DOE Bioenergy Technologies Office (BETO) 2023 Project Peer Review

Electrochemical Production of Formic Acid from Carbon Dioxide in Solid Electrolytes

April 7th, 2023
Carbon Dioxide Utilization

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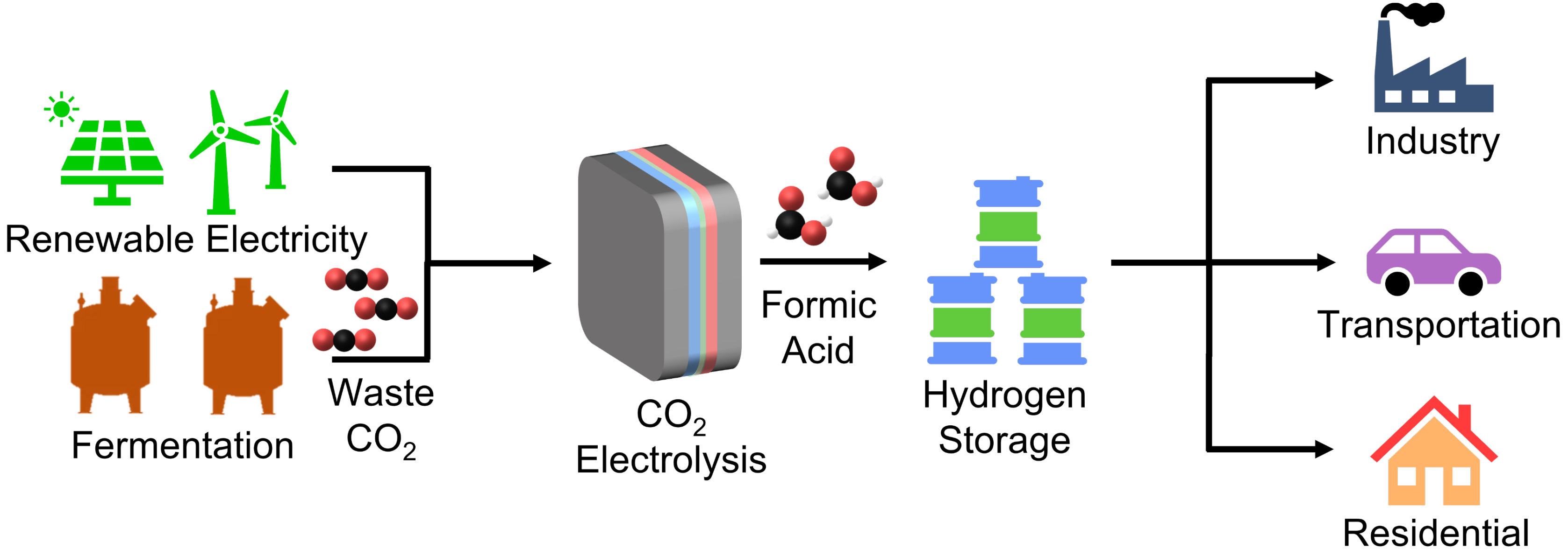
University of Delaware

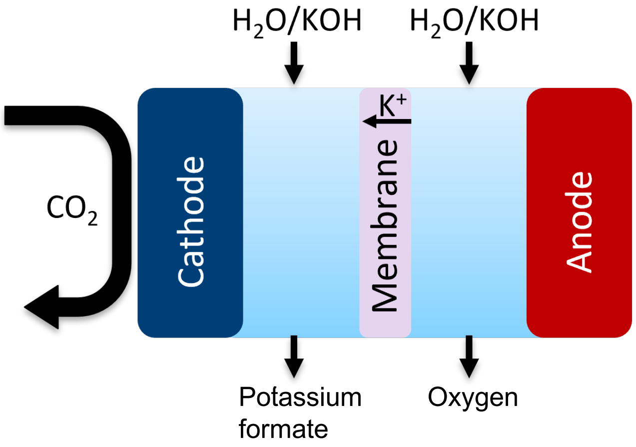
Project Overview



CO_2 electrolysis can utilize waste CO_2 from bioreactors to produce market competitive formic acid at commercial scales.

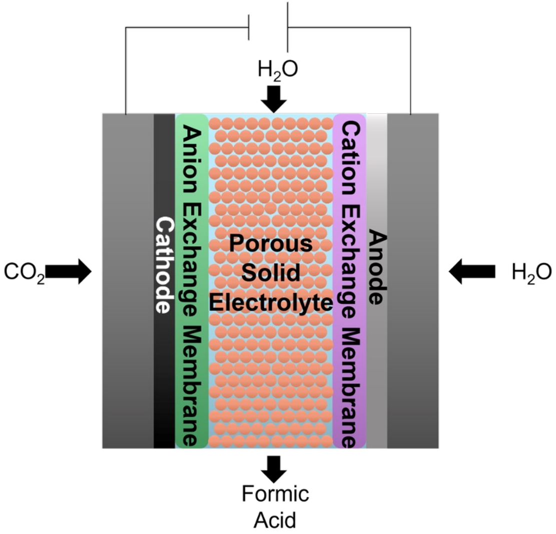
Project Overview

Conventional Design



Energy and cost intensive downstream separations

Solid Electrolyte Design



- Tunable formic acid concentration
- Elimination of downstream separations
- *Not demonstrated beyond lab scale*

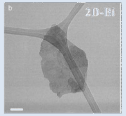
1 – Approach – Task Overview

Phase I – 3 Months

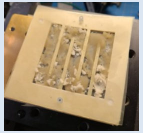
Task 1:
Initial verification

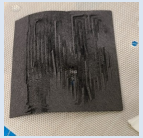
Phase II – 18 Months

Task 2: Electrode and membrane development

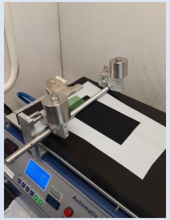


Task 3: Development and execution of durability protocols

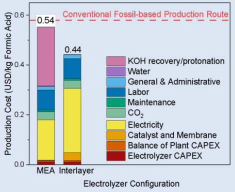




Task 4: Catalyst and reactor scale up



Task 5: Preliminary techno-economic analysis and life-cycle assessment



Phase III – 15 Months

Task 6: Design and fabrication of 750 cm^2 electrochemical cell

Task 7: Performance and durability assessment of 750 cm^2 electrochemical cell

Task 8: Bioreactor integration and comprehensive techno-economic analysis and life-cycle assessment

1 – Approach – Go/No Go Objectives

Validation Table	Instructions	Units				
Parameter/Performance			**Benchmark (Current)**	**Initial Verification (Go/No Go I Results)**	**Intermediate Target (Go/No Go II)**	**Final Target (Go/No Go III)**
General Information						
Current Density	The operation current for the generation of formic acid	mA/cm^2	100	100	200	200-300
Faradaic Efficiency	The selectivity of target product under benchmark current density	%	>80	87	>90	>90
Cell Size	The size of electrolyzer	cm^2	5	6.25	>100	>750
Durability	Operation time for the long-term stability experiment	h	100	130	>200	1000
Current Density for Durability	The operation current density for the long-term stability experiment	mA/cm^2	30	30	>100	200
Production Rate	Mole generation rate of liquid formic acid per hour	mM/h	2	6.3	N/A	N/A

1 – Approach – Project Structure

Catalyst Synthesis and Scale-up

RICE

Solid Electrolyte Interlayer Scale-up

NREL Transforming ENERGY

TEA and LCA

Stability Testing

RICE

NREL Transforming ENERGY

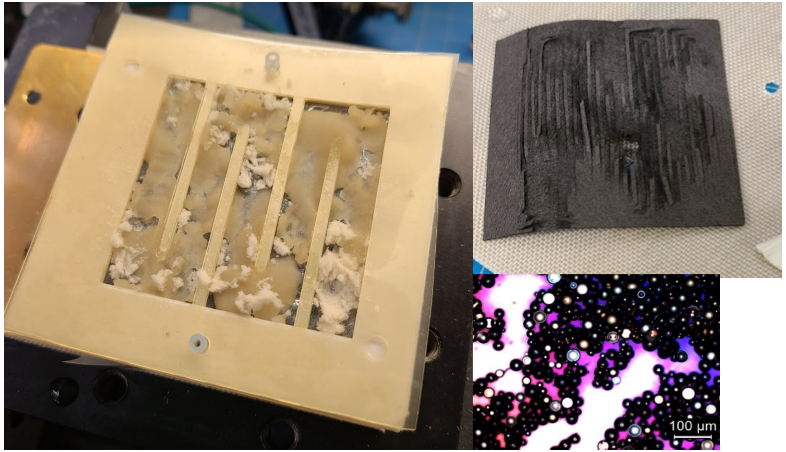
Commercial Scale-up

CHEM

NREL Transforming ENERGY

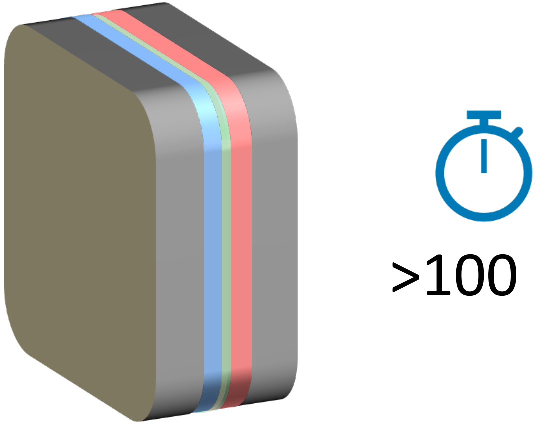
1 – Approach - Major Technical Challenges

Scale-up of solid-state interlayer



Lack of methods to fabricate large-scale interlayers while keeping uniform wetting, consistency, and pressure drop.

Stability of the full cell



>100 h

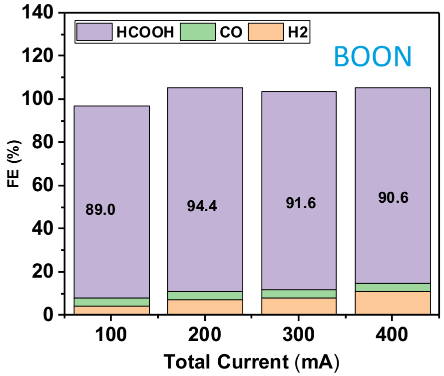
A stable operation for formic acid production has never been demonstrated in any CO_2 electrolyzers larger than 100 cm^2.

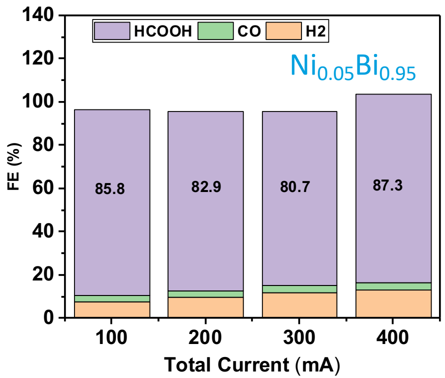
1 – Approach – Risk Mitigation

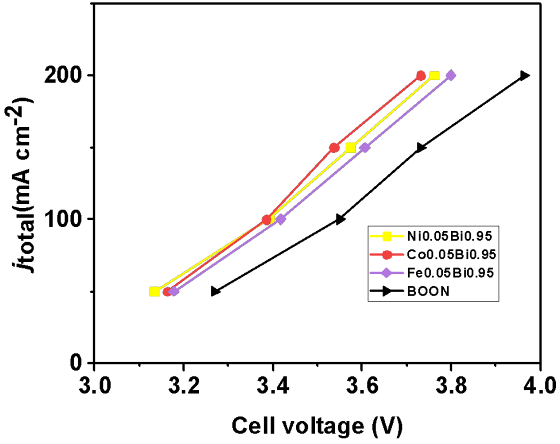
The team is tackling the technical challenges by exploring a variety of approaches.

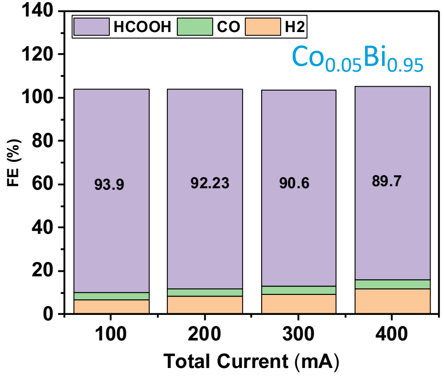
Risks	Mitigation
Scaling up current generation solid-state interlayer materials could be challenging due to its powder nature.	Alternative solid electrolyte layer materials are being investigated.
Current electrolyzer design may experience a significant loss of formic acid Faradaic efficiency at large cell sizes.	Several different electrolyzer cell designs have been studied.
Difficult to probe the falling mechanism at the full cell level.	A 5-electrode full cell diagnostic tool has been developed to probe the major voltage losses in the electrolyzer.

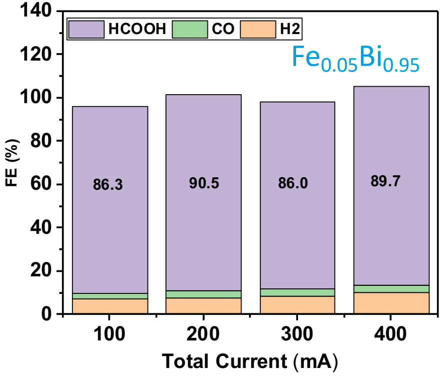
2 – Progress and Outcomes – Catalyst Testing and Effects of Doping









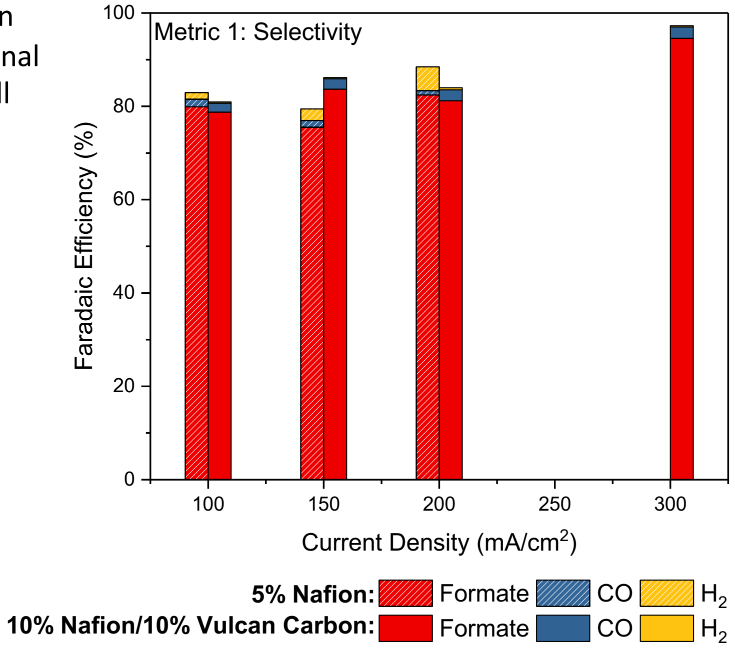


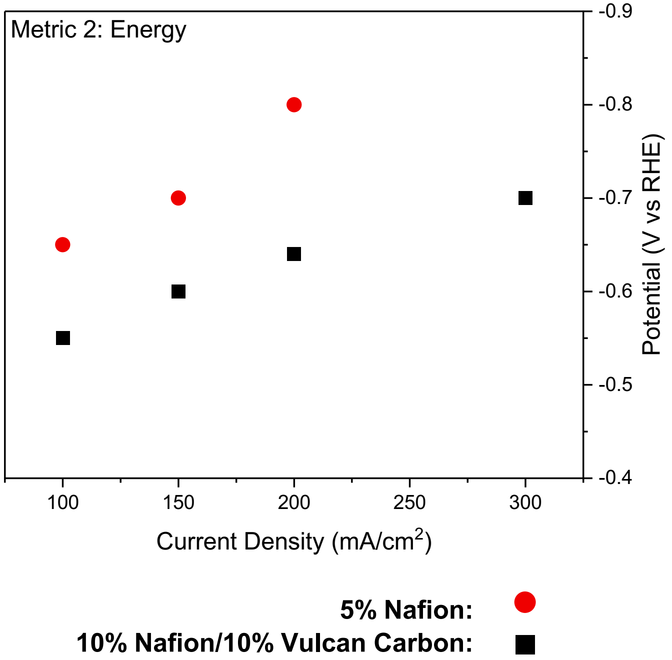
Milestone 2.1.1: Complete the identification of cathode catalysts that meet the performance target 90% FE and 200 mA/cm^2 [completed]

0.5 mg cm^{-2} loading , 30 sccm CO_2 feed, DI water anolyte 3 ml/min, Middle layer with water of~1 ml/min, IrO_2 anode

2 – Progress and Outcomes – Binder Material Evaluation

Tested in conventional flow cell



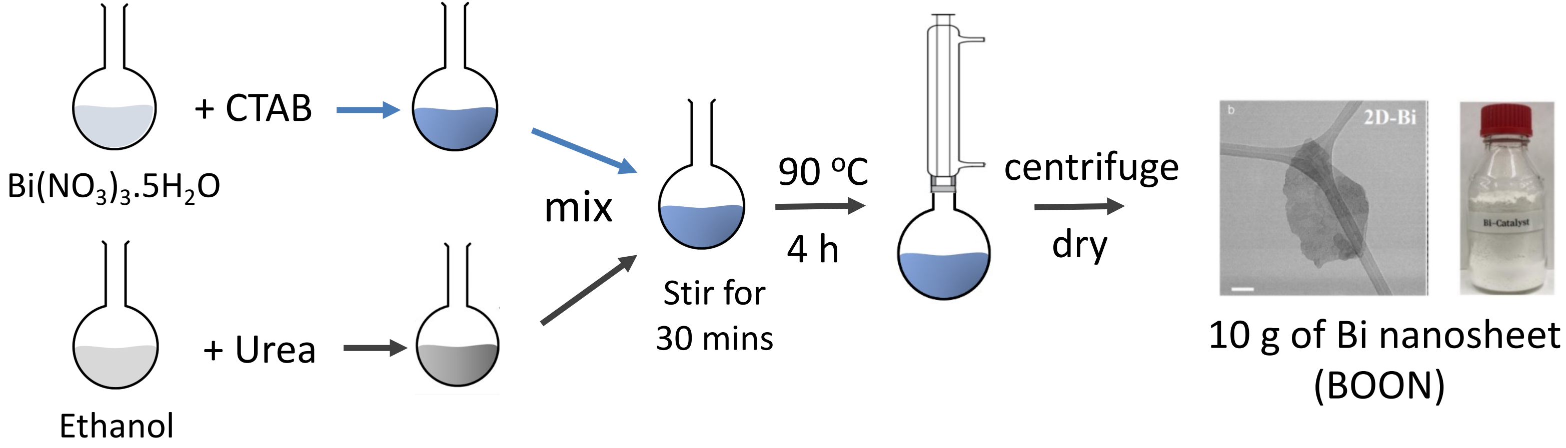


Milestone 2.2.1: Complete the selection of membrane and binder materials that can achieve at least 90% FE and 200 mA/cm^2. [completed]

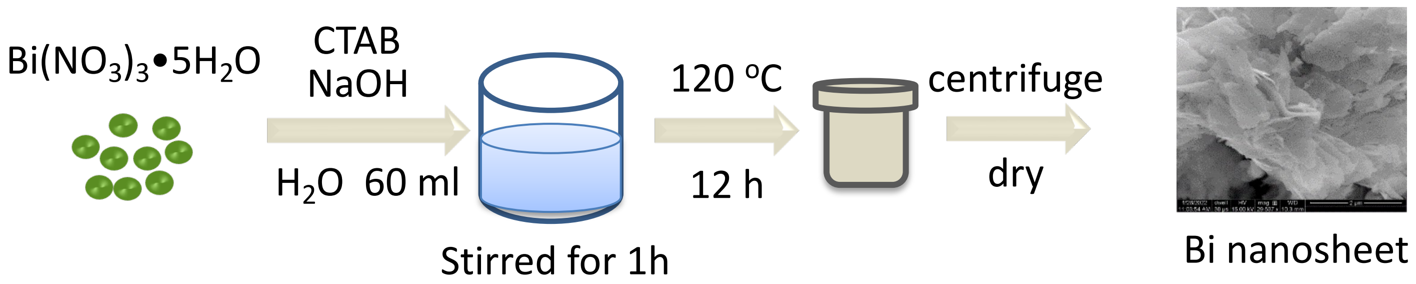
1 cm^2 reactor, 1 M KOH catholyte, 1 M KOH anolyte, Nafion 117, 0.5 mg/cm^2 BOON

2 – Progress and Outcomes – Catalyst Scale-up Routes

Synthesis Route 1: Hydrolysis



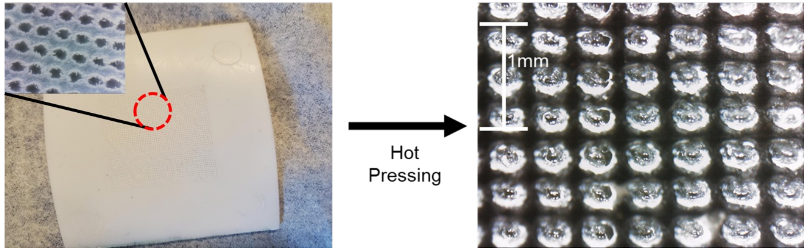
Synthesis Route 2: Hydrothermal



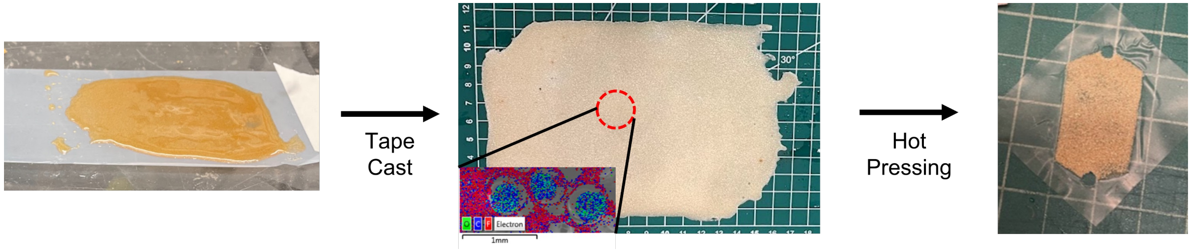
2 – Progress and Outcomes – Redesigning the Solid Electrolyte Interlayer

Task 3.0: Development and execution of durability protocols

Textured Membrane:

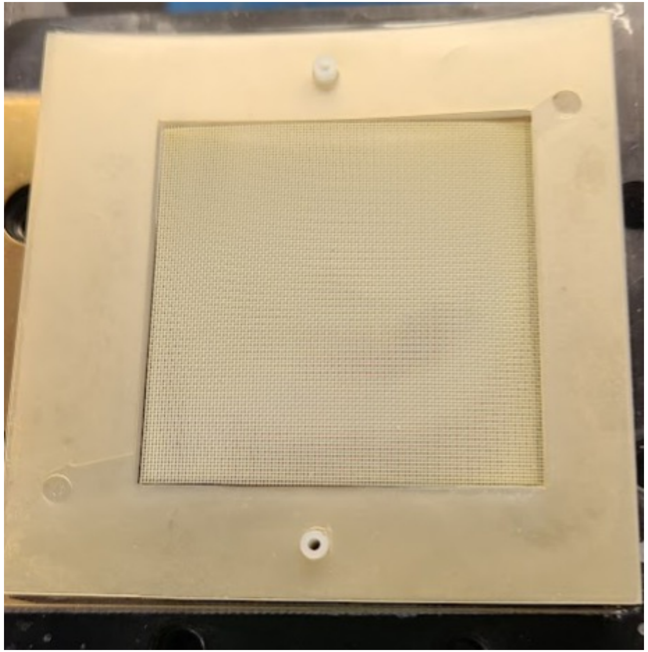


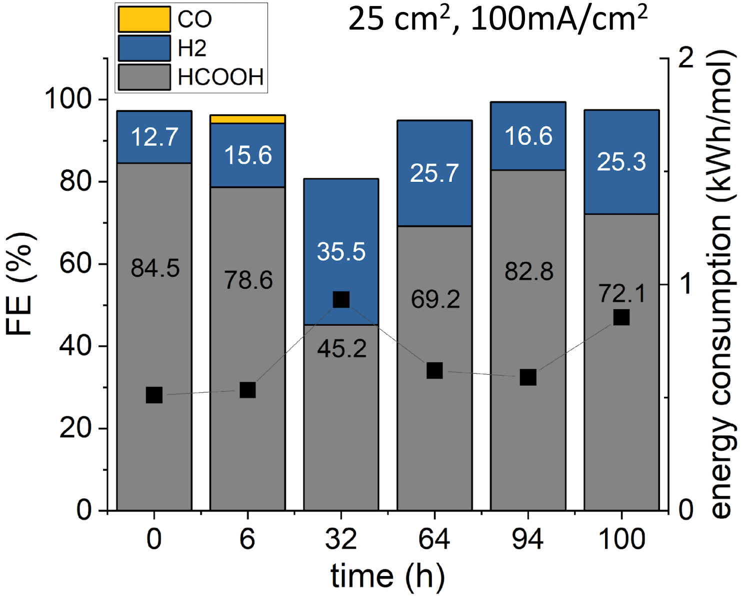
Confined Resin Composite:



2 – Progress and Outcomes – Redesigning the Solid Electrolyte Interlayer

Ionomer Coated Scaffold





Recovery of FE from 45% to >80% through doubling cathode gas flow rate

0.5 mg/cm² BOON, 1 mg/cm² IrO_2, 0.6 SLM CO_2 humidified 95%, Reinforced AEMion, Nafion, 10 mL/min DI water interlayer

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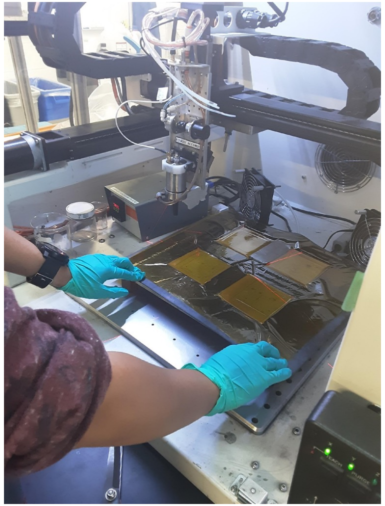
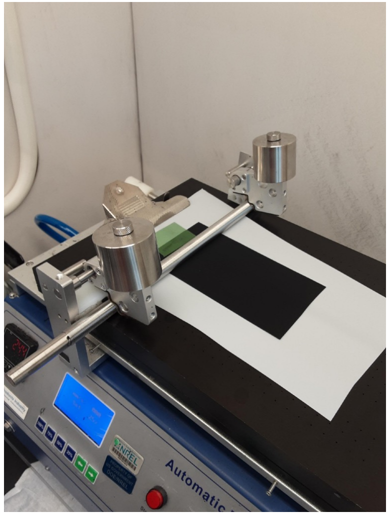
2 – Progress and Outcomes – Scaling-up Fabrication of Electrodes

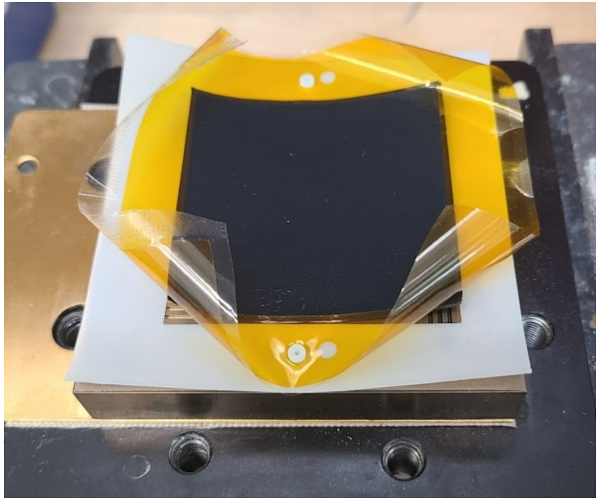
Subtask 4.2: 100-250 cm^2 reactor fabrication and evaluation



Automated spray deposition of catalyst ink



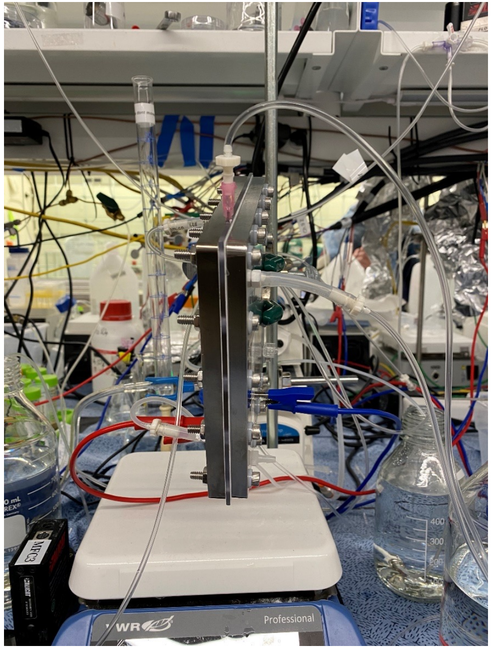
Automated rod-coating as a pilot to roll-to-roll electrode fabrication

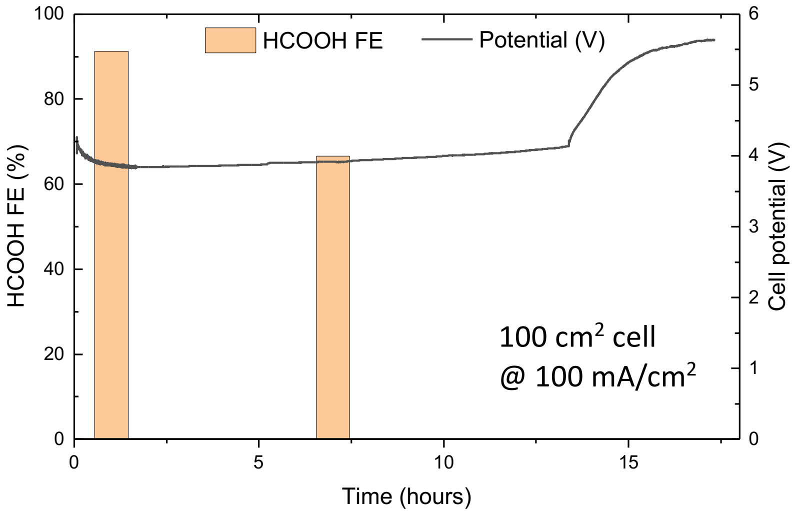


IrO_2 anode interfaced with Nafion membrane, 25 cm^2

2 – Progress and Outcomes – Electrochemical Measurements at 100 cm^2

Subtask 4.2: 100-250 cm^2 reactor fabrication and evaluation

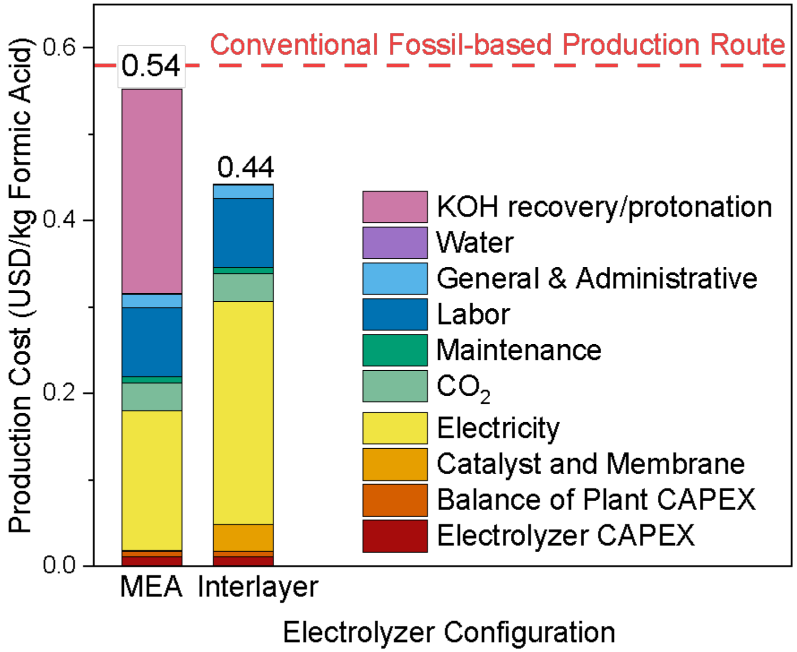


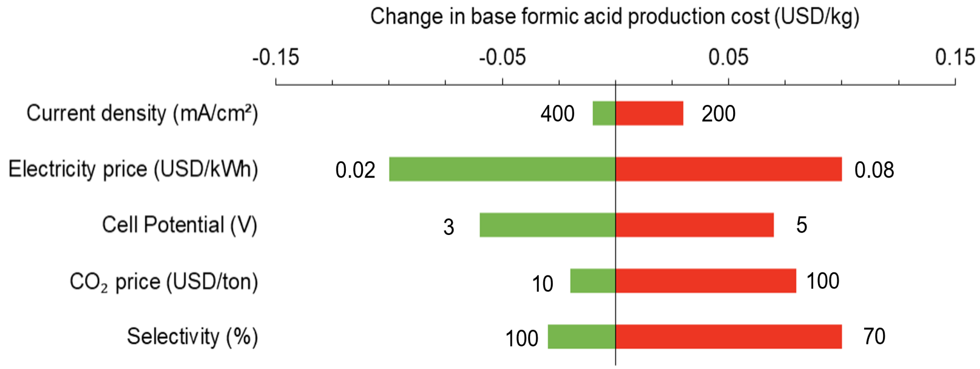


- Formic acid Faradaic efficiency >90%
- Anion exchange membrane (AEM) ruptured after 14 hours of operation. Alternative membrane materials will be tested.

0.5 mg cm^{-2} loading , 400 sccm CO_2 humidified, feed, DI water anolyte 50 ml/min, Middle layer with water of 30 ml/min, IrO_2 anode, Amberchrom 50 mesh interlayer

2 – Progress and Outcomes - TEA

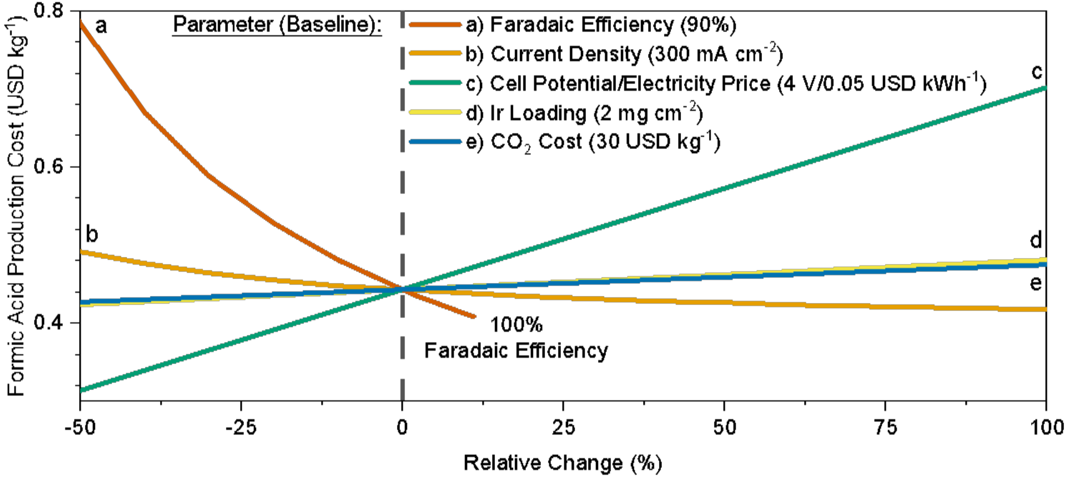


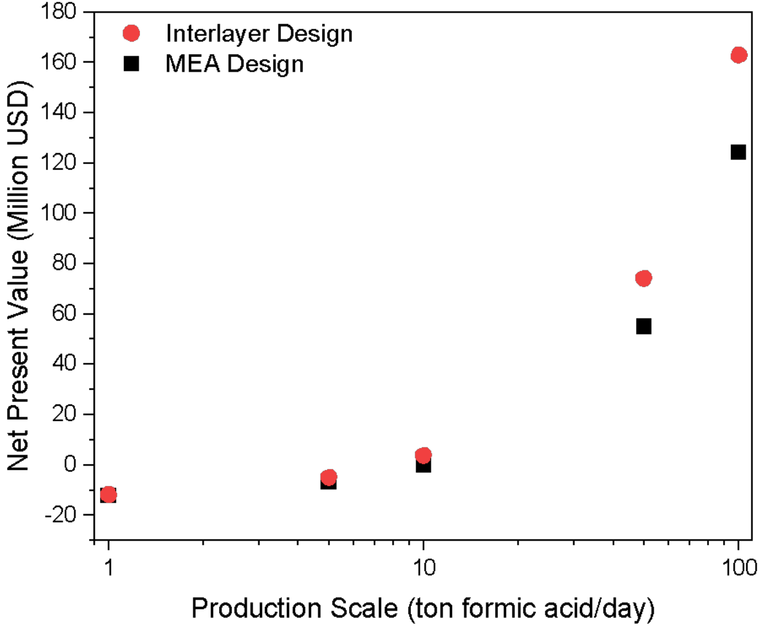


Expected 33% cost reduction of formic acid compared to conventional fossil fuel route

Milestone 5.1.1: Complete the preliminary techno-economic analysis including models of capital and operation costs, and sensitivity analysis. [completed]

2 – Progress and Outcomes - TEA





Most impactful parameters on production cost:

- Electricity Usage/Price
- Current Density
- Faradaic Efficiency

Milestone 5.1.1: Complete the preliminary techno-economic analysis including models of capital and operation costs, and sensitivity analysis. [completed]

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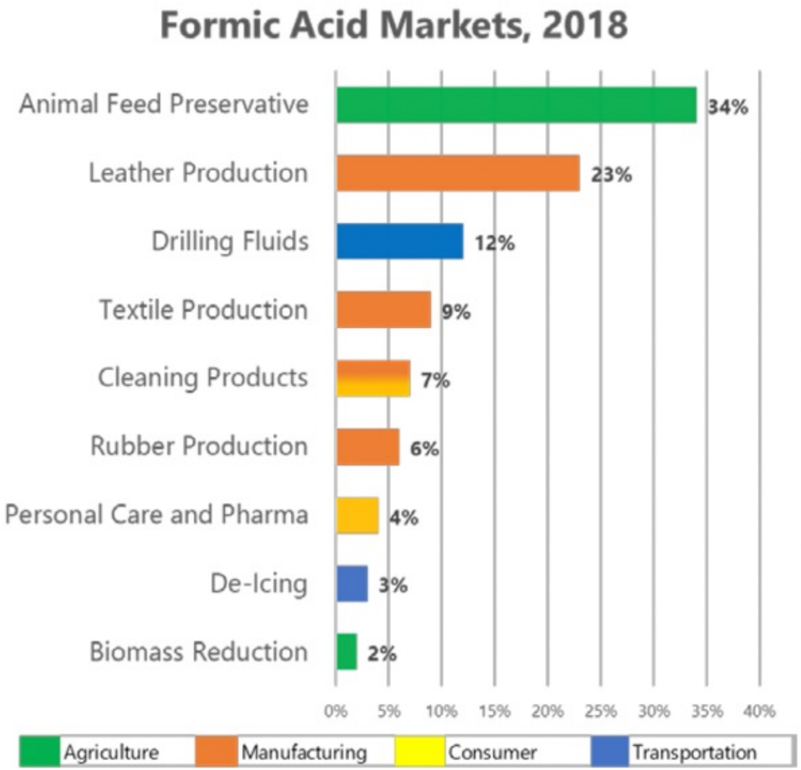
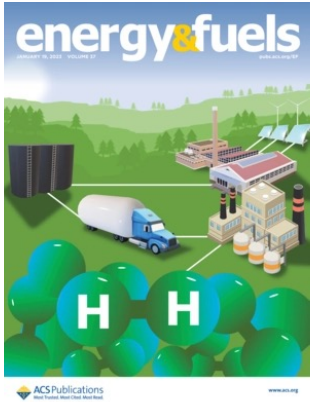
3 – Impact - Potential Market Effected

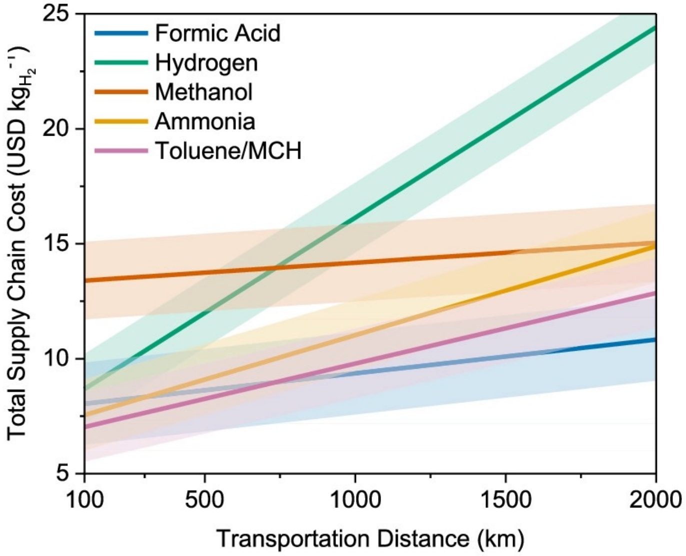


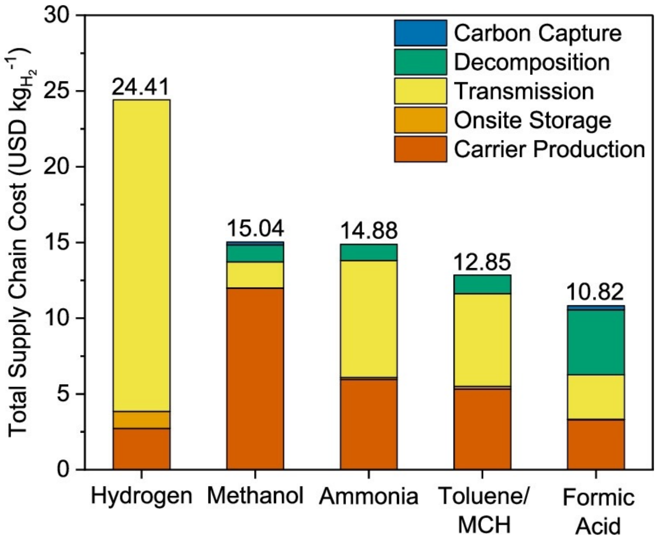
In addition to creating a foundation for a hydrogen economy, our cheaper green formic acid will contribute to decreasing CO_2 emissions in multiple sectors

3 – Impact - Evaluation of Hydrogen Carriers (Case Study)



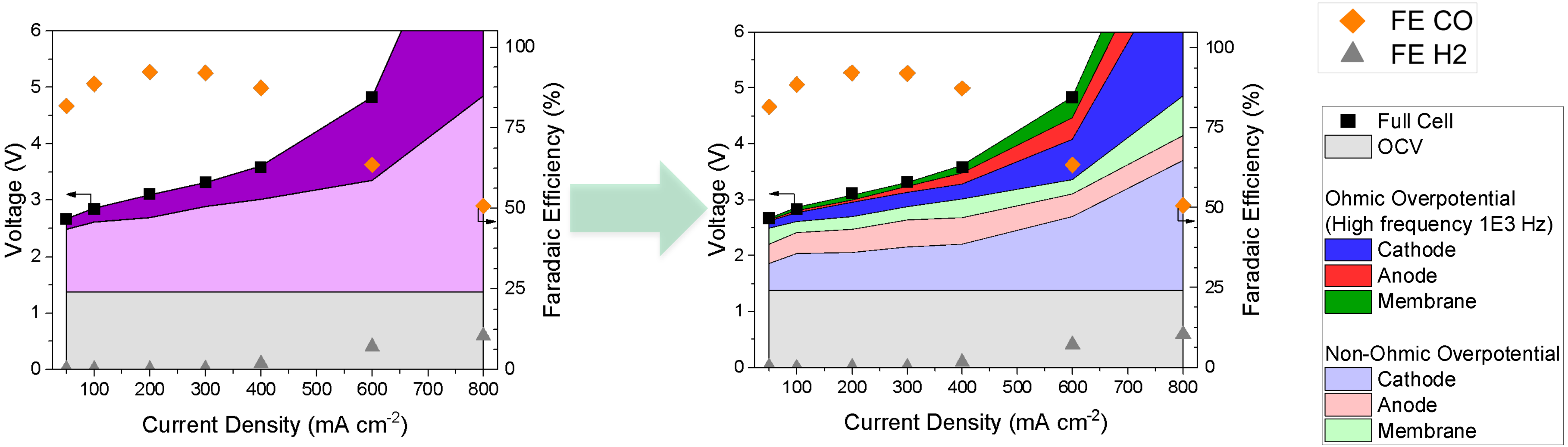
Crandall, B. S. Brix, T., Weber, R. S., Jiao, F. *Energy Fuels*, (2023) **37**, 2, 1441-1450





Formic acid is an economical green hydrogen carrier.

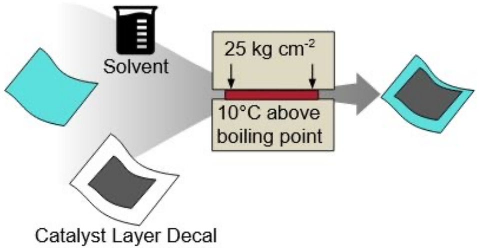
3 – Impact – Development of *Operando* Diagnostics

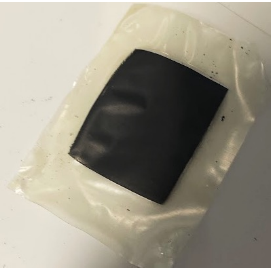


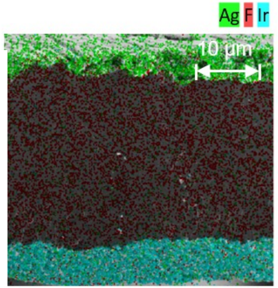
Development of novel *operando* diagnostic tool for overpotential breakdown in electrolyzers. The new tool has a high potential to be used at the industrial level.

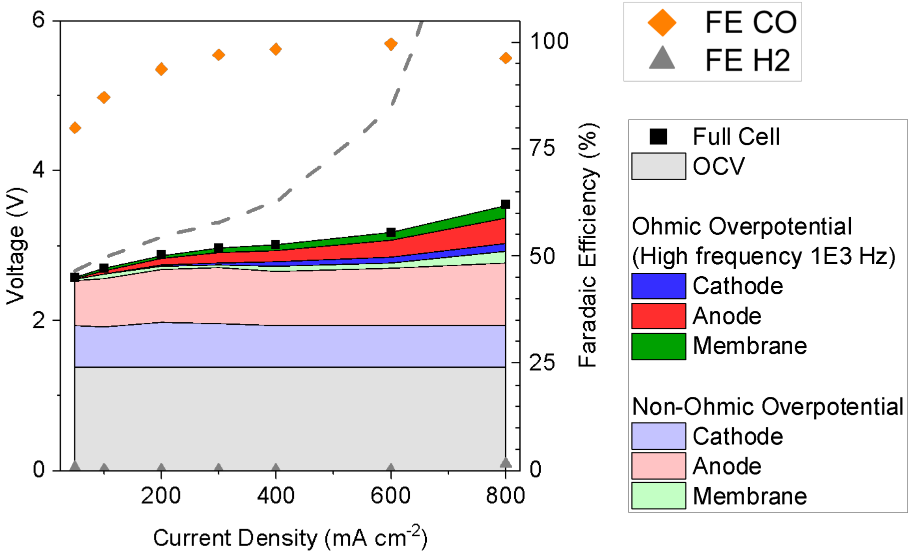
Hansen, K. U., Cherniack, L. H, Jiao, F. *ACS Energy Lett.* (2022) **7**, 12, 4504-4511

3 – Impact - Evaluation of Hydrogen Carriers

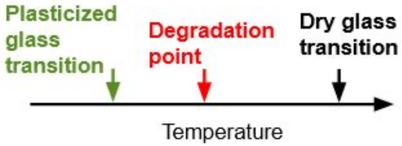








Failure to translate dry hot-pressing technique used for Nafion®!



- Identification and improvement of major energetic losses in CO_2 electrolyzers
- Development of hot-pressing technique for catalyst coating anion exchange membranes

Hansen, K. U., Cherniack, L. H, Jiao, F. *ACS Energy Lett.* (2022) **7**, 12, 4504-4511

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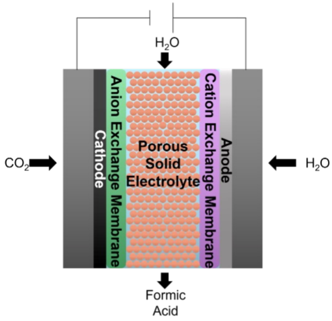
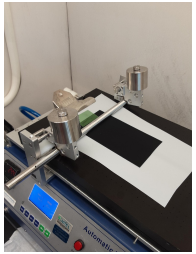
Summary

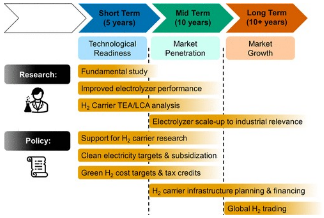


Our novel solid electrolyte CO_2 electrolyzer can produce clean, market competitive formic acid without additional downstream separations. The goal of this project is to scale electrochemical formic acid production from biowaste CO_2 to an industrially relevant size.



We have completed our task of electrolyzer component selection, catalyst scale-up, and preliminary TEA results. Our project currently remains on schedule as all teams have now moved on to stability testing and 100 cm^2 electrolyzer fabrication and evaluation as specified in SOPO.

Through cooperation with our industry partner, we have developed a techno-economic model to prove that electrochemical formic acid has high potential to be an economical hydrogen carrier. Thus, we expect a successful outcome of this project to greatly decrease CO_2 emissions.



Quad Chart Overview

Timeline

- *Start: 10/01/2021*
- *End: 9/30/2024*

	FY22 Costed	Total Award
DOE Funding	*(10/01/2021 – 9/30/2022)*	*(negotiated total federal share)*
Project Cost Share *		

TRL at Project Start: TRL-3

TRL at Project End: TRL-5

Project Goal

The goal of this project is to develop an industrially relevant CO_2 electrolyzer to produce clean formic acid from waste bioreactor streams at a market competitive price.

End of Project Milestone

Demonstrate formic acid production at a Faradaic efficiency of >90%, current density of >200 mA/cm^2, 1000 hours durability at 200 mA/cm^2 in a continuous electrolysis or in a noncontinuous electrolysis with interval system regeneration., cell size of >750 cm^2

Funding Mechanism

DE-FOA-0002203, DE-EE0009287.0001, Carbon Dioxide Utilization, 2020

Project Partners

- Haotian Wang (Rice University)
- Kenneth Neyerlin (NREL)
- Todd Brix (OCO Chem)

Additional Slides

TEA Major Assumptions

Parameter	Value	Reference
Bioethanol CO_2 Cost	$30/kg	Sanchez, D. L. et al. PNAS. 19, 4875-4880 (2018).
Electricity Cost	$0.05/kWh	"Renewable power generation costs in 2021" IRENA (2022).
Electrolyzer Lifetime	20 years	Shin, H. et al. Nat. Sustain. (2021).
Electrolyzer Reference Cost	$450/kW	Peterson, D. et al. Hydrogen production cost from PEM electrolysis. (2020).
Electrolyzer Maintenance	2.5% of Electrolyzer CAPEX	Peterson, D. et al. Hydrogen production cost from PEM electrolysis. (2020).
Electrolyzer Major Component Replacement Cost	15% of Electrolyzer CAPEX	Peterson, D. et al. Hydrogen production cost from PEM electrolysis. (2020).
Ir Cost	$26.91/g	"Historical Iridium Price" Mining.com [pre-covid 5-year average].
Labor Cost	$4000/day	DOE "Current Central Hydrogen Production from Polymer Electrolyte Membrane (PEM) Electrolysis (2019) version 3.2018"
General & Administrative Cost	20% of Labor Cost	DOE "Current Central Hydrogen Production from Polymer Electrolyte Membrane (PEM) Electrolysis (2019) version 3.2018"
Balance of Plant CAPEX	35% of Total CAPEX	Peterson, D. et al. Hydrogen production cost from PEM electrolysis. (2020).
Catalyst Cost	50% of Electrolyzer Reference Cost	Peterson, D. et al. Hydrogen production cost from PEM electrolysis. (2020).
Electrolyte Regeneration & Formate Protonation Cost	$0.24/kg formate	Overa, S. et al. Nat. Catal. (2022).

Electrochemical Reactions

Cathode Products	Anode Products
Formate $CO_2 + H_2O + 2e^- \rightarrow HCOO^- + OH^-$	Oxygen $4OH^- \rightarrow 2O_2 + 2H_2O + 4e^-$ (Alkaline)
Carbon Monoxide $CO_2 + H_2O + 2e^- \rightarrow CO + 2OH^-$	Oxygen $2H_2O \rightarrow 4H^+ + O_2 + 4e^-$ (Acidic)
Hydrogen $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	Formate Oxidation $HCOO^- + OH^- \rightarrow CO_2 + H_2O + 2e^-$

Publications, Patents, Presentations, Awards, and Commercialization

Funded Publications:

- Crandall, B. S. Brix, T., Weber, R. S., Jiao, F. *Energy Fuels*, (2023) **37**, 2, 1441-1450
- Hansen, K. U., Cherniack, L. H, Jiao, F. *ACS Energy Lett.* (2022) **7**, 12, 4504-4511