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Intensified Catalytic Conversion of CO_2 into High Value Chemicals

Project Number: DE-FE0031920

Performing Organization: University of Kentucky CAER

Principal Investigator: Jesse Thompson

caer.uky.edu/power-generation/

National Energy Technology Laboratory
Carbon Management and Natural Gas & Oil Research Project Review Meeting
Virtual Meetings, August 2 through August 31, 2021

Project Overview

- Develop technology to convert CO_2 to valuable products to partially offset carbon capture costs from the utility and industrial sectors.
- Contribute to the production of a formic acid at a lower cost than is currently available, potentially disrupting C1 feedstock markets

- **Project Period:** 10/1/2020 - 9/30/2022 (2 years)

- **Funding**: Federal - $1M; CS - $250K; Total - $1.25M

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TRIMERIC CORPORATION

Project Objectives

Developing CO_2 utilization technologies to reduce the cost of post-combustion CO_2 capture through:

1. Screening and production of engineered CO_2 reducing catalysts capable of producing C1/C2 products, including formic acid
2. Immobilization and protection of the catalyst within a flow-through process for increase catalyst lifetime and continuous production
3. Develop a pressurized electrochemical reactor to increase production rates
4. Long-term stable operation with high selectivity towards formic acid

Project Team

Principal Investigator
Jesse Thompson

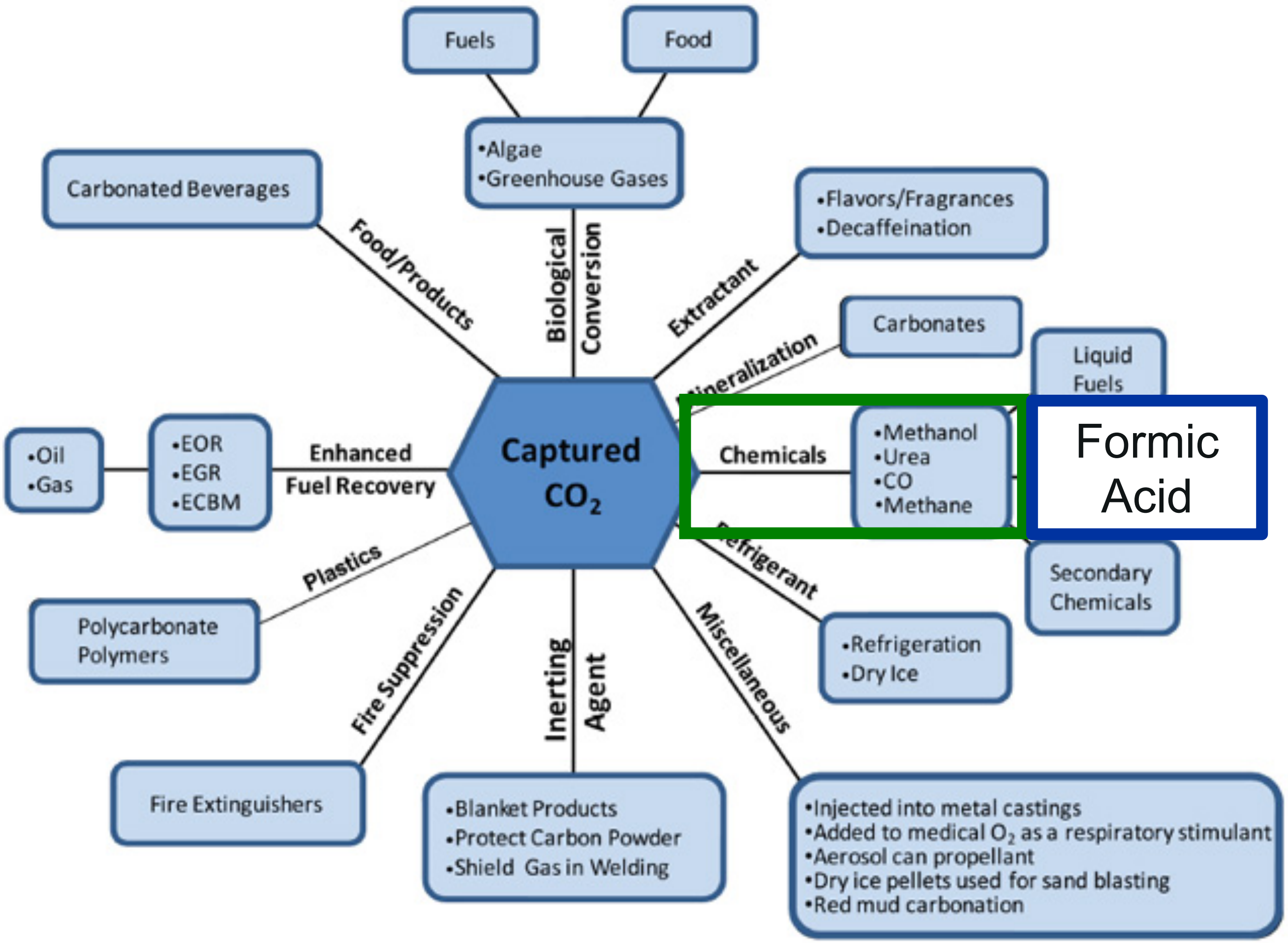
CO_2-U Catalyst
Muthu Gnanamani (Co-I)

CO_2-U Reactor
Ayo Omosebi (Co-I)

LCA
Naser Matin

TEA (Trimeric)
Andrew Sexton

Motivation



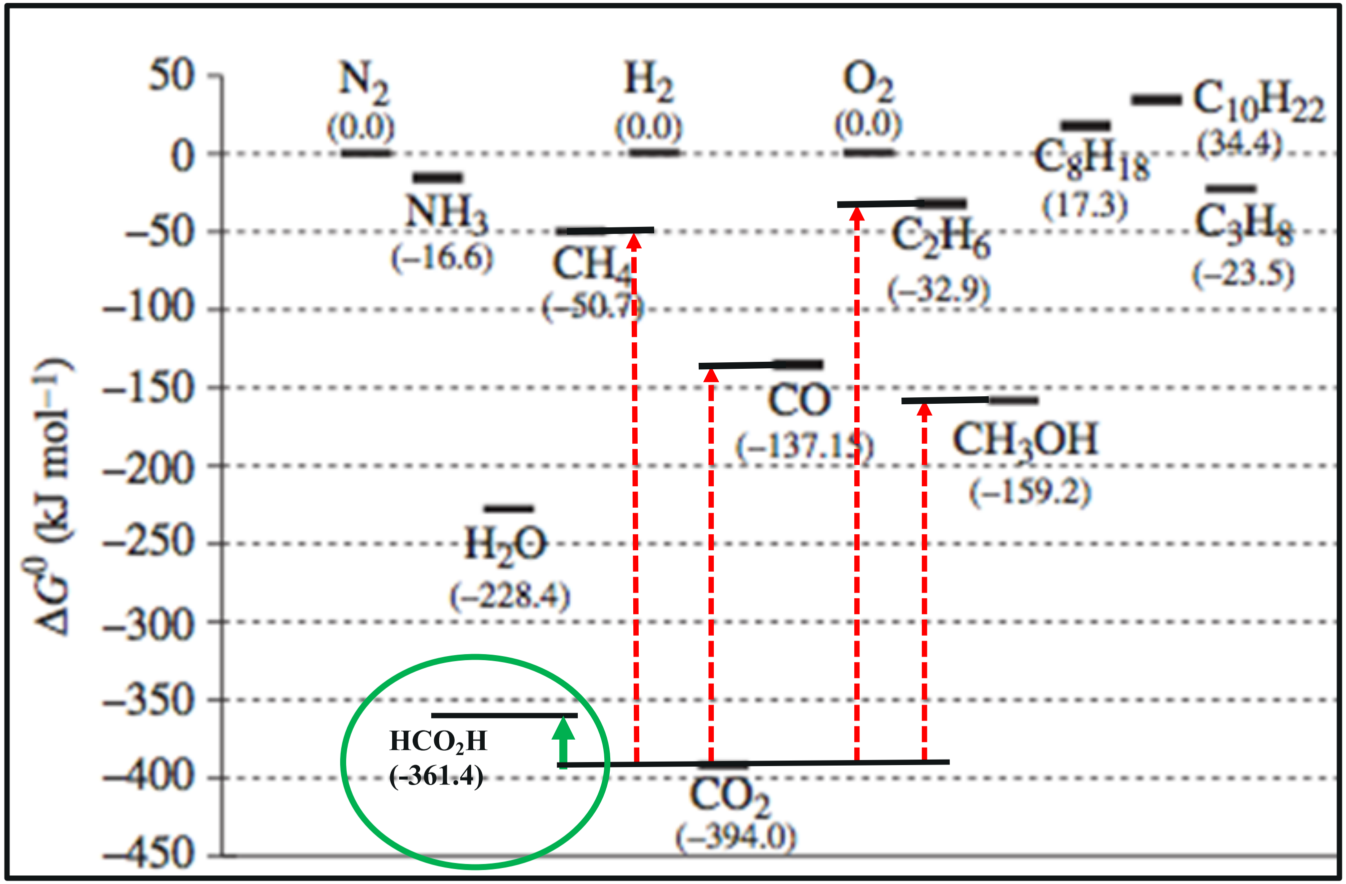
The current commercial market for formic acid is relatively small at <1M tonnes per year

Two potential new markets with lower cost formic acid:

- Formic acid-based fuel cells
- Liquid H_2 storage medium

http://www.netl.doe.gov/research/coal/carbon-storage/research-and-development/co2-utilization

Formic Acid Production

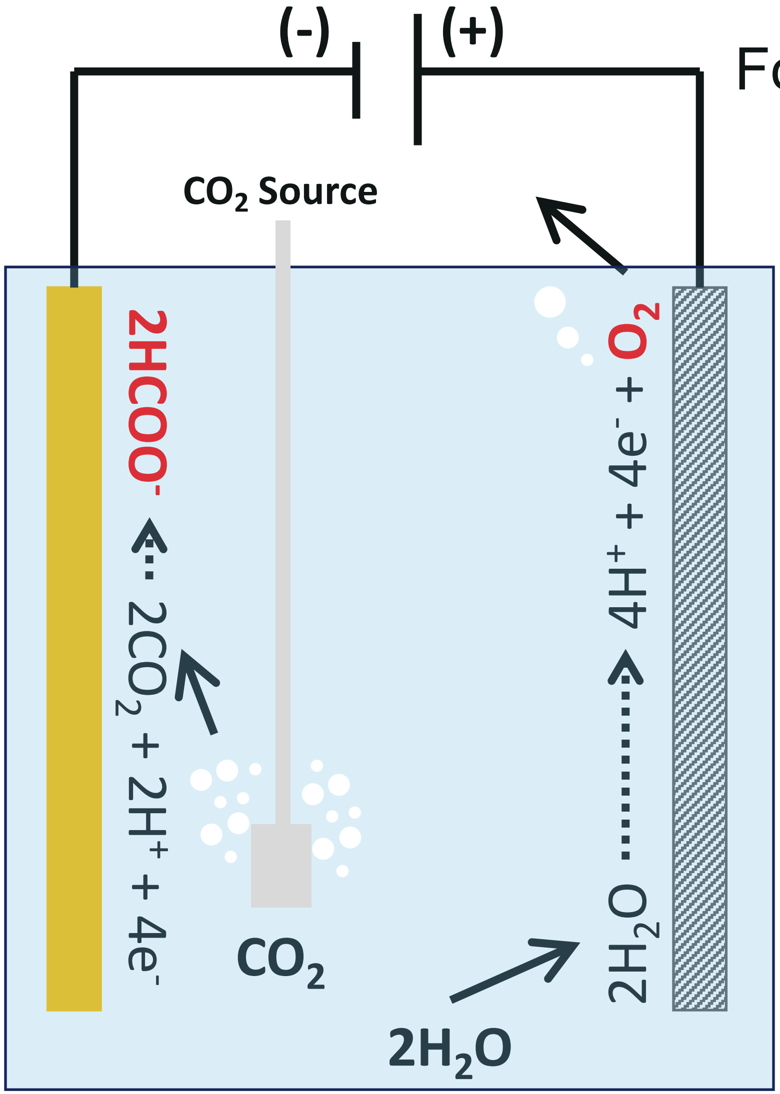


Formic acid (HCO_2H) has been selected as the target:

1) Lowest Gibbs energy input
2) Lowest atomic (proton/electron) input
3) High potential for growth in commercial market for formic acid

Phil. Trans. R. Soc. A **2010**, *368*, 3343; *ACS Catal.* **2017**, *7*, 5381; *J. Phys. Chem. Lett.* **2015**, *6*, 4073

Alternative Production Pathway -- Electrochemical CO_2 Reduction



Formic Acid with CO_2 and H_2O as inputs:

Anode Reaction:

$$2H_2O \rightarrow 4H^+ + 4e^- + O_2$$

Cathode Reaction:

$$2CO_2 + 2H^+ + 4e^- \rightarrow 2HCOO^-$$

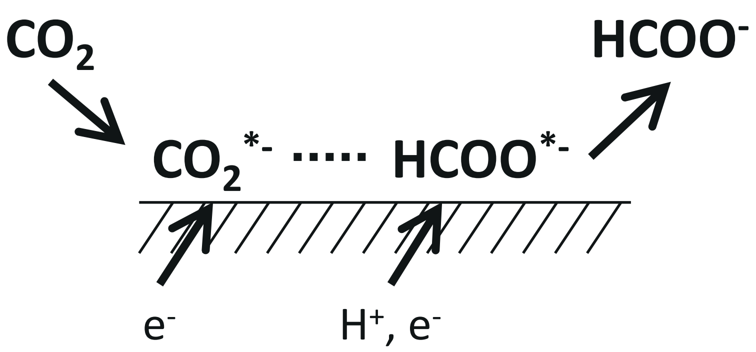
Net Reaction:

$$2H_2O + 2CO_2 \rightarrow 2HCOO^- + 2H^+$$

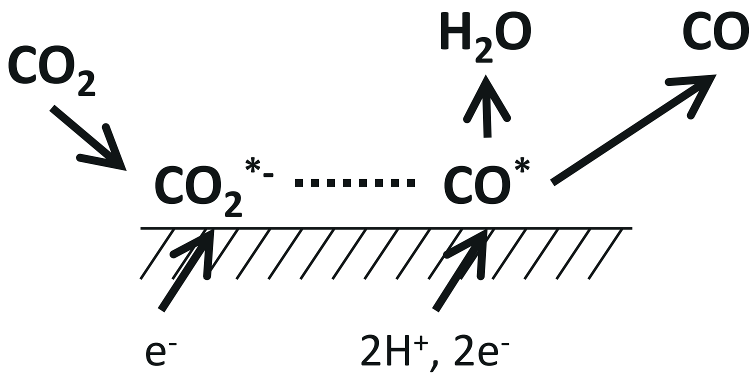
Water or hydrogen gas can be used to generate protons and electrons at the anode, but the reaction product at the cathode will depend on the *electrode/catalyst*.

Why So Many Reaction Products?

Weakly Bound CO_2^*:



Stably Bound CO_2^*:



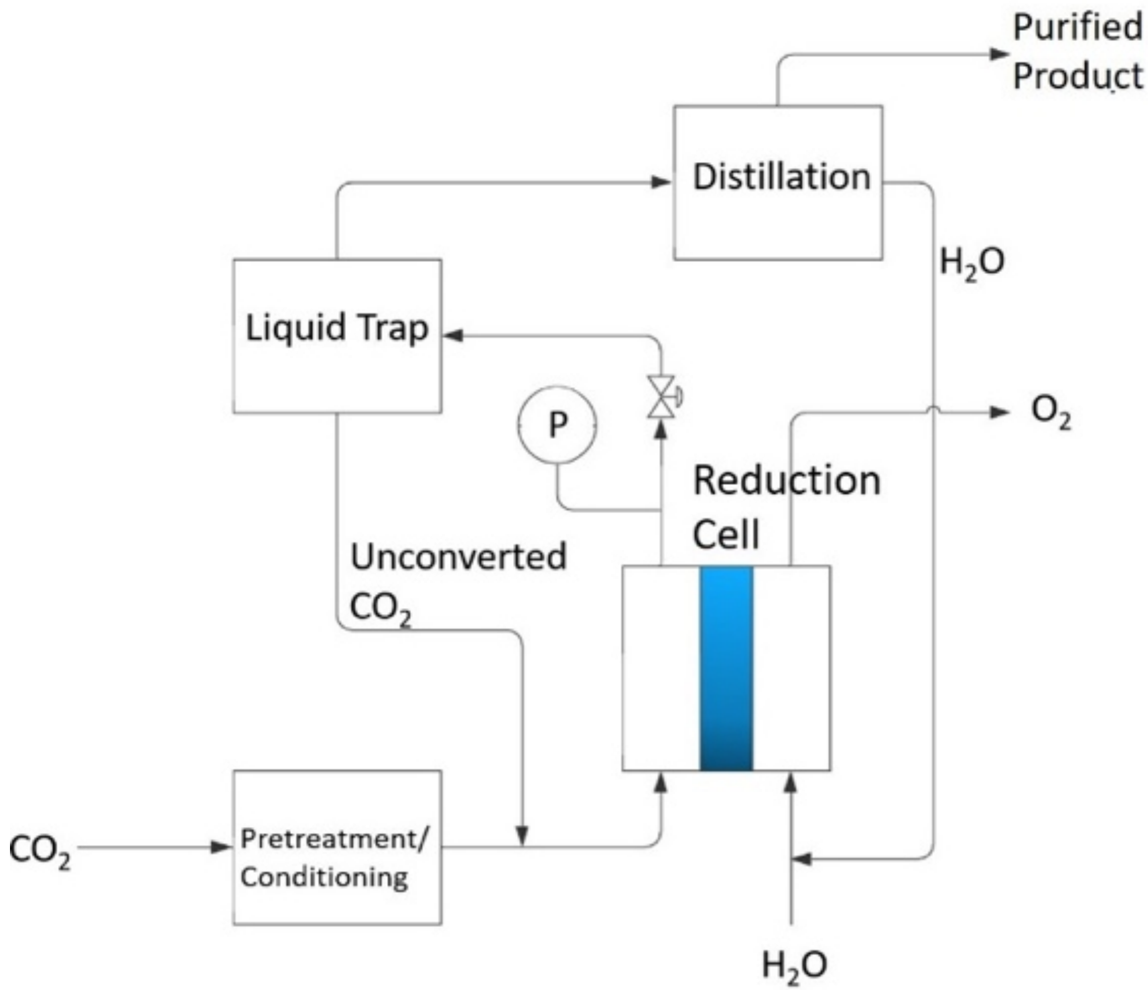
While the reduction of CO_2 to formic acid can be a relatively simple process (requiring H^+ and $2e^-$), when more reduced products are desired the protonation of CO_2 on the catalyst surface can be quite difficult and leads to a range of reaction products.

Peterson et al. JPCL 2012

Challenges and Limitations to CO_2-U

- **Reaction rate – Matching CO_2 source**
- **Catalyst stability**
  - Degradation due to overpotential
  - Faradic inefficiencies
  - Oxidants/inhibitors
- **Electrode charge density and stability**
  - Active surface area
  - Degradation
- **Purification**
  - Catalyst selectivity
  - Separation of co-products

UK CAER EBOCU Process



To provide a highly selective and robust process, the UK CAER *Enhanced Bi-Metallic Oxide Carbon Utilization* (EBOCU) process focuses on:

1. Using bi-metallic metal oxide catalyst with tailored/optimized properties
2. Leverage pressurized operation to enhance CO_2 conversion

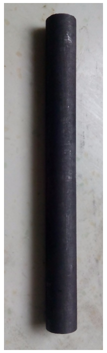
Our Approach to Address Limitations

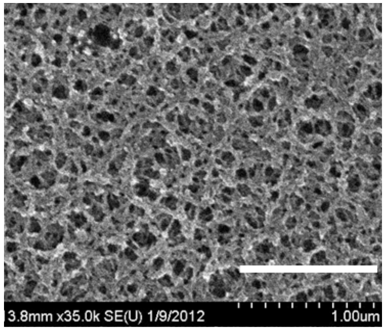
- Reaction rate
- Catalyst Stability

1 Catalyst Development

- Electrode degradation
- Electrode charge density

2 Carbon Electrodes





- Purification of Formic Acid

3 Maximizing selectivity

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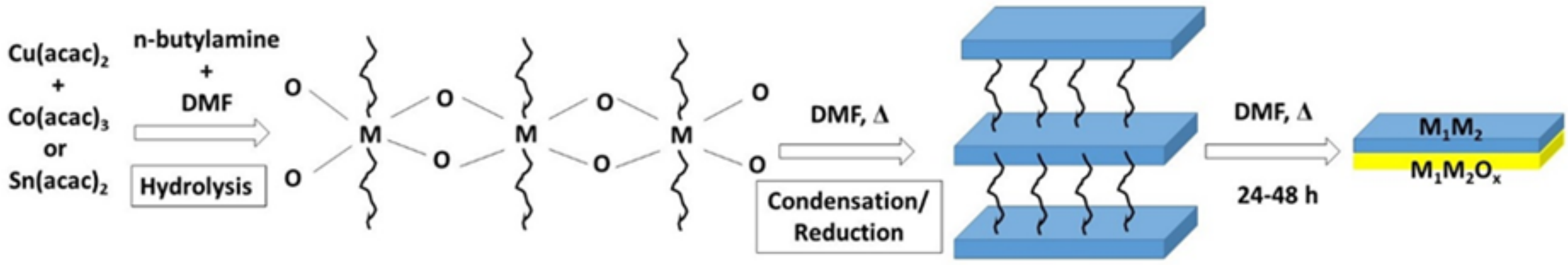
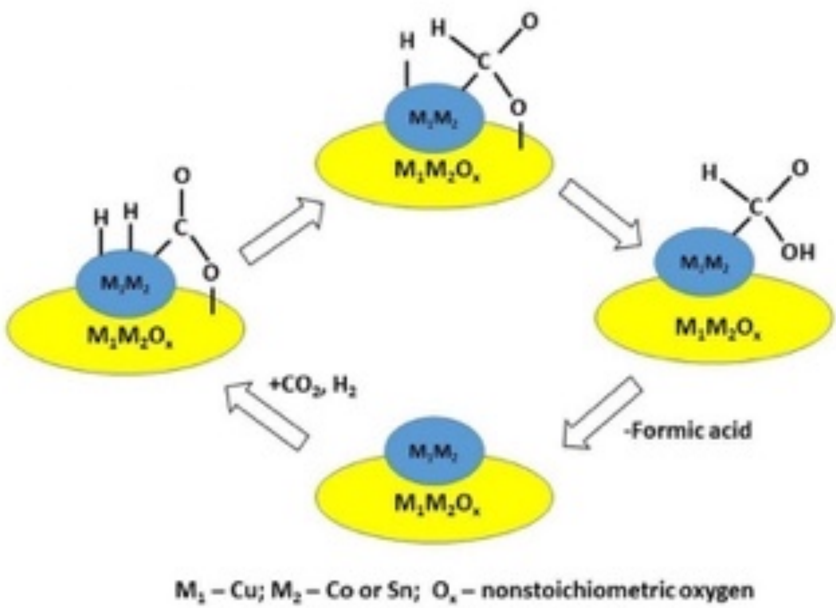
Catalyst for CO_2 Reduction



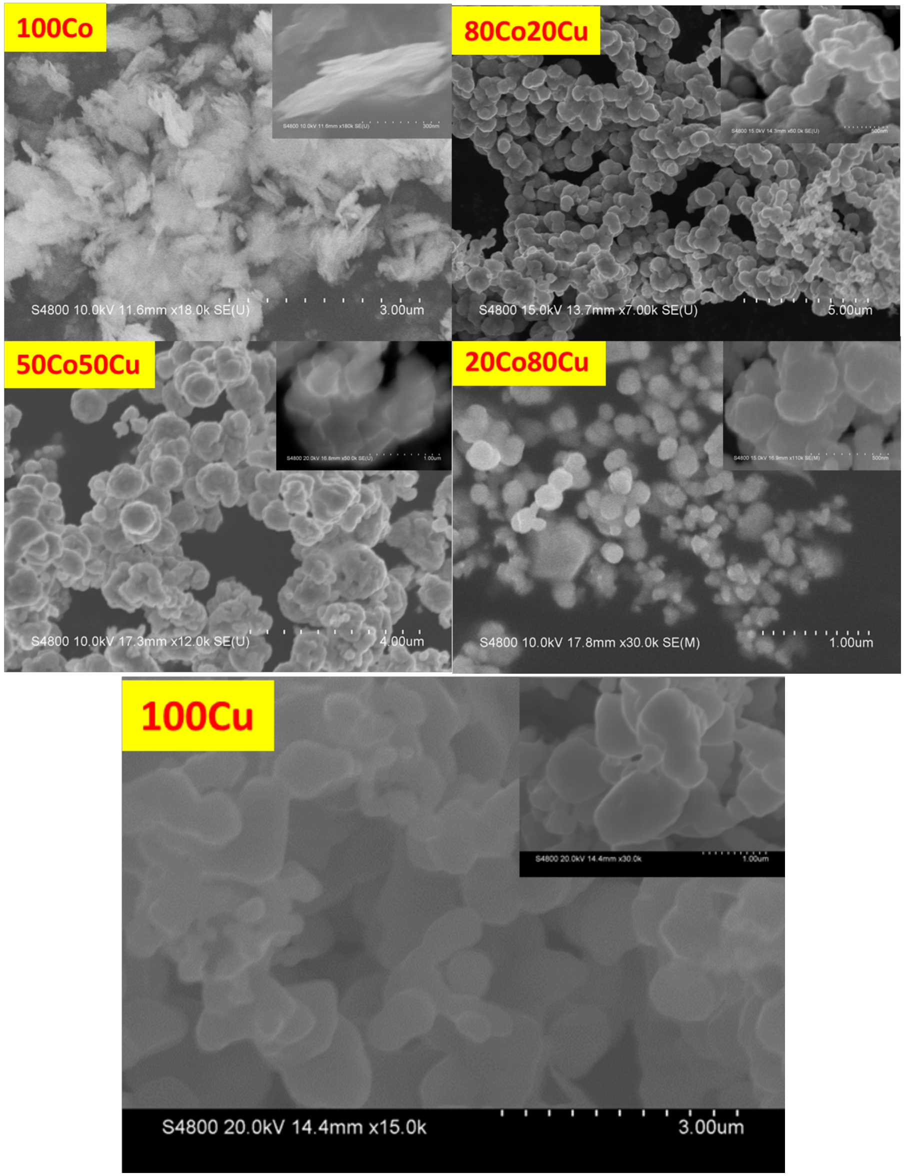
Hydrothermal synthesis of bimetal/oxide (CuSn/CuSnOx and CuCo/CuCoOx) catalysts



Proposed mechanism of formation of formic acid on bimetal/oxide catalysts from CO_2

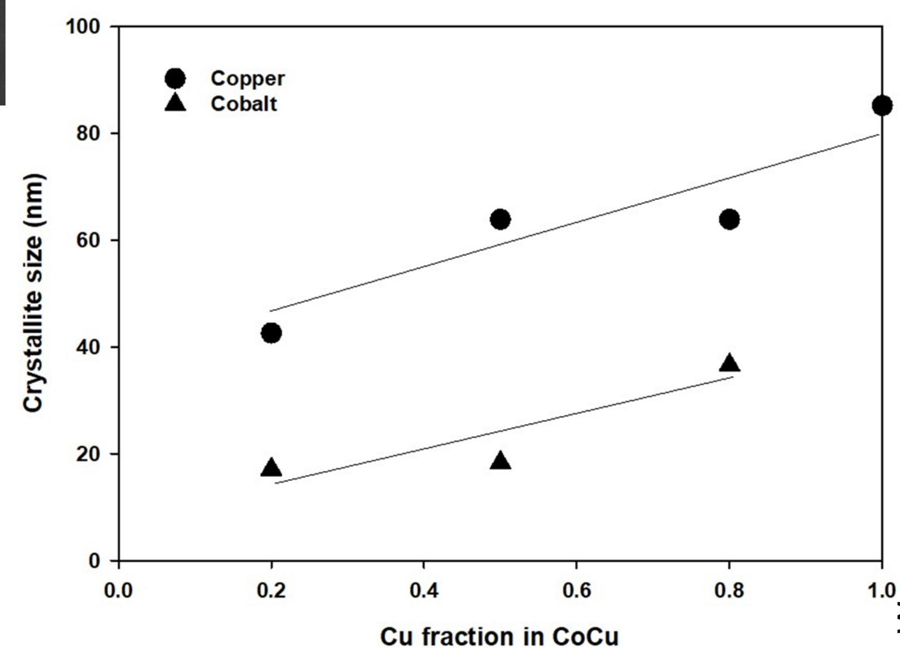
Goal: Synthesized and tested different ratios of Co, Cu and Sn bimetal/oxide nano-catalysts for production of C1/C2 compounds from CO_2

Catalyst for CO_2 Reduction

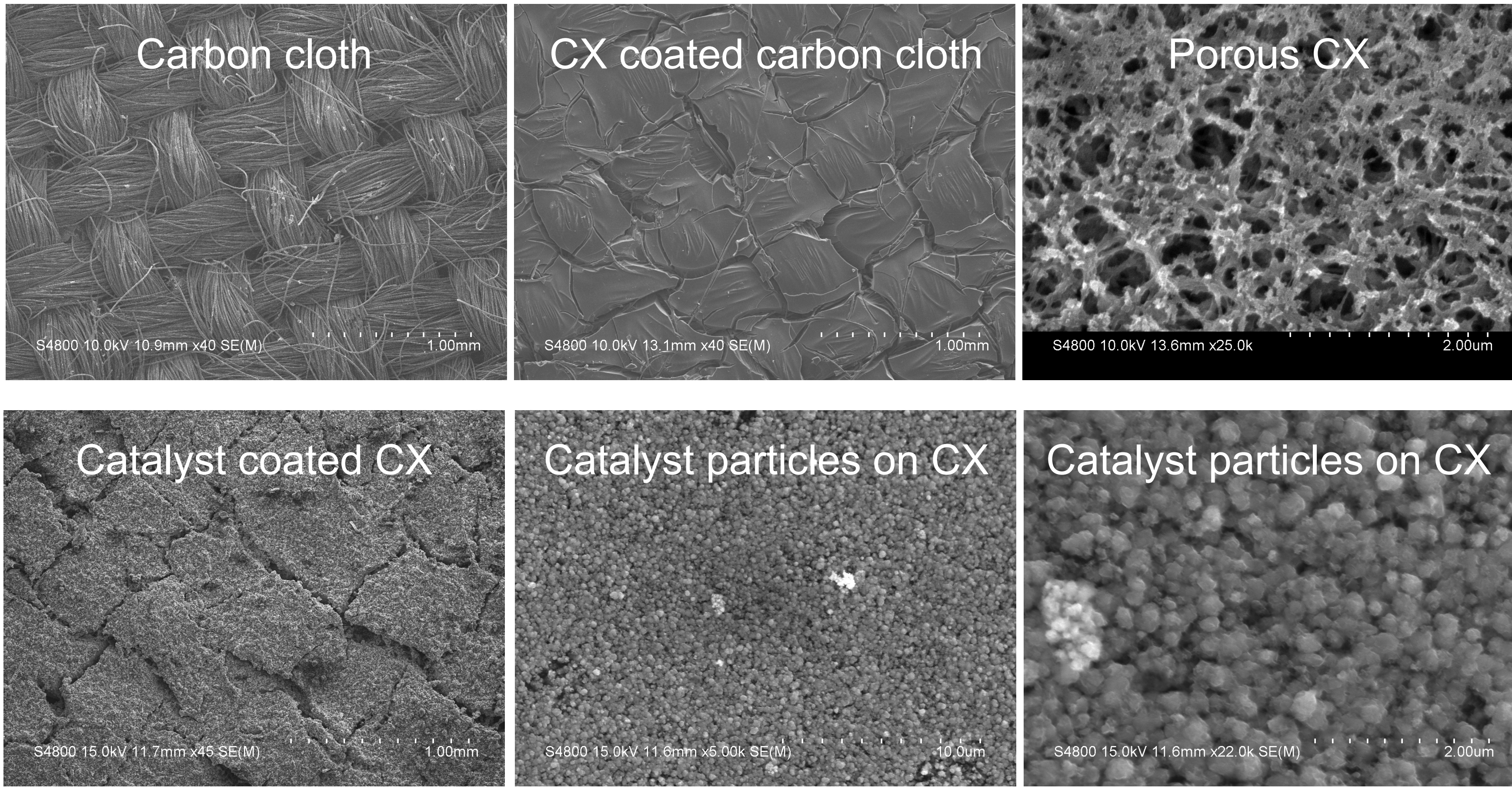


Starting with a combination of Co and Cu, bare Co (hydroxide) consists of needles.

Introducing Cu to Co changes the morphology as well as crystallinity yielding relatively flat nano-catalyst sheets



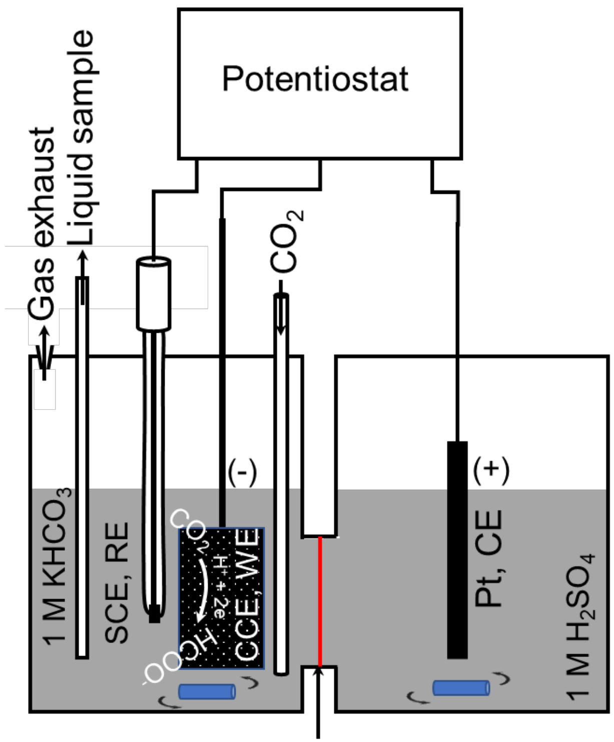
Electrode for CO_2 Reduction

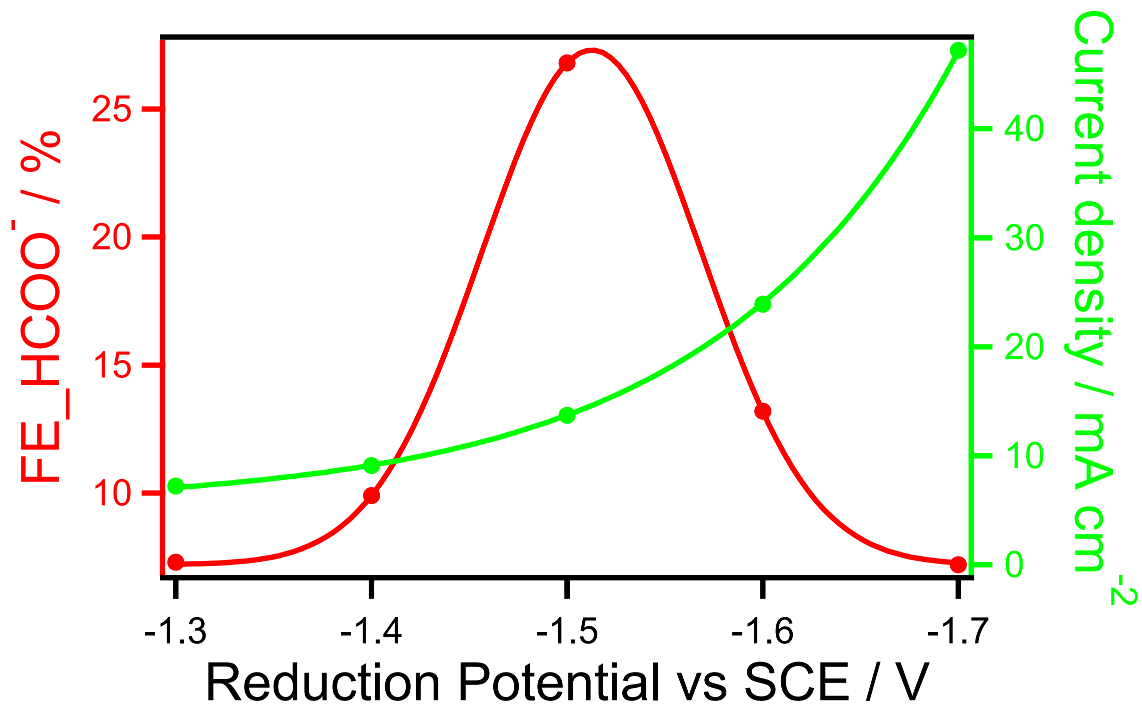


Carbon Xerogel (CX) is a good scaffold to immobilize the catalyst while also maintaining good conductivity

Catalyst: Nano Cu (discs) made by hydrothermal synthesis (Airbrush catalyst loading: 2.85 mgcm^{-2})

Electrodes for CO_2 Reduction





- H-cell using 1 M $KHCO_3$ (cathode) and 1 M H_2SO_4 (anode)
- CO_2 purge
- Nano-Cu catalyst loading: 2.85 mg/cm^2
- Electrode area: 2.4 cm^2
- Production of 44 mM Formate (-1.5V) (3 hr.)

Additional Tasks – TMP, LCA, TEA

Technology Maturation Plan (TMP)

- Describes the current technology readiness level (TRL) of the proposed technology/technologies, relates the proposed project work to maturation of the proposed technology, describes the expected TRL at the end of the project, and describes any known post-project research and development necessary to further mature the technology.

Life-Cycle Analysis (LCA)

- An LCA will be performed to demonstrate the potential of the proposed intensified electro-catalyst process to be a substantive CO_2 mitigation option by verifying the life cycle GHG reduction potential of the products(s) and technology (on a percent reduction basis) relative to current state-of-the-art pathways.

Final Techno-Economic Assessment with Technology Gap Analysis

- A high-level return-on-investment (ROI) analysis will be conducted to assess the viability of the proposed process to reduce GHG emissions from power plants based on the collected lab-scale data.

Success Criteria

24-month timeline	Due Date	Success Criteria (Task #)
12 months into project	9/30/2021	Catalyst capable of formic acid selectivity of > 80% (Task 2)
18 months into project	3/31/2022	CCE electrode with ohmic impedance contribution < 10 ohm (Task 3)
End of project	9/30/2022	Flow cell with production of 25 mM Formic acid, 50% Faradaic Efficiency, and operating at < 4 V (Task 4)
End of project	9/30/2022	Long-term production of formic acid for >50 hours at 5 mM/hr (Task 4)

Project Schedule

Task Number and Name	Length (months)	Start	End	Primary Personal	Federal FY 20/21 and 21/22 Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
1. Project Management and Planning	24	10/1/20	9/30/22	Jesse	■	■	■	■	■	■	■	■
1.1 Project Management Plan	24	10/1/20	9/30/22	Jesse	■	■	■	■	■	■	■	■
1.2 Technology Maturation Plan	24	10/1/20	9/30/22	Jesse	■	■	■	■	■	■	■	■
2. Development of Electrocatalysts for CO_2 reduction	18	10/1/20	3/31/21	Muthu	■	■	■	■	■	■		
2.1 Eectrocatalysis Formulation	12	10/1/20	9/30/21	Muthu	■	■	■	■				
2.2 Electrocatalysis Characterization	6	10/1/21	3/31/22	Muthu					■	■		
M4. Synthesis of four homogeneous bi-metal oxide catalyst with different molar ratios of Cu and Sn/Co.			9/30/21					★				
3. Reactor Design and Catalyst Evaluation	18	10/1/20	3/31/22	Daniel	■	■	■	■	■	■		
3.1 Evaluation of Catalyst Coated Electrodes (CCE)	9	10/1/20	6/30/21	Daniel	■	■	■					
3.2 Half-cell Parametric Testing of CCE	18	10/1/20	3/31/22	Daniel	■	■	■	■	■	■		
M5. 30% decline in cathode/anode after 50 CV cycles			9/30/21					★				
4. Integrated Reactor and Catalyst Testing	18	4/1/21	9/30/22	Daniel			■	■	■	■	■	■
4.1 Full Cell Design and Integration	12	4/1/21	3/31/22	Daniel			■	■	■	■		
4.2 Stability Testing	12	10/1/21	9/30/22	Daniel					■	■	■	■
4.3 Long-term Reactor Operation	18	4/1/21	9/30/22	Daniel			■	■	■	■	■	■
M6. Flow cell capable of 25 mM Formic Acid production at 2 mL/min with Faradaic Efficiency of 40%			6/30/22								★	
5. Final Techno-Economic Assessment with Technology Gap Analysis	6	4/1/22	9/30/22	Jesse/Ayo							■	■
6. Life Cycle Analysis	6	4/1/22	9/30/22	Jesse							■	■

Acknowledgements

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