ELECTROCHEMICAL REDUCTION OF FLUE GAS CO$_2$ TO COMMERCIALY VIABLE C2 – C4 PRODUCTS

PROJECT: DE-FE0031916

Joshua M. Spurgeon
University of Louisville, Louisville, KY

Program Manager: Andy Aurelio

U.S. Department of Energy
National Energy Technology Laboratory
Carbon Management and Natural Gas & Oil Research Project Review Meeting
Virtual Meetings August 2 through August 31, 2021
PROJECT OVERVIEW

Funding
- DOE: $1,000,000
- Cost Share: $252,536 (UofL - $188,536, UND - $64,000)

Overall Project Performance Dates
- One budget period
- Start: October 1, 2020
- End: September 30, 2022

Project Participants
- Recipient – University of Louisville
  - PI – Joshua Spurgeon – Theme Leader for Solar Fuels, Conn Center for Renewable Energy Research
  - Co-PI – Craig Grapperhaus, Professor, Chemistry Department
- Subrecipient – University of North Dakota
  - Co-PI – Nolan Theaker, Research Engineer, Institute for Energy Studies
- Partner – Minnkota Power Cooperative
Overall Project Objectives

- **Objective 1** – Establish mechanistic pathway for product formation in methanol and characterize vs potential and pH

- **Objective 2** - Build an electrolysis flow cell reactor for high current density performance stable for > 100 h

- **Objective 3** - Design an electrolyzer for direct conversion of flue gas to C2 - C4 species with > 90% of the initial faradaic efficiency maintained for > 100 h and > 50% of the product partial current achieved in an analogous system with pure CO$_2$ feedstock

- **Objective 4** - Combine flue gas feed with the optimized flow cell reactor to demonstrate performance and stability targets for commercial viability

- **Objective 5** - Perform a TEA with late-stage project performance parameters, and complete a life cycle analysis (LCA) for the energy usage and CO$_2$ emissions reduction
Technology Overview:
• Use of power plant flue gas derivatives for CO₂ reduction
• Electrolysis flow cell reactor for stable high current, high faradaic efficiency
• Nonaqueous catholyte to enable high selectivity production of novel products not found in aqueous CO₂ reduction
• Dual electrolyte approach with aqueous anolyte to have sustainable water oxidation

Technology Background:

T = 25 °C
P = 1 atm
V_{app} = 2.5 - 4.0 V
**Technology Background**

Methanol electrolyte enables

- Higher CO\textsubscript{2} solubility (0.17 M compared to 0.033 M in water)
- Chemical addition of CO\textsubscript{2} with electrolyte as an intermediate for non-standard CO\textsubscript{2} reduction products

**Methyl formate**

- **Initial** target C2 product
- Not an aqueous electrochemical CO\textsubscript{2}RR product
- Must come from waste CO\textsubscript{2}, rigorously exclude anodic methanol oxidation
- Combined CO\textsubscript{2}RR to HCOOH and in-situ esterification reaction with methanol
- Similar C3 – C4 product routes in ethanol and propanol to be pursued later

**Chemical Equation**

\[ \text{CO}_2 + 2e^- + 2H^+ + CH_3OH \rightarrow HCOOCH_3 + H_2O \]

\[ H_2O \rightarrow \frac{1}{2} O_2 + 2 e^- + 2 H^+ \]
### Technology Background

#### Technical Advantages
- Flow cell for high current, high selectivity operation
- Nonaqueous catholyte for high solubility and intermediate reactant addition
- Aqueous anolyte for sustainable water oxidation rather than methanol oxidation which does not incorporate $\text{CO}_2$
- Membrane to incorporate methanol barrier layer for minimal crossover – similar concepts successfully developed for direct methanol fuel cells

#### Economic Advantages
- Electroreduction – room temperature, atmospheric pressure, rapid response, use for intermittent or curtailed electricity
- Waste $\text{CO}_2$ turned into value added product - 45Q tax credit - $35/\text{ton} \text{CO}_2$ utilized
- Byproduct $\text{H}_2$ is still valuable
- Direct utilization of flue gas – no CAPEX for $\text{CO}_2$ capture plant
- Methanol ~ $375/\text{ton}$, methyl formate ~ $1000-2000/\text{ton}$

#### Technical Challenges
- Flue Gas - Mitigate contaminants degrading stability ($\text{SO}_x$, $\text{NO}_x$, Hg, PM), dilute $\text{O}_2$ decreasing faradaic efficiency (FE), lower $\text{CO}_2$ concentration
- Chemistry – Maintain low pH for high FE to methyl formate, low methanol crossover

#### Economic Challenges
- Achieving high current density and FE for acceptable capital costs
- Minimizing methanol anodic oxidation as an operating expense
- Market size for chemicals vs. industrial $\text{CO}_2$ output – need for diversified products with favorable TEA

---

**Funding Information**

- University of Louisville
- UofL Conn Center
- Institute for Energy Studies, University of North Dakota
- National Energy Technology Laboratory (NETL)
Work Plan
- Task 1 (Q1) – Project Management and Planning
- Task 2 (Q1-7) – Improvement of Faradaic Efficiency to C2-4 Products
- Task 3 (Q1-7) – Develop Electrolysis Reactor for High-current CO₂ Reduction
- Task 4 (Q3-7) – CO₂ Electrolysis System from Power Plant Flue Gas Derivatives
- Task 5 (Q5-8) – Full System Integration with Commercially Relevant Performance
- Task 6 (Q7-8) – Technoeconomic Analysis and Life Cycle Analysis

<table>
<thead>
<tr>
<th>Quarter</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Key Milestone</td>
<td>Fabricate Flow Cell Electrolyzer</td>
<td>Complete pH and Applied Potential Study</td>
<td>Demonstrate C2⁺ FE &gt; 40%</td>
<td>Complete Flue Gas Contaminants Study</td>
<td>Methanol Crossover &lt; 5% FE CH₃OH Oxidation</td>
<td>Current Density &gt; 600 mA cm⁻²</td>
<td>Flue Gas Performance &gt; 100 h with &gt; 40% FE C2⁺</td>
<td>Operation on Utility Site Flue Gas &gt; 1 Week</td>
</tr>
</tbody>
</table>

- Faradaic Efficiency
- Potential (V vs Ag/AgCl)
## Project Success Criteria

- Complete TEA and LCA for realistic system parameters with sensitivity analysis
- Completion of a reactor operating from flue gas at performance metrics for profitability as determined by the TEA (Target Metrics: 600 mA cm\(^{-2}\) at > 40% FE C2-4s for > 100 h)

<table>
<thead>
<tr>
<th>Perceived Risk</th>
<th>Risk Rating</th>
<th>Mitigation/Response Strategy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Probability</td>
<td>Impact</td>
</tr>
<tr>
<td></td>
<td>(Low, Med, High)</td>
<td></td>
</tr>
<tr>
<td><strong>Cost/Schedule Risks:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Parameter effect studies take too long to keep up with reactor development</td>
<td>Med</td>
<td>Med</td>
</tr>
<tr>
<td><strong>Technical/Scope Risks:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flue gas feed performance and stability issues</td>
<td>Med</td>
<td>Med</td>
</tr>
<tr>
<td>Insufficiently high current density</td>
<td>Med</td>
<td>Med</td>
</tr>
<tr>
<td>Difficulty achieving or maintaining high FE of C2 - C4 product</td>
<td>Med</td>
<td>Med</td>
</tr>
<tr>
<td><strong>ES&amp;H Risks:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Covid-19 inhibiting research</td>
<td>High</td>
<td>Low</td>
</tr>
</tbody>
</table>
Task 2 – Improvement of Faradaic Efficiency to C2-4 Products

- Determination of System Parameter Effects – Effect of pH
- Again, the initial focus is on methyl formate as the desired product

Faradaic efficiency vs. initial catholyte pH for a Pb wire at -1.85 V vs Ag/AgCl for 30 min in KCl-saturated methanol catholyte/56 mM KCl in water anolyte.

Direct H-cell studies with a Pb wire cathode

- pH < 2.5 to favor methyl formate
- pH < 1 starts to promote H₂ evolution and hurt methyl formate FE

Conversion of the CO₂ reduction liquid product to methyl formate (black triangles) and measured NMR peak chemical shift (red squares) as a function of the final pH value in the saturated KCl in CH₃OH catholyte.
Task 2 – Improvement of Faradaic Efficiency to C2-4 Products
• Determination of System Parameter Effects – Effect of Water Content in Catholyte

Effect of water in the catholyte. (A) NMR spectra and corresponding (B) molar percent conversion of formic acid to methyl formate for formic acid dissolved in 3 mM HCl in methanol with increasing water content by volume %.

• Maintain catholyte water content to < 20% to keep more than 75% of CO₂ product going to methyl formate
• Increased H₂O and decreased MeOH can disfavor the esterification by Le Chatlier principle
PROGRESS AND CURRENT STATUS OF PROJECT

Task 2 – Improvement of Faradaic Efficiency to C2-4 Products
• Determination of System Parameter Effects – Effect of Applied Potential

Sat. KCl, pH ~ 1.5 CH₃OH catholyte and 3 mM HCl, 56 mM KCl in water anolyte separated by Nafion.

Current density vs. potential for a Pb or Pt wire.

- H₂ evolution strongly suppressed on Pb relative to Pt
- Up to 75% FE methyl formate at -2.0 V vs. Ag/AgCl
- Methyl formate FE decreases and HCOOH/HCOO⁻ FE increases with time and/or charge passed – corresponds to increased catholyte pH

Partial current densities and FE vs. applied potential measured after potentiostatic operation for (A, B) 30 min and (C, D) 120 min.
PROGRESS AND CURRENT STATUS OF PROJECT

Task 2 – Improvement of Faradaic Efficiency to C2-4 Products
- Determination of System Parameter Effects – Increasing H₂ FE and Surface Film

![Graph showing H₂ FE vs. time at a Pb wire under CO₂ in sat. KCl, CH₃OH catholyte.](image)

- Increasing H₂ FE correlated to black film formation – Pb catalyst deactivation
- XPS indicates a likely Cl-containing carbonaceous layer
- Substitution of KCl with KPF₆ led to suppression of the black film formation

![Microscope images of Pb wire after electrolysis.](image)

XPS on Pb wire cathode.
Task 3 – Develop Electrolysis Reactor for High-current CO₂ Reduction

• Electrolyzer Chassis Design

- Acid-stable components for low pH operation
- Porous carbon Toray paper gas diffusion electrodes (GDE) for high catalyst loading and high mass flux of reactants
- Three-compartment arrangement with methanol through central compartment and gaseous CO₂ through cathode flowfield
- Peristaltic and/or syringe pumps for electrolyte flow
- Catholyte/anolyte reservoirs with density measurement to monitor water/methanol content
**Progress and Current Status of Project**

**Task 3 – Develop Electrolysis Reactor for High-current CO₂ Reduction**

- CO₂ Feed to the Cathode – Optimizing Pb-decorated GDE Cathodes

Various cathodes in an H-cell.

<table>
<thead>
<tr>
<th>Electrode Type</th>
<th>CO₂RR FE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb Wire</td>
<td>59.6</td>
</tr>
<tr>
<td>Blank GDE</td>
<td>4.9</td>
</tr>
<tr>
<td>Spray-deposited Pb NP GDE</td>
<td>6.9</td>
</tr>
<tr>
<td>Doctor-bladed Pb NP GDE</td>
<td>23.1</td>
</tr>
<tr>
<td>Pb NP Immersion GDE</td>
<td>55.9</td>
</tr>
<tr>
<td>Electrodeposited Pb GDE</td>
<td>29.1</td>
</tr>
<tr>
<td>Pulse-electrodeposited Pb GDE</td>
<td>75.2</td>
</tr>
</tbody>
</table>

-1.85 V vs. Ag/AgCl

(A) Potential profile during Pb pulsed-electrodeposition. (B) SEM and (C) EDS map cross-section of pulse-deposited Pb-GDE.

- Pulsed-electrodeposited Pb on GDEs has worked best with > 75% FE for formate/methyl formate in methanol in the H-cell
- 96% FE formate achieved in aqueous KHCO₃ in flow cell
- Working to optimize flow and current density in the flow cell in aqueous system before returning to methanol catholyte
Task 3 – Develop Electrolysis Reactor for High-current CO₂ Reduction

- Methanol Crossover and Oxidation – Membrane Testing Apparatus and Characterization

- Methodology for monitoring crossover via density measurements established – extend to data logging digital hydrometer
- In-situ EIS measurements of resistance
- Optimize crossover vs. conductivity, hydrophobicity of PTFE
- Perform in flow cell and characterize anode products

**Anolyte methanol concentration vs. time for membranes between sat. KCl in CH₃OH/56 mM KCl in H₂O catholyte/anolyte.**

- Porous PTFE membranes, from Sterlitech

- Digital Wifi hydrometer for continuous density readings
PROGRESS AND CURRENT STATUS OF PROJECT

Task 4 – CO₂ Electrolysis System from Power Plant Flue Gas Derivatives
• Impurity and CO₂ Concentration Effects – Flue Gas Composition and Testing

<table>
<thead>
<tr>
<th>Species</th>
<th>Flue Gas Composition</th>
<th>Electrochemical Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>14 - 16 vol%</td>
<td>N/A</td>
</tr>
<tr>
<td>N₂</td>
<td>80 - 85 vol%</td>
<td>Diluent</td>
</tr>
<tr>
<td>O₂</td>
<td>2 - 4 vol%</td>
<td>Loss of Faradaic Efficiency</td>
</tr>
<tr>
<td>NO</td>
<td>~ 80 ppm</td>
<td>Catalyst Poisoning/Parasitic Current</td>
</tr>
<tr>
<td>SO₂</td>
<td>~ 45 ppm</td>
<td>Catalyst Poisoning/Parasitic Current</td>
</tr>
<tr>
<td>PM</td>
<td>~ 9 ppm</td>
<td>Catalyst Coverage, Impedance</td>
</tr>
<tr>
<td>Hg</td>
<td>~ 1.2 ppb</td>
<td>Catalyst Poisoning</td>
</tr>
</tbody>
</table>

• Delayed: Staffing issues at collaborator so work relocated to University of Louisville
• Flue gas testing setup nearly complete - Early experiments show no effect on performance with 100 ppm SO₂ over 2 h

Experiments to be done:
• Simulated flue gas and contaminants for testing – SO₂, NO, Hg, PM
• Stability and materials characterization with varying impurity concentration to establish threshold values
• Performance characterization with variable CO₂ concentration
• Measure faradaic efficiency effects of dilute O₂ in feed gas

Alternative electrocatalysts to Pb to promote HCOOH/HCOOCH₃: Sn, Bi
**PROGRESS AND CURRENT STATUS OF PROJECT**

**Current Status**
- Task 2 understanding the electrochemical system and improving the faradaic efficiency of methyl formate production is on target.
- Task 3 flow cell electrolyzer design and methanol crossover testing has made progress, but the group needs to solve engineering challenges to increase the current density.
- Task 4 flue gas electrolysis work was delayed by staffing issues at our collaborator and subsequent reassignment of experimental work to the University of Louisville, but testing apparatus and simulation gas setup is almost ready.

<table>
<thead>
<tr>
<th>Quarter</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Key Milestone</td>
<td>Fabricate Flow Cell Electrolyzer</td>
<td>Complete pH and Applied Potential Study</td>
<td>Demonstrate C2+ FE &gt; 40%</td>
<td>Complete Flue Gas Contaminants Study</td>
<td>Methanol Crossover &lt; 5% FE CH₃OH Oxidation</td>
<td>Current Density &gt; 600 mA cm⁻²</td>
<td>Flue Gas Performance &gt; 100 h with &gt; 40% FE C2+</td>
<td>Operation on Utility Site Flue Gas &gt; 1 Week</td>
</tr>
</tbody>
</table>
Collaboration and Synergy Opportunities

- **Flow Cell Reactor** – A collaborator experienced in flow cell operation for CO₂ reduction could be very beneficial to helping us solve engineering issues to increase the current density.
- **Membranes** – Collaboration could benefit the project with new approaches to minimize both aqueous and nonaqueous crossover with minimal resistance.
- **Flue Gas** – Collaboration would be welcome with strategies to maintain high current with low concentration CO₂.

**POSTDOC OPPORTUNITY!!!** – We would love to hire an additional researcher with proven CO₂ electroreduction expertise.
PLANS FOR FUTURE TESTING/DEVELOPMENT/COMMERCIALIZATION

Plans for the future
- On-site flue gas testing of flow cell electrolyzer at a power plant
- Continue development of high performance nonaqueous catholyte CO₂ electrolyzers for additional novel products

Three-carbon products
- Ethyl formate, C₃H₆O₂ – like methyl formate route, CO₂ reduction to formic acid and esterification in ethanol
- Methyl acetate, C₃H₆O₂ – CO₂ reduction to acetate and esterification in methanol

Four-carbon products
- Propyl formate, C₄H₈O₂ – CO₂ reduction to formic acid and esterification in propanol

Commercialization plan
- Provisional/non-provisional patent applications of generated IP
- Pursue SBIR funding for device scale-up
- Look for collaborative opportunities with large electrolyzer manufacturers
- Customer discovery through utilities, cement producers, chemical manufacturers, oil companies
- Potentially license technology to CO₂ electrolysis companies like Dioxide Materials or Opus 12

Ethyl formate
Methyl acetate
Propyl formate
Waste $\text{CO}_2$ can be electrochemically upgraded in nonaqueous solvent to species not produced in aqueous systems, like methyl formate. Conversion can be accomplished with high selectivity and current, but challenges must be overcome including system stability of pH, catalysts, and electrolyte composition.

- Up to 75% FE HCOOCH$_3$ achieved
- System needs catholyte to maintain $1 < \text{pH} < 2.5$ for methyl formate
- Supporting electrolyte plays a critical role in conductivity, pH, membrane permeability, and catalyst deactivation
THANK YOU FOR LISTENING

Co-PIs:
CRAIG GRAPPERHAHUS
NOLAN THEAKER

Researchers:
DILLON HOFSOMMER
MANU GAUTAM
SANDESH UTTARWAR
HANK PAXTON
ARJUN THAPA
<table>
<thead>
<tr>
<th>Task Name</th>
<th>Task Duration</th>
<th>Completed Work</th>
</tr>
</thead>
<tbody>
<tr>
<td>Task 1.0 - Project Management and Planning</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Task 2.0 – Improvement of Faradaic Efficiency to C2-4 Products</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Task 3.0 – Develop Electrolysis Reactor for High-current CO₂ Reduction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Task 4.0 - CO₂ Electrolysis System from Power Plant Flue Gas Derivatives</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Task 5.0 – Full System Integration with Commercially Relevant Performance</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Task 6.0 – Technoeconomic Analysis and Life Cycle Analysis</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>