Electrochemical Reduction of Flue Gas CO_2 to Commercially Viable C2 – C4 Products

Project: DE-FE0031916

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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

University of Louisville

UofL Conn Center

UND Institute for Energy Studies, University of North Dakota

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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

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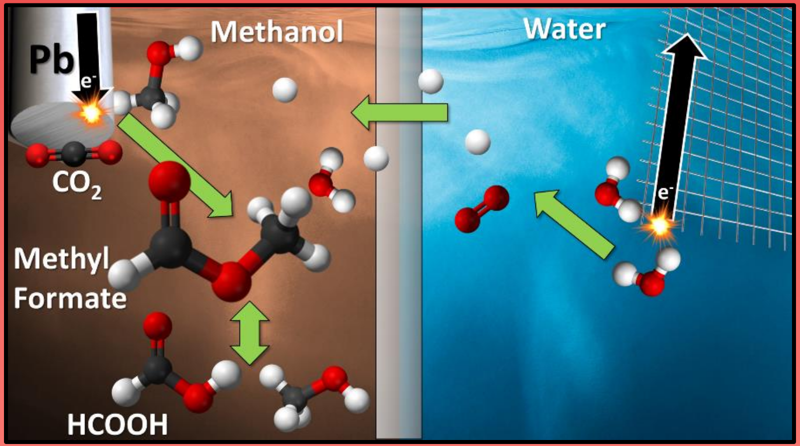
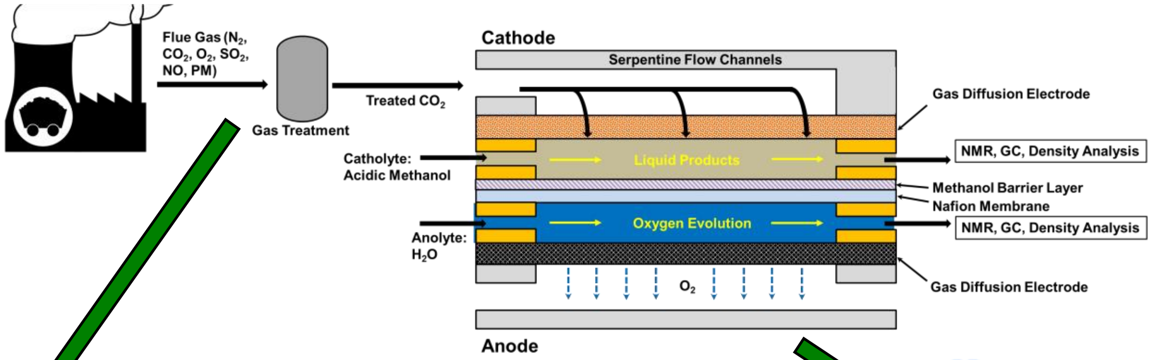
Overall Project Objectives

- **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

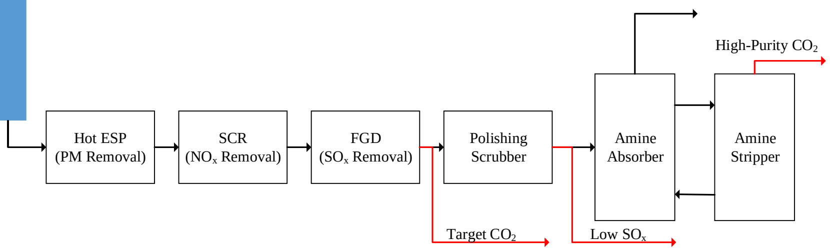
Technology Background

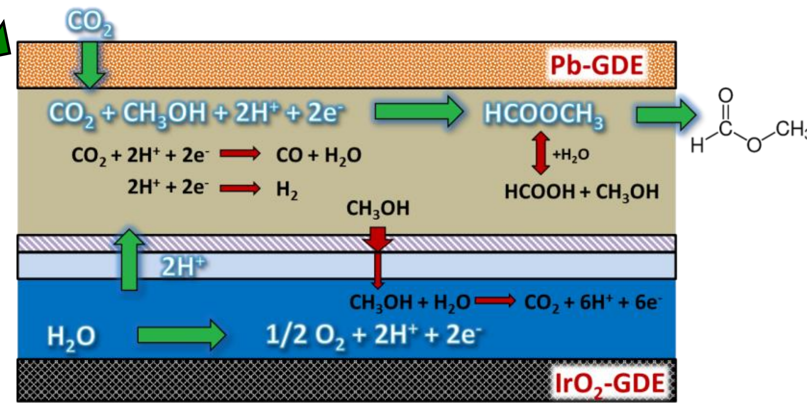


T = 25 °C

P = 1 atm

V_{app} = 2.5 – 4.0 V





Technology Overview:

- **Use of power plant flue gas derivatives for CO_2 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 CO_2 reduction**
- **Dual electrolyte approach with aqueous anolyte to have sustainable water oxidation**

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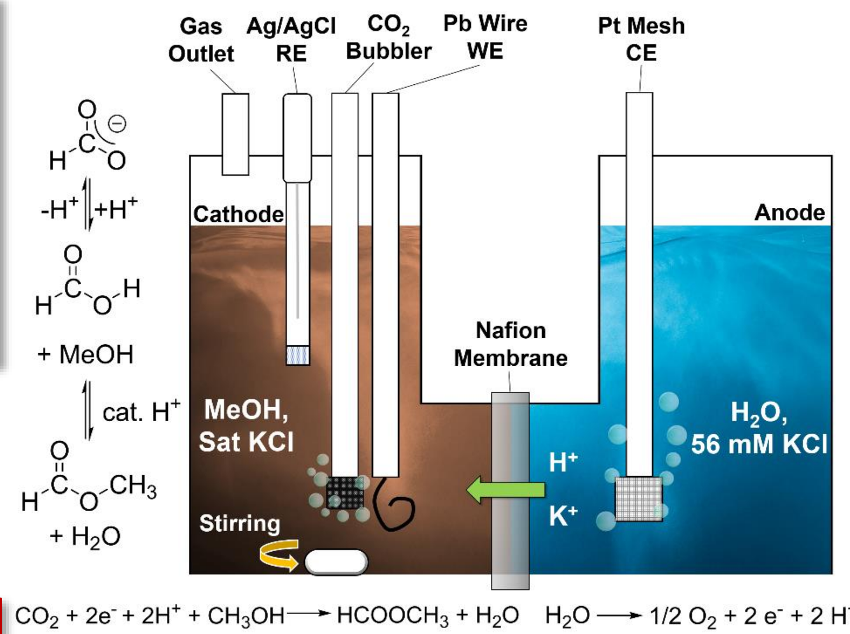
TECHNOLOGY BACKGROUND

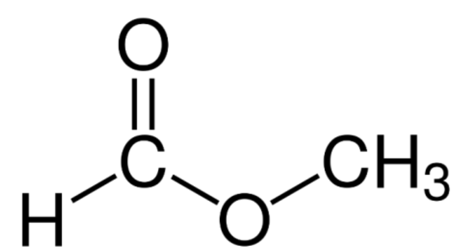
Methanol electrolyte enables

- Higher CO_2 solubility (0.17 M compared to 0.033 M in water)
- Chemical addition of CO_2 with electrolyte as an intermediate for non-standard CO_2 reduction products



Methyl formate

- <u>Initial</u> target C2 product
- Not an aqueous electrochemical CO2RR product
- Must come from waste CO_2, rigorously exclude anodic methanol oxidation
- Combined CO2RR to HCOOH and in-situ esterification reaction with methanol
- Similar C3 – C4 product routes in ethanol and propanol to be pursued later



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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 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 CO_2 turned into value added product - 45Q tax credit - \$35/ton CO_2 utilized
- Byproduct H_2 is still valuable
- Direct utilization of flue gas – no CAPEX for CO_2 capture plant
- Methanol ~ \$375/ton, methyl formate ~ \$1000-2000/ton

Technical Challenges

- Flue Gas - Mitigate contaminants degrading stability (SO_x, NO_x, Hg, PM), dilute O_2 decreasing faradaic efficiency (FE), lower 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 CO_2 output – need for diversified products with favorable TEA

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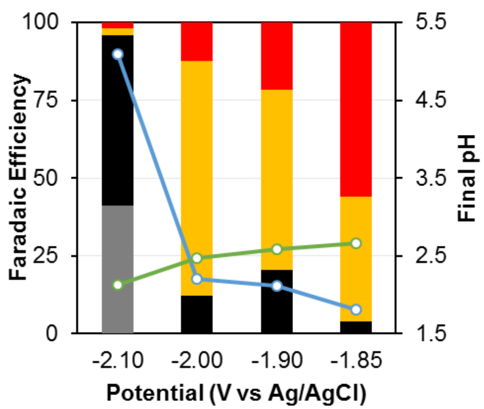
Technical Approach/Project Scope

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 CO_2 Reduction**
- **Task 4 (Q3-7) – CO_2 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**

Quarter	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Key Milestone	Fabricate Flow Cell Electrolyzer	Complete pH and Applied Potential Study	Demonstrate C2+ FE > 40%	Complete Flue Gas Contaminants Study	Methanol Crossover < 5% FE CH_3OH Oxidation	Current Density > 600 mA cm^{-2}	Flue Gas Performance > 100 h with > 40% FE C2+	Operation on Utility Site Flue Gas > 1 Week



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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)**

Perceived Risk	Risk Rating			Mitigation/Response Strategy
	Probability	Impact	Overall	
	(Low, Med, High)			
Cost/Schedule Risks:				
Parameter effect studies take too long to keep up with reactor development	Med	Med	Med	Constant communication between catalyst and reactor teams/redirection of priorities
Technical/Scope Risks:				
Flue gas feed performance and stability issues	Med	Med	Med	Multiple catalyst options (Pb, Sn, Bi), decontamination, CO_2 absorber, CO_2 concentration studies
Insufficiently high current density	Med	Med	Med	Flow cell condition optimization, maximize aqueous systems first
Difficulty achieving or maintaining high FE of C2 - C4 product	Med	Med	High	Product distribution mapping, CO_2 mass transfer optimization, pH stabilization
ES&H Risks:				
Covid-19 inhibiting research	High	Low	Low	Safety protocols, remote meetings, limited lab capacity

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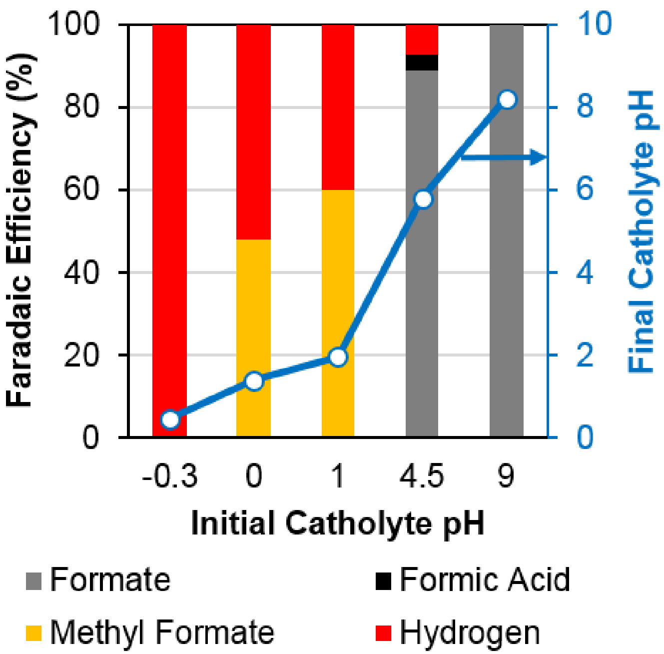
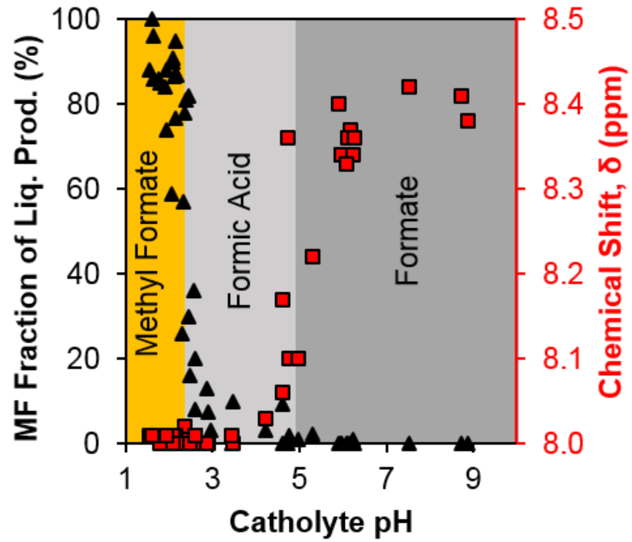
Task 2 – Improvement of Faradaic Efficiency to C2-4 Products

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

Direct H-cell studies with a Pb wire cathode



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.

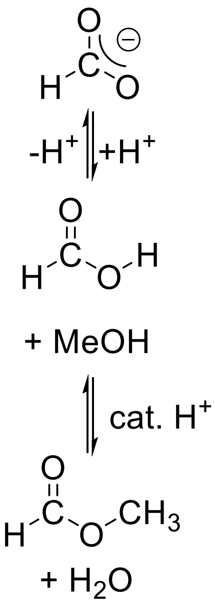


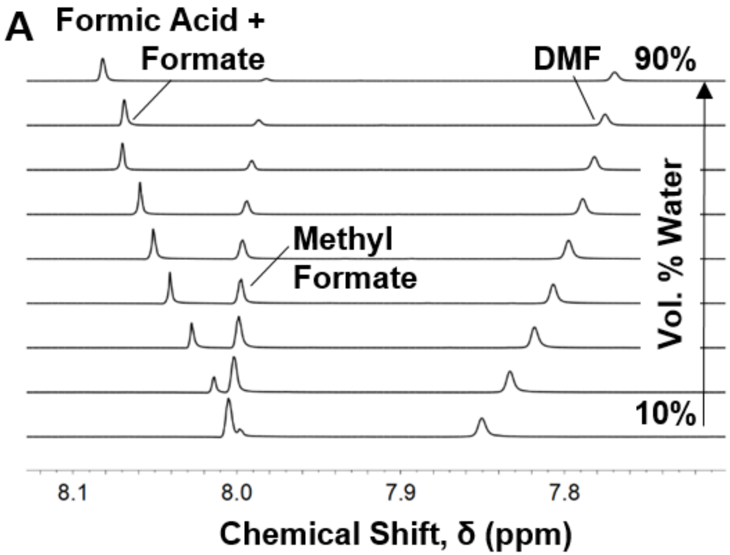
Conversion of the CO_2 reduction liquid product to methyl formate (black triangles) and measured NMR peak chemical shift (red squares) as a function of the final pH value in the saturated KCl in CH_3OH catholyte.

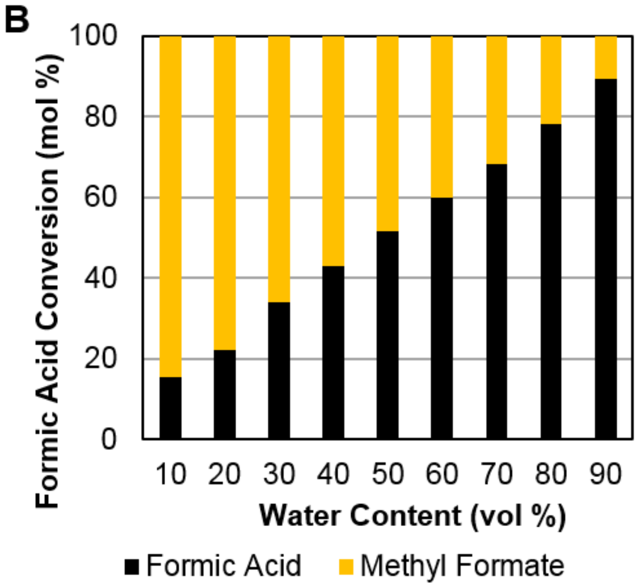
- **pH < 2.5 to favor methyl formate**
- **pH < 1 starts to promote H_2 evolution and hurt methyl formate FE**

Task 2 – Improvement of Faradaic Efficiency to C2-4 Products

- Determination of System Parameter Effects – Effect of Water Content in Catholyte







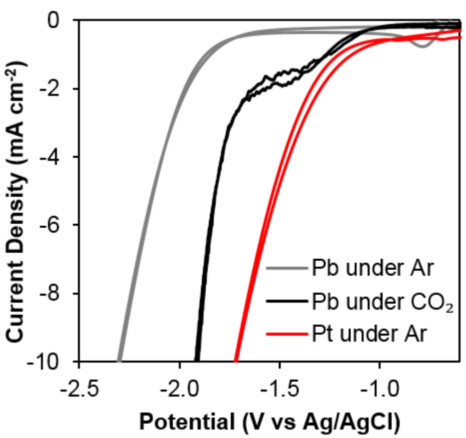
Effect of water in the catholyte. (A) NMR spectra and corresponding (B) molar percent conversion of formic acid to methyl formate for formic acid dissolved in 3 mM HCl in methanol with increasing water content by volume %.

- **Maintain catholyte water content to < 20% to keep more than 75% of CO_2 product going to methyl formate**
- **Increased H_2O and decreased MeOH can disfavor the esterification by Le Chatlier principle**

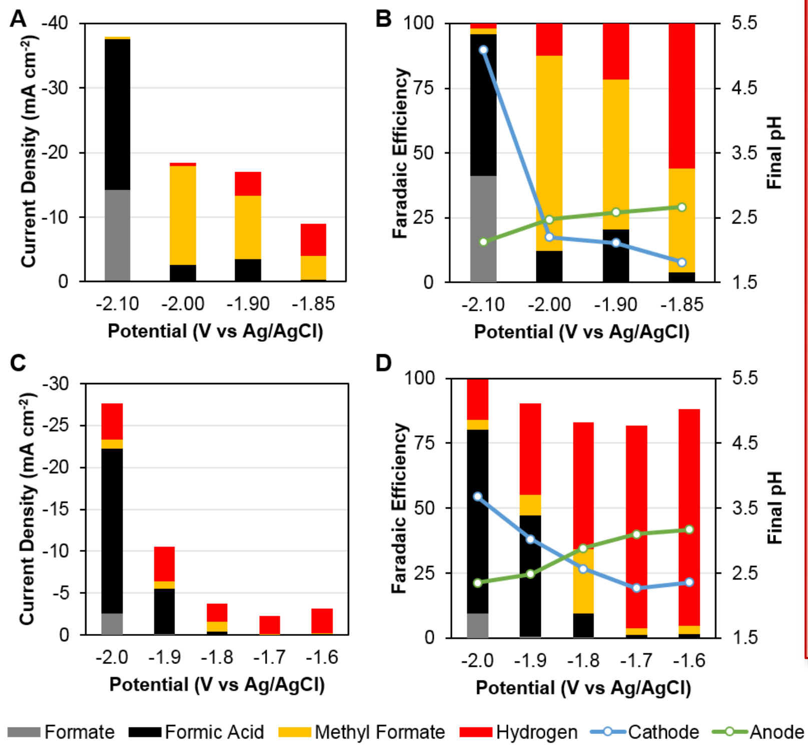
Task 2 – Improvement of Faradaic Efficiency to C2-4 Products

- **Determination of System Parameter Effects – Effect of Applied Potential**

Sat. KCl, pH ~ 1.5 CH_3OH catholyte and 3 mM HCl, 56 mM KCl in water anolyte separated by Nafion.



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



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

- **H_2 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**

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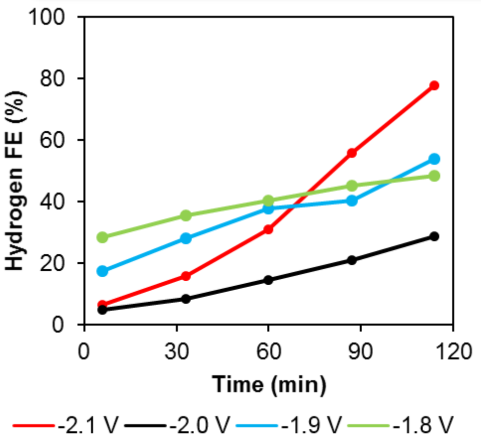
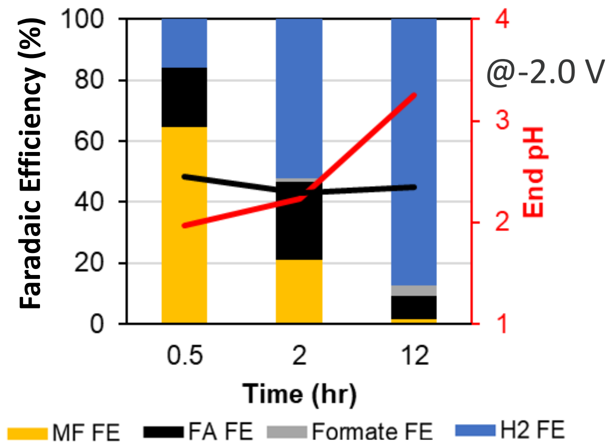
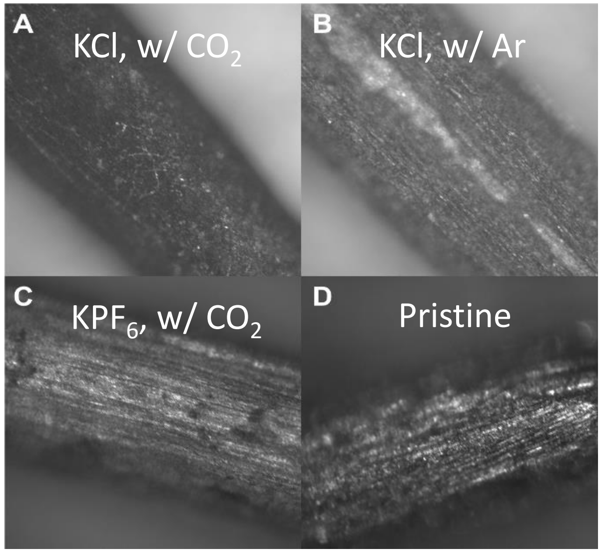
Task 2 – Improvement of Faradaic Efficiency to C2-4 Products

- **Determination of System Parameter Effects – Increasing H_2 FE and Surface Film**

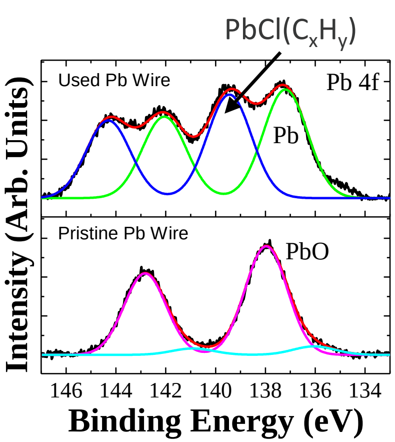




H_2 FE vs. time at a Pb wire under CO_2 in sat. KCl, CH_3OH catholyte.



Microscope images of Pb wire after electrolysis.



XPS on Pb wire cathode.

- **Increasing H_2 FE correlated to black film formation – Pb catalyst deactivation**
- **XPS indicates a likely Cl-containing carbonaceous layer**
- **Substitution of KCl with KPF_6 led to suppression of the black film formation**

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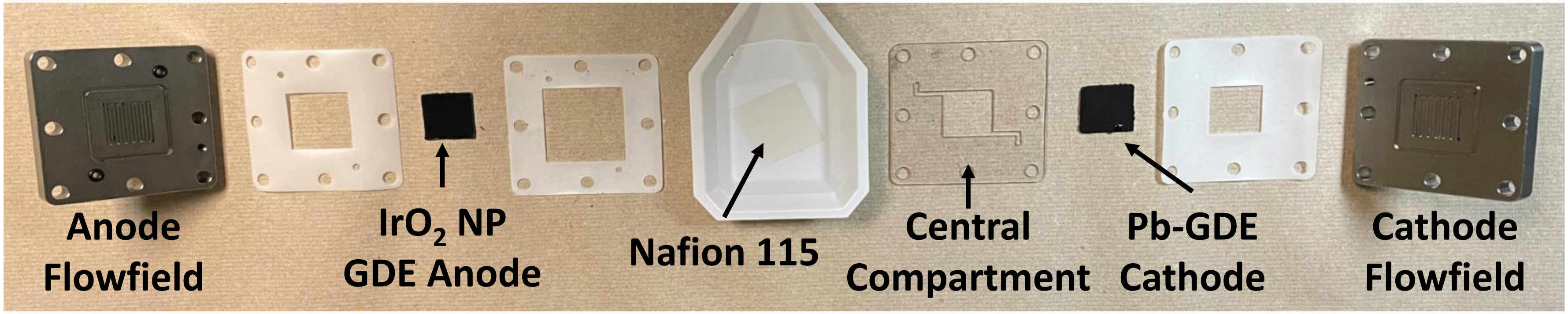
Task 3 – Develop Electrolysis Reactor for High-current CO_2 Reduction

- Electrolyzer Chassis Design



Flow cell exploded view.

Flow cell system setup.

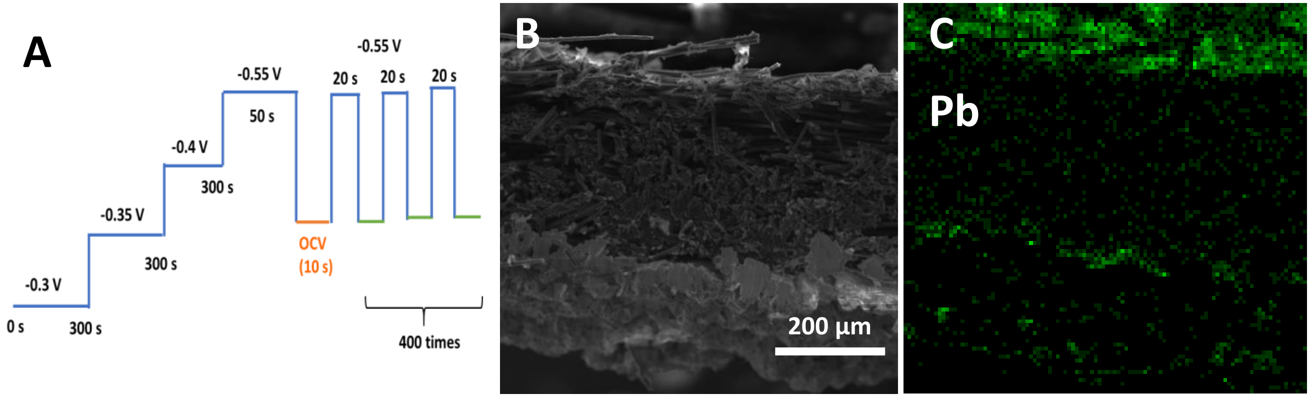
- Acid-stable components for low pH operation
- Porous carbon Toray paper gas diffusion electrodes (GDE) for high catalyst loading and high mass flux of reactants
- Three-compartment arrangement with methanol through central compartment and gaseous CO_2 through cathode flowfield
- Peristaltic and/or syringe pumps for electrolyte flow
- Catholyte/anolyte reservoirs with density measurement to monitor water/methanol content

Task 3 – Develop Electrolysis Reactor for High-current CO_2 Reduction

- **CO_2 Feed to the Cathode – Optimizing Pb-decorated GDE Cathodes**

Various cathodes in an H-cell.
-1.85 V vs. Ag/AgCl

Electrode Type	CO2RR FE (%)
Pb Wire	59.6
Blank GDE	4.9
Spray-deposited Pb NP GDE	6.9
Doctor-bladed Pb NP GDE	23.1
Pb NP Immersion GDE	55.9
Electrodeposited Pb GDE	29.1
Pulse-electrodeposited Pb GDE	75.2



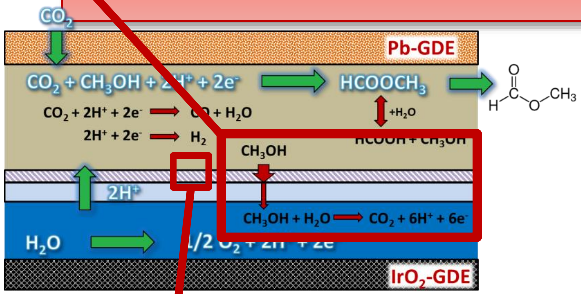
(A) Potential profile during Pb pulsed-electrodeposition. (B) SEM and (C) EDS map cross-section of pulse-deposited Pb-GDE.

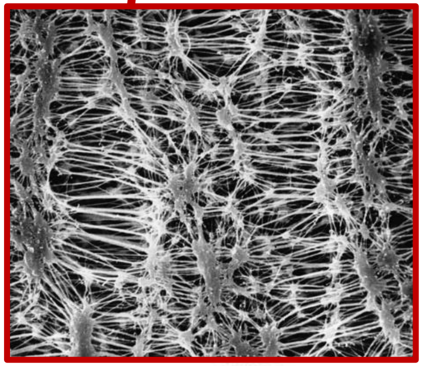
Full size pulse-deposited Pb-GDE

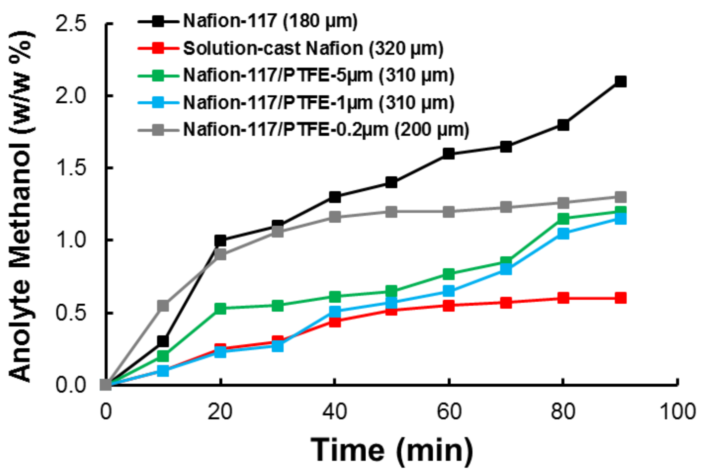
- **Pulsed-electrodeposited Pb on GDEs has worked best with > 75% FE for formate/methyl formate in methanol in the H-cell**
- **96% FE formate achieved in aqueous $KHCO_3$ in flow cell**
- **Working to optimize flow and current density in the flow cell in aqueous system before returning to methanol catholyte**

Task 3 – Develop Electrolysis Reactor for High-current CO_2 Reduction

- Methanol Crossover and Oxidation – Membrane Testing Apparatus and Characterization

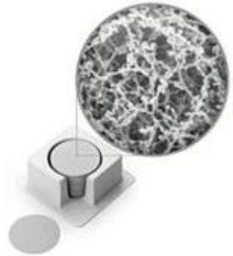






Anolyte methanol concentration vs. time for membranes between sat. KCl in CH_3OH/56 mM KCl in H_2O catholyte/anolyte.

Digital Wifi hydrometer for continuous density readings



Porous PTFE membranes, from Sterlitech

- 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

Task 4 – CO_2 Electrolysis System from Power Plant Flue Gas Derivatives

- **Impurity and CO_2 Concentration Effects – Flue Gas Composition and Testing**

Species	Flue Gas Composition	Electrochemical Effect
CO_2	14 - 16 vol%	N/A
N_2	80 - 85 vol%	Diluent
O_2	2 - 4 vol%	Loss of Faradaic Efficiency
NO	~ 80 ppm	Catalyst Poisoning/Parasitic Current
SO_2	~ 45 ppm	Catalyst Poisoning/Parasitic Current
PM	~ 9 ppm	Catalyst Coverage, Impedance
Hg	~ 1.2 ppb	Catalyst Poisoning

- **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 SO_2 over 2 h**

Experiments to be done:

- **Simulated flue gas and contaminants for testing – SO_2, NO, Hg, PM**
- **Stability and materials characterization with varying impurity concentration to establish threshold values**
- **Performance characterization with variable CO_2 concentration**
- **Measure faradaic efficiency effects of dilute O_2 in feed gas**

Alternative electrocatalysts to Pb to promote HCOOH/$HCOOCH_3$: Sn, Bi

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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**

Quarter	1	2	3	4	5	6	7	8
Key Milestone	Fabricate Flow Cell Electrolyzer	Complete pH and Applied Potential Study	Demonstrate C2+ FE > 40%	Complete Flue Gas Contaminants Study	Methanol Crossover < 5% FE CH_3OH Oxidation	Current Density > 600 mA cm^{-2}	Flue Gas Performance > 100 h with > 40% FE C2+	Operation on Utility Site Flue Gas > 1 Week

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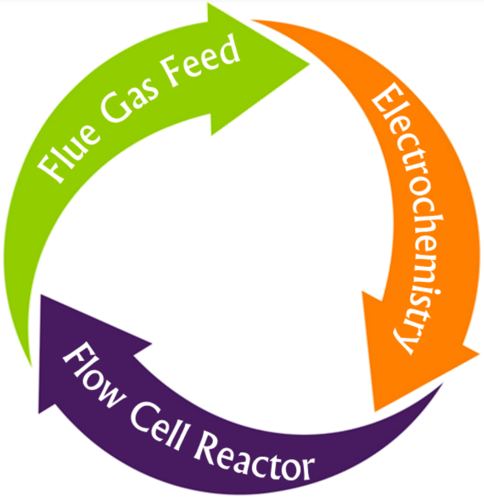
Collaboration and Synergy Opportunities

- **Flow Cell Reactor – A collaborator experienced in flow cell operation for CO_2 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 CO_2**



POSTDOC OPPORTUNITY!!! – We would love to hire an additional researcher with proven CO_2 electroreduction expertise.

Plans for Future Testing/Development/Commercialization

Plans for the future

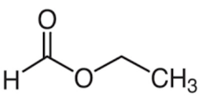
- On-site flue gas testing of flow cell electrolyzer at a power plant
- Continue development of high performance nonaqueous catholyte CO_2 electrolyzers for additional novel products

Three-carbon products

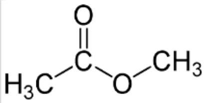
- Ethyl formate, $C_3H_6O_2$ – like methyl formate route, CO_2 reduction to formic acid and esterification in ethanol
- Methyl acetate, $C_3H_6O_2$ – CO_2 reduction to acetate and esterification in methanol

Four-carbon products

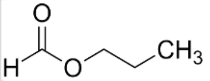
- Propyl formate, $C_4H_8O_2$ – CO_2 reduction to formic acid and esterification in propanol



Ethyl formate



Methyl acetate



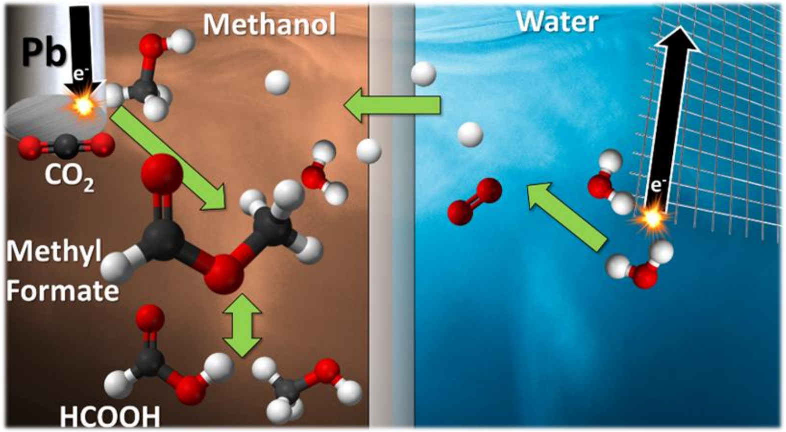
Propyl formate

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 CO_2 electrolysis companies like Dioxide Materials or Opus 12

Summary Slide

Waste 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 $1 < pH < 2.5$ for methyl formate**
- **Supporting electrolyte plays a critical role in conductivity, pH, membrane permeability, and catalyst deactivation**

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Appendix

- Organization Chart
- Gantt Chart

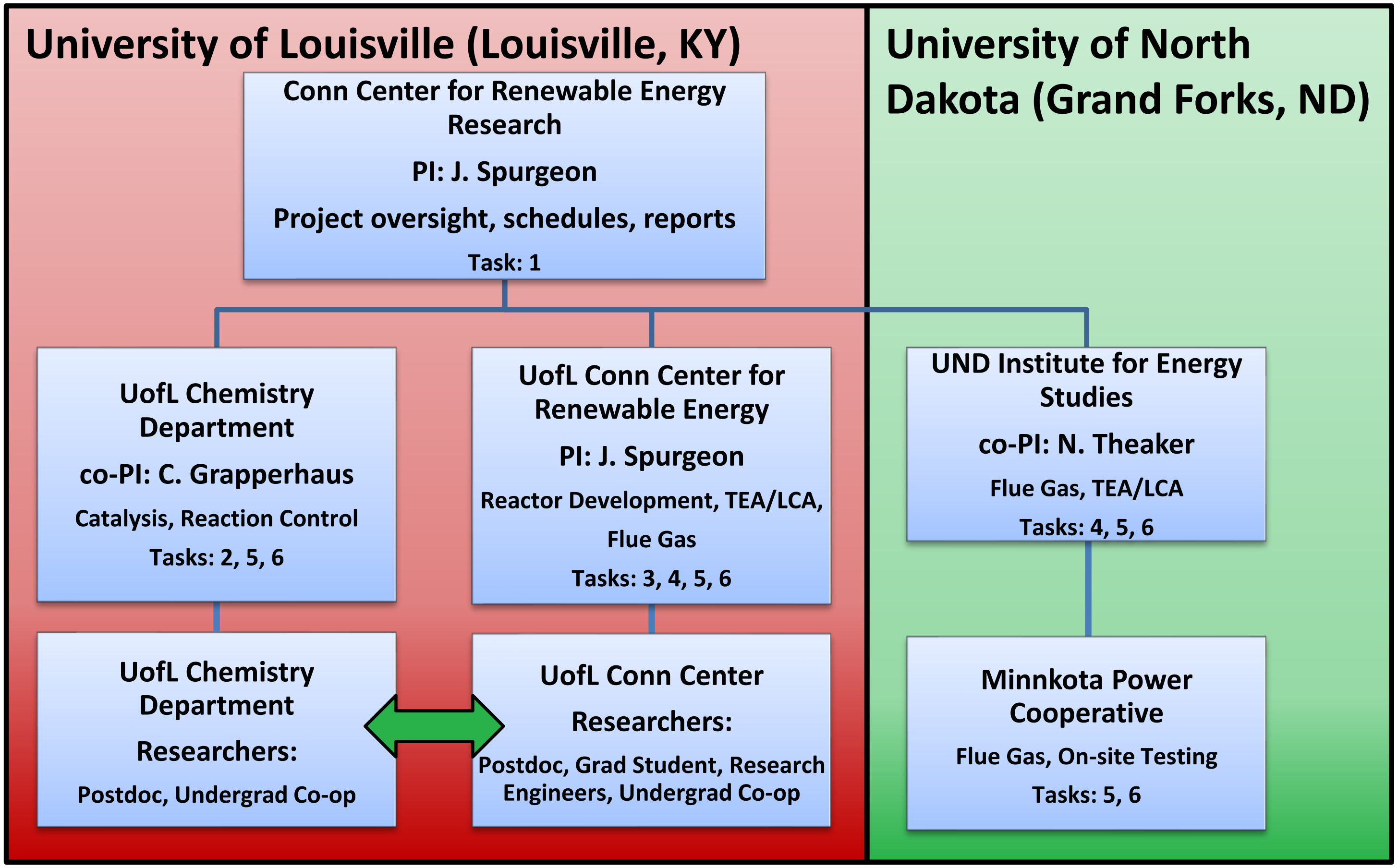
Thank you for Listening

<u>Co-PIs:</u>
Craig Grapperhahus
Nolan Theaker

<u>Researchers:</u>
Dillon Hofsommer
Manu Gautam
Sandesh Uttarwar
Hank Paxton
Arjun Thapa

University of Louisville. UofL Conn Center. UND Institute for Energy Studies, University of North Dakota. NETL National Energy Technology Laboratory

Organization Chart



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GANTT CHART

Task Name	Year 1				Year 2			
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Task 1.0 - Project Management and Planning	O							
Task 2.0 – Improvement of Faradaic Efficiency to C2-4 Products		O		O		X		
Task 3.0 – Develop Electrolysis Reactor for High-current CO_2 Reduction	O		X		X	X		
Task 4.0 - CO_2 Electrolysis System from Power Plant Flue Gas Derivatives				X			X	
Task 5.0 – Full System Integration with Commercially Relevant Performance								X
Task 6.0 – Technoeconomic Analysis and Life Cycle Analysis								X

Task Duration

Completed Work

O – Complete Milestone

X – Incomplete Milestone

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