ChemCatBio
Chemical Catalysis for Bioenergy

BETO 2021 Peer Review

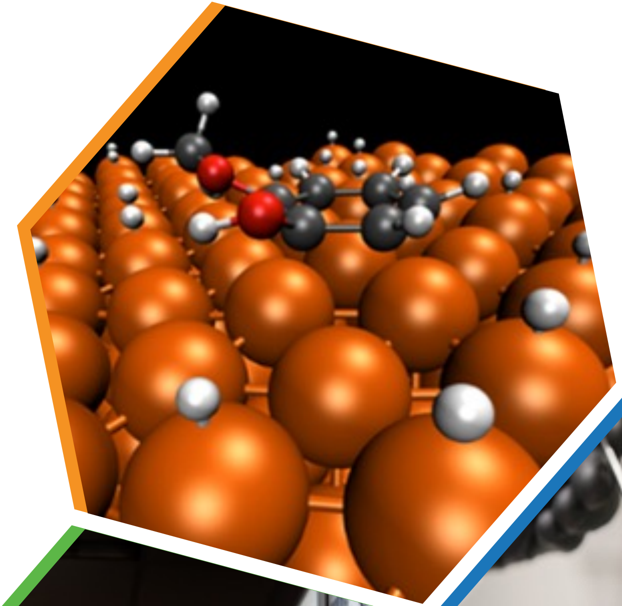
ChemCatBio DFA with Opus 12

Catalyst Development for Selective Electrochemical Reduction of CO_2 to High-value Chemical Precursors

WBS # 2.5.4.707

Frederick Baddour

3/11/2021



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BIOENERGY TECHNOLOGIES OFFICE

Project Overview

Project Goal: To ***enable the scalable synthesis and reactor integration*** of high-performance metal nanoparticle catalysts for deployment in commercial electrocatalytic CO_2 reduction applications

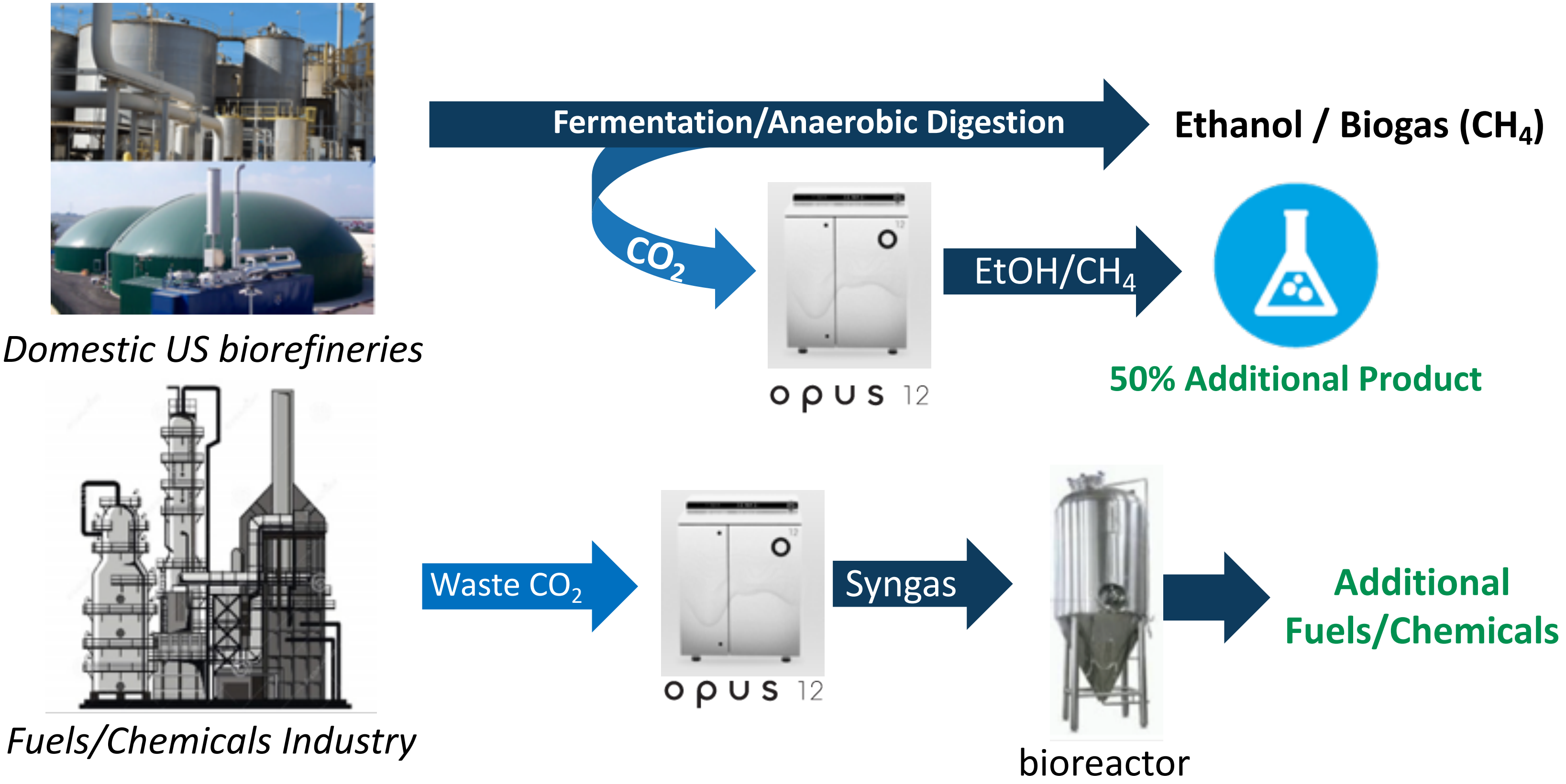
Approach: To couple unique national lab ***synthesis, characterization, and diagnostic expertise with industrial device fabrication and catalytic evaluation*** to accelerate the commercialization of tunable, industrial-scale CO_2 electrolyzers

Research Progress & Outcomes

- Stabilized ***higher catalyst loadings*** than commercially available analogues
- ***Increased scale*** of nanocatalyst synthesis by over 900x compared to published reports
- ***Increased stability*** of catalysts relative to commercial analogues (23% slower current decay rate)
- ***Increased current efficiency*** to CO by 12% compared to baseline catalyst

Impact: Demonstrated performance improvements at the 25 cm^2 membrane scale and competed follow-on funding to scale this technology to the ≥ 100 cm^2 scale

Overview – Revenue from Waste



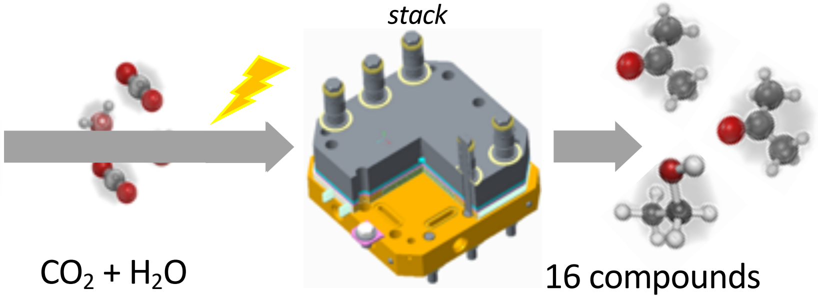
Opus 12's platform technology for CO_2 conversion could increase profitability across the bioenergy sector

Overview – The Opus 12 Platform

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

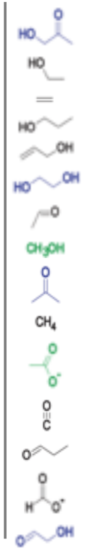
Phase I
Catalyst
Development

MEA electrolyzer stack



$CO_2 + H_2O$

16 compounds demonstrated to date

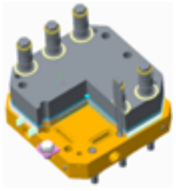


A clear path to large scale deployment

Phase II
Catalyst
Scale Up

$25 cm^2$

$100 cm^2$



Stack of $100 cm^2$

5 kW CO_2 Electrolyzer

Scale up to MW systems

Market Trends

Product
- Anticipated decrease in gasoline/ethanol demand; diesel demand steady
- Increasing demand for aviation and marine fuel
- Demand for higher-performance products
- Increasing demand for renewable/recyclable materials

Feedstock
- Sustained low oil prices
- Decreasing cost of renewable electricity
- Sustainable waste management
- Expanding availability of green H_2
- Closing the carbon cycle

Capital
- Risk of greenfield investments
- Challenges and costs of biorefinery start-up
- Availability of depreciated and underutilized capital equipment

Social Responsibility
- Carbon intensity reduction
- Access to clean air and water
- Environmental equity

NREL's Bioenergy Program Is Enabling a Sustainable Energy Future by Responding to Key Market Needs

Value Proposition

Reduce the time to commercial deployment of cost-effective CO_2 electrolysis systems can by applying the ***unique synthesis, characterization, and membrane diagnostics capabilities*** of the ChemCatBio consortium to industrial materials and scaling challenges.

Key Differentiators

- Comprehensive access to in-house synthesis expertise, state-of-the-art membrane diagnostics, and scale-up infrastructure
- Opus 12's industry leading CO_2 electrolysis testing platform

1 – Management: ChemCatBio Foundation – FY21

Integrated and collaborative portfolio of catalytic technologies and enabling capabilities

Catalytic Technologies

- **Catalytic Upgrading of Biochemical Intermediates** (NREL, PNNL, ORNL, LANL)
- **Upgrading of C1 Building Blocks** (NREL)
- **Upgrading of C2 Intermediates** (PNNL, ORNL)
- **Catalytic Fast Pyrolysis** (NREL, PNNL)
- **Electrocatalytic CO_2 Utilization** (NREL)

Enabling Capabilities

- **Advanced Catalyst Synthesis and Characterization** (NREL, ANL, ORNL)
- **Consortium for Computational Physics and Chemistry** (ORNL, NREL, PNNL, ANL, NETL)
- **Catalyst Deactivation Mitigation for Biomass Conversion** (PNNL)

Industry Partnerships

Phase II

Directed Funding

- **Opus12** (NREL)
- **Sironix** (LANL)
- **Visolis** (PNNL)

Cross-Cutting Support

- **ChemCatBio Lead Team Support** (NREL)
- **ChemCatBio DataHUB** (NREL)

1 – Management: Highly Integrated Approach

Project is a two-phase directed funding partnership between NREL and Opus 12

ChemCatBio DFA with Opus 12

NREL: Task 1	Opus 12: Task 2	NREL: Task 3
Synthesis and Design	**MEA Assembly and Testing**	**PEM Diagnostic 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	• Development of membrane diagnostics techniques • Modification of diagnostics tools for CO_2 electrolyzer MEAs • Membrane quality 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***

1 – Management: Highly Integrated Approach

Project is a two-phase directed funding partnership between NREL and Opus 12

ChemCatBio DFA with Opus 12

NREL: Task 1

Synthesis and Design

- Synthesis and characterization of metal nanoparticle (NP) catalysts
- NP scale-up methodology development
- NP supporting procedure development

Opus 12: Task 2

MEA Assembly and Testing

- Determination of material and physical property requirements
- Membrane electrode assembly (MEA) fabrication
- MEA performance testing

NREL: Task 3

PEM Diagnostic Testing

- Development of membrane diagnostics techniques
- Modification of diagnostics tools for CO_2 electrolyzer MEAs
- Membrane quality testing

ChemCatBio Interfaces

Enabling Technologies

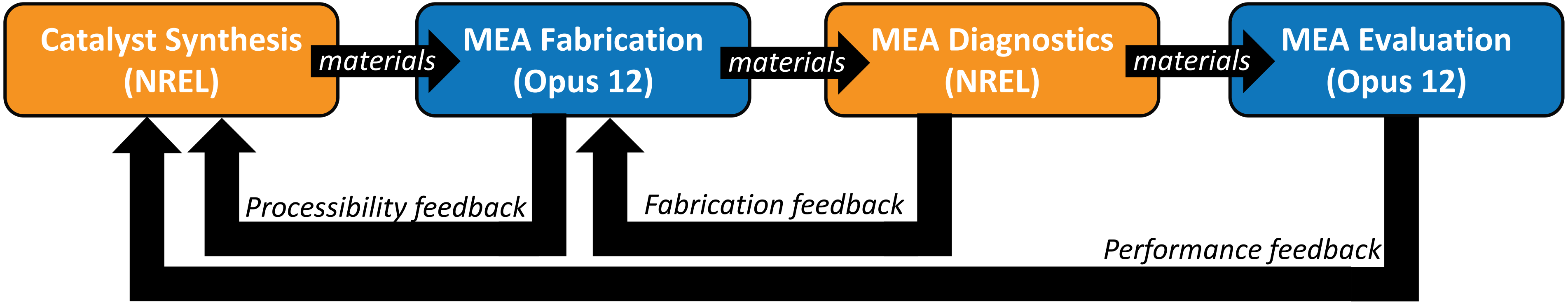
CatCost (2.6.3.500)

ACSC (2.5.4.304)

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

1 – Management

Highly collaborative, multi-component approach to accelerate catalyst design



Rapid feedback and frequent iteration to mitigate risks

- ***Processibility feedback*** to determine optimal support identity and surface chemistry
- ***Fabrication feedback*** to ensure catalyst and membrane fabrication are defect free
- ***Performance feedback*** to inform next-generation catalyst targets and develop fundamental understanding of structure-performance relationships

2 – *Phase I* Approach: Coupling unique capabilities to industrial expertise

Fundamental Research Challenges

New Cathode Catalyst Development

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

- Novel materials synthesis
- Characterization (e.g., TEM, SEM, XRD, XRF)
- Supporting methodologies
- Surface treatment methodologies
- Scalable-synthesis
- Advanced diagnostics

Advanced materials,
Fundamental understanding

Performance Feedback
Processing Requirements

Applied Research and Industrial Deployment

Reactor Integration and Catalytic Evaluation

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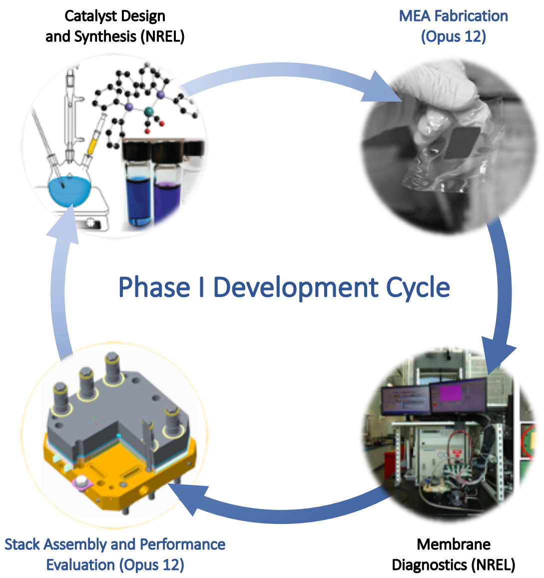
- Ink preparation
- MEA incorporation strategies
- Performance evaluation
- Lifetime evaluation

Coupling unique synthesis and characterization capabilities with industrial system fabrication and evaluation expertise to accelerate commercial deployment

2 – *Phase I* Approach

Challenges with commercially available technology:

- ***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

- ***Development of synthetic platform*** to optimize and evaluate material candidates that meet the physical properties identified by Opus 12
- ***Optimize 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

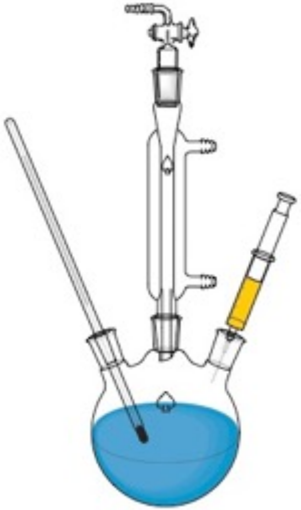
Technical approach applies unique consortia capabilities to industry specified needs

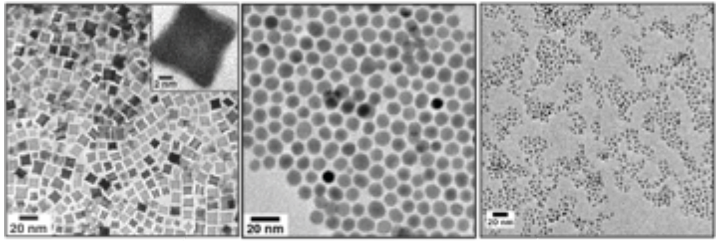
2 – *Phase I* Approach: Applying Advanced Synthesis

Challenges with commercially available technology:

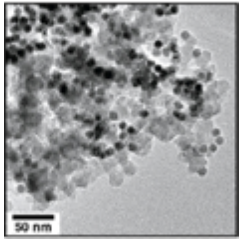
- ***Poor uniformity and large size*** *of commercial catalyst particles limits metal utilization*
- ***Low loading*** *of commercial catalyst requires additional MEAs to reach performance targets*
- ***Defect detection*** *in MEAs is critical for stack operation and non-trivia*

Advanced routes to controlled nanostructured materials





Excellent uniformity and small size *compared to commercial catalyst particles*



Support agnostic and high loading compatible

Phase I Target Metrics

- 10% reduction in overpotential
- 10% higher current density to target products compared to commercial analogue

3 – Impact: Improving the economic viability of the electrolyzer stack

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***

Membrane diagnostics development

- Membrane integrity and reproducibility in manufacturing is critical in electrolyzer commercialization
- Provides ***immediate feedback*** on commercial membrane fabrication methods
- Provides ***insight into failure*** modes and degradation during operation

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 Opus 12 plans to dedicate more resources to catalyst development in the future as a result of the project." – *Opus 12*

3 – Impact

Unique capabilities within ChemCatBio enabled fundamental evaluation of commercially relevant catalysts

"Through this project, Opus 12 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…" *– Opus 12*

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

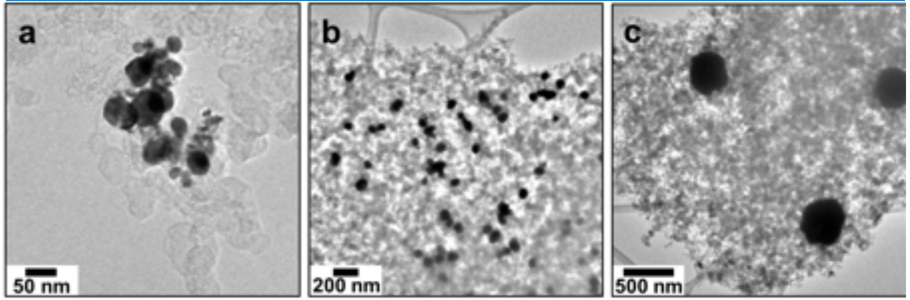
4 – Technical Accomplishments: Catalyst Development

Task 1
Catalyst Development

Target: *More uniform and smaller catalyst NPs*

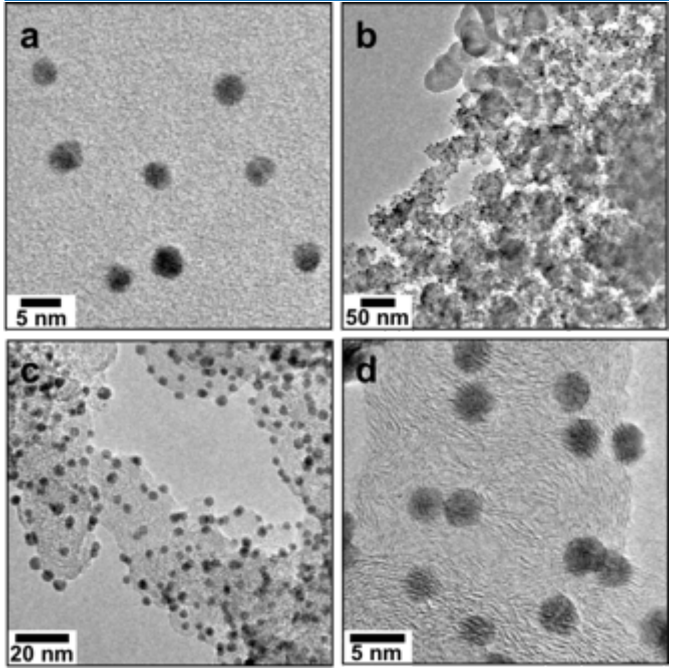
Evaluated state-of-the-art synthesis methodologies for materials of interest

Incipient Wetness Impregnation



vs.

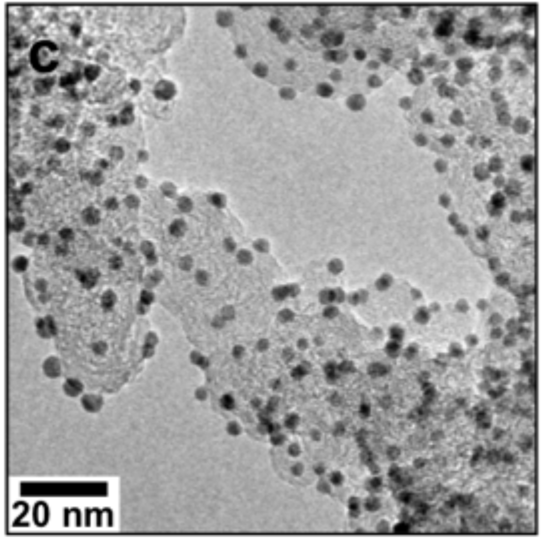
Aqueous Solution Synthesis



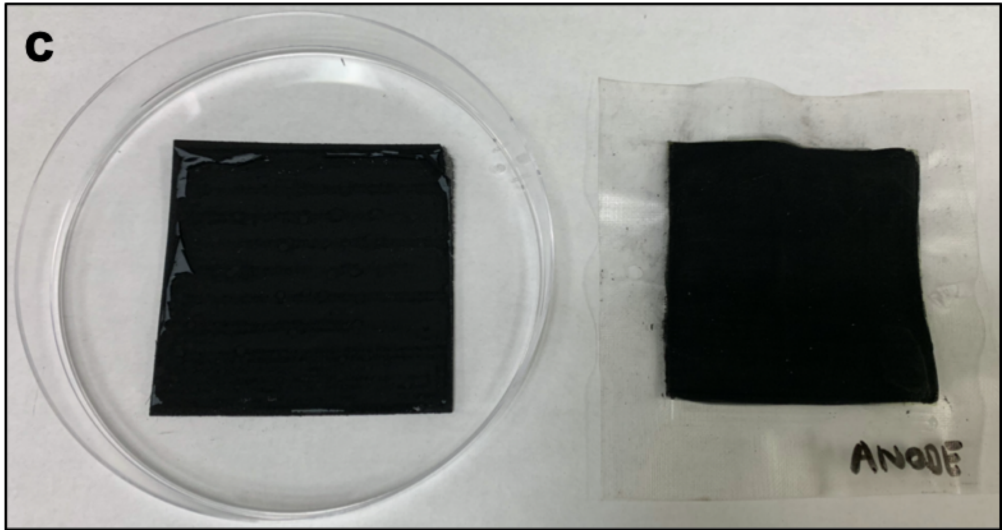
- Solution-based route met size and morphology requirements set by Opus 12
  - Particles < 25 nm
- Highly amenable to supporting on identified carbon support
  - Loadings > 10 wt%

***Target:* Scaled synthesis for membrane fabrication**

Carbon-supported particles



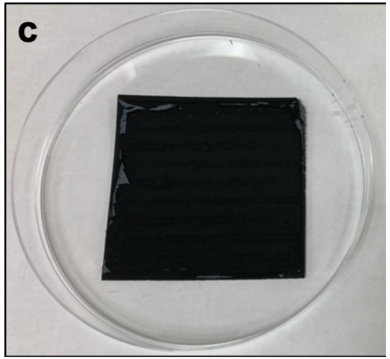
Catalysts successfully incorporated into MEAs

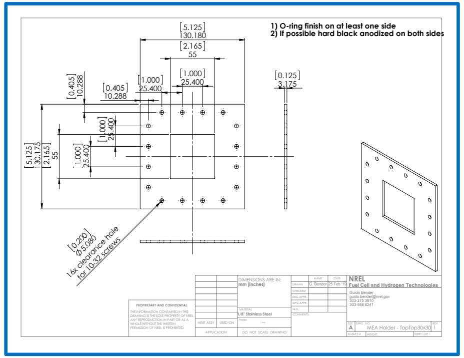


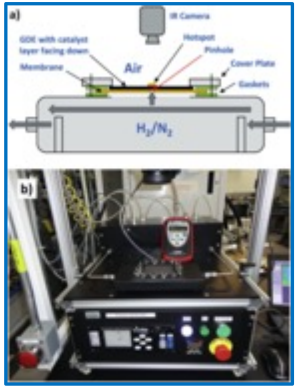
- Solution-based route ***scaled 932-fold*** while maintaining required morphology
- Opus 12 successfully fabricated MEAs with NREL catalysts

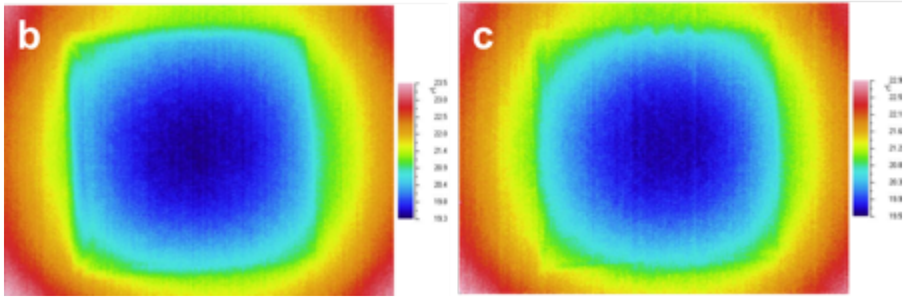
Target: ***Assessment of membrane integrity***

Designed assembly to test Opus 12 MEAs using pinhole detection apparatus (PDA)









Prepared membranes were determined to be ***free of pinhole defects***

4 – Technical Accomplishments: Performance Evaluation

Task 2
MEA Evaluation

Target: Performance evaluation of Generation 1 Catalysts

All values relative to baseline commercial catalyst @160mA/cm^2

Catalyst Description	Prod. Current Efficiency (%)	Prod. Current Efficiency Change (%/hr)	Voltage (V)	Voltage Decay (mV/hr)
Commercial Baseline	–	–	–	–
Cat 1	-1.4%	450%	4%	-1080%
Cat 2 (oxidized)	1.7%	50%	-4%	120%
Cat 3 (oxidized)	1.5%	200%	-5%	420%

Material Requirements

↓

CatCost™

↓

Catalyst 2: ~2-fold improvement in current efficiency per USD

Performance feedback identified:

- ***Higher loading*** identified to improve current efficiency
- High rate of decay indicated need for ***improved supporting methodology***
- ***Oxidation to remove surfactants*** negatively impacted performance
- ***Doping by chemical reductant*** may influence stability

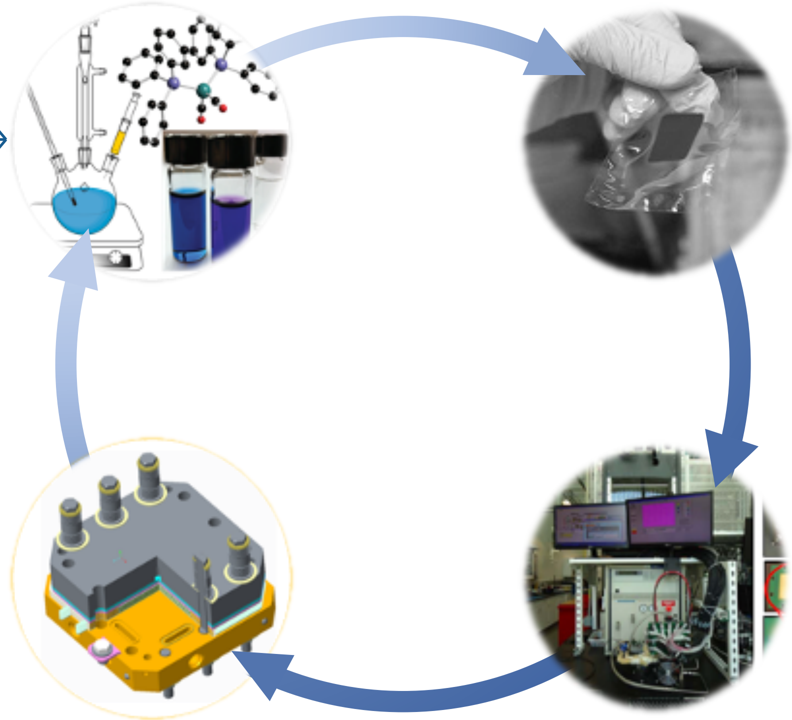
Catalytic evaluation of NREL MEAs delivered actionable insight to improve catalyst performance

4 – Technical Accomplishments: A Successful Development Cycle

- Synthesized higher catalyst with higher loading
- Synthesized material with excess $NaBH_4$ to assess doping
- Improved supporting procedure with high shear mixing

Catalyst Design and Synthesis (NREL)

MEA Fabrication (Opus 12)

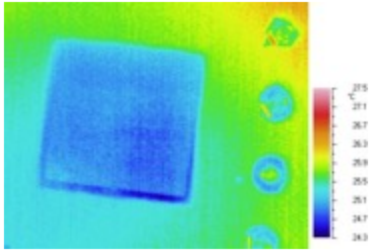


Stack Assembly and Performance Evaluation (Opus 12)

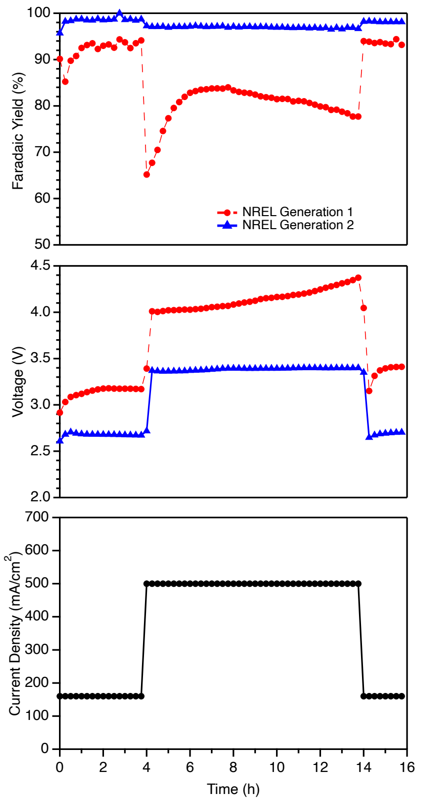
Membrane Diagnostics (NREL)

MEA fabrication not impacted by modifications

Remained defect free



4 – Technical Accomplishments: Performance Improvements



All values relative to baseline commercial catalyst @500 mA/cm²

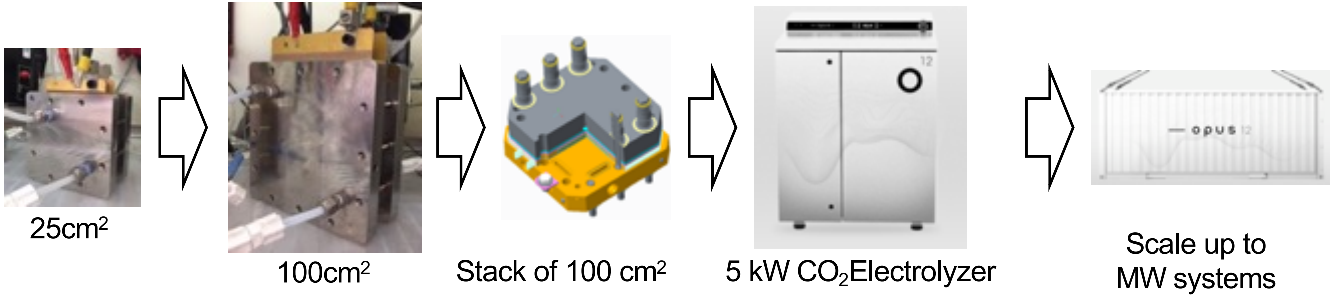
Catalyst	Prod. Current Efficiency (%)	Prod. Current Efficiency Decay (%/hr)	Voltage (V)	Voltage decay rate (%/hr)
Commercial Baseline	–	–	–	–
Gen. 2 – Short supp.	99%	209%	99.10%	124%
Gen. 2 – Long supp.	104%	77%	93.80%	96%

- Stabilized high wt% catalysts with improved supporting methodologies
- Generation 2 catalysts exhibited no degradation over 10h
- Operating voltage reduced by >16 %
- Faradaic efficiency to CO increased by >12 %

Catalyst development cycle resulted in rapid improvement of <u>catalyst performance in a commercial system</u>

3 – *Phase II* Approach: Challenge of Scale

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

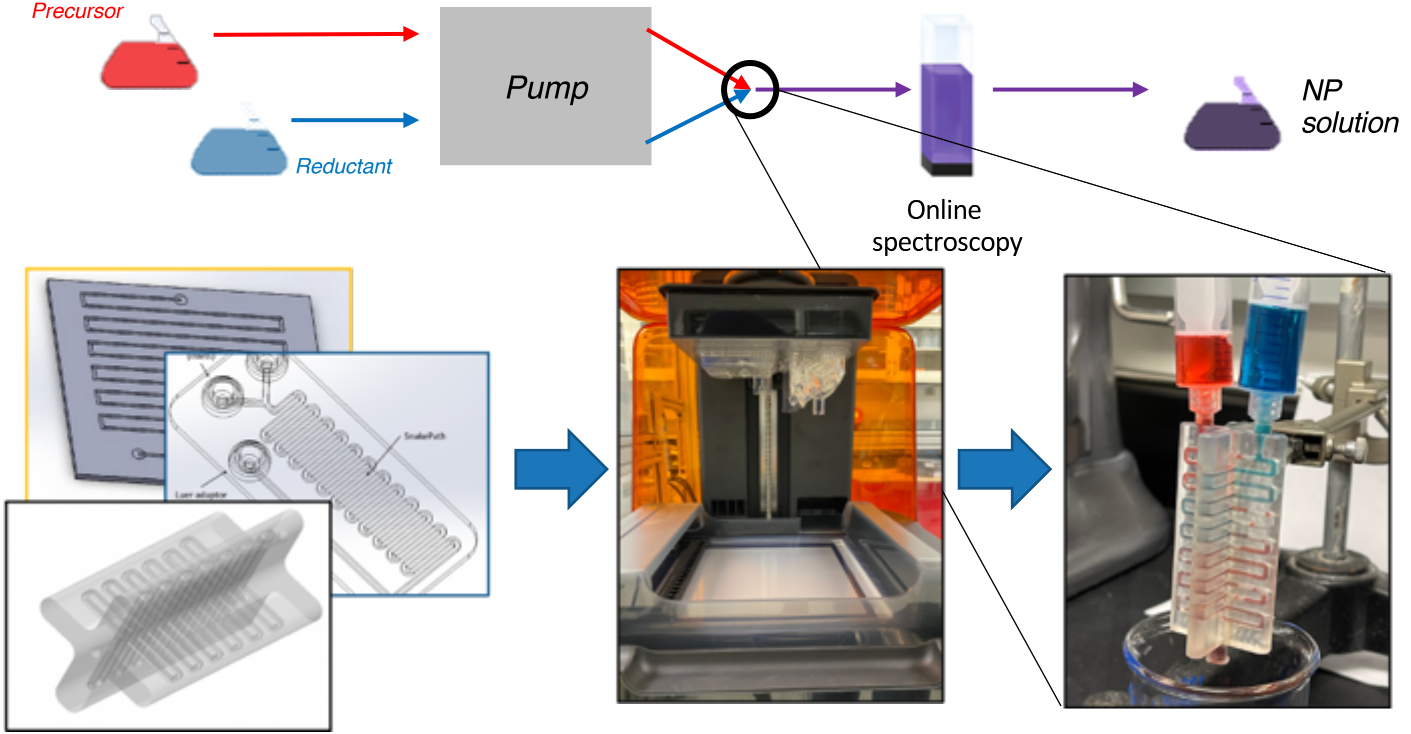


Translating from batch methods to millifluidics can offer higher throughput without impacting physical properties

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

3 – *Phase II* Approach: Designing an open-source synthetic platform

Rapid prototyping of mixing elements with SLA 3D printing to increase synthesis throughput



Design of millifluidic elements ***Part fabrication*** ***Reaction evaluation***

3 – Approach: Phase II Roadmap

FY 2021

Quarter 1
ID Critical Catalyst Elements
Synthesis Criteria (NREL)

Identify critical catalyst physical properties that must be faithfully reproduced and review continuous/semi-continuous methods for NP fabrication and survey existing technologies

Quarter 2
Develop
Synthesis Platform (NREL)

Develop synthetic platform and prepare suitable quantity of NPs to prepare 25 cm^2 MEAs for evaluation

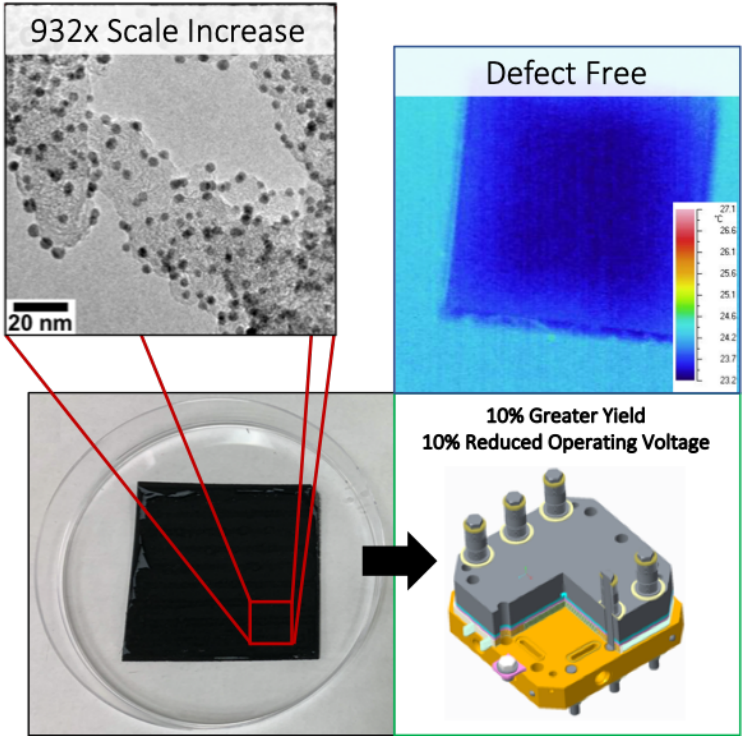
Quarter 3
Assembly of
MEAs and performance
evaluation (Opus 12)

Prepare baseline MEA using the catalysts synthesized using the methods developed in Q2

Quarter 4
Develop Continuous
Supporting Method
(NREL)

Develop continuous capability for adsorption and supporting of NPs onto a hydrophobic carbon surface

Summary



- ***Developed synthetic methods*** to prepare quantities of nanoparticle with physical properties specified by Opus 12 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 600 mA/cm^2*
  - *>12%* CO current efficiency compared to gen. 1

- Future efforts will focus on translating batch methods to flow for ***continuous synthesis and scale up***

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Opus 12

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ChemCatBio
Chemical Catalysis for Bioenergy

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BIOENERGY TECHNOLOGIES OFFICE

Quad Chart Overview

Timeline

- Phase I (January 1, 2018 – December 31, 2019)
- Phase II (October 1, 2020 – 9/30/2022)

	Total Costs Pre-FY20	FY20	Active Project
DOE Funding	$189k	$54k	Phase I – $250k (FY18-FY20) Phase II – $364k (FY21 – FY22)

Project Partners

- Opus 12, Inc. ($107k cost share FY18–FY20)

Barriers addressed

Ot-B. *Converting CO_2 waste streams (expenses) into desirable products (revenue)*

Ct-G. *Decreasing the time and cost to developing novel industrially relevant catalysts*

Project Goal

The goal of this project is to gain a fundamental understanding of the impact of metal nanoparticle and carbon support physical properties on electrochemical CO_2 reduction performance. This insight will enable the development of customizable reactors that can convert CO_2 with high selectivity to CO, CH_4, or C_{2+} products for the specific needs of customer segments within the biofuels and bio-products industry.

End of Project Milestone

The end of project goal is to *demonstrate a 10% reduction in overpotential and 10% higher partial current* to carbon-containing products compared to baseline MEAs with commercially available catalysts.

Funding Mechanism

FY18 ChemCatBio Directed Funding Opportunity

Additional Slides

Partner Statement at End of Phase I (FY18 Q2 – FY20 Q1)

"Through this project, Opus 12 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. The increased performance of CO_2 electroreduction with new catalysts demonstrates the potential for further improvement with more work in this area and Opus 12 plans to dedicate more resources to catalyst development in the future as a result of the project."

– Opus 12

Presentations

- Cave, E.; 255th ACS National Meeting, New Orleans, LA, March **2018**.
- Baddour, F. G.; BETO 2019 Peer Review, Denver, CO, March **2019.**

Responses to Previous Reviewers' Comments

- This targeted project seems to have a logical partnership between the performers. Results appear promising, both in catalyst development and performance. While scant on some details which could be valuable in assessing fully the current and future trajectory of the project, the NREL portion provides a unique expertise in catalyst synthesis and characterization that is clearly valued by the industrial partner.

- The ability to convert CO_2 to fuel and chemicals would be a major boon to the fight against global warming. Electrochemical catalysis is one of the more promising approaches since it would allow the conversion of renewable electricity available from a variety of sources into an easy to store high energy density liquid fuel. Demonstrating improved performance and determining the potential costs are critical for the continued development of the technology.