Intensified Catalytic Conversion of CO$_2$ into High Value Chemicals

Project Number: DE-FE0031920
Performing Organization: University of Kentucky CAER
Principal Investigator: Jesse Thompson
caec.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 CO₂ 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
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 H₂ storage medium
Formic Acid Production

**Formic acid (HCO$_2$H)** 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

Alternative Production Pathway -- Electrochemical CO₂ Reduction

Formic Acid with CO₂ and H₂O as inputs:

Anode Reaction:

\[2H₂O \rightarrow 4H^+ + 4e^- + O₂\]

Cathode Reaction:

\[2CO₂ + 2H^+ + 4e^- \rightarrow 2HCOO^-\]

Net Reaction:

\[2H₂O + 2CO₂ \rightarrow 2HCOO^- + 2H^+\]

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$_2^*$:

\[
\text{CO}_2 \rightarrow \text{CO}_2^- \cdots \text{HCOO}^- \rightarrow \text{HCOO}^- \rightarrow \text{CO}_2^- \rightarrow \text{CO}_2 \rightarrow \text{H}_2\text{O} \rightarrow \text{CO}
\]

Stably Bound CO$_2^*$:

\[
\text{CO}_2 \rightarrow \text{CO}_2^- \cdots \text{CO}^- \rightarrow \text{CO}^- \rightarrow \text{CO} \rightarrow \text{CO}_2 \rightarrow \text{H}_2\text{O} \rightarrow \text{CO}
\]

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.
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
Catalyst for CO₂ Reduction

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

Goal: Synthesized and tested different ratios of Co, Cu and Sn bimetal/oxide nano-catalysts for production of C1/C2 compounds from CO₂

Proposed mechanism of formation of formic acid on bimetal/oxide catalysts from CO₂
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.
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 mg cm⁻²)
Electrodes for CO$_2$ Reduction

- H-cell using 1 M KHCO$_3$ (cathode) and 1 M H$_2$SO$_4$ (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 CO₂ 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

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

<table>
<thead>
<tr>
<th>Task Number and Name</th>
<th>Length (months)</th>
<th>Start</th>
<th>End</th>
<th>Primary Personal</th>
<th>Q1</th>
<th>Q2</th>
<th>Q3</th>
<th>Q4</th>
<th>Q1</th>
<th>Q2</th>
<th>Q3</th>
<th>Q4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Project Management and Planning</td>
<td>24</td>
<td>10/1/20</td>
<td>9/30/22</td>
<td>Jesse</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.1 Project Management Plan</td>
<td>24</td>
<td>10/1/20</td>
<td>9/30/22</td>
<td>Jesse</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.2 Technology Maturation Plan</td>
<td>24</td>
<td>10/1/20</td>
<td>9/30/22</td>
<td>Jesse</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Development of Electrocatalysts for CO₂ reduction</td>
<td>18</td>
<td>10/1/20</td>
<td>3/31/21</td>
<td>Muthu</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.1 Electrocatalysis Formulation</td>
<td>12</td>
<td>10/1/20</td>
<td>9/30/21</td>
<td>Muthu</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.2 Electrocatalysis Characterization</td>
<td>6</td>
<td>10/1/21</td>
<td>3/31/22</td>
<td>Muthu</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M4. Synthesis of four homogeneous bi-metal oxide catalyst with different molar ratios of Cu and Sn/Co.</td>
<td></td>
<td></td>
<td>9/30/21</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.1 Evaluation of Catalyst Coated Electrodes (CCE)</td>
<td>9</td>
<td>10/1/20</td>
<td>6/30/21</td>
<td>Daniel</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.2 Half-cell Parametric Testing of CCE</td>
<td>18</td>
<td>10/1/20</td>
<td>3/31/22</td>
<td>Daniel</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M5. 30% decline in cathode/anode after 50 CV cycles</td>
<td></td>
<td></td>
<td>9/30/21</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. Integrated Reactor and Catalyst Testing</td>
<td>18</td>
<td>4/1/21</td>
<td>9/30/22</td>
<td>Daniel</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.1 Full Cell Design and Integration</td>
<td>12</td>
<td>4/1/21</td>
<td>3/31/22</td>
<td>Daniel</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.2 Stability Testing</td>
<td>12</td>
<td>10/1/21</td>
<td>9/30/22</td>
<td>Daniel</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.3 Long-term Reactor Operation</td>
<td>18</td>
<td>4/1/21</td>
<td>9/30/22</td>
<td>Daniel</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M6. Flow cell capable of 25 mM Formic Acid production at 2 mL/min with Faradaic Efficiency of 40%</td>
<td></td>
<td></td>
<td>6/30/22</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5. Final Techno-Economic Assessment with Technology Gap Analysis</td>
<td>6</td>
<td>4/1/22</td>
<td>9/30/22</td>
<td>Jesse/Ayo</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6. Life Cycle Analysis</td>
<td>6</td>
<td>4/1/22</td>
<td>9/30/22</td>
<td>Jesse</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Acknowledgements

• DOE-NETL: Kyle Smith, Katharina Daniels

• UK CAER: Muthu Gnanamani (Co-I), Ayo Omosebi (Co-I), Pom Kharel, Lisa Richburg, Kunlei Liu