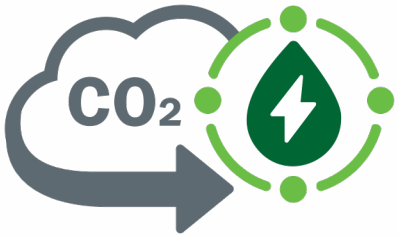


CO_2 Reduction and Upgrading for e-Fuels Consortium

U.S. DEPARTMENT OF ENERGY

DOE Bioenergy Technologies Office (BETO) 2023 Project Peer Review

Electrocatalytic CO_2 Utilization (2.3.1.316)

April 6th, 2023

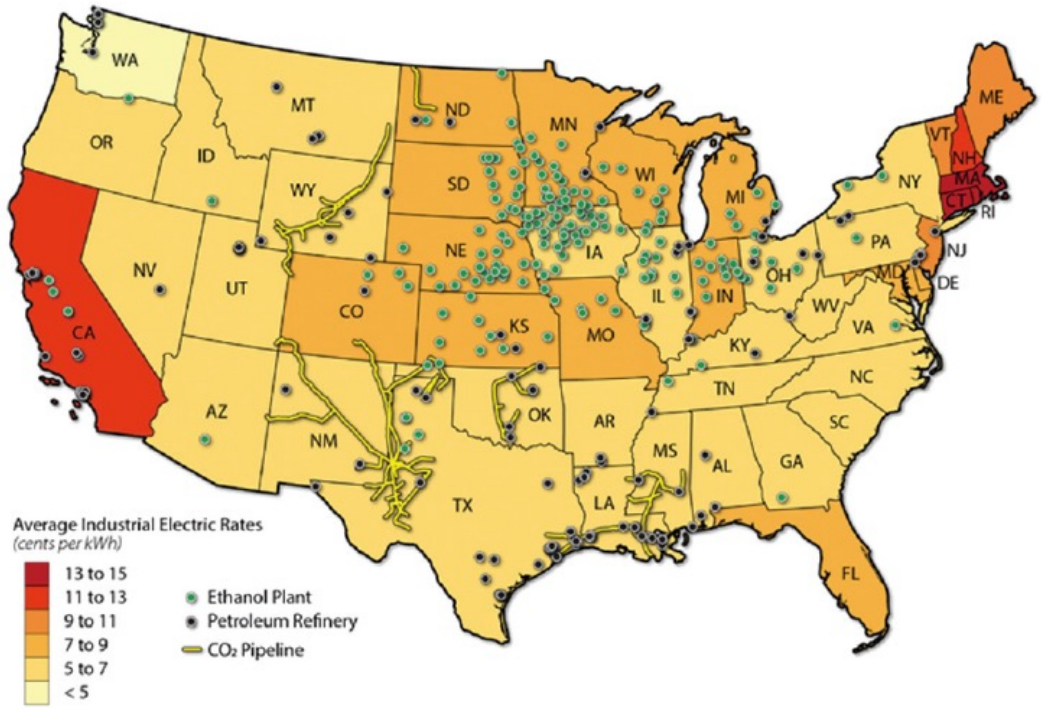
Carbon Dioxide Utilization

Jack Ferrell

NREL

Project Overview

- In addition to biomass, waste CO_2 is needed as a sustainable carbon source for difficult-to-electrify sectors and chemical production
- Low-temperature CO_2 electrolysis is a promising pathway to produce low carbon intensity fuels and chemicals, offering advantages in scalability, process efficiency, and intermittent operation
- Significant risks must be overcome for CO_2 electrolysis to help meet 2050 decarbonization goals
- This project works alongside CO_2RUe Consortium analysis projects to identify/quantify risks, and performs targeted experimental work to address risks



Biorefineries represent early opportunity for deployment of CO_2 utilization technologies

Energy Env. Sci., 2020, 13, 472-494

1. Approach

- **History**
  - Project began in FY18, collaboration with Feasibility Study (2.1.0.304, PI Gary Grim) to determine technical feasibility and research needs;[1] experimental focus on electro- and thermo-catalytic CO_2 conversion. Joined the Chemical Catalysis for Bioenergy Consortium (ChemCatBio) in FY20, spun off thermocatalytic work to Upgrading of C_1 Building Blocks project (2.3.1.305, PI Dan Ruddy)
- **Joined CO_2RUe Consortium in FY23**
  - Regular meetings with both analysis and electrolysis projects
  - Frequent contact with BETO TM and External Advisory Board
- **Retain connection to ChemCatBio**
  - Leverage ChemCatBio capabilities in catalyst synthesis & characterization
  - Facilitate information transfer between CO_2Re and ChemCatBio

CO_2 Reduction and Upgrading for e-Fuels Consortium
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ChemCatBio
Chemical Catalysis for Bioenergy

[1] *Energy Env. Sci.*, 2020, 13, 472-494

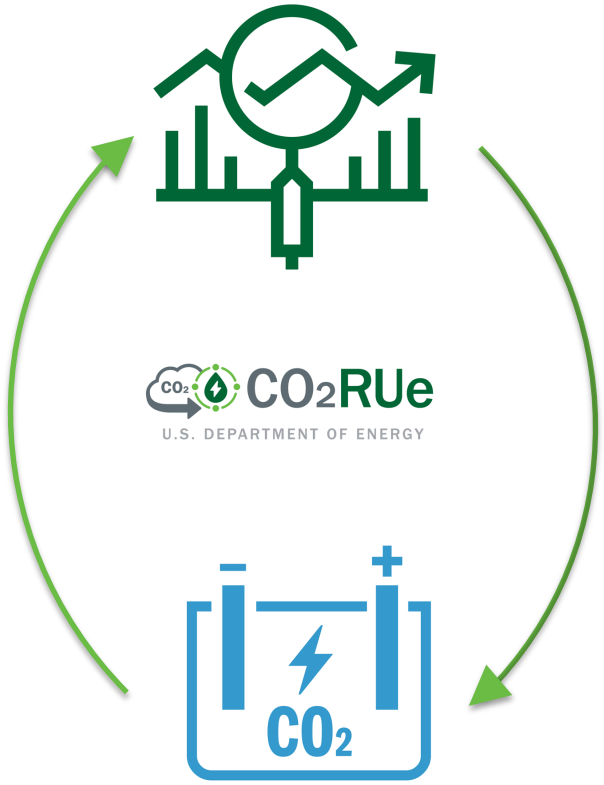
1. Approach – Milestone Table

Milestone Name/Description	Criteria	End Date	Type
Whole cell MEA carbon corrosion testing	Continue with carbon corrosion testing that began in FY22 using operating alkaline exchange membrane MEAs. Gas diffusion electrodes (GDEs) will be characterized pre- and post-mortem.	12/31/2022	Quarterly Progress Measure
Ex-Situ carbon corrosion test	Setup and execute an ex-situ test for CO_2 utilization gas diffusion electrodes (GDEs). This ex-situ test will allow for online detection of CO_2, providing a direct quantification of carbon corrosion. Quantification of carbon corrosion is challenging in an operating MEA where the CO_2 feedstock masks the CO_2 produced from the carbon corrosion process.	3/31/2023	Quarterly Progress Measure
Carbon corrosion manuscript draft	Complete a draft of a manuscript focused on carbon corrosion in low-temperature CO_2 electrolyzers. Summarize work to-date on carbon corrosion in CO_2 electrolyzers, from the literature as well as work in this project. Provide a perspective on the path forward to understand and mitigate carbon corrosion.	6/30/2023	Quarterly Progress Measure
Quantify catalyst degradation at base current density	Cathode electrocatalyst degradation (aggregation/agglomeration) during MEA testing will be quantified via pre- and post-mortem characterization (by microscopy and/or spectroscopic techniques) at standard operating conditions (200 mA/cm^2). In collaboration with projects in the CO_2RUe Consortium Electrolysis group. Also, in collaboration with ChemCatBio.	9/30/2023	Annual
Quantify catalyst degradation at elevated current density	Cathode electrocatalyst degradation (aggregation/agglomeration) during MEA testing will be quantified via pre- and post-mortem characterization (by microscopy and/or spectroscopic techniques) at elevated current densities (>300 mA/cm^2). In collaboration with projects in the CO_2RUe Consortium Electrolysis group. Also, in collaboration with ChemCatBio.	9/30/2024	Annual
Determine the economically feasible region of current density and MEA replacement interval	Determine the economically feasible region of current density and MEA replacement interval: electrocatalyst durability studies at different current densities will provide heuristics for MEA lifetime, which will be incorporated into techno-economic projections (at each corresponding current density) delineating thresholds in both current and lifetime for achieving cost-competitiveness.	9/30/2025	Annual

Go/No Go	Description	Criteria	Date
Cathode Electrocatalyst Degradation	Determine whether there are appreciable differences in electrocatalyst degradation at different current densities.	Based on MEA testing for longer times (>100 hours), quantify cathode electrocatalyst degradation (aggregation/agglomeration) at base (200 mA/cm^2) and elevated (>300 mA/cm^2) current densities. If no appreciable difference is seen (No Go), pivot to higher currents and/or longer times. In collaboration with ChemCatBio.	3/31/2024

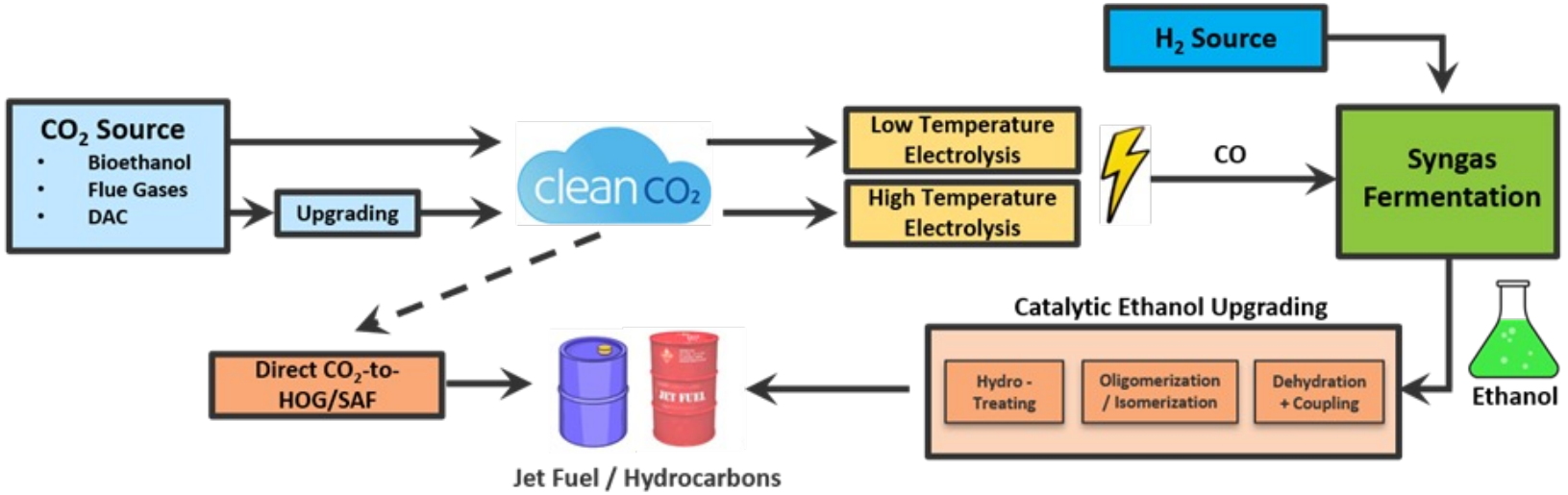
1. Approach

- First, in collaboration with CO_2RUe analysis projects, **identify largest risks** that must be overcome to enable commercialization of low-temperature CO_2 electrolysis
- Next, perform **targeted experimental work to help address risks**
  - Membrane-electrode-assembly (MEA) lifetime too short, needs to be > 4 years to enable commercialization
    - Quantify carbon corrosion on the anode (FY23 Q1 - Q3)
    - Catalyst degradation issues impacting lifetime (FY23 Q4 - FY25)
      - Go/No Go (Q2 FY24): Quantify cathode electrocatalyst degradation at existing (200 mA/cm^2) and elevated (>300 mA/cm^2) current densities. In collaboration with ChemCatBio.
- Finally, combine techno-economic (TEA) and life cycle analysis (LCA) with risk mitigation experimental work
  - End of Project Milestone (Q4 FY25): Determine the economically feasible region of current density and MEA replacement interval



2. CO_2 to Sustainable Aviation Fuel (SAF)

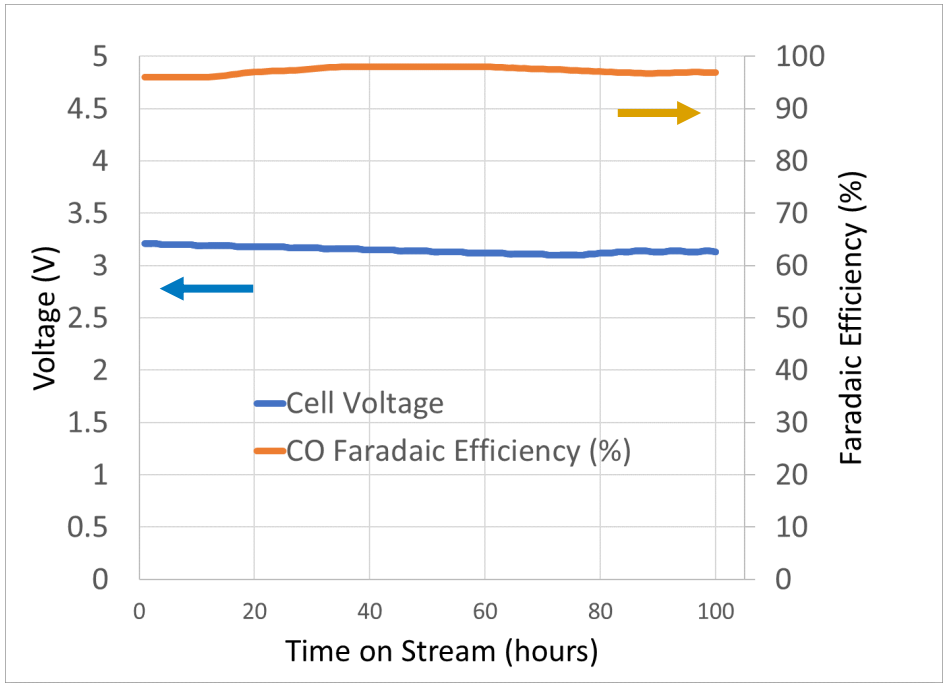
- **Quantified risks for an integrated CO_2-to-sustainable aviation fuel (SAF) process**
  - Q3 FY21 milestone (joint milestone with Feasibility Study, 2.1.0.304)
- **Technical, market, and systems integration risks quantified based on probability and impact**
  - Electrolysis risks: variable CO_2 feeds, stability of electrolyzer and balance of plant, poor performance metrics, membrane irreproducibility, corrosion of carbon supports, accumulation of electrolyte contaminants, thermal management, intermittent operation
  - Biggest risks: ***lack of long-term stability data*** and ***testing with real-world process streams*** containing contaminants
  - TEA analyses showed that higher currents (>500 mA/cm^2) needed alongside long lifetime (>7 years) to enable cost-competitiveness

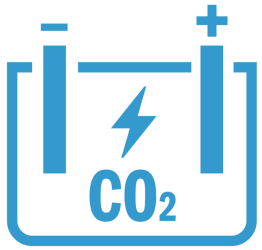


- Electrolysis-based risks for commercialization quantified
- Experimental plan to help address risks related to electrolyzer lifetime

2. MEA Testing System

- Designed & built testing system for membrane-electrode-assemblies (MEAs)
  - Online analytical (GC) on both anode and cathode – mass balance closure and quantification of CO_2 on anode
  - Tracer employed for calculation of production rates and single-pass conversion
- Stable performance over 100-hour tests in 5 cm^2 cell
  - 200 mA/cm^2 hold: 3.1V, 98% Faradaic efficiency



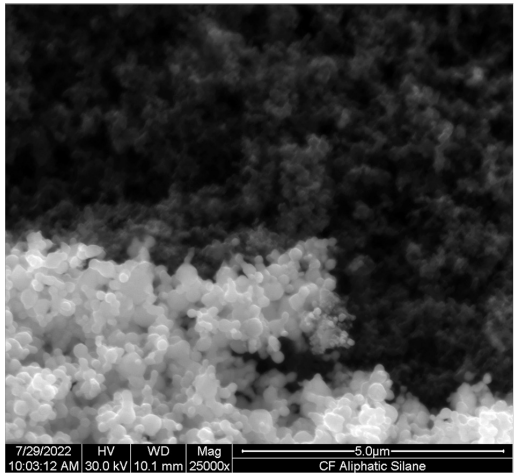


Cathode	Silver (Dioxide Materials)
Anode	IrO_2 (Dioxide Materials)
Electrolyte	Sustainion Membrane (Dioxide Materials)
Catholyte	CO_2: 38 sccm N_2: 5 sccm 100% RH
Anode	5 mM $KHCO_3$ 5 mL/min
Line temperatures	50 °C
Humidifier water flow	1.54 microL/min
Humidifier temp	150 °C

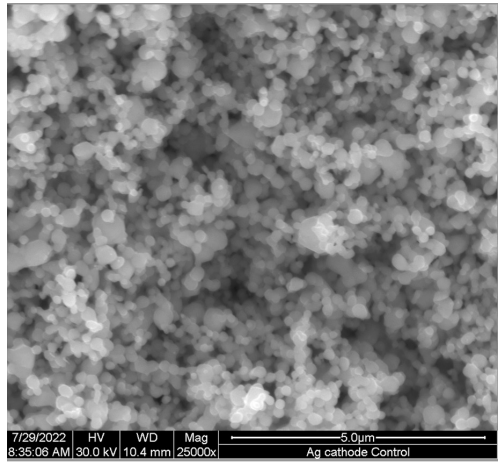
2. Catalyst Durability

- MEA testing with Ag cathode, Sustainion membrane. 200 mA/cm^2
  - No degradation seen in 100-hour tests via SEM:

Spent Electrode



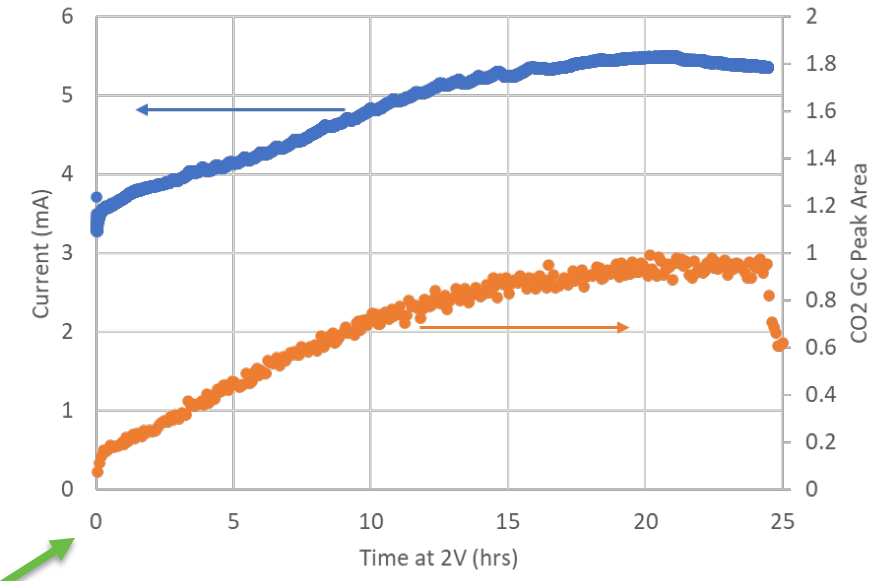
Fresh Electrode



- Catalyst degradation believed to be a persistent issue for achieving sufficient MEA lifetime (> 4 years)
- Future work will focus on quantifying catalyst agglomeration/aggregation at base (200 mA/cm^2) and elevated (>300 mA/cm^2) current densities
  - Combined TEA analyses to define economically feasible region of current density and lifetime

2. Carbon Corrosion

- Corrosion of carbon-based anodes could lead to short MEA lifetimes
  - Carbon corrosion has been seen in other low-temperature electrochemical devices (e.g., fuels cells and water electrolyzers)
- Detection of CO_2 produced from carbon corrosion is challenging in operating MEAs
- Developed ***Ex Situ* carbon corrosion test** relevant to CO_2 anodes
  - Gas diffusion electrode immersed in electrolyte solution, subjected to oxidizing potentials relevant to CO_2 anodes (1-2 V)
  - Online detection of CO_2 from carbon corrosion
    - No CO_2 fed; CO_2 detected was produced from anodic carbon corrosion
  - CO_2 detected follows corrosion current (phosphate buffer)
  - Mass loss in $KHCO_3$ solutions matches phosphate buffer

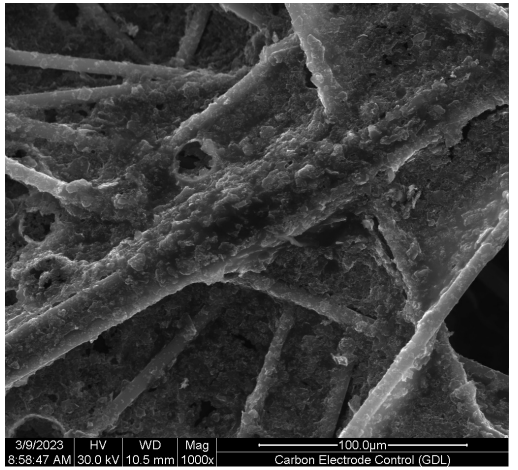


- 24-hour mass loss: 12% of electrode at 2V
- **Good repeatability** with 5.3% relative standard deviation

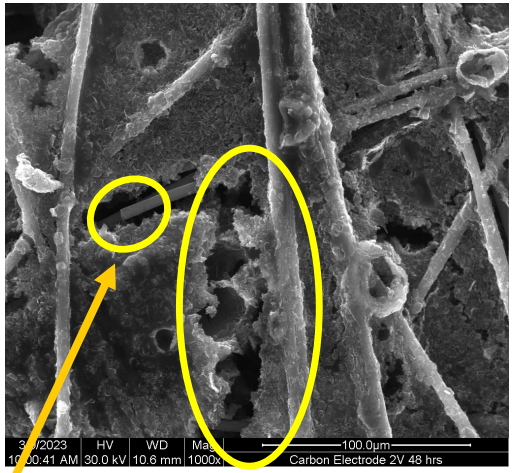
2. Carbon Corrosion

- In addition to mass loss, loss of carbon was seen via SEM for both sides of the gas diffusion electrode (microporous layer and carbon paper)
- Fracturing of carbon fibers and loss of carbon seen for carbon paper
- Energy Dispersive Spectroscopy (EDS) showed a loss of carbon for both sides of electrode
  - Consistent decrease in C:F Ratio due to loss of carbon

Fresh Carbon Paper



Corroded Carbon Paper

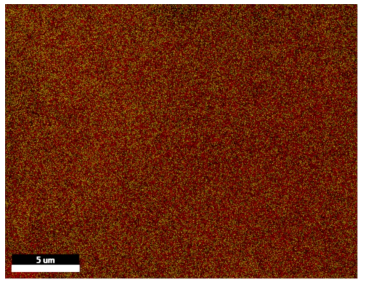


Fracturing of carbon fibers

Degradation of interstitial region

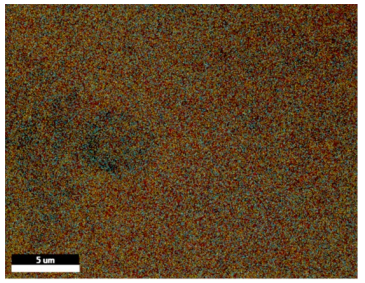
- Moving forward: lower voltages, longer times
  - Manuscript submission planned (FY23 Q3)
- *Ex Situ* test available to CO_2RUe Consortium
  - Anodes/contaminants of interest

Fresh Microporous Layer



C:F Ratio = 2.7

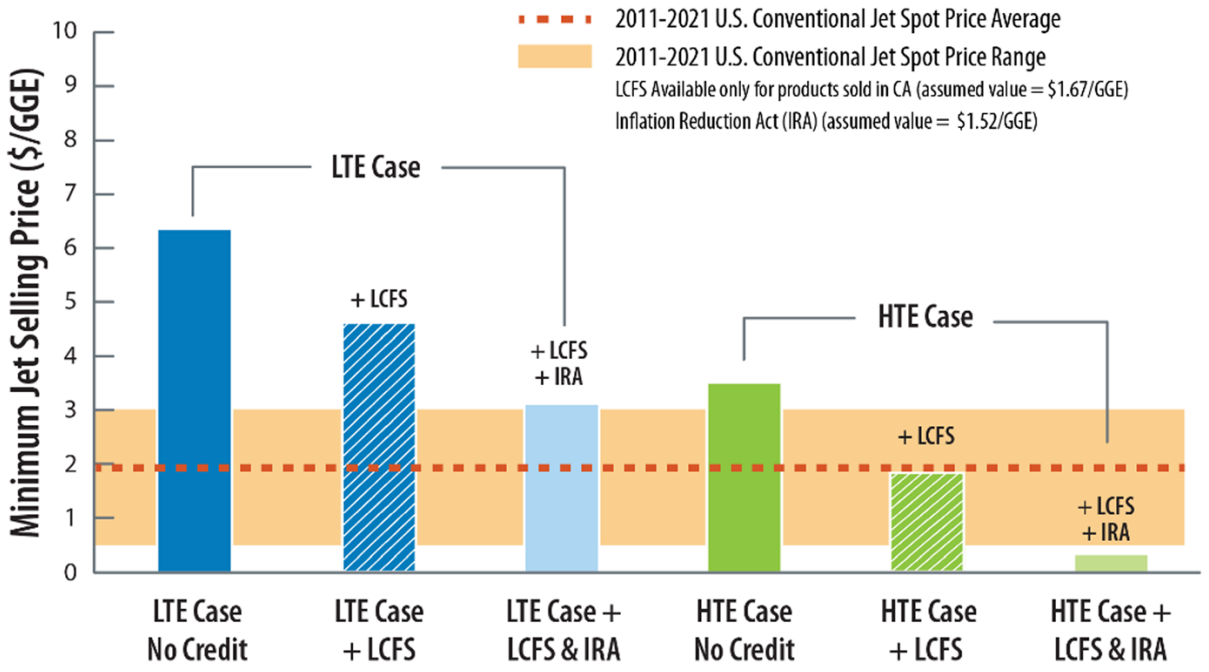
Corroded Microporous Layer



C:F Ratio = 1.3

3. Impact

- Identified risks incorporated into TEA/LCA analyses; in collaboration with CO_2RUe analysis projects
  - Published paper in *Energy & Environmental Science*[1] on CO_2-to-SAF
- CO_2-derived SAF, via both low-temperature (LTE) and high-temperature (HTE) electrolysis, has potential to be competitive in terms of both costs and carbon intensity



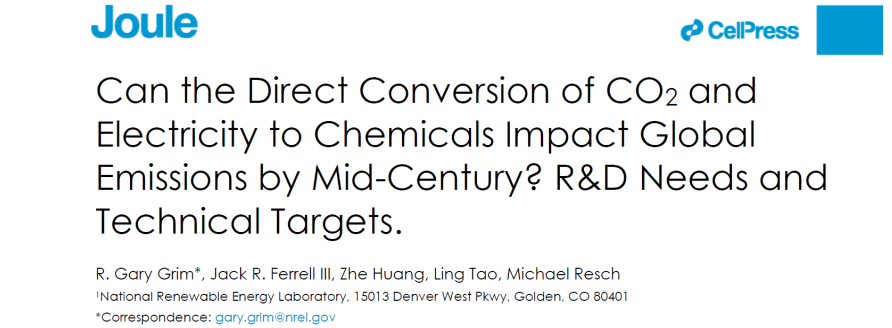
- Largest cost drivers are *electricity price* and *electrolyzer CAPEX*
- Increasing current density (500 mA/cm^2) and MEA lifetime (7 years) critical for cost-competitiveness
- Biorefinery CO_2-derived SAF has lowest carbon intensity of all pathways studied

[1] *Energy Env. Sci.*, 2022, 15, 4798-4812

3. Impact

- Risk mitigation – quantification of risks in collaboration with analysis projects
- Risks incorporated into **Strategic Plan** for CO_2RUe Consortium
  - TEA showed electricity and electrolyzer CAPEX largest cost drivers
    - Higher currents (>1000 mA/cm^2) needed alongside longer MEA lifetimes (>4 years) to enable cost-competitiveness
    - Tradeoffs between current density and MEA lifetime need to be quantified
- Future work
  - Quantify catalyst degradation at different current densities
    - Do higher currents lead to faster catalyst aggregation/agglomeration?
  - Incorporate data into TEA/LCA analysis efforts to help inform economically feasible region of current and MEA lifetime

- Manuscript submitted to *Joule* based on results from Strategic Plan



Summary

- Project focused on identification & mitigation of risks for CO_2 electrolysis
  - Identify largest risks in collaboration with CO_2RUe analysis projects
  - Perform targeted experimental work to address risks
  - Incorporate experimental work with techno-economic (TEA) and life cycle analysis (LCA)
- Risk mitigation work[1,2] shows advancements needed to overcome hurdles in current density, single pass CO_2 conversion, and lifetime
  - R&D advancements necessary to meet BETO's decarbonization goals
- Future work to help define cost-competitive region of current density and lifetime

CO2RUe
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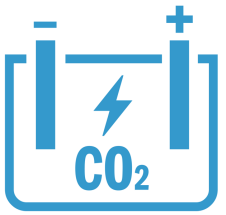

[1] *Energy Env. Sci.*, 2020, 13, 472-494
[2] *Energy Env. Sci.*, 2022, 15, 4798-4812

Quad Chart

Timeline

- 10/1/2022
- 9/30/2025

	FY22 Costed	Total Award
DOE Funding		$900,000
Project Cost Share		

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

Project Goal

This project will de-risk the low-temperature electrochemical conversion of CO_2 by identifying/quantifying risks and performing targeted experimental efforts to increase electrolyzer lifetime

End of Project Milestone

Determine the economically feasible region of current density and MEA replacement interval: electrocatalyst durability studies at different currents will provide heuristics for MEA lifetime, which will be incorporated into techno-economic projections

Funding Mechanism

BETO FY23 Lab Call, subtopic 2c: Conversion Technologies – ChemCatBio Consortium

Project Partners

- CO_2RUe Consortium Analysis group
- CO_2RUe Consortium Electrolysis group
- Chemical Catalysis for Bioenergy Consortium (ChemCatBio)

Q&A

NREL

- Gary Grim
- Mat Rasmussen
- Wilson McNeary
- Jenny Huang
- Josh Schaidle
- Randy Cortright
- Ling Tao
- Michael Resch
- K.C. Neyerlin
- Susan Habas
- Fred Baddour

Bioenergy Technologies Office

- Ian Rowe
- Sonia Hammache
- Kevin Craig

CO_2 Reduction and Upgrading for e-Fuels Consortium
U.S. DEPARTMENT OF ENERGY

ChemCatBio
Chemical Catalysis for Bioenergy

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Publications

- Electrifying the Production of Sustainable Aviation Fuel: The Risks, Economics, and Environmental Benefits of Emerging Pathways Including CO2, Gary Grim*, Dwarak Ravikumar, Eric Tan, Zhe Huang, Jack Ferrell, Michael Resch, Zhenglong Li, Chirag Mev, Steven Phillips, Lesley Snowden-Swan, Ling Tao, Josh Schaidle*, *Energy & Environmental Science*, 2022, 15, 4798-4812. DOI: 10.1039/d2ee02439j
- Can the Direct Conversion of CO2 and Electricity to Chemicals Impact Global Emissions by Mid-Century? R&D Needs and Technical Targets. Gary Grim*, Jack Ferrell, Zhe Huang, Lingo Tao, Michael Resch. *Joule*, 2023, Submitted

2021 Peer Review Comments

- Comment: The development of systematic testing protocols to evaluate AEMs under CO2 electrolysis conditions is a worthy goal because it could bring clarity to a question that is a source of uncertainty in modeling and analysis.
- Comment: It is not clear how this project is directly related to the BETO goals. The project does not need to work on the biologic systems or biocatalysts, but making connections to other BETO efforts would be important.
  - Response: We believe this project is a good fit within the BETO portfolio, as BETO has recently developed a CO2 utilization program and this project was one of the first efforts here.
- Comment: This project has significant potential to help define performance metrics, identify technical barriers to MEA scaling and implementation, and develop best practices for assessing MEA durability and degradation. All are crucial for practical electrolyzer development.
- Comment: While the development of these new catalysts and materials is important, there is not a clear pathway to implement them commercially, in particular to test the catalysts using a real-world feedstock.
  - Response: MEA testing on real-world feedstocks has not been in scope to-date on this project; this work has been a part of another BETO project on CO2 utilization
- Comment: The technical objectives of the project are modest relative to reported state-of-the-art in the field. Published results from Dioxide Materials in 2018 showed >3000 of stable operation at 200 mA/cm2 and 3 V for CO2 to CO electrolysis with sustainion (J. Electrochem. Soc. 165 (15) J3371-J3377 (2018)).
  - Response: We do agree that there is a large disparity between the long-term MEA testing data produced by Dioxide Materials (>3000 hours) and the rest of the community, this project included. However, while the Dioxide Materials long-term data is very promising, it needs to be validated and more detailed data is also desired. Notably, the Dioxide Materials long-term data did not provide any characterization of different components of the MEA before and after testing, and this data is needed to determine the most prevalent degradation pathways at play, and to quantify degradation rates. We have taken the approach of first understanding the system in detail at shorter times (up to 100 hours), and we have closed the carbon balance on this system, producing complete analysis of both anode and cathode streams. Moving forward, we plan to collect this detailed data in conjunction with longer-term durability tests, where the nature of the catalyst, catalyst support, and membrane will be quantified before and after testing.