Reducing Carbon Dioxide to Oxalic Acid Using Copper-Based Electrocatalysts

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Objective
The goal of this research is to develop energy-efficient catalysts capable of electrocatalytic reductive coupling of carbon dioxide (CO₂) to oxalate. Oxalate can be further reduced to other products that can be used for liquid fuel production or in alternative, sustainable syntheses of industrially important chemicals produced on the million-ton scale.

Background
The production of carbon-based fuels and chemicals from renewable energy and materials is important for a sustainable energy-based society. Transforming surplus solar energy into high energy density, storable fuels can help address the intermittent and diffuse availability of sunlight. One approach is to develop energy-efficient processes that convert CO₂, an abundant and renewable carbon source, into fuels or industrial chemicals.

The synthesis of long-chain carbon products and fuels from CO₂ is significantly limited by the extreme challenges associated with carbon-carbon (C-C) bond formation under energy-efficient conditions. The simplest C-C bond-forming reaction with CO₂ produces oxalate, an industrially important chemical that can be further transformed to other value-added chemicals, such as ethylene glycol, ethylene and more complex hydrocarbons (Figure 1).¹,²

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2 \text{CO}_2 \xrightarrow{2 \text{e}^-} \text{oxalate} \xrightarrow{[\text{H}]} \text{ethylene glycol} \xrightarrow{[\text{H}]} \text{fuels}
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Figure 1: Proposed pathway to the production of industrial chemicals and fuels via the reduction of CO₂.

The reductive coupling of CO₂ is the critical step in an electrochemical pathway to oxalate. Most electrochemical reductions of CO₂ non-selectively form a mixture of products through multiple proton-coupled electron transfer processes. Copper electrodes can reduce CO₂ in methanol to ethylene. Developing catalysts capable of efficiently coupling CO₂ to yield first oxalate and then other compounds would provide a game-changing strategy to make value-added chemicals independent of fossil fuel reserves.
**Approach**

The proposed research will involve a variety of laboratory and analytical approaches including: ligand synthesis; homogeneous catalyst screening; catalyst imprinting and immobilization on electrode surfaces; and mechanistic analyses, along with complementary density functional theory (DFT) calculations. The overall goal is to develop robust and efficient copper complexes capable of the electrocatalytic reduction of CO$_2$ with minimal energy (Figure 2).

The design principles will include ligation with charge-neutral amines to assure modest Cu$^{II}$/I redox potentials for energy-efficient processes and a macrocyclic arrangement of the amines to assure durable copper-based electrocatalysts. The initial research will include a modular synthetic approach to a family of ligands along with screening of the resulting Cu$^+$ complexes for CO$_2$ coupling under homogeneous conditions. To inform the design of more advanced catalysts, kinetic studies will be done in conjunction with DFT-reaction profiles. Promising candidates will be synthesized with copper complexes immobilized as discrete electrocatalysts onto electroactive heterogeneous surfaces, which may ultimately be more amenable for applications at scale.

**References**


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Figure 2: Redox potentials of mono- (left and right) versus di-nuclear (middle) molecules, and pyridine versus thioether coordination (right).$^3$ Note the positive shifts in the dimeric complex and thioether ligation (right).$^4$