
ELECTROCHEMICAL TRANSFORMATION OF CARBON DIOXIDE INTO CHEMICALS, FUELS, MATERIALS, AND FOOD

Bradie S. Crandall

Thesis Advisor: Prof. Feng Jiao

Committee Members: Prof. Yushan Yan, Prof. Raul F. Lobo, Prof. Dongxia Liu

Tuesday, June 11th at 1:00 PM (ET) in Colburn 366

Zoom: <https://udel.zoom.us/j/98973000791> (password: CO2)

The urgent need for affordable carbon capture technology in the fight against climate change has prompted the exploration of innovative approaches for carbon utilization. Bolstered by the emergence of affordable renewable electricity, the electrochemical conversion of CO₂ into valuable products presents a promising strategy. This frontier in carbon utilization has previously been largely confined to the production of chemicals and fuels at the watt-scale, limiting industrial insights and carbon sequestration potential. Here, I present the first-of-its-kind kW-scale CO₂ electrolysis system and explore its potential to transform CO₂ into chemicals, fuels, materials, and food.

I first examine a physical vapor deposition catalyst testing platform to probe a variety of Cu-based dilute alloys for tuning CO₂ electrolysis selectivity. CuAl, CuB, CuGa, CuSc, CuAu, CuPd, and pure Cu were all prepared via magnetron sputtering with a uniform porosity, morphology, and catalyst layer thickness then tested experimentally and examined using grand canonical density functional theory simulation.

Next, I build a custom techno-economic supply chain model to study the potential to use formic acid derived from CO₂ electrolysis as a green hydrogen carrier. Given the high costs of hydrogen storage and transportation, green hydrogen carriers have a critical role to play in enabling an affordable green hydrogen economy. This work directly compares green formic acid with green methanol, green ammonia, toluene/methylcyclohexane as a two-way carrier, and pure green hydrogen and finds formic acid to be a promising hydrogen carrier candidate.

After studying the potential of CO₂ electrolysis for delivering sustainable fuel, the electrochemical sequestration of carbon into materials is examined. Here, a strategy to 3D print advanced CO₂-derived carbon nanocomposites is demonstrated. An integrated system is developed to directly connect the CO output of CO₂ electrolysis to a thermochemical reactor for producing carbon nanotubes at up to 84% yield which are then converted to carbon nanocomposites via additive manufacturing. This strategy offers a pathway for carbon sequestration at the gigaton-scale by converting CO₂ into materials for construction, vehicles, and electronics.

Following an examination of direct CO₂ electrolysis, a tandem CO₂ electrolysis cascade to produce multi-carbon products at high efficiency by avoiding (bi)carbonate formation is offered.

A kW-scale system for producing ethylene and acetate from CO₂ is successfully designed, fabricated, and operated at performances similar to that achieved at smaller scales. Over 125 h of stable operation is demonstrated using a 1,000 cm² CO electrolyzer stack to generate nearly 100 L of 1.2 M acetate at 96% purity. This represents the largest scale system ever publicly reported substantially accelerating commercialization.

This tandem CO₂ electrolysis system is then used to produce sustainable food from CO₂-derived acetate via electro-agriculture. For millennia, humanity has relied upon photosynthesis to meet our caloric needs at relatively low solar-to-crop efficiency (~1%) which has led to half of earth's habitable land being used for agriculture today. A radical reimagining of a more efficient global food system will be offered by engineering food crops to circumvent photosynthesis and instead utilize electrosynthesized acetate for heterotrophic growth which can improve solar-to-crop efficiency by an order of magnitude. Analysis is performed to demonstrate how these efficiency improvements can result in a 94% decrease in U.S. agricultural land usage, liberating nearly half of the U.S. for rewilding efforts to promote natural carbon sequestration. The efficiency of our food system can also be improved by coupling CO₂ electrolysis with precision fermentation technology to produce animal proteins without the need for highly inefficient and resource intensive animal agriculture.

After demonstrating the feasibility of electro-agriculture, a prototype system is developed to enable a human mission to Mars and beyond as part of NASA's Deep Space Food Challenge. Electro-agriculture offers great promise to maximize resource efficiency in deep space, thereby reducing the need for resupply missions. A fully integrated, user-friendly electro-agriculture prototype is designed to support a 4-person astronaut crew representing a significant step towards enabling deep space exploration and establishing a self-sufficient human colony on Mars. Additionally, this prototype could be deployed to produce fresh food in urban cities, arid deserts, or in the wake of a natural disaster.

Finally, future research directions will be discussed to further develop and scale tandem CO₂ electrolyzer stacks beyond 1 kW and new opportunities for enabling electro-biomanufacturing by integrating CO₂ electrolysis with bioprocesses will be offered. It will be demonstrated that CO₂ electrolysis has a critical role to play in making meaningful progress towards resolving some of the most critical challenges facing humanity: climate change, world hunger, and enabling humans to become a multi-planetary species.