Intensified Catalytic Conversion of CO₂ into High Value Chemicals

Project Number: DE-FE0031920
Performing Organization: University of Kentucky
Principal Investigator: Jesse Thompson

National Energy Technology Laboratory
2022 Carbon Management Project Review Meeting
Pittsburgh, PA - August 15 -19, 2022
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
Project Objectives

Developing CO₂ utilization technologies to reduce the cost of post-combustion CO₂ capture through:

1. Screening and production of engineered CO₂ reducing catalysts capable of producing C1/C2 products, including formic acid (formate)
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 (formate)
Project Team

Principal Investigator
Jesse Thompson

CO₂-U Catalyst
Muthu Gnanamani (Co-I)

CO₂-U Reactor
Ayo Omosebi (Co-I)

LCA
Naser Matin

TEA (Trimeric)
Andrew Sexton
Captured CO₂

UK CAER Andora Process
DE-FE0031720

UK CAER EBOCU Process
Options for CO₂

http://www.netl.doe.gov/research/coal/carbon-storage/research-and-development/co2-utilization
Formic acid (HCO$_2$H) 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
Formic Acid Market

• Current commercial uses include as a preservative for animal feeds, leather tanning, and in rubber production.

• Production is almost exclusively in Europe and China. Almost no formic acid production within US.

• Potential future markets include in formic acid fuel cell, and as a liquid hydrogen storage medium for transportation applications.
Formic Acid Production

Industrial formic acid is produced from methanol (BASF/Kemira Process) (methanol typically comes from energy intensive steam methane reforming)

\[
\text{CH}_3\text{-OH} + \text{C} \equiv \text{O} \xrightarrow{\text{NaOMe}} \xrightarrow{80 \degree \text{C}, 40 \text{ atm}} \text{HOO} \xrightarrow{} \text{H} \xrightarrow{} \text{COOH} + \text{CH}_3\text{-OH}
\]

Distillation is used to separate formic acid from methanol, followed by solvent extraction to separate formic acid from water.
The energy required to separate and purify formic acid makes up the majority of the GWP for the comparative system.

CPS = Methyl Formate route

CO₂ conversion to formic acid by the Andora Process LCA report DE-FE0031720 (2022)
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 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\textsubscript{2}*:

\[
\text{CO}_2 \rightarrow \text{CO}_2^* \rightarrow \text{HCOO}^- \rightarrow \text{e}^- \quad \text{H}^+, \text{e}^- 
\]

Stably Bound CO\textsubscript{2}*:

\[
\text{CO}_2 \rightarrow \text{H}_2\text{O} \rightarrow \text{CO}^* \rightarrow \text{CO} \rightarrow \text{H}_2\text{O} \rightarrow \text{e}^- \quad 2\text{H}^+, 2\text{e}^- 
\]

While the reduction of CO\textsubscript{2} to formic acid can be a relatively simple process (requiring H\textsuperscript{+} and 2e\textsuperscript{-}), when more reduced products are desired the protonation of CO\textsubscript{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

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 CO₂ 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 CO$_2$ Reduction

Hydrothermal synthesis of bimetal/oxide (CuCo/CuCoO$_x$ and CuSn/CuSnO$_x$) catalysts

**Goal:** Synthesized and tested different ratios of Co, Cu and Sn bimetal/oxide nano-catalysts for production of C1/C2 compounds from CO$_2$

Proposed mechanism of formation of formic acid on bimetal/oxide catalysts from CO$_2$
Catalyst for CO$_2$ Reduction

Synthesizing a series of Sn:Cu catalysts with different molar ratios was our primary focus.
Electrode for CO$_2$ Reduction

Carbon Xerogel (CX) is a good scaffold to immobilize catalysts while also maintaining good conductivity and gas permeability.
H-Cell Screening

95Sn:5Cu UK catalyst
Pressure: 0 - 4 psi
FE - formate: 68.5% - 76%

FE_formate / %
Pressure / psi

Potential vs RHE / V

Pressure / psi

FE_formate / %

Id / mA cm²
Flow Cell Optimization

- CO₂ + Gas products
- CO₂

Catholyte
Anolyte
Anolyte
Catholyte

0.5 M KHCO₃
0.5 M H₂SO₄

Cell Potential = 3.45 V

- CD: 48 mA/cm²
- FE: 81.2% (energy)
- 29% conversion (CO₂ input)
- 1.65 g/hr formic acid
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.
## Technology Maturation Plan (TMP) - Update

<table>
<thead>
<tr>
<th>Component</th>
<th>TRL at beginning of Project</th>
<th>TRL at end of Project</th>
<th>Performance Attribute/Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bimetallic catalyst</td>
<td>2</td>
<td>3</td>
<td>Catalyst capable of formic acid selectivity of &gt; 80%</td>
</tr>
<tr>
<td>Anode/cathode materials</td>
<td>3</td>
<td>4</td>
<td>CCE electrode with ohmic impedance contribution &lt; 10 ohm.</td>
</tr>
<tr>
<td>Fully integrated combined system</td>
<td>2</td>
<td>3</td>
<td>Production of 25 mM Formic acid, 50% Faradaic Efficiency, and operating at &lt; 4 V. Long-term production of formic acid for &gt;50 hours at 5 mM/hr</td>
</tr>
</tbody>
</table>
LCA and TEA

- Comparison system is formic acid produced from the Kemira process with European data added into our LCA, but using US power (openLCA)

- The main GHG source in the comparison system is steam used to separate methanol from formic acid.

- In our system we are anticipate using IEX to isolate and separate formic acid from the catholyte solution.

- The main equipment costs will come from construction of the electrolyzer, and the ion exchange system to separate the formic acid from the process solution.
<table>
<thead>
<tr>
<th>Due Date</th>
<th>Success Criteria (Task #)</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>9/30/2021</td>
<td>Catalyst capable of formic acid selectivity of &gt; 80% (Task 2)</td>
<td>100%</td>
</tr>
<tr>
<td>3/31/2022</td>
<td>CCE electrode with ohmic impedance contribution &lt; 10 ohm (Task 3)</td>
<td>100%</td>
</tr>
<tr>
<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>
<td>100%</td>
</tr>
<tr>
<td>9/30/2022</td>
<td>Long-term production of formic acid for &gt;50 hours at 5 mM/hr (Task 4)</td>
<td>25%</td>
</tr>
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</table>
Key Project Takeaways

• Using KHCO$_3$ catholyte is a way to potentially match with CO$_2$ capture systems in the future

• Operating at slight pressure to boost CO$_2$ in catholyte solution can increase production

• Previous TEA and LCA’s showed that the separation processes are important and need to be considered in this project
# 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>Federal FY 20/21 and 21/22</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>Q1 Q2 Q3 Q4 Q1 Q2 Q3 Q4</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>
</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>
</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>
</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>
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<tr>
<td>2.2 Electrocatalysis Characterization</td>
<td>6</td>
<td>10/1/21</td>
<td>3/31/22</td>
<td>Muthu</td>
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<tr>
<td>M4. Synthesis of four homogeneous bi-metal oxide catalyst with different molar ratios of Cu and Sn/Co.</td>
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<td></td>
<td>9/30/21</td>
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<tr>
<td>3. Reactor Design and Catalyst Evaluation</td>
<td>18</td>
<td>10/1/20</td>
<td>3/31/22</td>
<td>Daniel</td>
<td>Q1 Q2 Q3 Q4 Q1 Q2 Q3 Q4</td>
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<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>
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<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>
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<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>
</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>Q1 Q2 Q3 Q4 Q1 Q2 Q3 Q4</td>
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<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>
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<tr>
<td>4.2 Stability Testing</td>
<td>12</td>
<td>10/1/21</td>
<td>9/30/22</td>
<td>Daniel</td>
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<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>
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<tr>
<td>M6. Flow cell capable of 25 mM Formic Acid production at 2 mL/min with Faradaic Efficiency of 40%</td>
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<td></td>
<td>6/30/22</td>
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<td></td>
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<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>Q1 Q2 Q3 Q4 Q1 Q2 Q3 Q4</td>
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<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>
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</tbody>
</table>
# State Point Table

<table>
<thead>
<tr>
<th>State Point Table</th>
<th>Units</th>
<th>Measured/Current Performance</th>
<th>Projected/Target Performance</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Synthesis Pathway Steps</strong>&lt;sup&gt;1&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Step 1 (based on CO&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>mol&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>( CO_2 + 2H^+ + 2e \rightarrow HCOOH (pH &lt; 3.75) )</td>
<td></td>
</tr>
<tr>
<td>Step 2 (anodic)</td>
<td>mol&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>( 2H_2O \rightarrow O_2 + 4H^+ + 4e )</td>
<td></td>
</tr>
<tr>
<td>Overall</td>
<td>mol&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>( 2CO_2 + 2H_2O \rightarrow O_2 + 2HCOOH )</td>
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</tr>
<tr>
<td>Source of external intermediate 1</td>
<td></td>
<td>(e.g., natural gas, oil, renewable energy, etc)</td>
<td></td>
</tr>
<tr>
<td>Source of external intermediate 2</td>
<td></td>
<td>(e.g., natural gas, oil, renewable energy, etc)</td>
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<tr>
<td>Source of external intermediate n</td>
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<td>(e.g., natural gas, oil, renewable energy, etc)</td>
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<tr>
<td><strong>Reaction Thermodynamics</strong>&lt;sup&gt;2,3&lt;/sup&gt;</td>
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<td></td>
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<tr>
<td>( \Delta H_{Rxn} )</td>
<td>KJ/mol</td>
<td></td>
<td>Electrochemical</td>
</tr>
<tr>
<td>( \Delta G_{Rxn} )</td>
<td>KJ/mol</td>
<td></td>
<td>264.2</td>
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<tr>
<td><strong>Conditions</strong></td>
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<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt; Source&lt;sup&gt;5&lt;/sup&gt;</td>
<td></td>
<td>+99.9% pure CO&lt;sub&gt;2&lt;/sub&gt; supplied from CO&lt;sub&gt;2&lt;/sub&gt; capture plant</td>
<td>+99.9% pure CO&lt;sub&gt;2&lt;/sub&gt; supplied from CO&lt;sub&gt;2&lt;/sub&gt; capture plant</td>
</tr>
<tr>
<td>Catalyst&lt;sup&gt;6&lt;/sup&gt;</td>
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<td>Sn&lt;sub&gt;95&lt;/sub&gt;Cu&lt;sub&gt;5&lt;/sub&gt;</td>
<td>Sn&lt;sub&gt;95&lt;/sub&gt;Cu&lt;sub&gt;5&lt;/sub&gt;</td>
</tr>
<tr>
<td>Pressure (bar)</td>
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<td>Ambient – 5 psi</td>
<td>Ambient – 5 psi</td>
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<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt; Partial Pressure (bar)</td>
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<td></td>
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</tr>
<tr>
<td>Temperature (°C)</td>
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<td>25°C</td>
<td>25°C</td>
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<tr>
<td><strong>Performance</strong></td>
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<tr>
<td>Nominal Residence Time&lt;sup&gt;7&lt;/sup&gt; (sec)</td>
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<td></td>
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<tr>
<td>Selectivity to Desired Product&lt;sup&gt;8&lt;/sup&gt;</td>
<td>%</td>
<td>81.2%</td>
<td>&gt;80%</td>
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<tr>
<td><strong>Product Composition</strong>&lt;sup&gt;9&lt;/sup&gt;</td>
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<tr>
<td>Desired Product</td>
<td>mol%</td>
<td>Formic acid 81%</td>
<td>Formic acid 99%</td>
</tr>
<tr>
<td>Desirable Co-Products</td>
<td>mol%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>&quot; Unwanted By-Products</td>
<td>mol%</td>
<td>CO 19%</td>
<td>CO &lt;1%</td>
</tr>
<tr>
<td>Grand Total</td>
<td>mol%</td>
<td>--</td>
<td>100%</td>
</tr>
</tbody>
</table>
Acknowledgements

- **DOE-NETL**: Isaac “Andy” Aurelio, Katharina Daniels, Kyle Smith
- **UK CAER**: Muthu Gnanamani, Ayo Omosebi, Pom Kharel, Naser Matin, Md Ariful Hoque, Lisa Richburg, Kunlei Liu