ChemCatBio
Chemical Catalysis for Bioenergy

DOE BETO 2023 Project Peer Review

CCB DFAs: Rapid Prototyping of High-Throughput Systems for CO2 Reduction Electrocatalyst Synthesis w/Opus 12 (Twelve)

2.5.4.707

April 7, 2023

Catalytic Upgrading

Frederick Baddour

NREL

U.S. DEPARTMENT OF ENERGY | Office of ENERGY EFFICIENCY & RENEWABLE ENERGY

BIOENERGY TECHNOLOGIES OFFICE

Project Overview

Project Goal: Derisk the commercialization of CO_2 electrolysis by supporting MEA scale-up through the ***development of high-throughput synthesis methods*** for high-performance nanocatalyst production

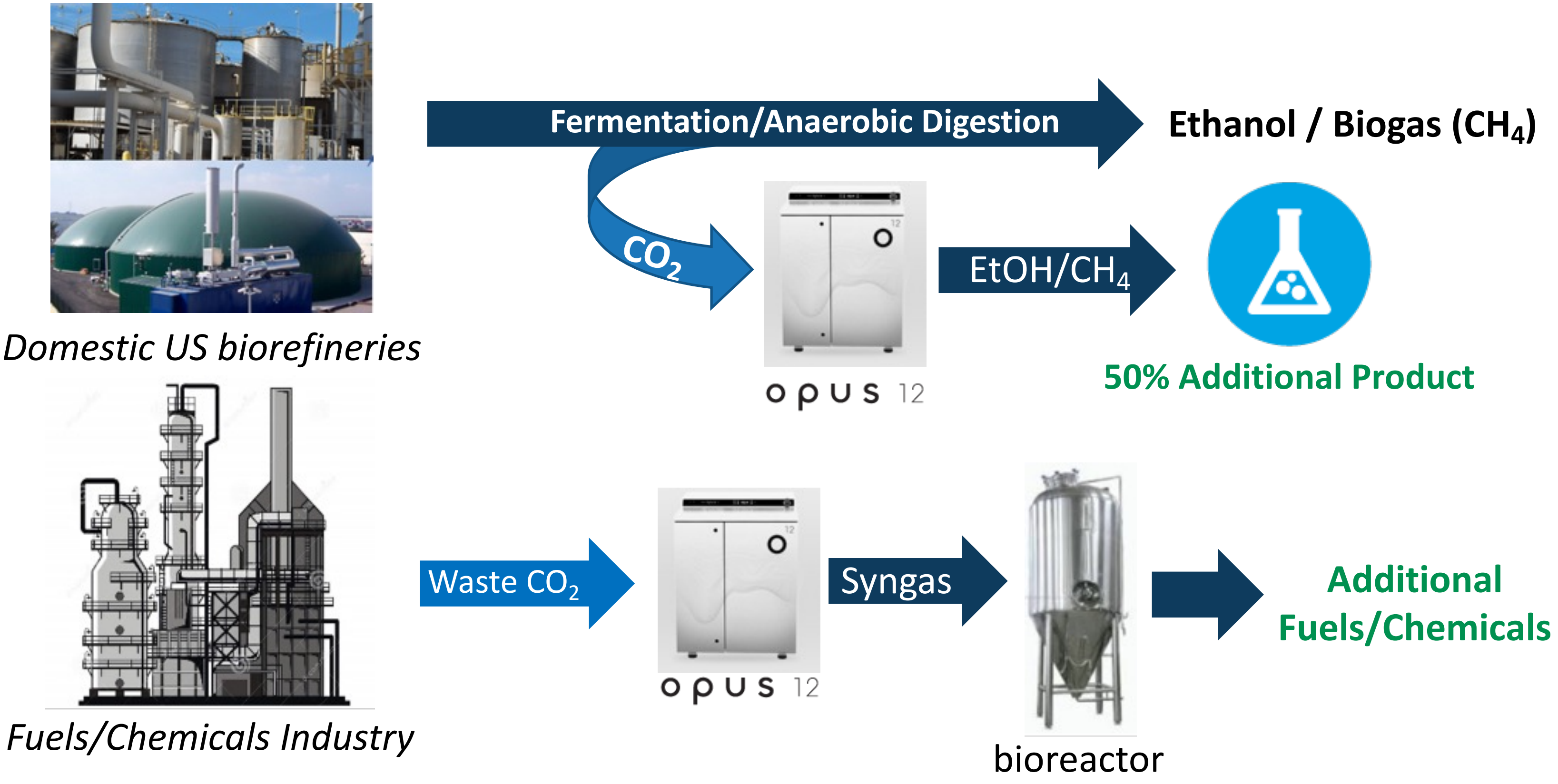
Approach: To couple unique national lab ***millifluidic synthesis & characterization, with industrial device fabrication and catalytic evaluation*** to accelerate the commercialization of tunable, industrial-scale CO_2 electrolyzers

Research Progress & Outcomes

- ***Translated*** state-of-the art batch electrocatalyst syntheses to continuous flow millifluidic methods
- ***Increased scale*** of nanocatalyst synthesis to 7.5 g particles (30 g catalyst) per day in a single channel
- ***Maintained catalyst performance*** upon translation to high-throughput synthesis
- ***Facilitated performance testing*** of MEAs at >750 cm^2 compared to previous 25 cm^2 (40x scale up)

Impact: Reduced commercialization risk by ***developing high-throughput methods*** that (1) are capable of ***satisfying commercial catalyst demand***, (2) ***maintain catalyst performance***, and (3) ***enabled large-scale MEA performance*** evaluation.

Overview – Revenue from Waste

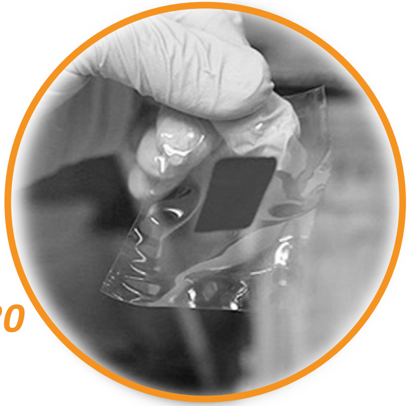


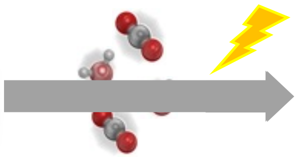
Twelve's platform technology for CO_2 conversion could increase profitability across the bioenergy sector

Overview – The Twelve Platform

Core Technology: *Uniquely formulated membrane-electrode assembly (MEA) converts a water electrolyzer stack into a CO_2 electrolyzer*

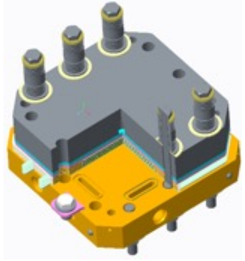
Phase I
Catalyst
Development
FY18-FY20

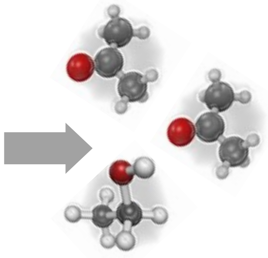




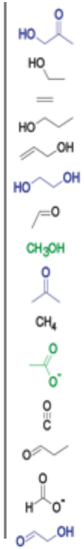
$CO_2 + H_2O$

MEA electrolyzer stack





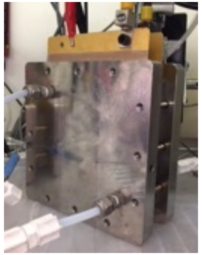
16 compounds demonstrated to date



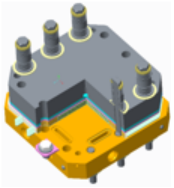
A clear path to large scale deployment

Phase II
Catalyst
Scale Up
FY21-FY22

25cm²



100cm²



Stack of 100 cm²

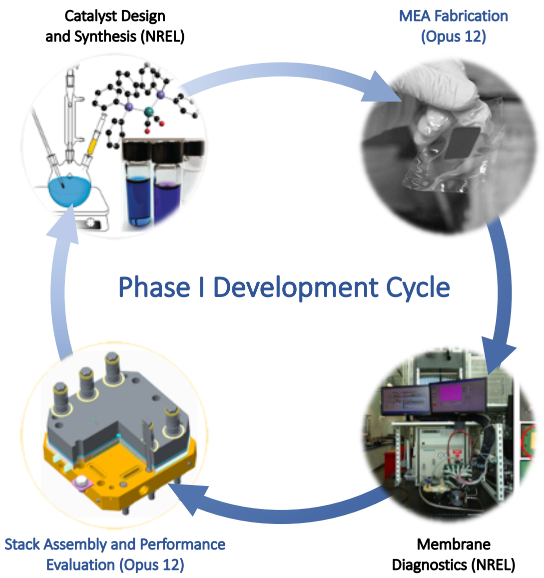
5 kW CO_2 Electrolyzer

Scale up to MW systems

Project Overview– Phase I Approach

Challenges with commercially available technology *addressed in Phase I*

- ***Poor uniformity and large size*** of commercial catalyst particles limits metal utilization
- ***Low loading*** of commercial catalyst requires additional MEAs to reach performance targets
- ***Defect detection*** in MEAs is critical for stack operation and non-trivia

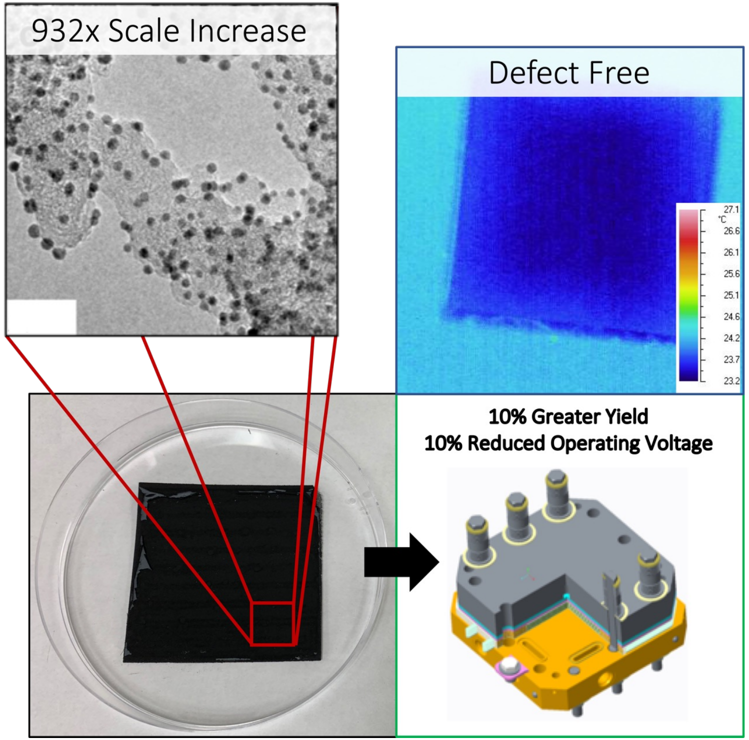


Approach – Phase I (FY18-FY22)

- **Developed synthetic platform** to optimize and evaluate material candidates that meet the physical properties identified by Twelve
- **Optimized supporting methodologies** to increase catalyst loading without reducing lifetime due to sintering
- **Determination of best practices** for MEA diagnostics
- Link synthesis, fabrication, diagnostic, and catalytic testing to **develop structure-performance** relationships to accelerate material discovery

Technical approach applied unique consortia capabilities to industry specified needs

Project Overview – Phase I Outcomes



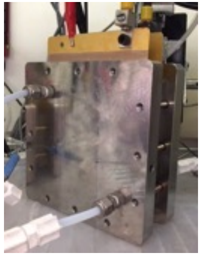
- ***Developed synthetic methods*** to prepare quantities of nanoparticle with physical properties specified by *Twelve* in quantities suitable to fabricate >3 25cm^2 MEAs
- ***Developed effective supporting methodologies*** to retain particle size and morphology at increased loadings
- ***Performance feedback*** enabled the preparation of catalysts with *higher performance than commercially available analogues*
  - *23% lower current efficiency decay rate*
  - *6.2% lower operating voltage at 500 mA/cm^2*
  - *>12%* CO current efficiency compared to gen. 1

Phase I established technical basis for incorporating nanocatalysts into Twelve's MEA platform

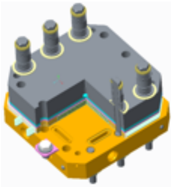
1 –Approach to Phase II: Challenge of Scale

Scaling to 100 cm² MEAs and beyond requires further scaling of synthetic methods beyond existing batch methods

25cm²



100cm²



Stack of 100 cm²

5 kW CO_2 Electrolyzer

Scale up to
MW systems

Translating from batch methods to millifluidics can offer higher throughput without impacting physical properties

- Increased concentration to ***reduce solvent use***
- Reduced reaction time to ***increase throughput***
- Inline supporting for ***controlled NP anchoring***

Inability to produce catalyst at scales commensurate with electrolyzer scale-up poses a significant commercialization risk

1 – Approach: Integrated Synthesis, Characterization, Evaluation

Project is the second phase of a directed funding partnership between NREL and Twelve

ChemCatBio DFO with Twelve

NREL: Task 1	Twelve: Task 2
Synthesis and Design	**MEA Assembly and Testing**
• Synthesis and characterization of metal nanoparticle (NP) catalysts • NP scale-up methodology development • NP supporting procedure development	• Determination of material and physical property requirements • Membrane electrode assembly (MEA) fabrication • MEA performance testing

- ***Monthly meetings*** between tasks to ensure efforts remain relevant to industrial partner and adapt to changes in needs
- ***Proprietary samples tracked and isolated*** to prevent information leakage
- Data transmitted only through ***DataHub and FedRAMP compliant services***

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ChemCatBio Interfaces

Enabling Technologies

CatCost (2.6.3.500)

ACSC (2.5.4.304)

- Synthesis and characterization support
- Estimation of manufacturing costs
- Estimation of materials costs

1 – Approach: Research Plan

Phase I – Catalyst Development & Membrane QC

Phase II – Catalyst Scale-up and large-scale evaluation

- **FY18:** 900x scaled synthesis of NPs developed
- **FY19:** Membrane diagnostics established
- **FY20:** Demonstration of catalyst dev cycle
- **FY21:** Develop mF platform for continuous synthesis
- **FY22:** Assess mF reactor designs & catalyst performance
- **FY25:** Demo integrated mF synthesis for large-scale MEA

Peer Review FY21 Focus

Current Progress & Outcomes

Phase I – Designing a Better Catalyst

- *Developed synthetic methods* to prepare quantities of nanoparticle with physical properties specified by Twelve in quantities suitable to fabricate 25cm^2 MEAs
- *Developed effective supporting methodologies* to retain particle size and morphology at increased loadings
- *Performance feedback* enabled the preparation of catalysts with *higher performance than commercially available analogues; (slower FE decay; lower operating voltage; greater CO FE compared to gen. 1)*

Phase II – Development of Scalable Methods

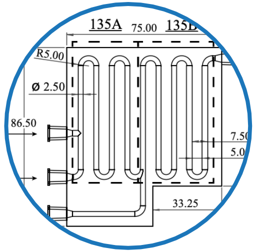
- *Design and fabricate mF reactors* utilizing rapid, additive-manufacturing techniques
- Developed approach for NP *synthesis in continuous flow* while maintaining critical properties of Phase I materials
- *Evaluated impact of mF reactor* on catalyst properties and synthesis throughput
- *Demonstrated end-to-end process* for NP synthesis, supporting, MEA fabrication, and performance evaluation

1 – Approach: Coupled Rapid Prototyping with MEA Evaluation

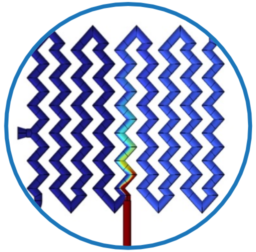
NREL

Catalyst Design (Phase I)

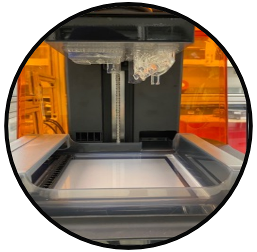
targets



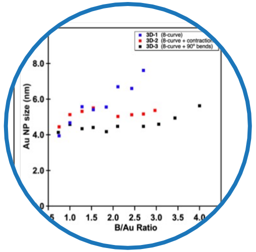
mF Reactor Design



Computational Modeling



mF Reactor Fabrication



Synthetic Evaluation

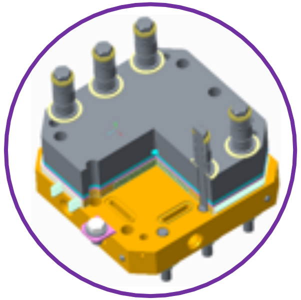
Rapid feedback and frequent iteration to mitigate scale-up risks

Materials

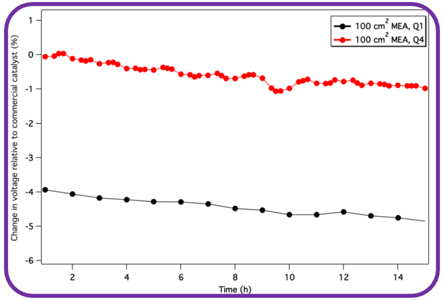
Performance feedback

Twelve

MEA Fabrication



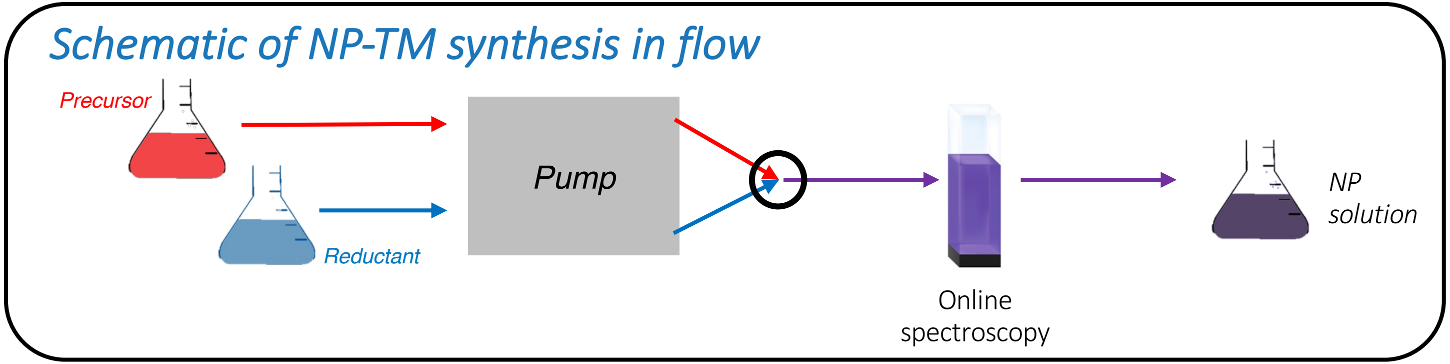
System Integration



Performance Evaluation

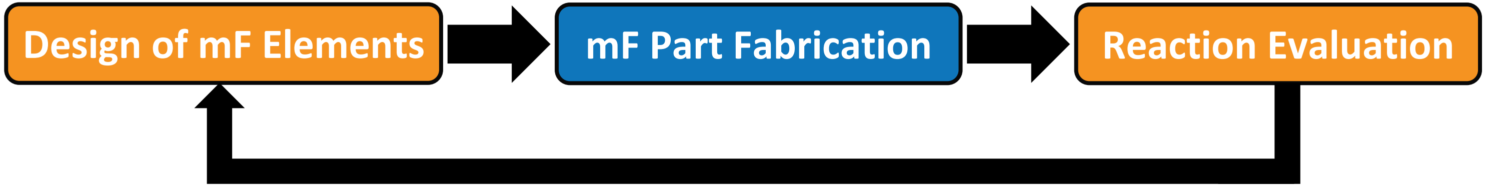
2 – Progress: Designing an Open-Source Synthetic Platform

Target: ***Design continuous flow approach for high-throughput catalyst synthesis***



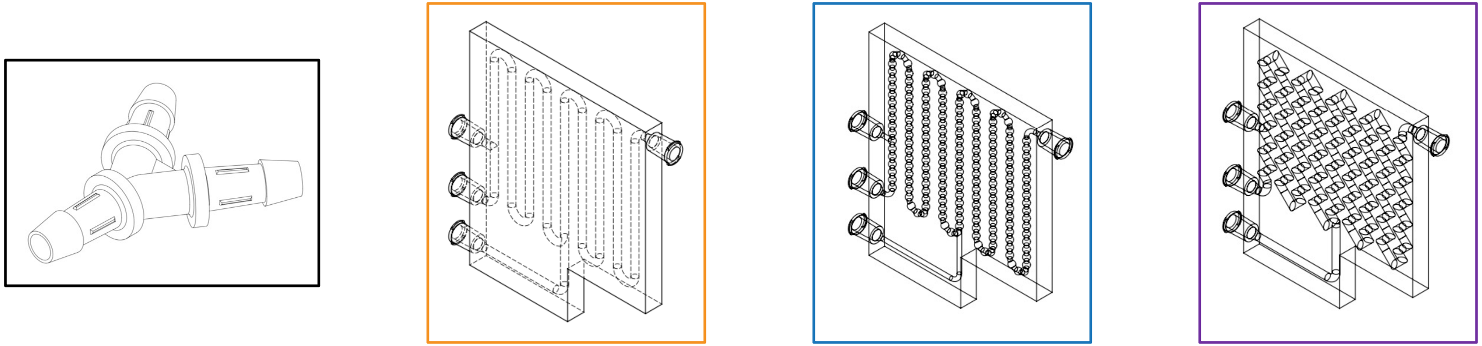
Challenge: ***Translating from batch methods to high-throughput methods needs to maintain critical catalyst physical properties (i.e., shape, size, performance)***

Approach: ***Prototyping of mF elements with SLA 3D printing to rapidly assess performance and viability***

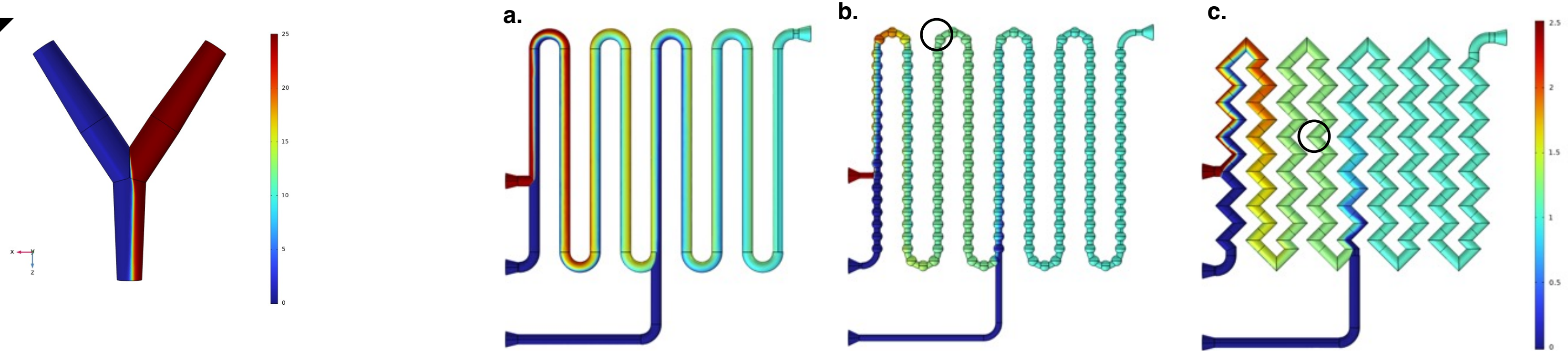


2 – Progress: mF Reactor Design

Drafted mF mixers in CAD software informed by literature with diverse internal architectures



Utilized COMSOL to model concentration profiles and identify high-performance mixer geometries



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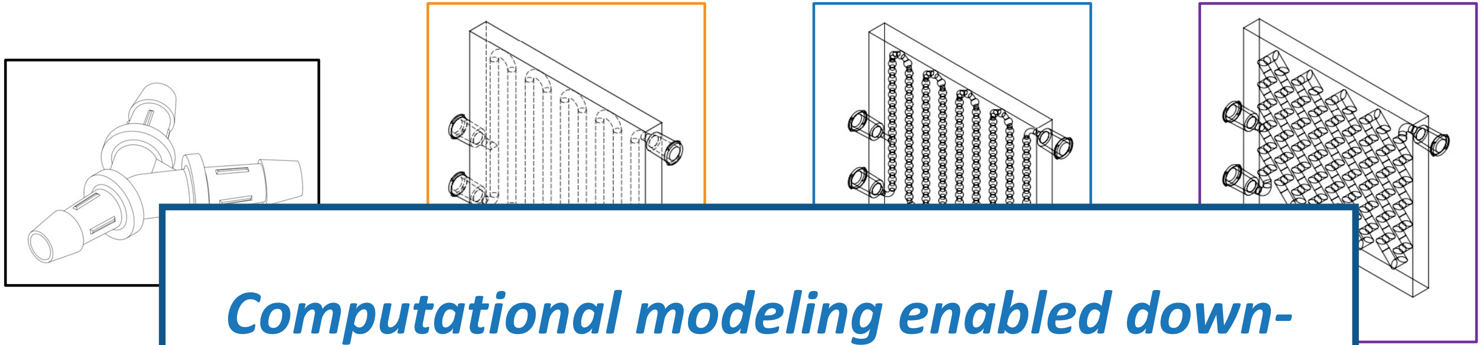
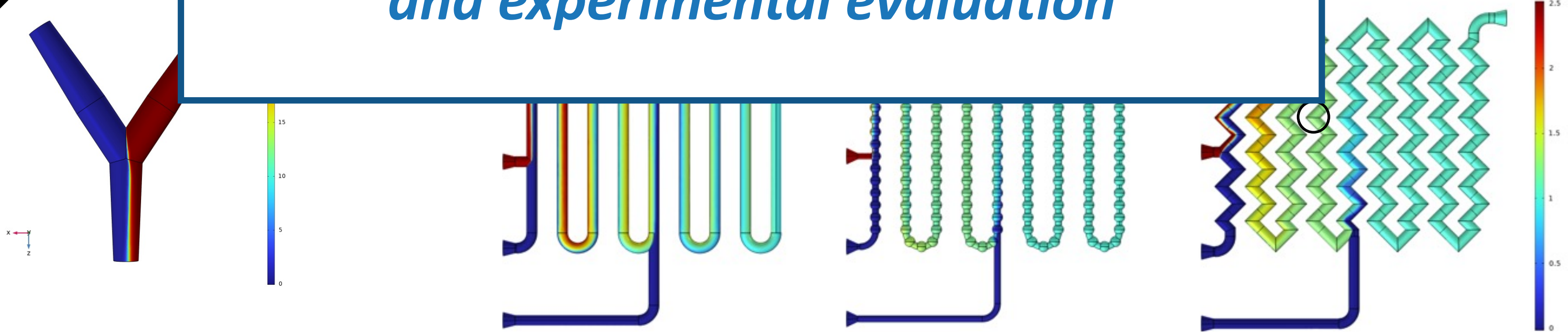


Utilized C ... *mixer geometries*

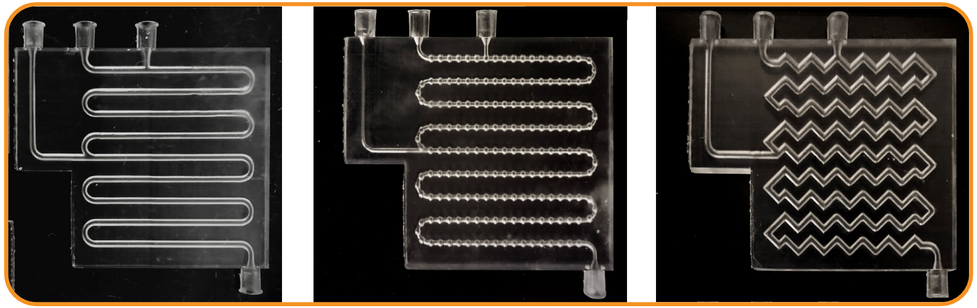


Computational modeling enabled down-selection of reactor designs for fabrication and experimental evaluation

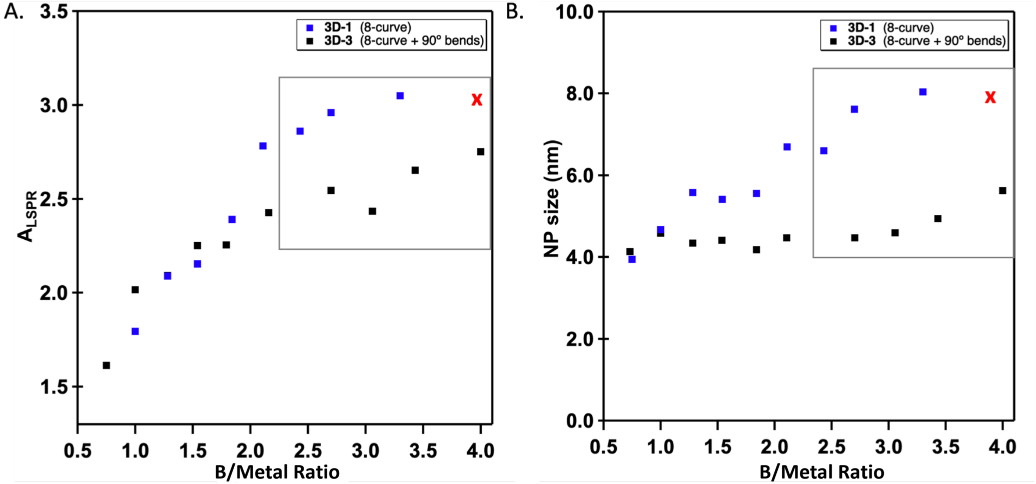
2 – Progress: Experimental mF Reactor Evaluation

3D Print

Process



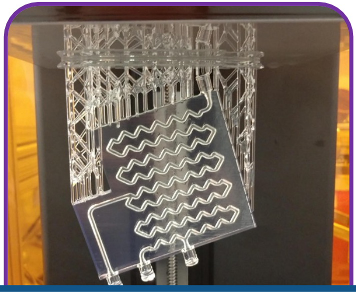
Evaluate

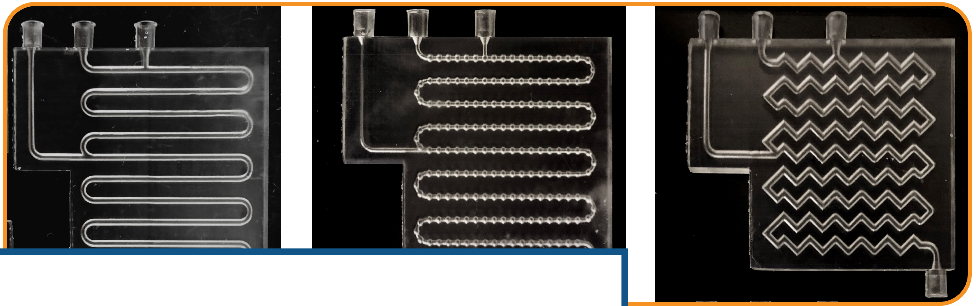


- Nodal mixer eliminated due to ***reproducibility challenges***
- 90º mixer produced ***smaller particles @ higher concentrations***

2 – Progress: Experimental mF Reactor Evaluation

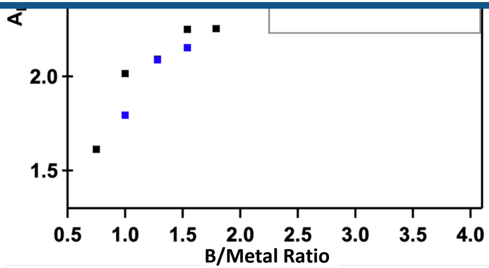
3D Print

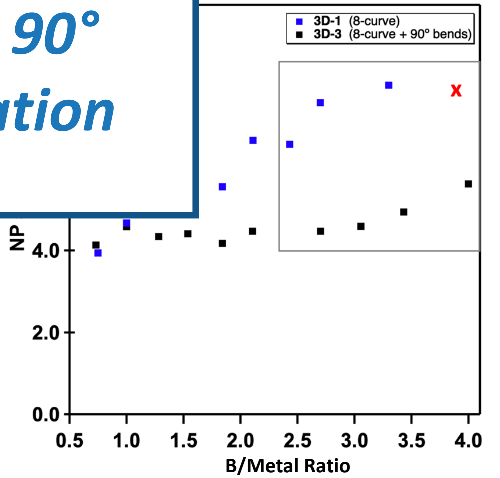




- Nodal mixer eli
reproducibility

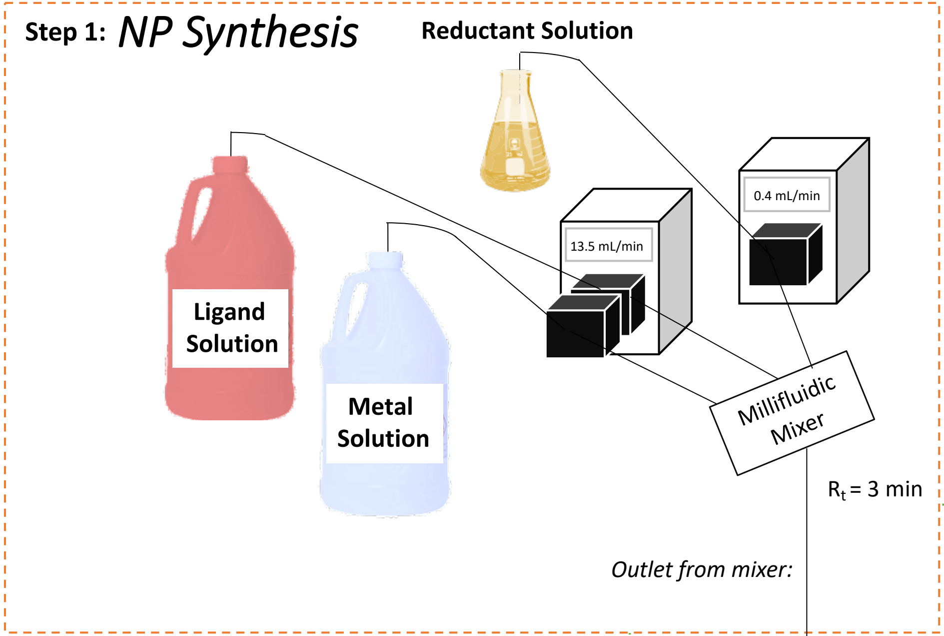
- 90º mixer produced ***smaller particles @ higher concentrations***

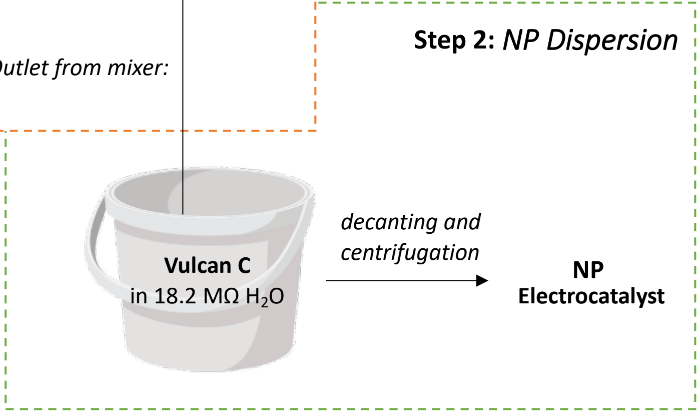


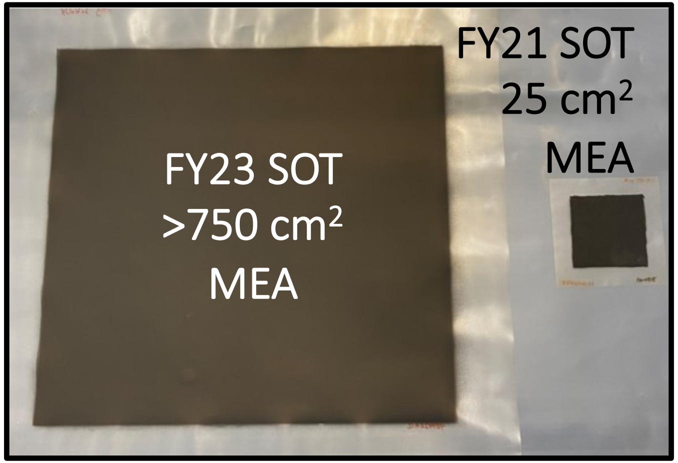


Computational modeling results consistent with experimental evaluation and 90° mixer selected for process optimization

2 – Progress: Integrated Testing

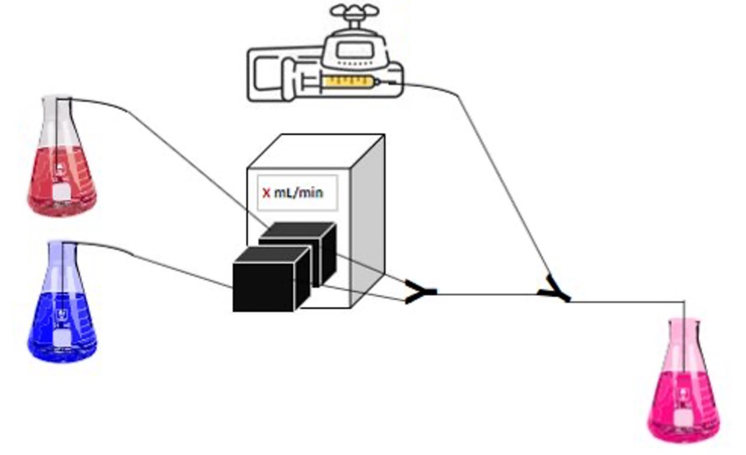




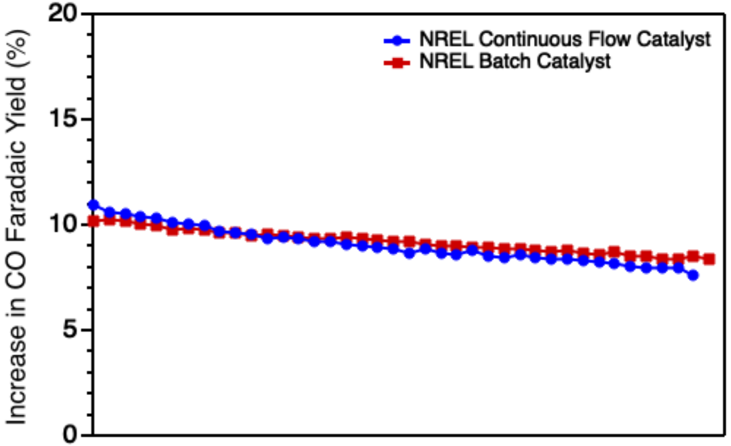


- *Reduced supporting time* from 71 h to 22 h
- *6.6-fold increase in throughput*

2 – Progress: Performance Results



Catalyst	Millifluidic mixing element	NP throughput (mg h^{-1})	Supporting duration (h)
Y-NP/C	Y-junction	54	70 h
⊿-NP/C	Right-angle	**357**	**21.5 h**



- NP catalysts prepared by continuous flow were **successfully integrated into 100 cm^2 MEAs**
- Faradaic efficiency was ***near parity with batch*** prepared catalysts
- ***6.6–fold increase in throughput***
- ***Maintained particle size*** and dispersity control
- ***Reduced supporting time*** from 71 h to 22 h

3 – Impact

Unique capabilities within ChemCatBio enabled fundamental evaluation of commercially relevant catalysts

"Through this project, Twelve was able to explore the effect of carbon-supported metal catalyst size and loading on CO_2 electroreduction performance. Catalysts synthesized and tested through the project are not commercially available, so exploring these effects would have been difficult if not for the support of ChemCatBio…" – *Twelve*

Direct industrial partnership leads to clear commercialization potential of jointly developed technologies

- Target metrics, materials, and scales directly address barriers to commercialization
- Transitioning from Phase I (catalyst development) to Phase II (materials scale-up) demonstrates continued industrial interest

3 – Impact: Improving the economic viability of the electrolyzer stack & Reducing Scale-Up Risk

Development of advanced synthetic methods

- Precious metal cathode catalyst is a ***major cost contributor*** to electrolyzer fabrication
- Increasing uniformity and decreasing size ***reduces MEA cost***
- Smaller particles may enable higher loading ***minimizing MEAs required per stack***

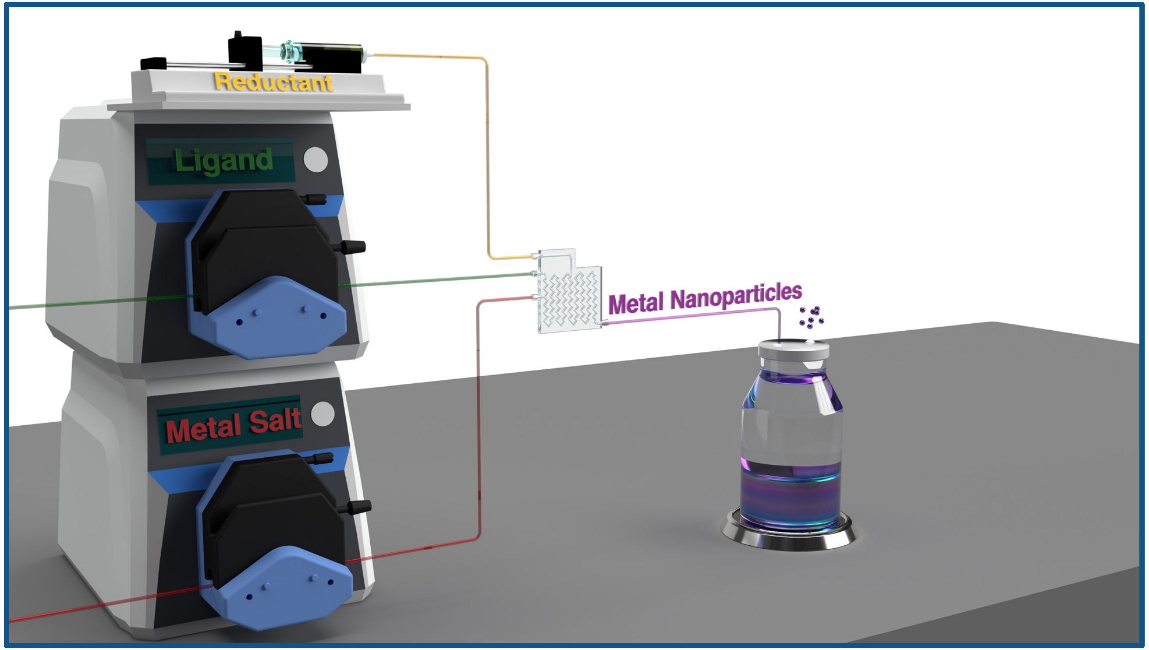
Electrocatalyst Scale-up and Manufacturing

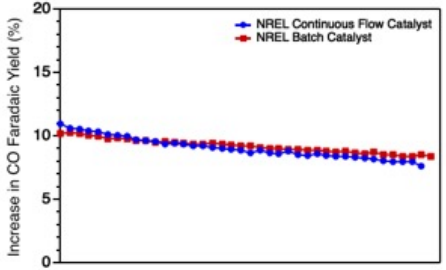
- Near-term electrolyzer scale-up targets require significant catalyst scale-up
- Inability do satisfy catalyst demand ***poses significant deployment risk***
- Development of ***material agnostic scale-up*** methods reduces risk as catalyst needs change

Achievement of Phase I performance metrics led to continued partner engagement and follow-on funding for scale-up activities in Phase II

"…The increased performance of CO_2 electroreduction with new catalysts demonstrates the potential for further improvement with more work in this area and Twelve plans to dedicate more resources to catalyst development in the future as a result of the project." – *Twelve*

Summary





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- ***Increased scale*** of nanocatalyst synthesis to > 7.5 g particles (30 g catalyst) per day in a single channel
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- ***Facilitated performance testing*** of MEAs at >750 cm^2 compared to previous 25 cm^2 (40x scale up)

Quad Chart Overview

Timeline

- *Project Start: 10/1/2020 (FY21)*
- *Project End: 09/30/2022 (FY22)*
- *Status: CLOSED*

	FY22 Costed	Total Award FY21-FY22
DOE Funding	*(10/01/2021 – 9/30/2022)* $204,638	$375k
Project Cost Share	$86k	$86k

TRL at Project Start: 3
TRL at Project End: 4

Project Goal

The primary goal of this project is to implement stereolithographic (SLA) 3D printing to rapidly prototype advanced millifluidics (mF) elements to develop a versatile mF synthesis platform for the preparation of nanostructured CO_2 electroreduction catalysts at throughputs greater than 10 g per day. This production capability will enable the systematic evaluation of catalyst properties and ink preparations for MEAs on the scale of 600 – 1500 cm^2.

End of Project Milestone

Design a high-throughput millifluidic system capable of producing ≥ 10/g day of carbon-supported NP catalysts and demonstrate their incorporation into a large-scale MEA system (> 600 cm^2) compared to the 25 cm^2 MEAs fabricated and evaluated in FY21. *Twelve* will fabricate large-scale MEAs with the material supplied in Q3 and evaluate the impact of synthesis reactor geometry optimization on performance and longevity of the prepared catalysts. This final catalyst synthesis/performance feedback loop of the fully realized high-throughput system will serve as the basis for a feasibility assessment of an integrated continuous flow NP-TM/C catalysts synthesis and adsorption methodology for supporting commercial MEA fabrication.

Funding Mechanism

FY21 ChemCatBio Directed Funding Opportunity

Project Partners

- **Twelve**

This research was supported by the DOE Bioenergy Technology Office under Contract no. DE-AC36-08-GO28308 with the National Renewable Energy Laboratory

This work was performed in collaboration with the Chemical Catalysis for Bioenergy Consortium (ChemCatBio, CCB), a member of the Energy Materials Network (EMN)

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- Sichao Ma

NREL NATIONAL RENEWABLE ENERGY LABORATORY

twelve

ChemCatBio Chemical Catalysis for Bioenergy

Energy Materials Network U.S. Department of Energy

Twelve/NREL DFO: Informed by 2021 Peer Review

"CO_2 electrolysis to products is a tall order, with many hurdles. This project attacks one of the key problems of resistance of the cell, often due to poor electrode structure and performance. "

- ➢ We agree with the reviewer and hope to address additional hurdles through the development of catalyst scale-up methodologies

"Overall, the project management is very good, with appropriate feed forward/feedback of information to facilitate iterative development.

- ➢ We have sought to maintain this level of organization within Phase II when implementing a feedback loop for continuous flow synthesis and catalyst evaluation

"The use of 3D printing, where appropriate, could help reduce fabrication costs."

- ➢ This is aligned well with FY21–FY22 efforts that included the development 3D printing methodologies for rapidly prototyping and evaluating millifluidic reactor designs for high-throughput synthesis

Publications, Patents, Presentations, Awards, and Commercialization

Publications

- B. E. Petel, K. M. Van Allsburg, F. G. Baddour, "Cost-Responsive Optimization of Nickel Nanoparticle Synthesis" Advanced Sustainable Systems, **2023**, *accepted*.
- B. E. Petel, A. Yung, Y. Wu, Z. Huo, S. E. Habas, F. G. Baddour "Design and Optimization of a High-Throughput Millifluidic Reactor System for Nanoparticles with Morphology Control for CO_2 Electrolysis" **2023**, *in prep.*

Presentations

- F. G. Baddour, FY21 BETO Project Peer Review, **March 2021**, Virtual Meeting.
- F. G. Baddour, FY19 BETO Project Peer Review, **March 2019**, Denver, CO.

Patents

- Fluidic Systems and Methods for the Manufacture of Nanoparticles, Application No. 63/313,011
- Fluidic Systems and Methods for the Manufacture of Nanoparticles, Application No. 18/173,317 February 2023