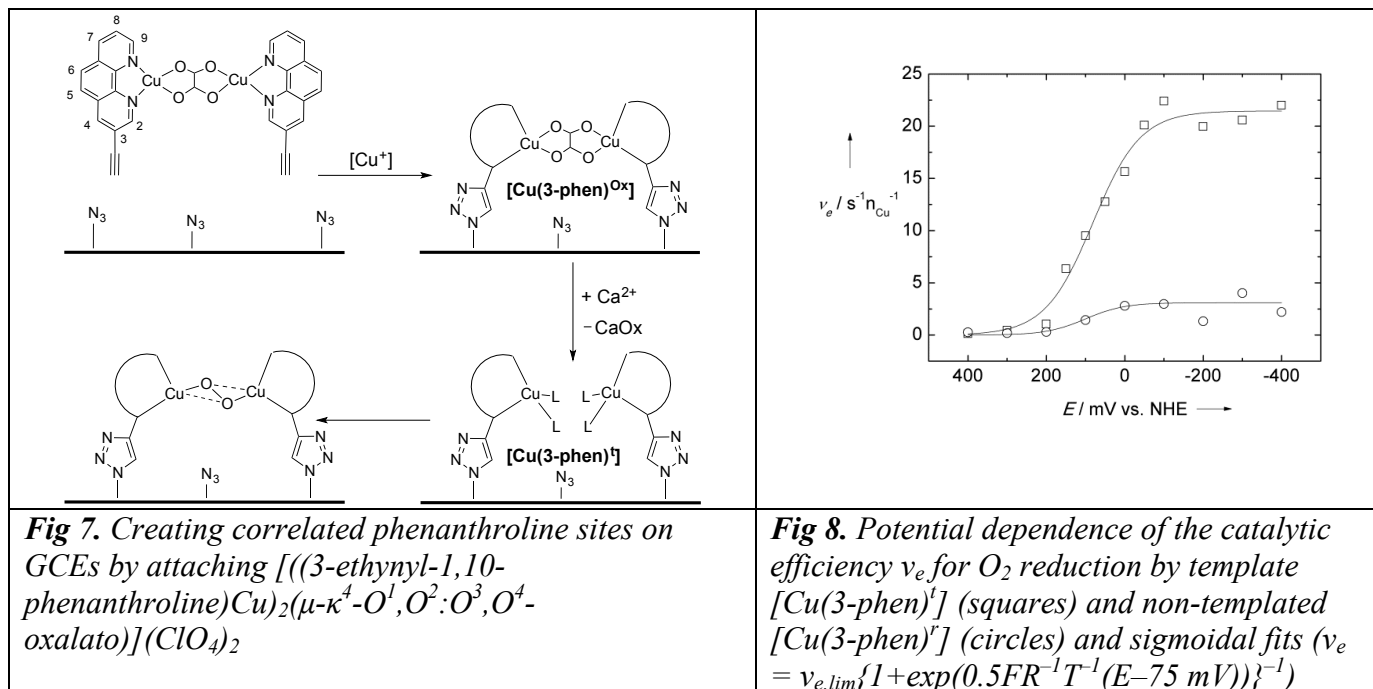
Water oxidation and dioxygen reduction are microscopic reverse processes (eqn 1) that share common reaction mechanisms. The ability of discrete copper complexes to catalyze the electro-oxidation/reduction of water/dioxygen is well documented.<sup>25-27</sup> Studies of dioxygen reduction inform on the design of electrocatalysts for efficient water oxidation. Using a methodology developed in our labs, Cu(1,10-phenanthroline) complexes have been attached covalently to glassy carbon electrodes (GCE). The ability to reduce  $\text{O}_2$  efficiently is related to the number of dinuclear copper sites on the electrode.<sup>25</sup> 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.<sup>27</sup> Although our previous work has focused on  $\text{O}_2$  reduction, the principles for creating dinuclear species should be applicable to water oxidation (**Fig 6**).



**Fig 6.** Schematic illustrations of dioxygen reduction and water oxidation, two microscopic reversible steps, catalyzed by 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.<sup>28</sup> 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 bridge, an imprinting technique. The oxalate anion has been used successfully to imprint dinuclear Cu phenanthroline sites (**Fig 7**), even under surface-diluted conditions. A comparison of the kinetic current from  $\text{O}_2$  reduction versus copper

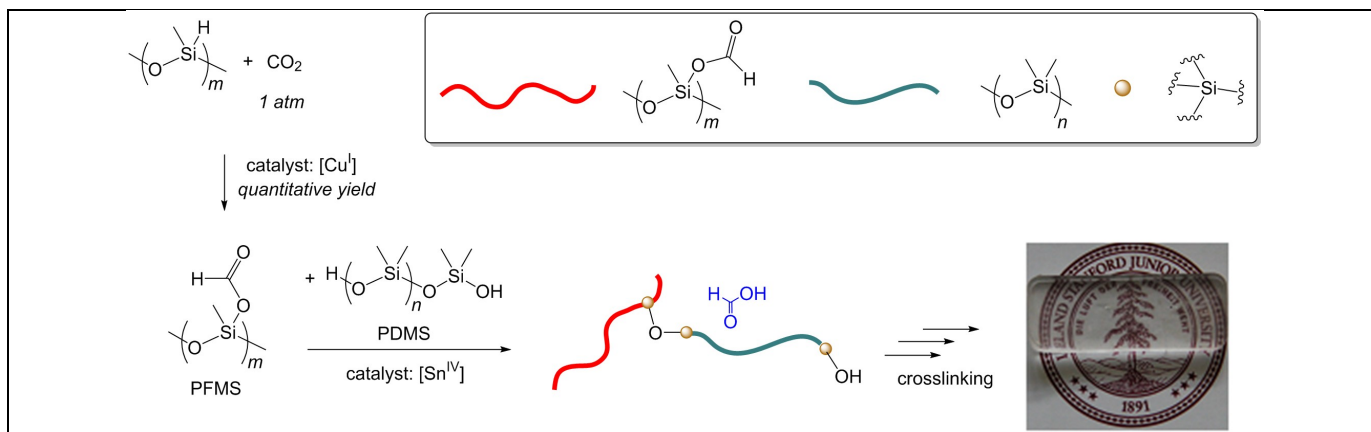
catalyst surface coverage of both randomly distributed Cu-phenanthroline complexes and imprinted dimeric sites shows significantly more current (~10-fold increase) with the latter exhibiting a greater faradaic efficiency to water (**Fig 8**), highlighting the importance of a correlated arrangement of the metal centers on the electrode surface for fast and energy efficient conversions.<sup>29</sup>



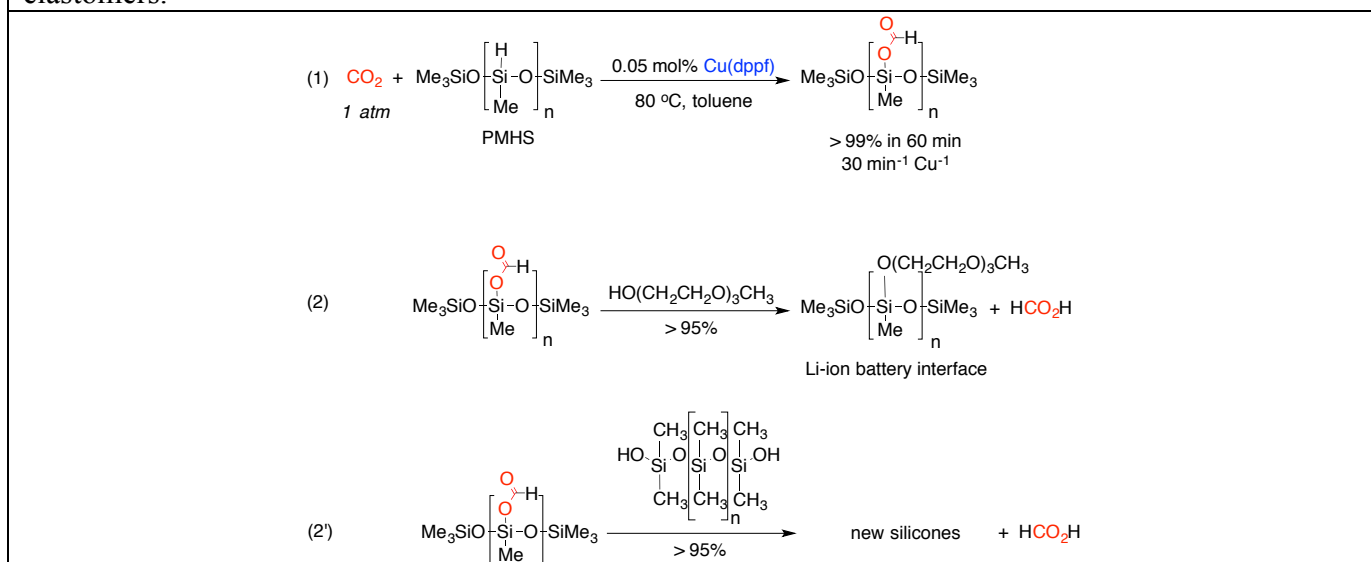
### Hydrosilylation of $\text{CO}_2$ – Reductive Coupling to Formic Acid and New Silicone Materials

In the process of investigating  $\text{CO}_2$  coupling with discrete copper complexes, we have discovered a facile, quantitative hydrosilylation of  $\text{CO}_2$  by polyhydrosiloxane to prepare formoxylated polysiloxane. The resulting formoxylated polysiloxane releases formic acid when treated with water or an alcohol, completing the  $\text{CO}_2$  to fuel objective, but more importantly, this material crosslinks readily to an elastomeric silicone that exhibits thermal self-healing behavior even in the presence of water (**Fig 9**). A highly efficient Cu(I) hydride catalyst is a key enabling step to these new smart materials from two by-products, polyhydrosiloxane and  $\text{CO}_2$ .<sup>30</sup>

This study details a new strategy for the reductive integration of  $\text{CO}_2$  into a polymeric elastomer with healing properties that is tolerant of wet conditions. Efficient  $\text{CO}_2$  hydrosilylation using an earth-abundant metal catalyst (copper) allows for the simple preparation of formoxylated polysiloxane (PFMS) from two abundant industrial by-products in 1 hour. Engineering of latent reactive groups that generate healing components *in situ* upon damages provides a new approach for future polymer-healing designs. Further exploration of PFMS as a crosslinking component in silicone rubbers may provide greener alternatives to commercial acetoxy silanes, in which the carbons are derived exclusively from fossil fuels. The remarkably high mass ratio of  $\text{CO}_2$  in the PFMS (*ca.* 40%) and in the formed elastomers (*ca.* 4-10%) unequivocally demonstrates the great potential of  $\text{CO}_2$  as a useful carbon source to make polymers via a reductive approach.



**Fig 9.** Water-activated healable silicone rubbers derived for CO<sub>2</sub> and polymethylhydrosiloxane elastomers.



**Fig 10.** Water-activated healable silicone rubbers derived for CO<sub>2</sub> and polymethylhydrosiloxane elastomers.

### Development of Robust and Reproducible Attachment Points on High-Surface Area Carbons

Developing efficient and reproducible covalent surface functionalization methods for high surface area, porous carbon materials is an area of considerable research interest due to their low cost. Surface modification allows for tuning the chemical and physical properties of these materials increasing the range of their applications, including energy storage and gas separations. Ideally, introduced functionality is robust and provides a versatile attachment point for further chemical modification. Current carbon surface functionalization strategies such as radical coupling of amines, coupling of alkynes at high temperatures, and photochemical coupling of alkynes are limited in scope, relatively unselective, and often require aggressive reaction conditions.

Chloromethylation of high-surface carbons is possible with good coverage of *ca.* 1.5 mmol g<sup>-1</sup>, yet the hazardous procedure is difficult to perform and yields an electrophile for nucleophilic displacement that is far from ideal if high derivatization yields are desired.<sup>31</sup> We have developed and optimized simple, safe and reproducible bromomethylation of high-surface area carbons. The bromomethylated materials

**Br-AC**) have high surface coverage (*ca.* 1.2 mmol g<sup>-1</sup>), exhibit excellent stability (100 days, < 5 % Br loss), and readily react with a variety of nucleophiles in high yields. Derivatization with azide is a particularly attractive material (**N<sub>3</sub>-AC**) for further derivatization using Cu(I) catalyzed azide-alkyne cycloaddition reaction (CuAAC). **N<sub>3</sub>-AC** also display excellent stability and can be coupled with various terminal alkynes to yield functional materials, as detailed below.

Treatment of **Br-AC** with sodium azide in DMSO affords **N<sub>3</sub>-AC** with typically greater than 90% conversion of Br to N<sub>3</sub>, as determined by nitrogen elemental analysis, and in agreement with XRF data for **N<sub>3</sub>-AC** showing only 4 – 8% of the initial Br content remaining after the reaction. The Br 3d and N 1s regions of the XPS spectrum of **N<sub>3</sub>-AC** confirm the high conversion of Br to N<sub>3</sub>. The intensity of the two diagnostic N 1s XPS features of azide (401 & 405 eV) deviate from the expected 1:2 ratio significantly (*ca.* 1:4), suggesting partial azide decomposition to yield amine-like nitrogen species on the surface. In addition to functionalization of **Br-AC** by simple nucleophilic displacement, CuAAC has been performed on **N<sub>3</sub>-AC** with various ethynylated substrates. Ethynyl-ferrocene was first chosen as a model substrate to provide an elemental tag (Fe) for characterization by XRF and XPS. CuAAC of ethynyl ferrocene on **N<sub>3</sub>-AC** resulted in ferrocene-functionalized materials (**Fc-AC**) with Fe loadings of up to 1.0 mmol g<sup>-1</sup> as measured by XRF, corresponding to approximately 90% conversion of azide from **N<sub>3</sub>-AC**. The N 1s region of the XPS spectrum of **Fc-AC** displays a single peak near 401 eV, suggesting good conversion of azide to triazole during the CuAAC reaction. The Fe 2p<sub>3/2</sub> region shows distinct features associated with Fe(II), confirming incorporation of Fe onto the surface of AC.

Additional functionalization of **N<sub>3</sub>-AC** using various ethynylated amines was explored as a first step toward creating discrete molecular functionalized carbon materials, including ones that should be capable of metal chelation. Most notably CuAAC of ethynyl ethylenediamine and ethynyl propylenediamine on **N<sub>3</sub>-AC** gave diamine-functionalized materials **cED-AC** and **cPD-AC**, respectively. The N 1s region of the XPS spectrum of **cED-AC** and **cPD-AC** suggests near complete conversion of the azide functionality to triazoles, and nitrogen elemental analysis confirms an efficient conversion. Surface loadings of *ca.* 1.0 mmol g<sup>-1</sup> of diamines are achieved from **Br-AC** materials containing *ca.* 1.2 mmol g<sup>-1</sup> of bromide.

We also explored additional functionalization of **Br-AC** using simple nucleophilic bromide displacement by diamines. Mixing previously characterized **Br-AC** with neat ethylenediamine or propylenediamine yields another set of diamine-functionalized materials (**ED-AC** and **PD-AC**, respectively). XRF of these materials show a 90% decrease in bromine content and elemental analysis confirms a diamine concentration of *ca.* 1.1 mmol g<sup>-1</sup> for both the **ED-AC** and **PD-AC** materials.

### **A Discrete, Surface-immobilized Ruthenium Electrocatalyst for Alcohol Oxidation**

A discrete ruthenium polypyridyl complex has been immobilized on carbon via CuAAC. From this precursor an electrochemically generated ruthenium species is formed that not only oxidizes benzyl alcohol with a modest overpotential, but also oxidizes methanol, the first example of a discrete metal species immobilized to an electroactive surface capable of this transformation.

The [RuCl(DMSO)(ethynyl-TPA)]PF<sub>6</sub> (TPA-Ru) complex was attached covalently to azide-functionalized carbon (GC-TPA-Ru). The carbon was prepared according to a previously reported procedure.<sup>32</sup> Cyclic voltammetry (CV) was used to characterize GC-TPA-Ru. A reversible redox couple is observed at 1.15 V vs NHE (all potentials reported vs NHE), and is assigned to the Ru<sup>II/III</sup> couple of

the  $[\text{RuCl}(\text{DMSO})(\text{ethynyl-TPA})]^+$  complex on the surface. The peak current shows a linear dependence on scan rate, corroborating surface immobilization of the complex. Integration of the area of the cathodic wave at 1.15 V corresponds to an average surface coverage of  $3 \times 10^{14}$  redox active Ru molecules  $\text{cm}^{-2}$ . A reduction wave is observed at 0.60 V that does not appear unless the oxidation sweep of the potential passes the  $\text{Ru}^{\text{II/III}}$  couple. The 0.60 V reduction wave has previously been assigned to the reduction of  $\text{Ru}^{\text{III}}\text{-DMSO}$ , whereas the reduction at 1.15 V is  $\text{Ru}^{\text{III}}\text{-DMSO}$ .<sup>33,34</sup>

GC-TPA-Ru exhibits electrocatalytic alcohol oxidation. In 0.1 M aqueous  $\text{HClO}_4$  the onset potential for benzyl alcohol oxidation is 0.95 V for a surface where the potential has been swept past previously to 1.15 V (in the absence of alcohol). GC-TPA-Ru also displays a pH dependent shift in onset potential for benzyl alcohol oxidation. Alcohol oxidation is observed at  $\text{pH}=7$  with a 0.55 V onset potential. The complex also oxidizes 2-propanol, ethanol, and methanol.

Water oxidation from surface discrete immobilized ruthenium polypyridyl complexes is known,<sup>13,14,35,36,37</sup> and benzyl alcohol provides a mechanistic probe into such catalytic activity.<sup>17</sup> In particular, reticulated vitreous carbon coated with indium doped tin oxide nanoparticles with its enhanced surface loading of polypyridyl ruthenium complexes is able to oxidize benzyl alcohol at 0.9 V vs NHE ( $\text{pH} = 5$ ). Controlled potential electrolysis at 1.25 V showed 400 TON with 75% Faradaic efficiency for 30 mM benzyl alcohol to benzaldehyde in 2 hr.<sup>37</sup> GC-TPA-Ru electrocatalytically oxidizes benzyl alcohol at 1.00 V under otherwise identical conditions with 4400 TON at >90% Faradaic efficiency in 4 hr. This magnitude increase in TON and decrease of the overpotential suggests that GC-TPA-Ru is the most efficient alcohol oxidation catalyst ever immobilized. It also oxidizes methanol at  $\text{pH}=7$ , the first example of a discrete molecular complex displaying electrocatalytic methanol oxidation. The homogeneous analog of GC-TPA-Ru has been investigated for alcohol oxidation and  $[\text{Ru}(\text{TPA})(\text{OH}_2)_2]^{2+}$  is proposed as the precursor complex to the catalyst, which is capable of electrocatalytic methanol oxidation. The active catalyst is proposed as a  $\text{Ru}^{\text{IV}}=\text{O}$  species.<sup>38</sup>

#### **Future Plans:**

In the last year of this grant, we will focus on those aspects of the research that will be most impactful to future energy related research, namely the imprinting of molecular catalysts on carbon electrodes and derivatization of high-surface area carbon materials.

#### **Budget:**

A one-year no-cost extension is currently projected to spend the majority of the balance. 2 graduate students are now working on carbon electrode modification/electrocatalysis and high-surface area carbon modifications.

#### **Scope of Project:**

The scope of the project has not changed.

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