An Intensified Electro-Catalytic Process for Production of Formic Acid from Power Plant CO₂ Emissions

Project Number: DE-FE0031720
Performing Organization: University of Kentucky CAER
Principal Investigator: Jesse Thompson
cae.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 and test a novel electro-catalytic method for the production of high-value formic acid from coal-derived CO\textsubscript{2} as a strategy to offset the cost of CO\textsubscript{2} capture.

• The project involves the development and testing of an engineered catalyst to selectively reduce CO\textsubscript{2} directly and exclusively to formic acid, along with process intensification aspects of the reactor design.

• **Project Period:** 1/1/2019 - 12/31/2021 (36 months)

• **Project Funding:** Federal - $800K; CS - $201K; Total - $1M

• **Project Team:** UK CAER and UNIST
Project Objectives

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

1. Screening and production of engineered CO₂ reducing catalyst capable of exclusively producing formic acid;

2. Protection of the catalyst within a flow-through process to continually produce formic acid and increase catalyst lifetime;

3. Long-term stable operation with high selectivity towards formic acid
**Motivation**

Formic acid is the closest to CO$_2$ from an energy perspective, i.e. smaller hill to climb compared to other common CO$_2$ reduction products.

The current commercial market for formic acid is relatively small, mainly as a preservative in animal feed, at ~1M tonnes per year.

Two potential new markets with lower cost formic acid:

- Formic acid-based fuel cells
- Liquid H$_2$ storage medium
Technology Background

Electrochemical CO₂ Reduction

Formic Acid produced with CO₂ and H₂O as inputs:

**Anode Reaction:**

\[ 2H₂O → 4H^+ + 4e^- + O_2 \]

**Cathode Reaction:**

\[ 2CO₂ + 2H^+ + 4e^- → 2HCOO^- \]

**Net Reaction:**

\[ 2H₂O + 2CO₂ → 2HCOO^- + 2H^+ + O_2 \]

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 material and catalyst.
UK CAER Andora Process

**Cathode Reaction (-): Reduction of Methyl Viologen (MV)**

\[
4MV^{2+} + 4e^- \leftrightarrow 4MV^+ \quad E = -0.67 \text{ vs. Ag/AgCl}
\]

**Anode Reaction (+): Water Oxidation**

\[
2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad E = 0.617 \text{ vs. Ag/AgCl, pH}=7
\]
Charge Carrier

Methyl Viologen (MV)

- MV$^{2+}$ has been demonstrated to be a stable electron mediator
- The active catalyst can accept an electron not from working electrode directly, but from reduced MV$^{•+}$.
- This type of electron transfer *minimizes* overpotentials and catalyst degradation.

Oxidized Methyl Viologen loses its blue color after $e^-$ transfer

Formic acid production cell where methyl viologen transfer $e^-$ to the catalyst

Reduced methyl viologen (blue) entering formic acid production cell
Three viable charge carriers evaluated; EV selected for continued development based on activity, stability and lowest environmental concern.

- Methyl Viologen (MV), Ethyl Viologen (EV) and Anthraquinonone Disulfonate (AQDS) charge mediators have low reduction voltages (-0.6 to -0.8 V vs. Ag/AgCl)
- Carbon felt electrode in H-cell, charged at -0.75 V vs. Ag/AgCl for 1.5 h (left), discharge (OCV run) for 4.5 h (right)
Flow-through Reactor Design

Operating variables:

- Anode materials (Pt and Pt-Ir)

- Cathode solution flow rates from 1-9 mL/min

- Catalyst immobilization with low pressure drop membranes

- Sulfuric acid used as anode solution (proton source) at lab-scale, but can be replaced with H₂ or OER in next iteration
Flow-through Reactor Operation

Achievement: > 500 mM Formate production with > 80% Faradaic efficiency (FE) and > 90% selectivity

Cathode: 200 mM phosphate buffer + 10 mM EV charge carrier; Carbon felt electrode operated at -0.74V vs Ag/AgCl

Anode: 100 mM Sulfuric acid proton source with platinum electrode and Nafion membrane

Pure CO₂ gas purge

2 mL/min cathode flow rate
Operating Options

Formate production achieved using both a phosphate and carbonate buffer system

- Pt wire anode
- Phosphate and carbonate buffer solutions
- CO₂ purging (15 mL/min)

Operating voltage
- 0.75V vs. Ag/AgCl
Formate/Formic Acid Separation

- Water + Formic Acid Azeotrope Distillation
- Membrane pervaporation pre-concentrating before distillation
- Liquid-liquid extraction
- Ion exchange (IEX)
  - Commercially available IEX with capacities up to 450 mg formate / g IEX from our process solution (viologen and buffer recycled)

Remaining Work

- Update Technology Maturation Plan (TMP)
  • Performance attributes and requirements will be re-evaluated. Post project maturation plans will be updated along with an assessment of the technology’s current TRL level.

- Life-Cycle Analysis (LCA)
  • Demonstrate the proposed process to be a substantive CO₂ mitigation option and verify 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.

- Initial Technical and Economic Feasibility Study (TEA)
  • 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.
LCA

System Boundaries

- **Upstream Processes**
  - Catalyst
  - EV (ethyl viologen)
  - Buffer
  - Acid
  - Miscellaneous (chemicals/metals)
  - Power (Energy)
  - Water

- **CO2U Process**
- **Product**
  - Formic Acid

- **Upstream Processes**
  - Material & Energy

- **Power or Industrial Plants**

- **CO2 Product**

- **Waste**
  - (solid, liquid)

Generated using openLCA 1.10.3
LCA

Contribution of Different Sections in Global Warming Potential (GWP) (TRACI 2.1 method)

Using sulfuric acid as proton source at lab-scale

Switch to H$_2$ as proton source for scale-up

By switching from sulfuric acid to H$_2$ the GWP was significantly reduced
TEA

- Detailed process design created for TEA
Knowledge Gained/Challenges

• Moving from a batch cell to a flow-through configuration can be challenging due to larger volumes, residence times, and matching reaction rates between both reactors/cells.

• Formate production achieved using both a phosphate and carbonate buffer system

• Proton (H\(^+\)) source in CO\(_2\) reduction is an important factor in LCA
# Milestones

<table>
<thead>
<tr>
<th>Budget Period</th>
<th>Task Number</th>
<th>Title</th>
<th>Planned Completion Date</th>
<th>Actual Completion Date</th>
<th>Verification Method</th>
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<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>Updated Project Management Plan</td>
<td>1/31/2019</td>
<td>1/31/19 (A)</td>
<td>Revised PMP Revision A</td>
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<td>3/14/19 (B)</td>
<td>Revised PMP Revision B</td>
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<td>2/28/20 (C)</td>
<td>Revised PMP Revision C</td>
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<td>Kickoff Meeting</td>
<td>3/31/2019</td>
<td>3/25/2019</td>
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<td>Subcontracts Established</td>
<td>3/31/2019</td>
<td>10/16/2019</td>
<td>Written Verification</td>
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<td>1</td>
<td>2</td>
<td>Issue Technology Maturation Plan</td>
<td>6/30/2019</td>
<td>6/30/2019</td>
<td>Appended to Quarterly Report</td>
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<td>1</td>
<td>3</td>
<td>Quarterly production and delivery of improved catalyst with verified formic acid production capabilities</td>
<td>12/31/2020</td>
<td>12/31/2020</td>
<td>Quarterly Report</td>
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<td>1</td>
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<td>Production cell capable of 25 mM formic acid during continuous production at 2 ml/min with Faradaic efficiency of at least 50%</td>
<td>9/30/2021</td>
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<td>Quarterly Report</td>
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<td>Long-term formic acid production for &gt;100 hours with produced concentrations of 25 mM</td>
<td>6/30/2020</td>
<td>7/6/2020</td>
<td>Quarterly Report</td>
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<td>High-performance cell capable of &gt;100 mM of continuous formic acid production</td>
<td>9/30/2021</td>
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<td>Quarterly Report</td>
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<td>Issue report on Life Cycle Analysis</td>
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<td>Appended to Quarterly Report</td>
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<td>1</td>
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<td>Issue Report on Technical and Economic Feasibility Study</td>
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## Success Criteria

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<tr>
<th>Success Criteria (Task #)</th>
<th>Status</th>
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<tr>
<td>(#4) Electrochemical cell carrier charge efficiency of greater than 60%</td>
<td>Average 60% efficiency achieved</td>
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<tr>
<td>(#4) Fabrication of the flow-through apparatus: Production cell capable of supporting flow rate of 2 mL/min during continuous operation</td>
<td>Achieved - operating between 2-9 mL/min</td>
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<tr>
<td>(#3) Catalyst production: Two grams of catalyst produced and supplied to UK CAER with stability (less than 25% deactivation) of greater than 100hr</td>
<td>Catalyst being provided in batches as needed</td>
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<td>(#4) Immobilization of catalyst: 90% of catalyst retained in production cell during continuous operation as verification by analysis</td>
<td>Above 95% retention</td>
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<td>(#5) Production of formic acid from CO₂: Continuous operation of reduction and production cells with a formic acid production of 25 mM and a selectivity of greater than 80%</td>
<td>25 mM formic acid production with high (&gt;90%) selectivity for &gt;100 hours</td>
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## Project Schedule

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<thead>
<tr>
<th>Task Number and Name</th>
<th>Start</th>
<th>End</th>
<th>FY2019</th>
<th>FY2020</th>
<th>FY2021</th>
<th>FY2022</th>
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<tr>
<td>1. Project Management and Planning</td>
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<td>12/31/21</td>
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<td>1.1 Task management and execution</td>
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<td>1.2 Update PMP</td>
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<td>2. Technology Maturation Plan</td>
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<td>4. Electro-catalyst flow-through reactor design, fabrication and commissioning</td>
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<td>4.1 Immobilization of electro-catalyst</td>
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<td>5. Lab-scale reactor testing</td>
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<td>5.2 Stability testing of flow-through reactor</td>
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<td>5.3 Evaluation of formic acid purification process</td>
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<td>25 mM formic acid productions with 50% efficiency</td>
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<td>6. Life cycle analysis</td>
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<td>7. Initial technical and economic feasibility study</td>
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<td>12/31/21</td>
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Acknowledgements

• DOE-NETL: Naomi O’Neil, Andy Aurelio

• UK CAER: Daniel Moreno, Ayo Omosebi, Keemia Abad, Lisa Richburg

• UNIST: Professor Yonghwan Kim, Byoung Wook Jeon