BETO 2021 Peer Review: 
Electrocatalytic CO₂ 
Utilization

Jack Ferrell – NREL
CO₂ Upgrading
March 11, 2021

This presentation does not contain any proprietary, confidential, or otherwise restricted information
**Project Overview: Motivation**

**CO₂ – a ubiquitous feedstock:**

- CO₂ is available from a range of point sources, as well as in the atmosphere. The only feedstock measured in gigatons
- Domestic biorefineries emit a very pure CO₂ waste stream, and represent an *early opportunity for deployment* of CO₂ utilization technologies
- Multiple forces combine to make capture + utilization of CO₂ attractive
  - Climate change (some incentives today for CO₂ capture/use)
  - Increase C utilization of existing processes
  - Inexpensive, intermittent electricity available & increasing

- *Additional R&D needed to enable the economical electrochemical conversion of CO₂ to value-added products, either through C₁ intermediates to be further upgraded (e.g., CO; TRL 3-4), or directly to products (e.g., C₂H₄, C₂H₅OH; TRL 1-3)*

*Energy Env. Sci.*, 2020, 13, 472-494
**Market Trends**

- 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
- Sustained low oil prices
- Decreasing cost of renewable electricity
- Sustainable waste management
- Expanding availability of green H₂
- Closing the carbon cycle
- Risk of greenfield investments
- Challenges and costs of biorefinery start-up
- Availability of depreciated and underutilized capital equipment
- Carbon intensity reduction
- Access to clean air and water
- Environmental equity

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

**Value Proposition**
- Enable long-term and stable operation of low-temperature CO₂ electrolyzers, by developing diagnostics, standard procedures for testing, and focusing on degradation pathways

**Key Differentiators**
- Focus on diagnostics and standard testing procedures
- Leverage NREL expertise on both low-temperature electrochemical technologies and enabling capabilities within the ChemCatBio Consortium
**Quad Chart Overview**

**Timeline**
- 10/1/2019
- 9/30/2022

<table>
<thead>
<tr>
<th>DOE Funding</th>
<th>FY20</th>
<th>Active Project</th>
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<tr>
<td>$300k</td>
<td>$900k</td>
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**Project Goal**
Enable stable and long-term operation of low-temperature CO₂ electrolyzers, by investigating scalable MEA architectures, studying catalyst and support degradation, and creating standard methods for testing and product quantification.

**End of Project Milestone**
Demonstrate stable (<10% change in cell voltage) and long-term (>100 hours) electrocatalytic CO₂ conversion in a membrane-electrode-assembly (MEA) at relevant current density (>200 mA/cm²).

**Project Partners**
- Feasibility Study of Utilizing Electricity to Produce Intermediates from CO₂ and Biomass (2.1.0.304)
- Advanced Catalyst Synthesis and Characterization (ACSC) (2.5.4.304)
- Consortium for Computational Physics and Chemistry (CCPC) (2.5.1.307)

**Barriers addressed**
- Ct-E: Efficient Low-Temperature Deconstruction
- Ct-H: Efficient Catalytic Upgrading of Gaseous Intermediates to Fuels and Chemicals

**Funding Mechanism**
AOP Project (continuing)

*Only fill out if applicable.*
1 – Management: Project Overview

• Project started in FY18
  • Collaboration with Feasibility Study (2.1.0.304) to determine technical feasibility and research needs
  • Focused on both electrochemical and thermochemical CO₂ upgrading
• Moved into ChemCatBio in FY20
  • Electrochemical pathway only
• Project Structure / Communication / Collaborators
  • 1 task, applied R&D
  • Regular contact with BETO TM
  • Frequent contact with other BETO CO₂ utilization projects
  • Collaborate with NREL researchers with expertise in low-temperature electrochemical systems (EERE - Hydrogen and Fuel Cell Technologies Office)
  • Leverage ChemCatBio capabilities in catalyst synthesis and characterization (ACSC project) and modeling (CCPC)

¹Energy Env. Sci., 2020, 13, 472-494
## 1. Management: ChemCatBio Foundation – FY21

### Integrated and collaborative portfolio of catalytic technologies and enabling capabilities

#### Catalytic Technologies

<table>
<thead>
<tr>
<th>Technology</th>
<th>Lead Institutions</th>
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<tbody>
<tr>
<td>Catalytic Upgrading of Biochemical Intermediates</td>
<td>NREL, PNNL, ORNL, LANL</td>
</tr>
<tr>
<td>Upgrading of C1 Building Blocks</td>
<td>NREL</td>
</tr>
<tr>
<td>Upgrading of C2 Intermediates</td>
<td>PNNL, ORNL</td>
</tr>
<tr>
<td>Catalytic Fast Pyrolysis</td>
<td>NREL, PNNL</td>
</tr>
<tr>
<td>Electrochemical CO₂ Utilization</td>
<td>NREL</td>
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#### Enabling Capabilities

<table>
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<th>Capability</th>
<th>Lead Institutions</th>
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</thead>
<tbody>
<tr>
<td>Advanced Catalyst Synthesis and Characterization (ACSC)</td>
<td>NREL, ANL, ORNL</td>
</tr>
<tr>
<td>Consortium for Computational Physics and Chemistry (CCPC)</td>
<td>ORNL, NREL, PNNL, ANL, NETL</td>
</tr>
<tr>
<td>Catalyst Deactivation Mitigation for Biomass Conversion</td>
<td>PNNL</td>
</tr>
</tbody>
</table>

#### Industry Partnerships (Phase II Directed Funding)

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

### Cross-Cutting Support

- ChemCatBio Lead Team Support (NREL)
- ChemCatBio DataHUB (NREL)
Advantages:
• High Faradaic efficiency to products
• Stable operation
• Scalable MEA architecture

Technical Challenges:
• CO₂ crossover (50%)
• Long-term membrane durability
• Catalyst & support degradation

Approach:
• Probe membrane durability in MEA environment
• Test new AEM membrane materials
• Quantify catalyst and carbon support degradation
• Standard methods for testing & product analysis

Go/No Go: Demonstrate Stable & Long-term Operation (March 2021)
2 – Approach: Proton Exchange Membrane MEAs

**Advantages:**
- Nafion durable & well-understood membrane material
- No CO₂ crossover issues

**Technical Challenges:**
- Acidic environment – significant hydrogen evolution
  - Buffer layer required at membrane/cathode interface
  - Stability & scalability of buffer layer architectures
- Catalyst & support degradation

**Approach:**
- Quantify hydrogen evolution kinetics
- *Use kinetics to develop integrated MEA model*
- Quantify catalyst and carbon support degradation
- Standard methods for testing & product analysis

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Proton Exchange Membrane (PEM)

100s mA/cm² @ ~3V

CCPC

U.S. DEPARTMENT OF ENERGY

Consortium for Computational Physics and Chemistry

ChemCatBio
3 – Impact: Addressing Technical Barriers

• Improving biorefinery carbon utilization
  • Ethanol biorefineries large source of pure industrial CO₂ waste stream
  • Valorization of this waste stream, enabled by inexpensive renewable electricity, will improve biorefinery economics

• Published review article in Energy & Environmental Science¹
  • Focused on key technical challenges CO₂ utilization
  • Identified research needs

• Addressing top technical barriers¹ for low-temperature CO₂ electrolysis
  • Increasing long-term stability
  • Scalable MEA architectures
  • Optimizing reaction conditions (electrolyte, pH, mass transport)
  • Increasing single-pass CO₂ conversion

¹Energy Env. Sci., 2020, 13, 472-494
Recent publications identify common needs for enabling CO₂ conversion

- Standardized testing protocols
- MEA fabrication
- Electrochemical testing

Product analysis: **Standard NMR method developed (FY21 Q2)**

- Accelerated durability test needed
- Cells and systems need to get to 1000s of hours – long-term durability testing not practical
- Degradation routes (catalysts, membranes, catalyst supports) must first be understood
  - **Catalyst and catalyst support degradation**
4 – Progress: Baselining Existing MEA Architectures

**PEM MEAs**
- Nafion membrane
- 150 mA/cm² @ ~3.5V (25 cm² cell)
- Flowing liquid buffer layer (K₂SO₄)
- SnO₂ catalysts selectively produce formate
- Significant hydrogen evolution occurred (~50% selectivity to H₂)

**AEM MEAs**
- Sustainion membrane (Dioxide Materials)
- 155 mA/cm² @ ~3.3V (5 cm² cell)
- High CO selectivity (98%) on Ag catalyst
- Significant CO₂ crossover (from cathode to anode) observed (50%)

![Diagram showing PEM and AEM MEAs with various components and flow directions.](image-url)
In situ Membrane Integrity

- CO₂ utilization MEAs employ very thin membranes (50 µm) – pinholes can develop during MEA fabrication
- Pinholes lead to parasitic losses and safety concerns

Electrochemical Impedance Spectroscopy (EIS)

- EIS is an easily-deployed, fast technique that can probe operating MEAs
- Test multiple MEAs with and without defects
- Membrane resistance defined as high-frequency (>38 kHz) limit of real impedance (Z’) - circled
- Method yields area specific resistance (ASR) for membrane of operating MEAs
  - 1.52 Ω-cm² (<10% RSD) – below this membrane is compromised

Diagnostic quickly detects if membrane has defects
4 – Progress: New Alkaline Exchange Membranes (AEMs)

**Durability concern for existing AEM materials**
- Nafion (PEM membrane) is well-developed and durable, due to perfluorinated membrane backbone
- Significant recent AEM development for alkaline fuel cells – with a goal of increased durability
- NREL developed a new perfluorinated AEM membrane\(^1\)
  - Showed enhanced durability in AEM fuel cell testing (>500 hours @ 600 mA/cm\(^2\)) and record performance with powdered ionomer in electrode
- Leading AEM for CO\(_2\)U is Sustainion – hydrocarbon backbone

**Testing Perfluorinated AEM for CO\(_2\)U**
- Promising results – 200 mA/cm\(^2\) @ -3.5V
- Ag cathode catalyst – CO main product
- No degradation seen in cell voltage over 1-hour test

New more durable membrane materials needed – initial results promising

\(^1\)Advanced Ionomers & MEAs for Alkaline Membrane Fuel Cells, DOE Hydrogen and Fuel Cells Program, PI Bryan Pivovar;
\(^2\)ECS Transactions, 80 (8) 957-966 (2017)
Kinetic info lacking for CO₂ U MEAs

- Setup experiment based on asymmetric Pt/Nafion/Pt MEA¹
  - High Pt loading (0.4 mg/cm²) at anode – HOR kinetics fast
  - Low Pt loading (0.03 mg/cm²) at cathode – HER kinetics dominate
  - Reproduced previous results on Pt

- Fabricated CO₂ U MEAs: Pt/Nafion/Ag
  - Ag catalyst used to selectively form CO from CO₂
  - 0.4 and 0.8 mg/cm² Ag catalyst loading at cathode

- Evaluated HER kinetics on CO₂ U MEAs
  - 40, 50, 60, 70 & 80 °C
  - Constant gas flow (1-2 s lpm H₂), RH (100%), and P (150 kPa)
  - Extract Tafel slopes (semi-log plot)
    - Simplification of Butler-Volmer equation
    - Extrapolate to η = 0 to get exchange current density (i₀)
  - HER 10³ – 10⁴ slower on Ag than Pt

- Moving forward: Integrated MEA modeling efforts in collaboration with CCPC

¹Journal of The Electrochemical Society, 154 7 B631-B635 2007
Summary

• Management
  • Moved into ChemCatBio Consortium – leverage capabilities in catalyst synthesis & characterization and modeling
  • Close connection with Feasibility Study – technical feasibility and analysis
• Approach
  • Applied R&D on scalable single-membrane MEAs
  • Focus on enabling long-term & stable operation
• Impact
  • Identified technical challenges, targeted R&D to address challenges
  • Addressing specific needs of CO₂ utilization community (standard protocols, degradation)
• Progress
  • Baselined PEM and AEM MEAs
  • Developed membrane integrity diagnostic
  • New alkaline membrane material tested
  • Hydrogen evolution kinetics will enable integrated modeling efforts
Bioenergy Technologies Office

- Ian Rowe
- Jesse Glover

NREL

- Erick White
- Liz Ware
- Renee Happs
- Josh Schaidle
- Randy Cortright
- Ling Tao
- Bryan Pivovar
- K.C. Neyerlin
- Ami Neyerlin
- Yingying Chen
- Tim Van Cleve
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- Guido Bender
- Jason Zach

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• This is a comprehensive project, and advancements were made in catalyst development. System design results can help demonstrate the viability of the approach. The connections between electrochemical and thermochemical pathways can be articulated to identify the synergies, and the linkage between the identified BETO barriers and deliverables can help shape future priorities.
  • Response: We thank the reviewer for the feedback and agree that there are clear synergies between the CO2 conversion routes such as the synthesis of catalyst materials that are being leveraged across both pathways and characterization efforts that focus on key intermediates that are similar in both cases. Future deliverables will have metrics that directly address BETO MYP barriers through the incorporation of TEA in upcoming years.

• This is a great team leveraging ChemCatBio efforts. Active collaborations with other expert groups. Thus, the team has a great potential to significantly advance the thermo and electrochemical catalysts for CO2 conversion to C2+. The consideration of using a wide range of CO2 sources (e.g., ambient to industrial sources beyond ethanol plants) and the investigation of challenges associated with different CO2 waste streams would further improve the potential impact of this study.
  • Response: We thank the reviewer for their positive comments and agree that the investigation of realistic CO2 sources will bring additional value to the project. In the initial 2-years of the project we focused on developing a synthetic platform of catalyst materials and an understanding of the corresponding reactivity. Additionally, we have developed capabilities for the testing of different membrane-electrode-assemblies which are required for performing relevant research (including screening of different CO2 sources).

• This project aims to benchmark and then further develop both electrochemical and thermochemical catalysts for the conversion of CO2.
This project aims to benchmark and then further develop both electrochemical and thermochemical catalysts for the conversion of CO2.

While the thematic goals are highly relevant to the BETO mission, the project has presented insufficient evidence to show that specific efforts in this project have a good chance of advancing the state of the art.

Response: On the thermochemical side, we sought to develop a synthetic strategy for a tunable catalyst system to develop a fundamental understanding of the impact of catalyst features on the resulting product slate. We acknowledge that the metal carbide system is only one type of catalyst system used for CO2 reduction, but we believe that it affords the ability to rationally tune the catalyst structure and advance the state of the art over industrial materials. On the electrochemical side, our catalyst development efforts have yet to find a material that can outperform the state-of-the-art copper catalyst. However, electrocatalyst development with a tunable materials platform (transition metal phosphides) have been useful for studying electrochemical CO2 reduction, and we are actively exploring new materials systems. Additionally, much work has been spent developing capabilities for catalyst testing in the relevant environment (in a membrane-electrode-assembly), and these capabilities are required to advance the current state-of-the-art.

The performers have proposed to improve both electrochemical and thermochemical conversion of CO2 to C2+ products. The performers will be collaborating with the Feasibility study from NREL. The performers are suggested to focus on one of the two approaches (likely electrochemical) to maximize chance of success. The performers should also more clearly list out what the metrics of success (MoS) and the rationale for choosing those targets.

Response: In the future we will more closely align metrics of success for the project with BETO MYP barriers which will be facilitated with ongoing TEA efforts to compare electrochemical and thermochemical approaches.


## FY20 Milestones

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<tr>
<th>Milestone Name/Description</th>
<th>Criteria</th>
<th>End Date</th>
<th>Type</th>
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<tbody>
<tr>
<td><strong>Develop in situ MEA Diagnostics</strong></td>
<td>Develop <em>in situ</em> electrochemical diagnostics tailored for CO₂ utilization MEAs. Electrochemical impedance spectroscopy (EIS) and supporting measurements will be used to quantify <em>in situ</em> electrocatalyst activity, CO₂ crossover (from cathode to anode), ohmic resistances of different parts of the MEA, and identify processes that lead to performance degradation (e.g., pH drift, membrane degradation, catalyst degradation, leakage current). Electrochemical process models will be developed, and model parameters will be used for benchmarking and MEA development in subsequent tasks. Target &lt;10% variability (defined as % RSD) for the whole cell resistance from the EIS measurement.</td>
<td>12/31/2019</td>
<td>Quarterly</td>
</tr>
<tr>
<td><strong>Alkaline Exchange Membrane (AEM) Membrane Development</strong></td>
<td>While AEM materials operate at a pH favorable for CO₂ utilization, persistent problems remain including loss of CO₂ reactant (via bicarbonate crossover from cathode to anode) and membrane degradation. We will adapt new fluorinated AEM membrane materials to improve durability while maintaining high current density. Demonstrate degradation rates &lt;10 mV/hr at current density &gt;100 mA/cm².</td>
<td>3/31/2020</td>
<td>Quarterly</td>
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<tr>
<td><strong>Proton Exchange Membrane (PEM) MEA Development</strong></td>
<td>While PEM materials (e.g., Naftion) are very durable and have been proven for other applications, they operate at a pH that is too low to facilitate electrochemical CO₂ utilization. Perform PEM MEA development, including efforts to reduce the pH at the membrane/cathode interface. Potential strategies to reduce the pH include the addition of solid or liquid-containing buffer layers, as well as the incorporation of AEM ionomer materials into the cathode catalyst layer. Demonstrate stable performance, defined here at maintaining &gt;50% Faradaic efficiency to non-hydrogen products for at least 4 hours.</td>
<td>6/30/2020</td>
<td>Quarterly</td>
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<tr>
<td><strong>Determine most promising type of membrane-electrode-assembly (MEA) for integration and <em>in situ</em> testing of state-of-the-art electrocatalysts.</strong></td>
<td>At least 2 different types of MEAs will be tested: proton exchange membrane (PEM) and anion exchange membrane (AEM) MEAs. By integration of the same state-of-the-art electrocatalyst (e.g., Ag catalyst for selective formation of CO), performance and any stability issues will be compared for PEM and AEM MEAs. The most promising MEA will be the focus of future MEA development in this project, and will be used for <em>in situ</em> testing and baselining of electrocatalysts in the electrolyzer environment. Target maintaining high Faradaic efficiency (&gt;50% to non-hydrogen products) for at least 8 hours, at a relevant current density (&gt;100 mA/cm²).</td>
<td>9/30/2020</td>
<td>Annual SMART</td>
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<tr>
<td>Evaluate Hydrogen Evolution Reaction Kinetics in the MEA Environment.</td>
<td>Measure kinetic parameters including Tafel Slopes and Exchange Current Densities for the Hydrogen Evolution Reaction (HER) in a proton exchange membrane (PEM) MEA. HER kinetics remain unexplored for CO₂ Utilization MEAs, and these parameters will inform modeling and scaleup efforts, as well as strategies to limit hydrogen evolution in PEM MEAs. Hydrogen evolution is a persistent problem that significantly reduces the Faradaic efficiency of CO₂ conversion in PEM MEAs. Kinetic data produced in this milestone will inform future meso-scale modeling efforts in collaboration with the CCPC.</td>
<td>12/31/2020</td>
<td>Quarterly</td>
</tr>
<tr>
<td>Develop Standard Method for Product Analysis from CO₂ Utilization MEAs.</td>
<td>Agreed-upon Standards remain a need in the CO₂ Utilization community. As electrochemical CO₂ conversion can create various products, standard analytical methods are needed to quantify these products. Currently, there is no consensus on product quantification, that is, many different techniques and analytical methods are used. We will develop at least one standard analytical method for product quantification and will deliver a Laboratory Analytical Procedure (LAP) with this milestone. The LAP can later be published on an NREL website, where it will be free and publicly available.</td>
<td>3/31/2021</td>
<td>Quarterly</td>
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<tr>
<td>Risk Identification</td>
<td>Based on subject matter expert interviews, critical literature review, and research to-date in the Electrocatalytic CO₂ Utilization Project (2.3.1.316) develop a risk register for the CO₂ reduction pathway evaluated in the FY21 Q4 Annual SMART milestone in the Feasibility Study Project (2.1.0.304), characterize the risks based on probability and impact, and identify responsible parties. Technical risks will be evaluated on both a unit operations level and a systems integration level. This is a joint milestone with the Feasibility Study of Utilizing Electricity to Produce Intermediates from CO₂ and Biomass (2.1.0.304).</td>
<td>6/30/2021</td>
<td>Quarterly</td>
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<tr>
<td>Integration of Electrocatalysts into CO₂ Utilization MEAs.</td>
<td>Integrate at least two (2) electrocatalysts into CO₂ utilization MEA cathodes. Develop methods for reliable application of electrocatalysts and identify any differences between electrocatalyst activity in the ex situ catalyst screening test (in aqueous solution) and in situ activity in the MEA cathode. This milestone is in collaboration with the Advanced Catalyst Synthesis and Characterization (ACSC) project within ChemCatBio.</td>
<td>9/30/2021</td>
<td>Annual SMART</td>
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### Go/No Go

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<tr>
<td>Long-term operation at relevant current density.</td>
<td>Stable and long-term electrocatalytic CO$_2$ conversion at significant current density remains a challenge. Develop MEA architectures that can enable stable operation at sufficient current density.</td>
<td>Demonstrate stable (degradation rates &lt; 10 mV/hr) and long-term (&gt;24 hours) electrocatalytic CO$_2$ conversion in a membrane-electrode-assembly (MEA) at relevant current density (&gt;100 mA/cm$^2$). This degradation rate represents an upper-bound for what will be needed for scale-up.</td>
<td>3/31/2021</td>
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*On track to complete the Go/No Go on time*