#### Intensified Catalytic Conversion of CO<sub>2</sub> into High Value Chemicals

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

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# **Project Overview**

- Develop technology to convert CO<sub>2</sub> 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:

- Screening and production of engineered CO<sub>2</sub> 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 <u>increase catalyst lifetime</u> and continuous production
- 3. Develop a <u>pressurized electrochemical reactor</u> to increase production rates
- 4. Long-term <u>stable operation with high selectivity</u> towards formic acid (formate)







# **Captured CO<sub>2</sub>**



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# **Options for CO<sub>2</sub>**



http://www.netl.doe.gov/research/coal/carbon-storage/research-and-development/co2-utilization



# Formic Acid (Formate)



Formic acid (HCO<sub>2</sub>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

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#### **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)





## **Formic Acid Production - LCA**



The energy required to separate and purify formic acid makes up the majority of the GWP for the comparative system

Comparison Product System: NETL Default

CPS = Methyl Formate route

CO<sub>2</sub> conversion to formic acid by the Andora Process LCA report DE-FE0031720 (2022)



### Alternative Production Pathway --Electrochemical CO<sub>2</sub> Reduction



Formic Acid with  $CO_2$  and  $H_2O$  as inputs: Anode Reaction:

 $2H_2O \rightarrow 4H^+ + 4e^- + O_2$ 

Cathode Reaction:

 $2CO_2 + 2H^+ + 4e^- \rightarrow 2HCOO^-$ 

Net Reaction:

 $2H_2O + 2CO_2 \rightarrow 2HCOO^- + 2H^+$ 

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 <u>electrode/catalyst</u>.



# Why So Many Reaction Products?



While the reduction of  $CO_2$  to formic acid can be a relatively simple process (requiring H<sup>+</sup> and 2e<sup>-</sup>), 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<sub>2</sub>-U**

- Reaction rate Matching CO<sub>2</sub> 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  $CO_2$  conversion



# **Our Approach to Address Limitations**

- Reaction rate
- Catalyst Stability

(1) Catalyst ⁻ Development

- Electrode degradation
- Electrode charge density





Purification of Formic Acid Maximizing selectivity



# **Catalyst for CO<sub>2</sub> Reduction**



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



M1 – Cu; M2 – Co or Sn; O2 – nonstoichiometric oxygen

Proposed mechanism of formation of formic acid on bimetal/oxide catalysts from CO<sub>2</sub>

<u>Goal</u>: Synthesized and tested different ratios of Co, Cu and Sn bimetal/oxide nano-catalysts for production of C1/C2 compounds from  $CO_2$ 



#### **Catalyst for CO<sub>2</sub> Reduction**





Synthesizing a series of Sn:Cu catalysts with different molar ratios was our primary focus



### **Electrode for CO<sub>2</sub> Reduction**



Carbon Xerogel (CX) is a good scaffold to immobilize catalysts while also maintaining good conductivity and gas permeability



# **H-Cell Screening**





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# **Flow Cell Optimization**









- CD: 48 mA/cm<sup>2</sup>
- FE: 81.2% (energy)
- 29% conversion (CO<sub>2</sub> input)
- 1.65 g/hr formic acid



# 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 CO<sub>2</sub> 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-ofthe-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.



#### TMP

#### Technology Maturation Plan (TMP) - Update

Performance attributes and targets after completion of this project						
Component	TRL at beginning of Project	TRL at end of Project	Performance Attribute/Target			
Bimetallic catalyst	2	3	Catalyst capable of formic acid selectivity of > 80%			
Anode/cathode materials	3	4	CCE electrode with ohmic impedance contribution < 10 ohm.			
Fully integrated combined system	Illy integrated 2 3		Production of 25 mM Formic acid, 50% Faradaic Efficiency, and operating at < 4 V. Long-term production of formic acid for >50 hours at 5 mM/hr			



### 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



#### **Success Criteria**

Due Date	Success Criteria (Task #)			
9/30/2021	Catalyst capable of <u>formic acid selectivity of &gt; 80%</u> (Task 2)	100%		
3/31/2022	CCE electrode with <u>ohmic impedance contribution</u> < 10 ohm (Task 3)	100%		
9/30/2022	Flow cell with production of <u>25 mM Formic acid</u> , <u>50% Faradaic Efficiency</u> , and operating at < 4 V (Task 4)	100%		
9/30/2022	Long-term production of formic acid for <u>&gt;50 hours</u> at 5 mM/hr (Task 4)	25%		



# **Key Project Takeaways**

- Using KHCO<sub>3</sub> catholyte is a way to potentially match with CO<sub>2</sub> capture systems in the future
- Operating at slight pressure to boost CO<sub>2</sub> 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**

					Feder	Federal FY 20/21 and 21/22						
	Length			Primary								
Task Number and Name	(months)	Start	End	Personal	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
1. Project Management and Planning	24	10/1/20	9/30/22	Jesse								
1.1 Project Management Plan	24	10/1/20	9/30/22	Jesse								
1.2 Technology Maturation Plan	24	10/1/20	9/30/22	Jesse								
2. Development of Electrocatalysts for CO2 reduction	18	10/1/20	3/31/21	Muthu								
2.1 Eectrocatalysis Formulation	12	10/1/20	9/30/21	Muthu								
2.2 Electrocatalysis Characterization	6	10/1/21	3/31/22	Muthu								
M4. Synthesis of four homogeneous bi-metal oxide catalyst with different molar ratios of Cu and Sn/Co.			9/30/21					*				
3. Reactor Design and Catalyst Evaluation	18	10/1/20	3/31/22	Daniel								
3.1 Evaluation of Catalyst Coated Electrodes (CCE)	9	10/1/20	6/30/21	Daniel								
3.2 Half-cell Parametric Testing of CCE	18	10/1/20	3/31/22	Daniel								
M5. 30% decline in cathode/anode after 50 CV cycles			9/30/21					★				
4. Integrated Reactor and Catalyst Testing	18	4/1/21	9/30/22	Daniel								
4.1 Full Cell Design and Integration	12	4/1/21	3/31/22	Daniel								
4.2 Stability Testing	12	10/1/21	9/30/22	Daniel								
4.3 Long-term Reactor Operation	18	4/1/21	9/30/22	Daniel								
M6. Flow cell capable of 25 mM Formic Acid production at 2 mL/min with Faradaic Efficiency of 40%			6/30/22								۴	
5. Final Techno-Economic Assessment with Technology Gap Analysis	6	4/1/22	9/30/22	Jesse/Ayo								
6. Life Cycle Analysis	6	4/1/22	9/30/22	Jesse								



#### **State Point Table**

	Units	Measured/Current Performance	Projected/Target Performance					
Synthesis Pathway Steps <sup>1</sup>								
Step 1 (based on CO <sub>2</sub> )	mol <sup>-1</sup>	$CO_2 + 2H^+ + 2e \rightarrow HCOOH (pH < 3.75) CO_2 + H^+ + 2e \rightarrow HCOO^- (pH > 3.75)$						
Step 2 (anodic)	mol <sup>-1</sup>	$2H_2O \rightarrow O_2 + 4H^+ + 4e$						
Overall	mol <sup>-1</sup>	$2CO_2 + 2H_2O \rightarrow O_2 + 2HCOOH$						
Source of external intermediate 1		(e.g., natural gas, oil, renewable energy, etc)						
Source of external intermediate 2		(e.g., natural gas, oil, renewable energy, etc)						
Source of external intermediate n		(e.g., natural gas, oil, renewable energy, etc)						
Reaction Thermodynamics <sup>2,3</sup>		1						
Reaction <sup>4</sup>		Electrochemical						
$\Delta H^{o}_{Rxn}$	KJ/mol	264.2						
$\Delta G^{\circ}_{Rxn}$	KJ/mol	697.6						
Conditions	1	(range)	(range)					
CO <sub>2</sub> Source <sup>5</sup>	 	+99.% pure $CO_2$ supplied from $CO_2$ capture	+99.% pure $CO_2$ supplied from $CO_2$ capture					
	1	plant	plant					
Catalyst <sup>6</sup>	   -	Sn <sub>95</sub> Cu <sub>5</sub>	Sn <sub>95</sub> Cu <sub>5</sub>					
Pressure (bar)	1	Ambient – 5 psi	Ambient – 5 psi					
$CO_2$ Partial Pressure (bar)	   							
Temperature (°C)	, 1 1	25°C	25°C					
Performance	1	(range)	(minimum)					
Nominal Residence Time <sup>7</sup> (sec)	1							
Selectivity to Desired Product <sup>8</sup>	%	81.2%	>80%					
Product Composition <sup>9</sup>	1	range)	(optimal)					
Desired Product	mol%	Formic acid 81%	Formic acid 99%					
Desirable Co-Products	mol%	-	-					
и и	mol%							
Unwanted By-Products	mol%	CO 19%	CO <1%					
и и	mol%							
Grand Total	mol%		100%					



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