CO2 Reduction and Upgrading for e-Fuels Consortium

U.S. DEPARTMENT OF ENERGY

DOE Bioenergy Technologies Office (BETO) 2023 Project Peer Review

Integration of CO_2 Electrolysis with MicrobialSyngas Upgrading to Rewire the Carbon Economy

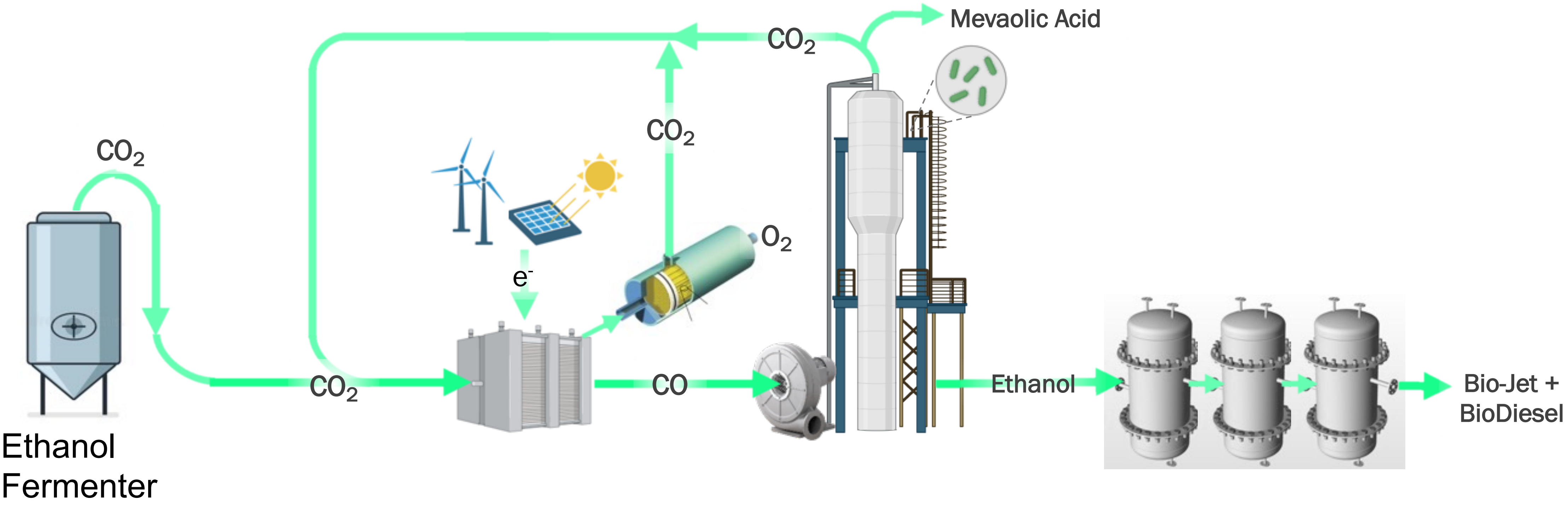
April 6, 2023

CO_2 Conversion Session

Michael G. Resch - Principal Investigator

NREL

Project Overview



- Improve electrolyzer robustness to industrial flue gas components, carbon and energy efficiency.

- Improve molecular biology tools and flux to mevalonic acid
- Evolve strains via ALE and directed strain engineering

- Integrate system to demonstrate the process of converting CO_2 into fuels and chemicals
- Identify two near term industrial sites with low cost electrical and CO_2 feedstocks

Project Goals

Increase the efficiency and durability of CO_2 conversion through electrolysis and syngas fermentation.

<u>Outcomes</u>

1. Reduce CO_2 membrane crossover by 20% in a MEA CO_2 electrolyzer.
2. Identify at least 2 near term sites with low carbon electricity and low-cost CO_2 feedstocks to identify opportunities to integrate this technology at scale.
3. Increase the carbon conversion efficiency from CO, H2 and CO2 into ethanol and mevolnic acid by at least 20%.

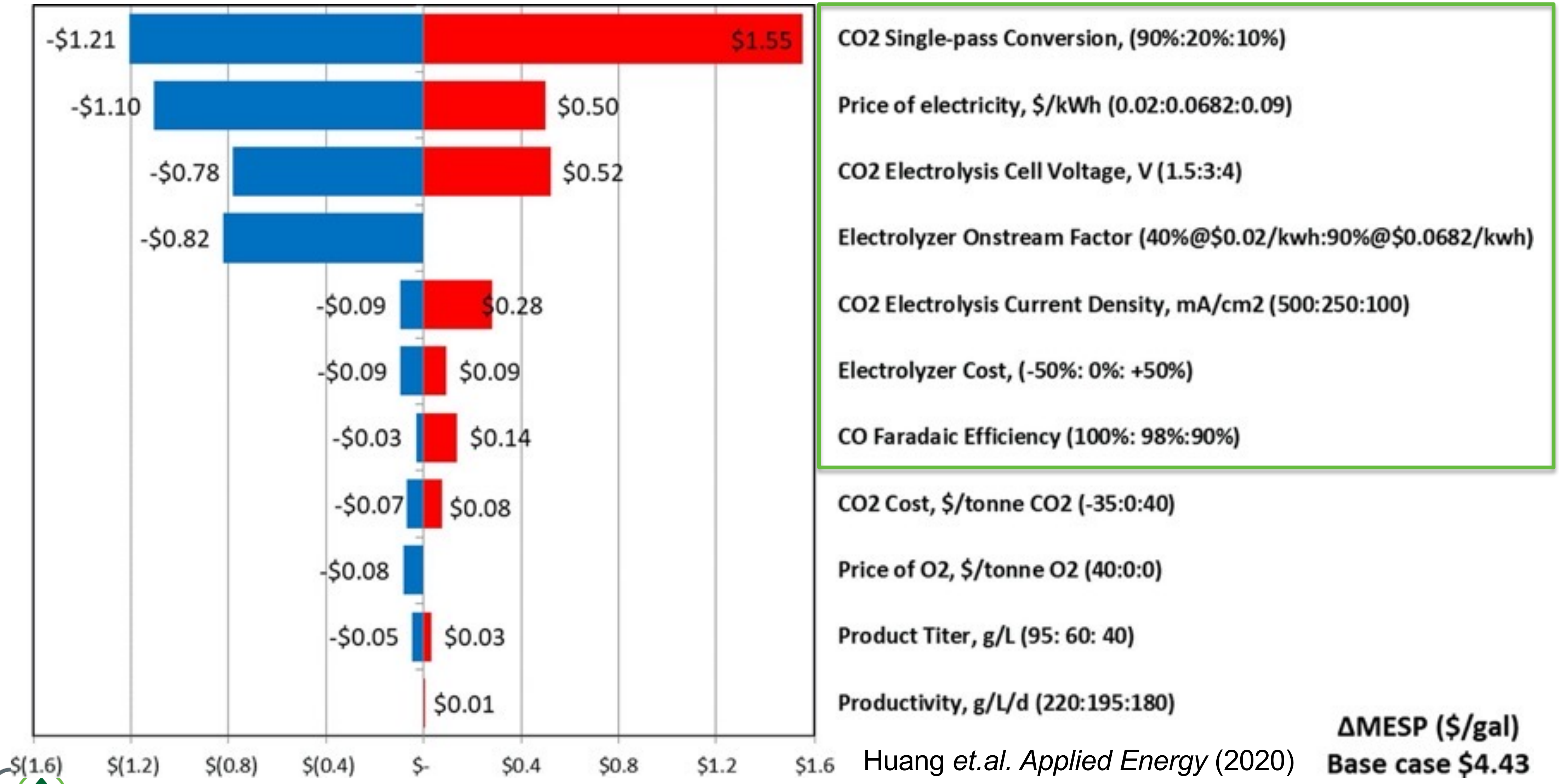
1. Approach - Project Management

Task 1 - Liu (DM)	Task 2 - Guarnieri	Task 3 - Resch
CO_2 Electrolyzer performance improvement	Gas fermentation strain optimization and tool development	Analysis and integration of CO_2 electrolysis with gas fermentation

- Bi-weekly Project Meetings
- Molecular Biology specific meetings monthly

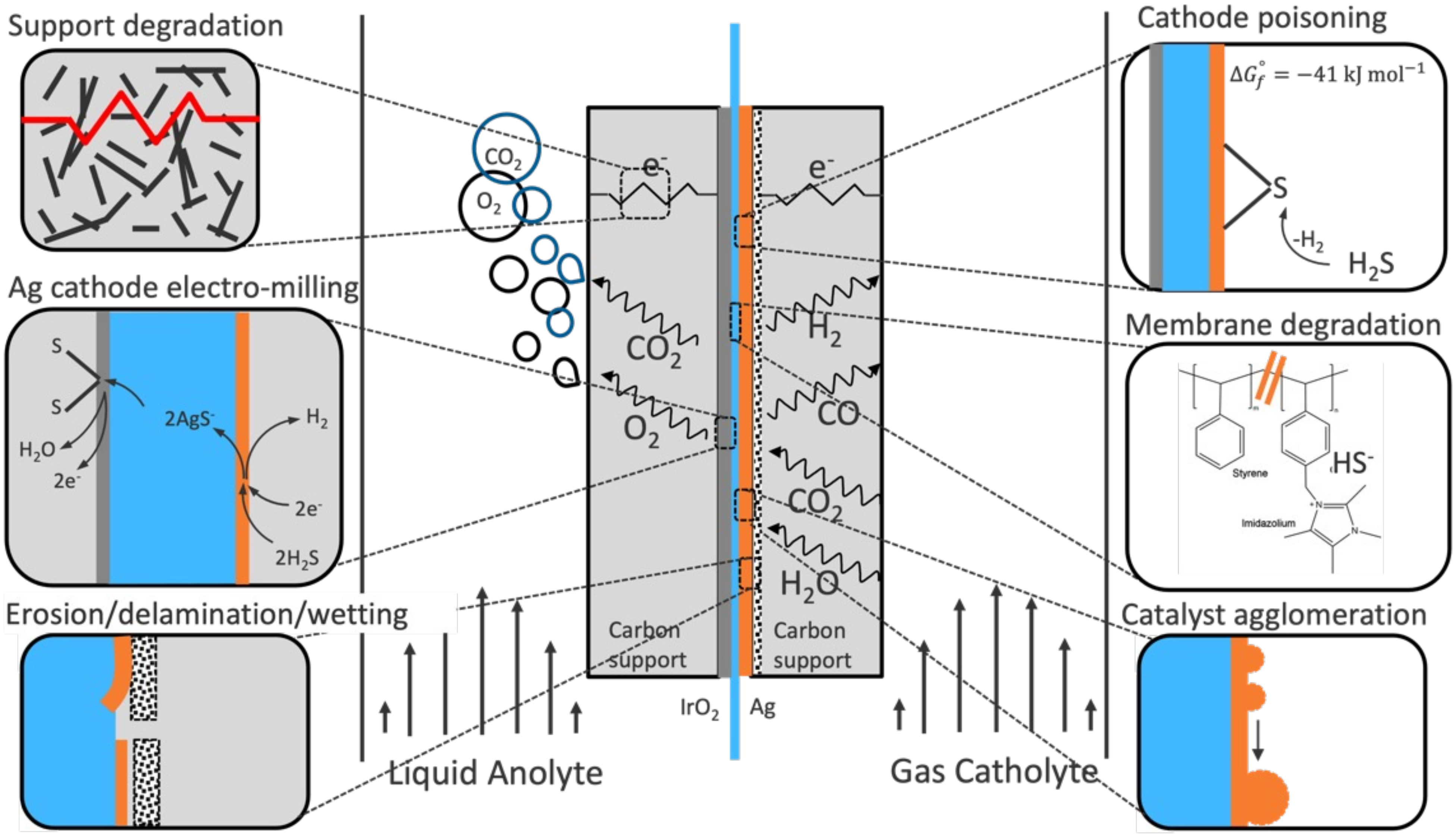
- Bi-monthly Working Groups E-COWG, B-COWG, A-COWG
- Site Visits with industrial partners

1. Approach – Research Focus Key Cost Drivers



Huang *et.al. Applied Energy* (2020)

1. Electrochemical CO_2 Reduction Gaps

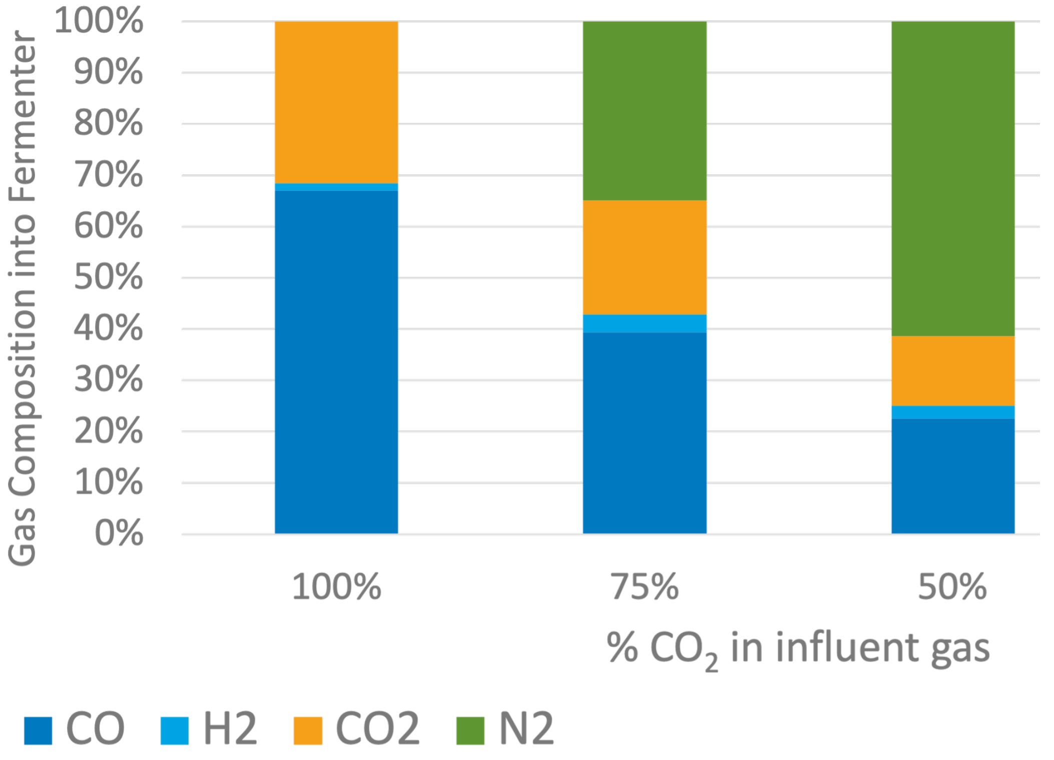


1. Flue Gas Components to Test on Electrolyzers

Components	[High] CO_2 Flue gas	Electrolyzer Testing Conditions	Results
CO_2	99%+	14-100%	
VOC	< 1000 ppm (combined)		
Acetic Acid	N.D.	100+ hrs.	OK up to 500 ppm
Acetone	0.6	100+ hrs.	OK up to 500 ppm
VSC	< 10 ppm (combined)		
Hydrogen Sulfide	2.3	0-50 ppm	Decrease @ 3 ppm
Methyl mercaptan	0.1	0-10 ppm	Decrease @ 2 ppm

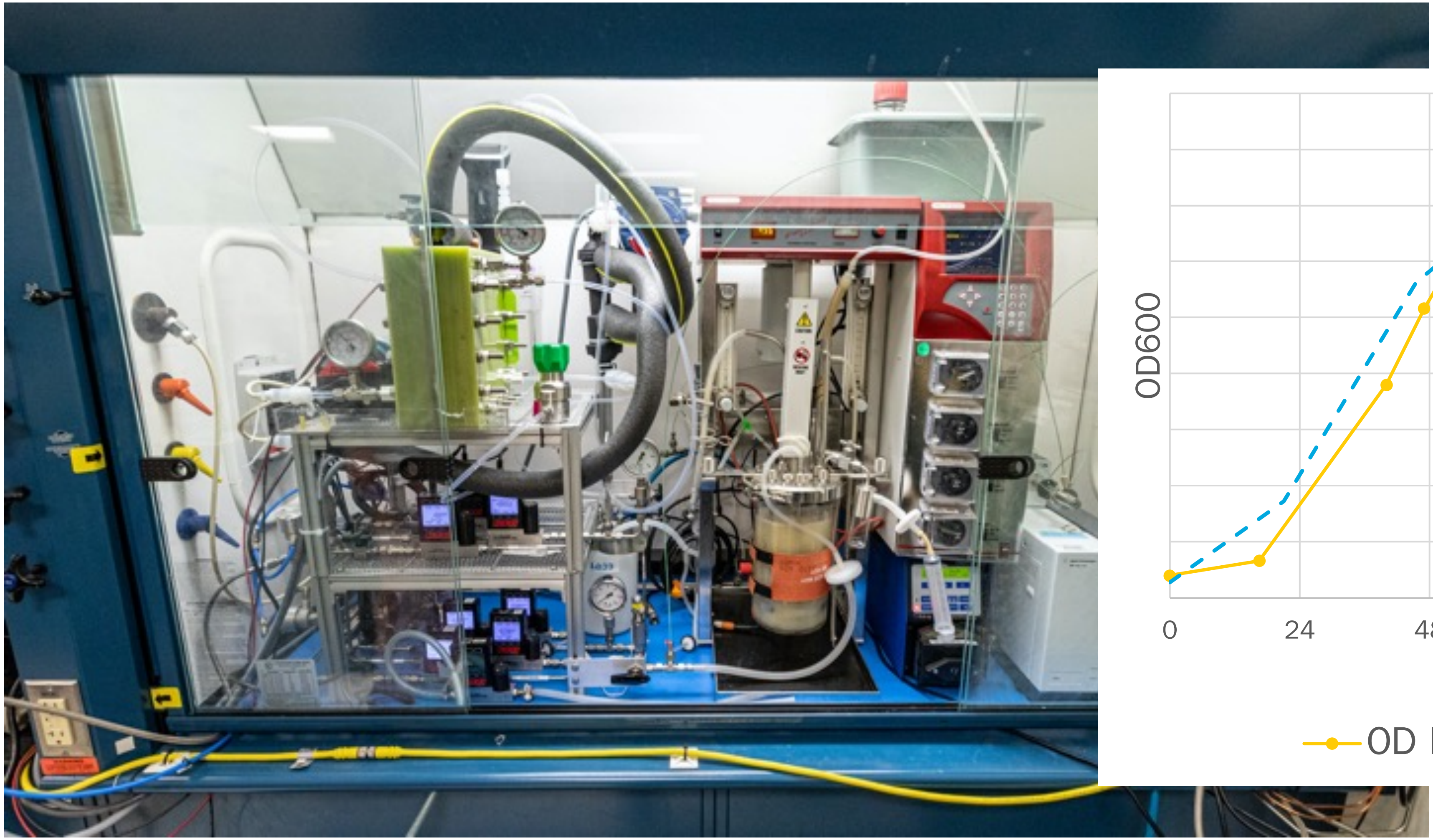
1. Waste Gas Compositions for Fermentation

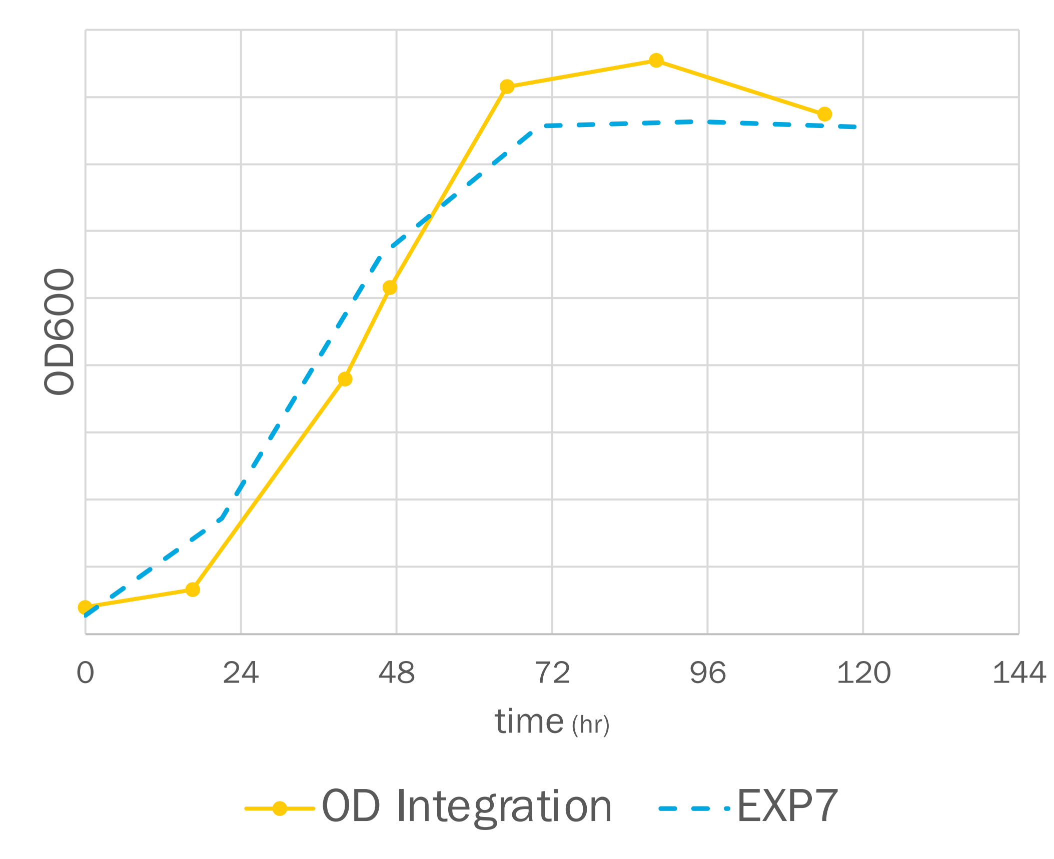
	H_2	CO	CO_2	N_2	ALE
High CO	2%	65%	33%	0%	O
Low CO	10%	45%	23%	22%	O
High H_2	50%	10%	30%	10%	x
SMOG	5%	55%	30%	10%	x
Syngas	30%	30%	30%	10%	x



High H2 gas: refinery off-gas.
Steel-Making Off Gas **(SMOG)**
Syngas: representative for gasification of municipal solid waste or biomass.

1. Electrolyzer Integration with Gas Fermenter





C. Auto Fermentation is identical with bottled gas or electrolyzer output

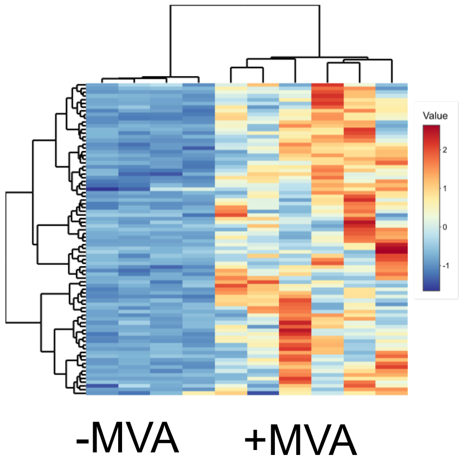
Construction of *de novo* Mevalonate biosensor

Why Mevalonic Acid?

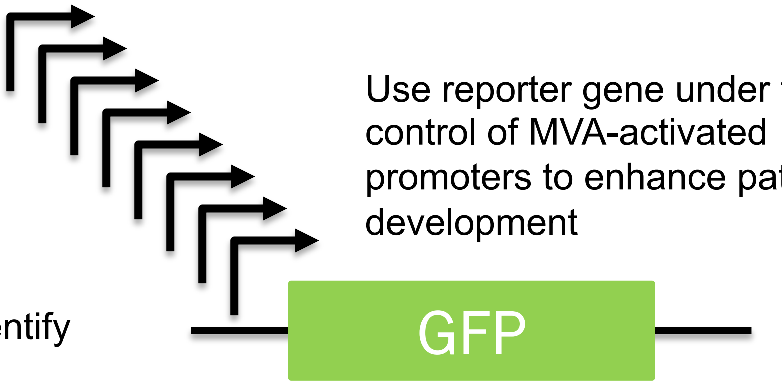
- Flexibility in feedstocks and end products beyond ethanol such as isopropyl alcohol, acetone, and **mevalonate**
- Mevalonate is the precursor for high value chemicals such as isoprene as a key ingredient for synthetic rubber.
- US has no domestic source of rubber, biomanufacturing will play a growing role in our domestic independence from both fossil-fuel based commodity chemicals and products.

A two-pronged approach to construct our biosensor

Strategy 1 will employ transcriptomic profiling of cells exposed to mevalonate to identify promoter with strong expression responses MVA

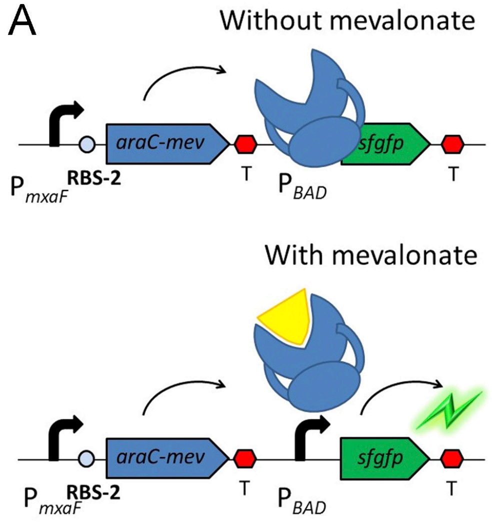


Transcriptomics (*E. coli/C. auto*) to identify gene responsive to MVA



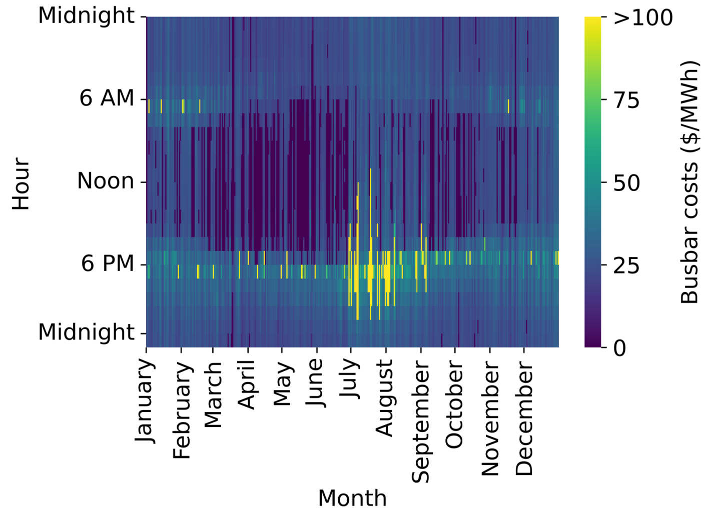
Use reporter gene under the control of MVA-activated promoters to enhance pathway development

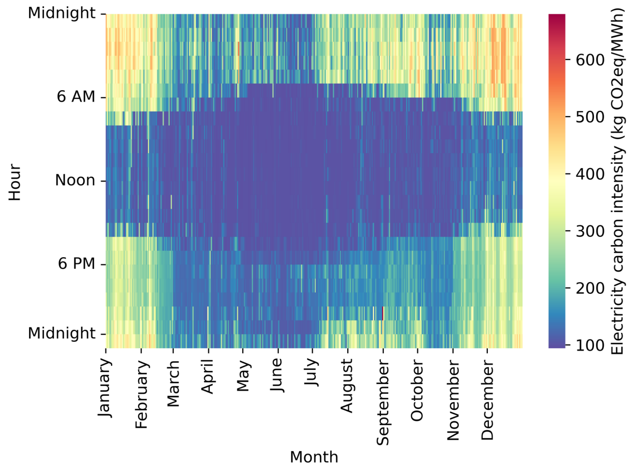
Strategy 2 will utilize both random and targeted mutagenesis to adapt known transcriptional regulators into responding to mevalonate

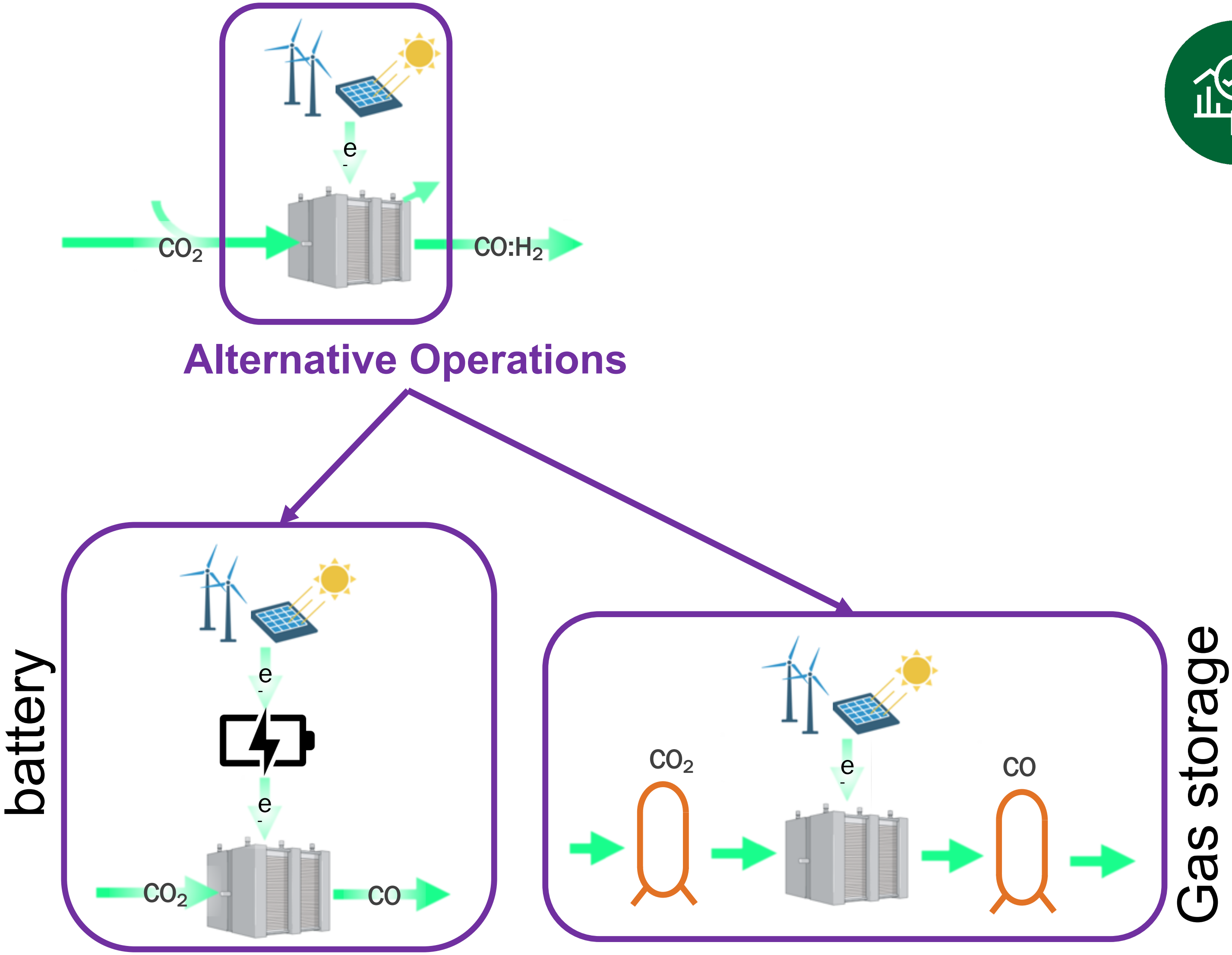


Adapted from Liang et al. 2017

1. How to design and operate an electrolyzer and the impact on economics







2. Progress and Outcomes

Year 1
Start Q2 FY22

- ✓Project kick-off
- ✓Demonstrate *C. auto* transformation protocols
- ✓Run Electrolyzer with CO_2 and 3 ppm H_2S for 250 hours with less than 10% increase in cell voltage

Year 2

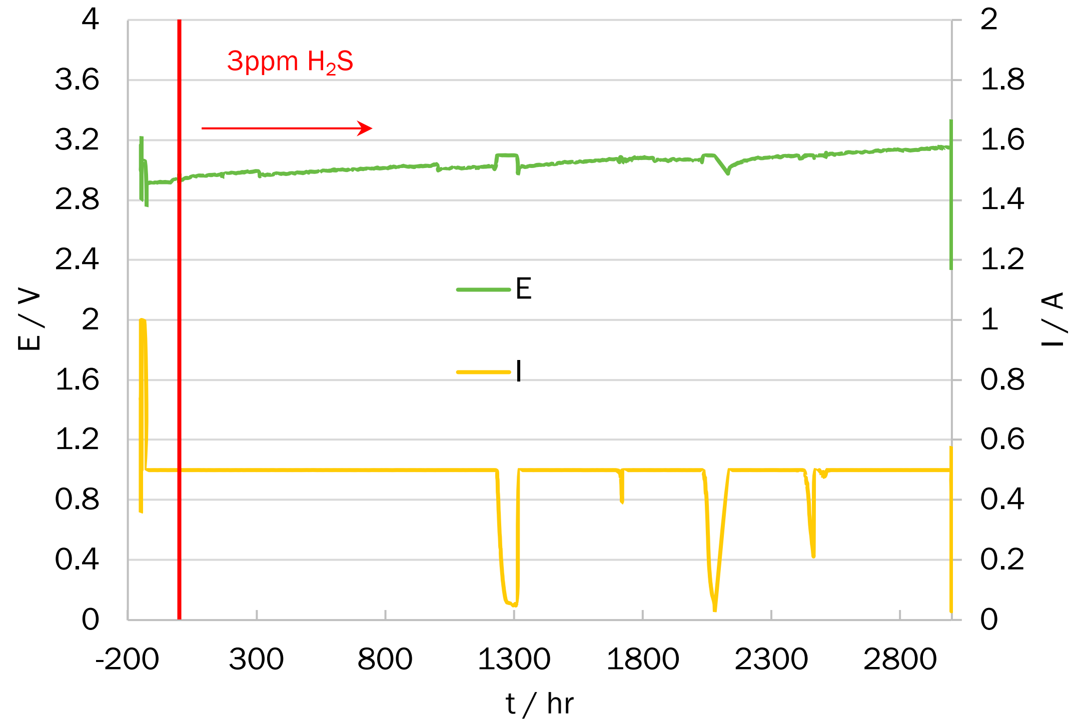
- ✓Demonstrate at least 2X increase in maximum expression level of a reporter gene
- Generate mevalonate biosensor
- Quantify electrolyzer performance as a function of H_2S concentration (>3 ppm)
- Report optimal operating strategies and system designs for electrolyzers
- Demonstrate membrane regeneration strategies to recover performance within 90% of initial performance.

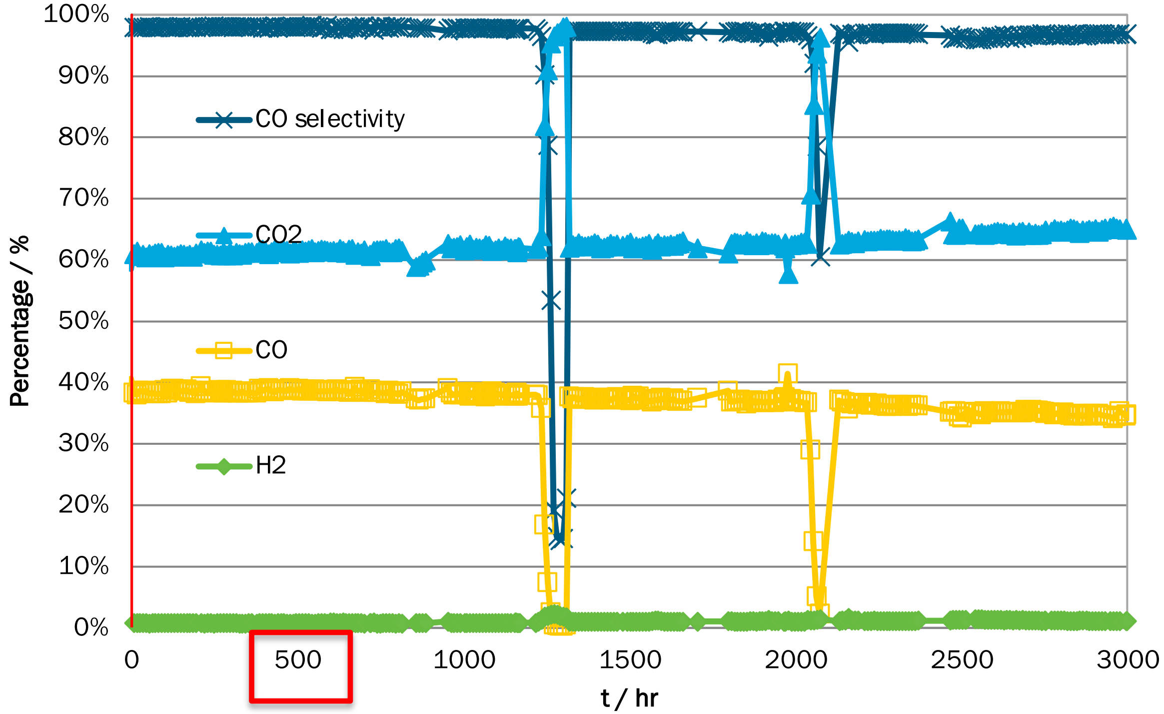
Year 3
End Q4 FY24

- Reduce CO_2 membrane crossover by 20% in a MEA CO_2 electrolyzer.
- Identify at least 3 near term sites with low carbon electricity and low-cost CO_2 feedstocks to identify opportunities to integrate this technology at scale.
- Increase the carbon conversion efficiency from CO_2 to ethanol and melonic acid by at least 20%.

2. Increased durability

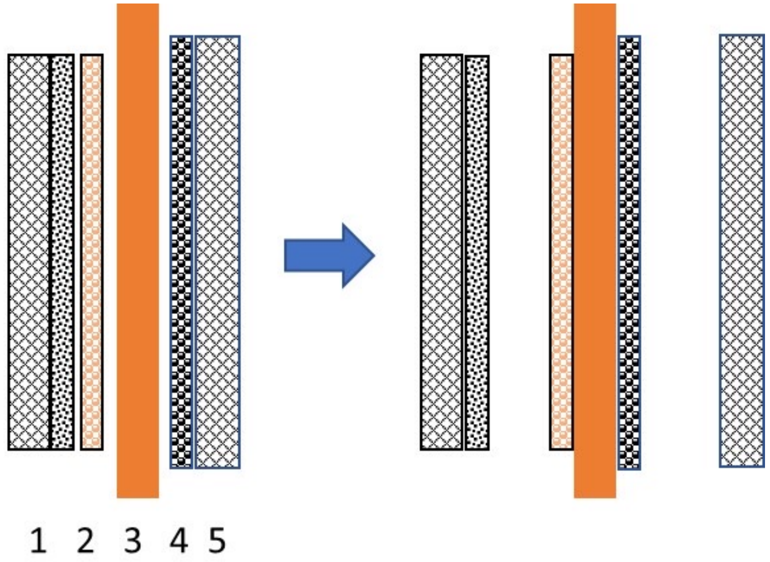
100 mA/cm² 3ppm of H_2S for up to 3000hr

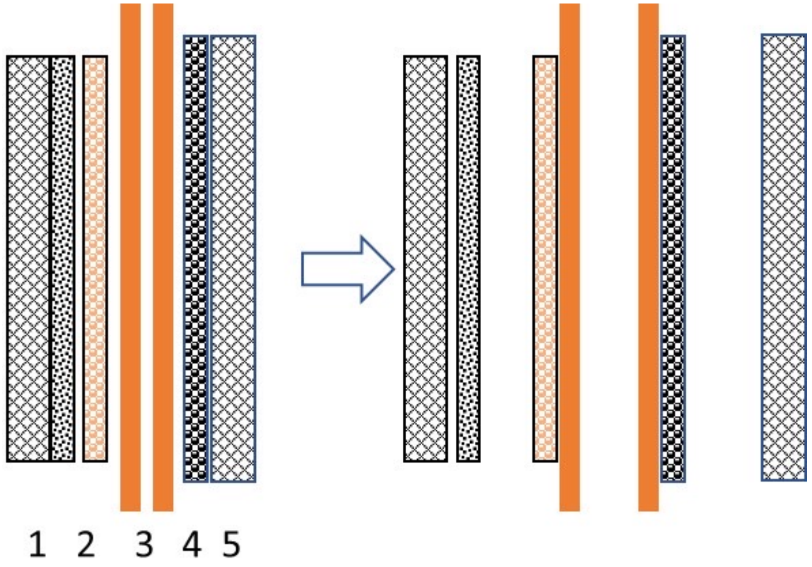




Go/ No-Go MS (3/30/23): No more than 5% increase in electrolyzer voltage when fed with 3 ppm of H_2S for 500 hours at 100 mA/cm².

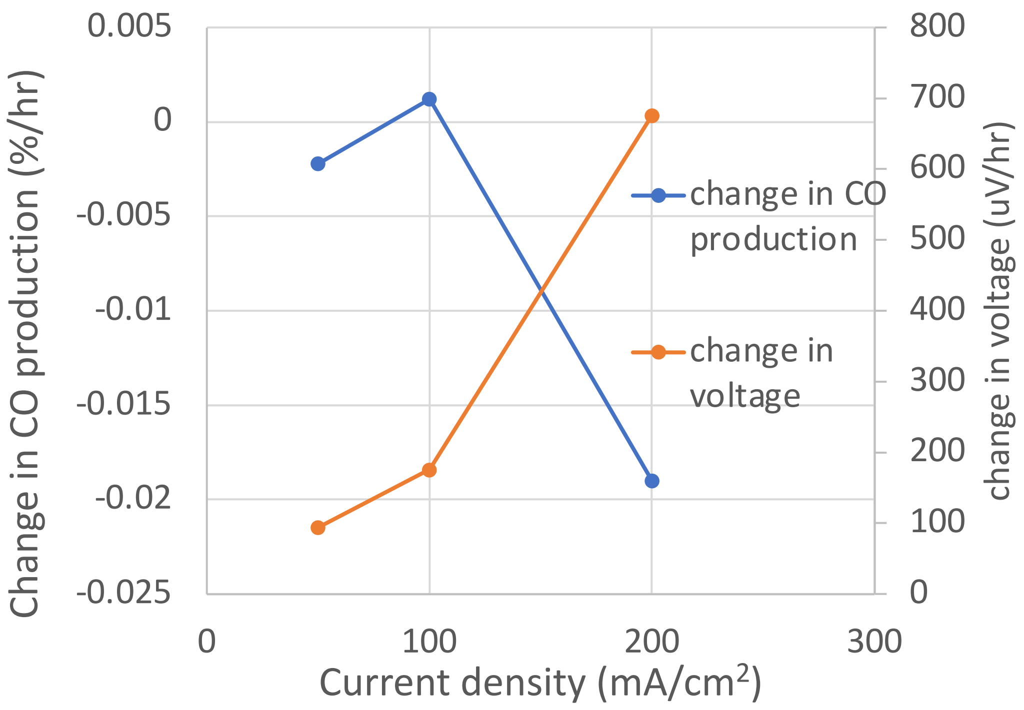
2. Improved Membranes

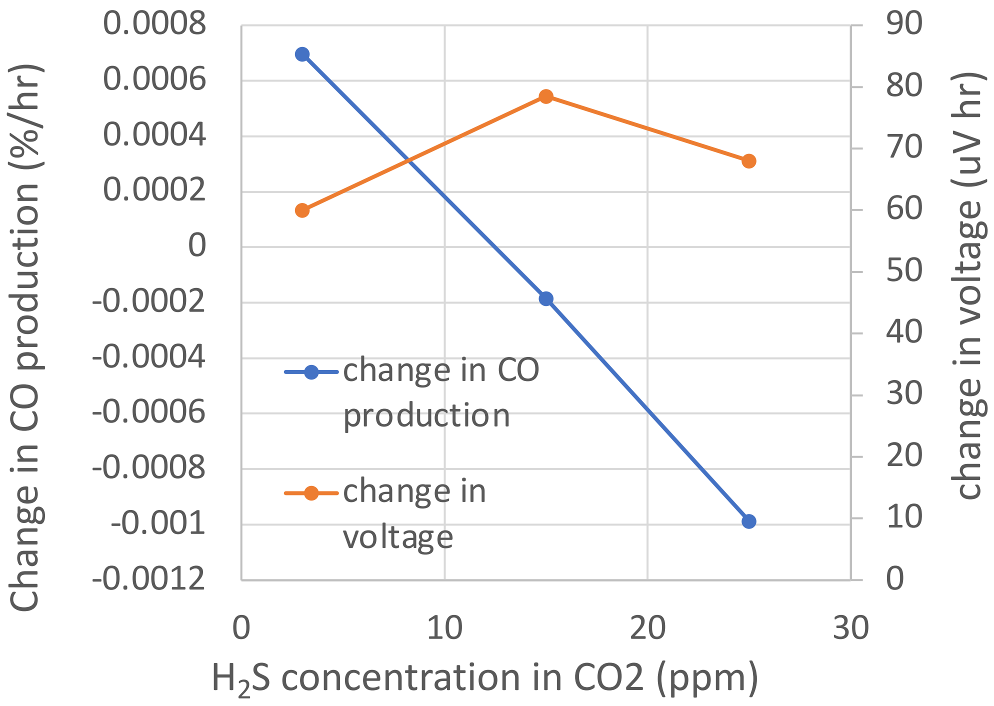




1 Avcarb GDS
2 Ag catalyst layer
3 Sustainion® membrane
4 IrO2 catalyst layer
5 Toray carbon fiber paper

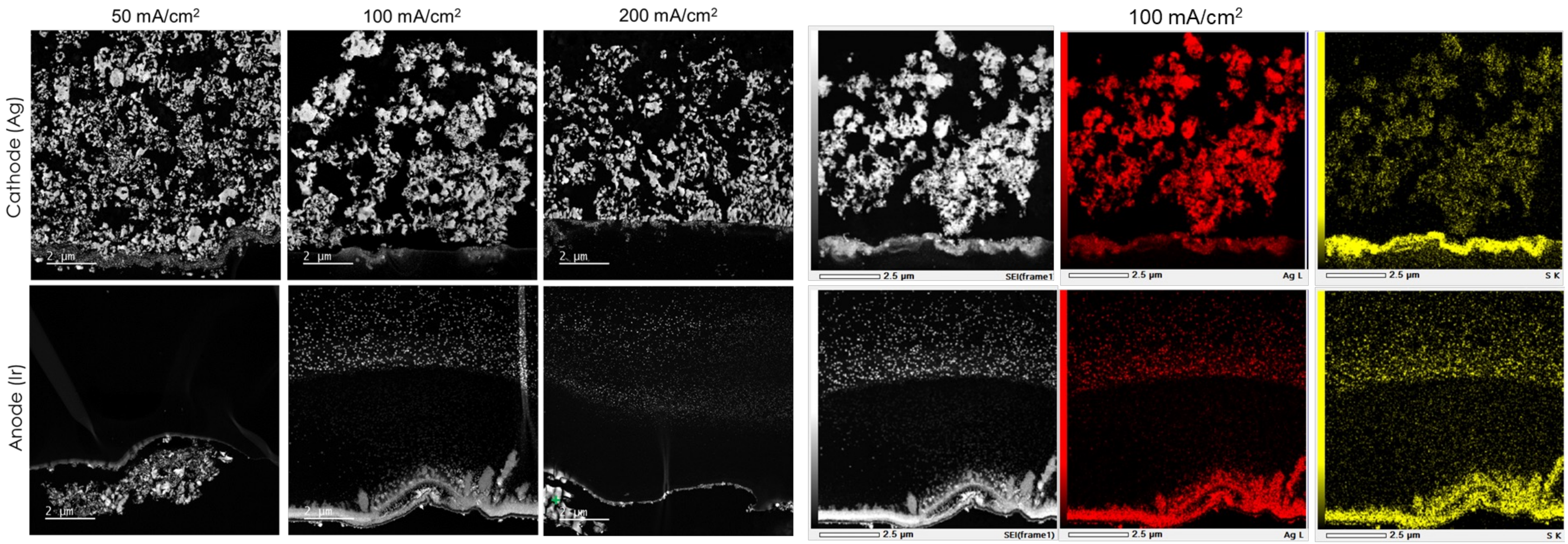
2. Summary of H_2S effect





2. Colocalization of Ag(S) Particles in Membrane

SEM-EDX element localization and quantification



Silver

Sulfur

2. Strain and Fermentation Engineering

NREL

- MVA Biosensor/selector Tool Development
- Small-scale ALE
- Metabolite, Offgas, and Compositional analyses

Lanzatech

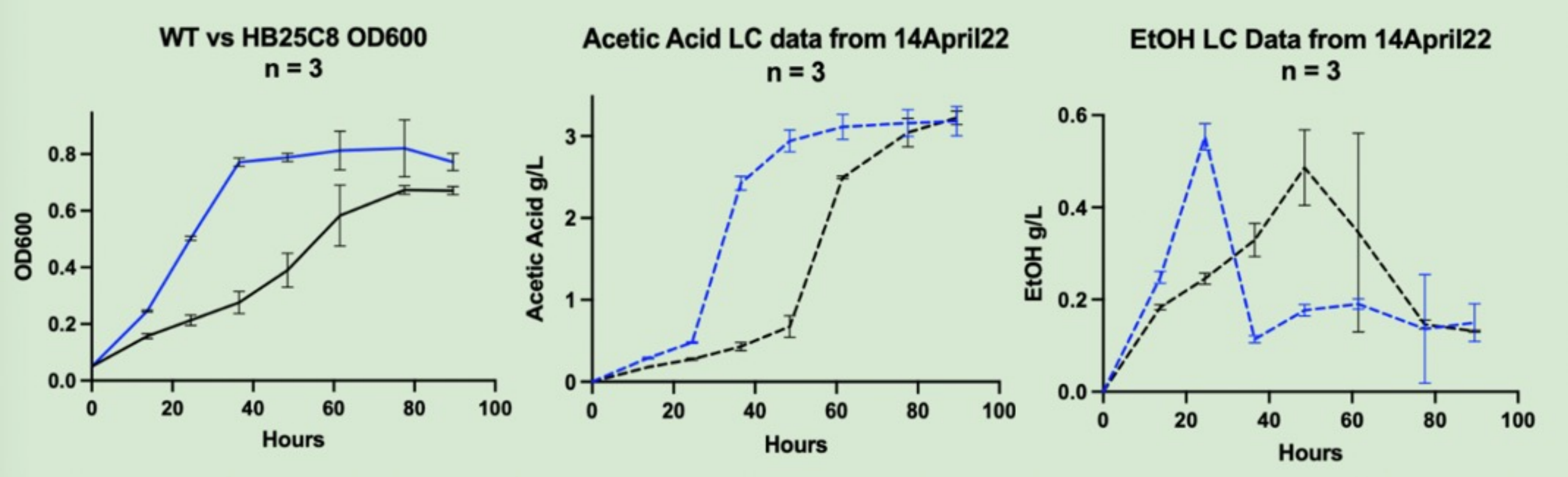
- Provide strains and plasmids
- ALE Scale-up
- Next-gen seq sequencing and genome-scale modeling

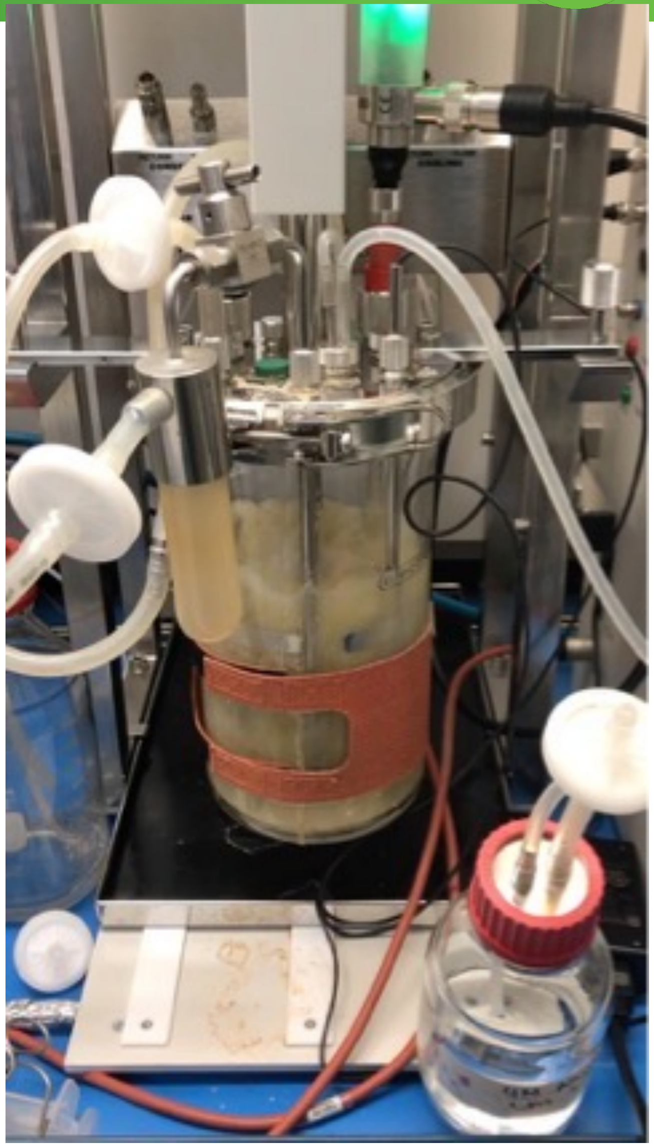
ORNL

- Toolbox expansion
  - ➢ High-copy number plasmids
  - ➢ Dynamic pathway control (w/ Agile)
  - ➢ Terminators and genetic insulators

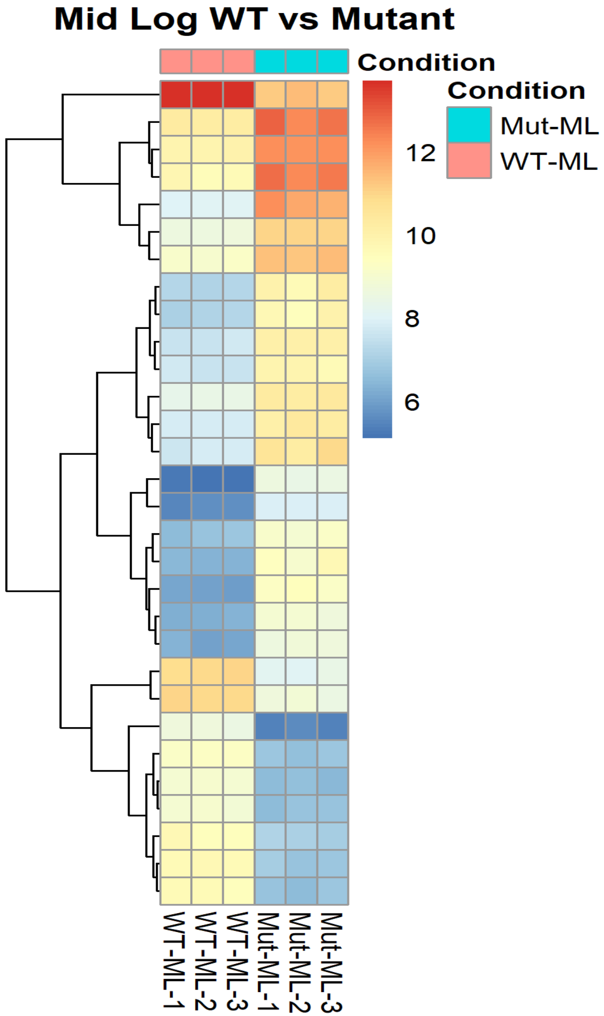
2. Adaptive Laboratory Evolution for Enhanced CO Utilization

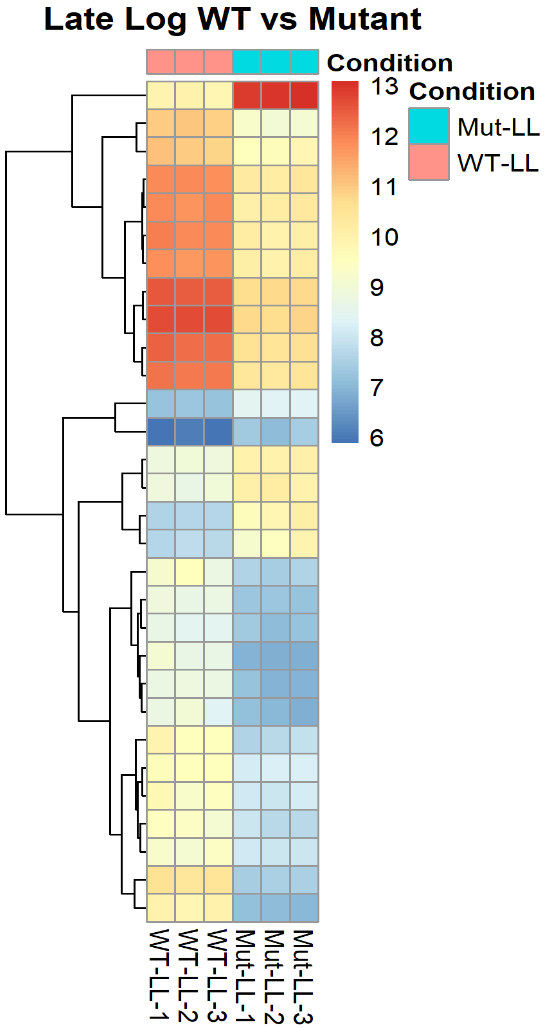
- We have identified mutants with enhanced growth rate and product formation relative to WT *C. autoethanogenum.*
  - Achieved **>57g/L acetate titer** under continuous gas feed (CO as sole carbon source)





2. Transcriptomic Results From High CO Adapted Mutant



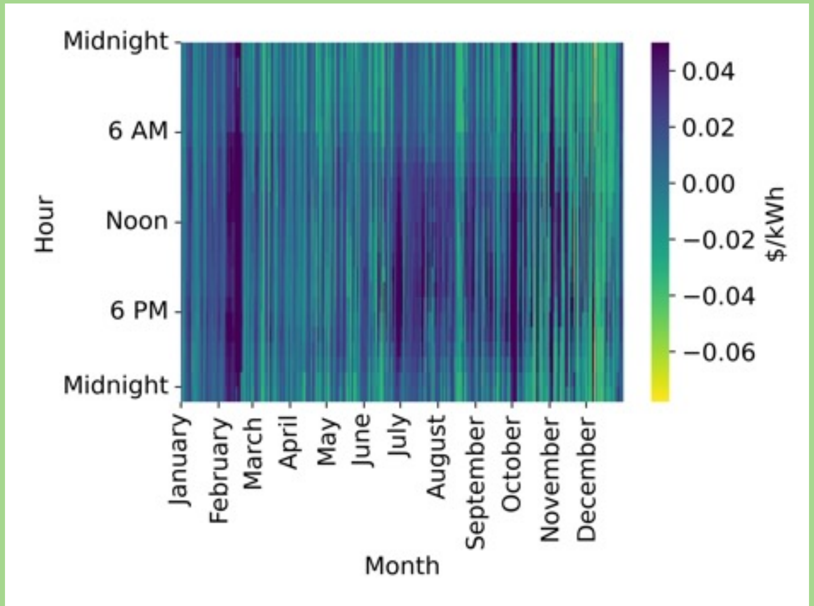


- Comparative genomic analyses have identified candidate mutations conferring enhanced phenotype.
- Currently conducting comparative transcriptomics to identify differentially expressed genes to inform targeted engineering efforts.

2. Accomplishments in Task 2

1. Establishment of CO delivery/cultivation/fermentation system at NREL
2. Reproduction of LT genetic engineering capabilities
3. Chemically mutagenized and adapted to low and high-CO electrolytic syngas streams
4. Genomic and transcriptional characterization of top-candidate mutant strains
5. Physiological characterization (growth rate, substrate utilization, and product formation) of top-candidate mutant strains.
6. Initiation of a MVA biosensor development

2. Optimization of System Integration

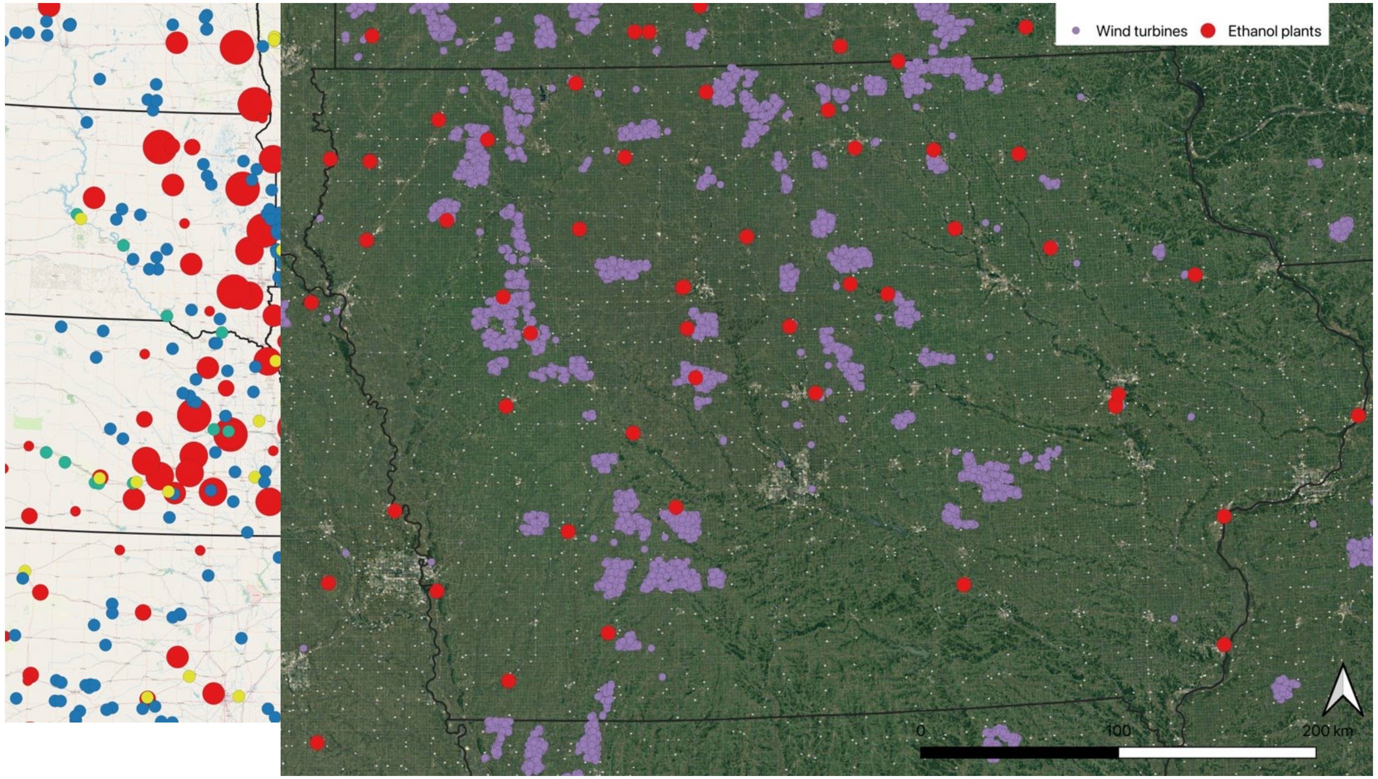


Economic tradeoff analysis of:

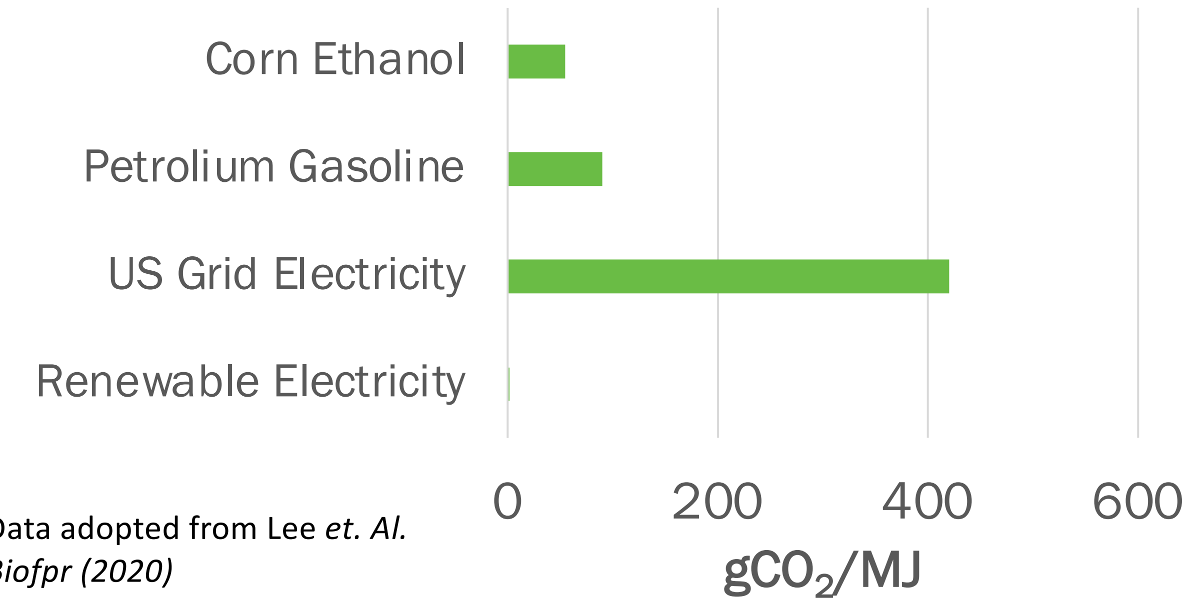
- Buffer tank storage of feedstock and products
- Battery energy storage to offset high energy costs

Geospatial feasibility and opportunity analysis

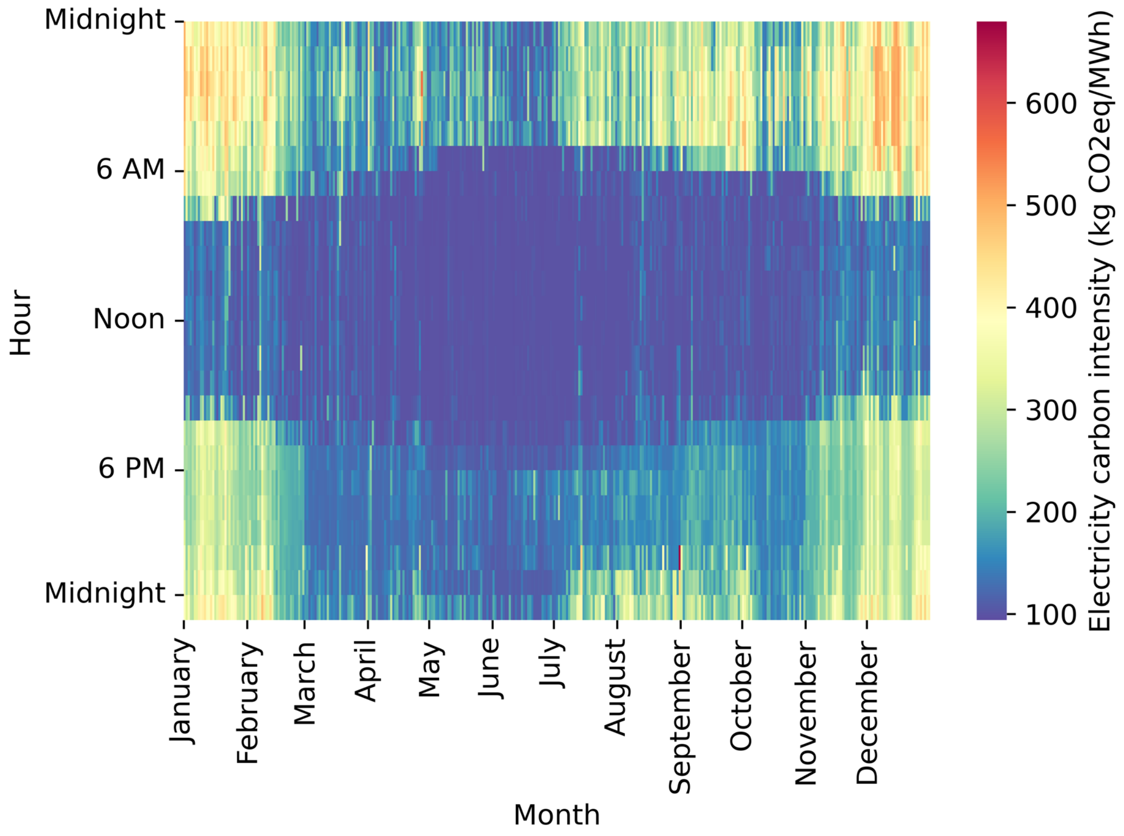
- High concentration CO_2 feedstock stream
- Low-cost wholesale power
- Highly renewable grid



3. Impact of CI



Data adopted from Lee *et. Al. Biofpr (2020)*



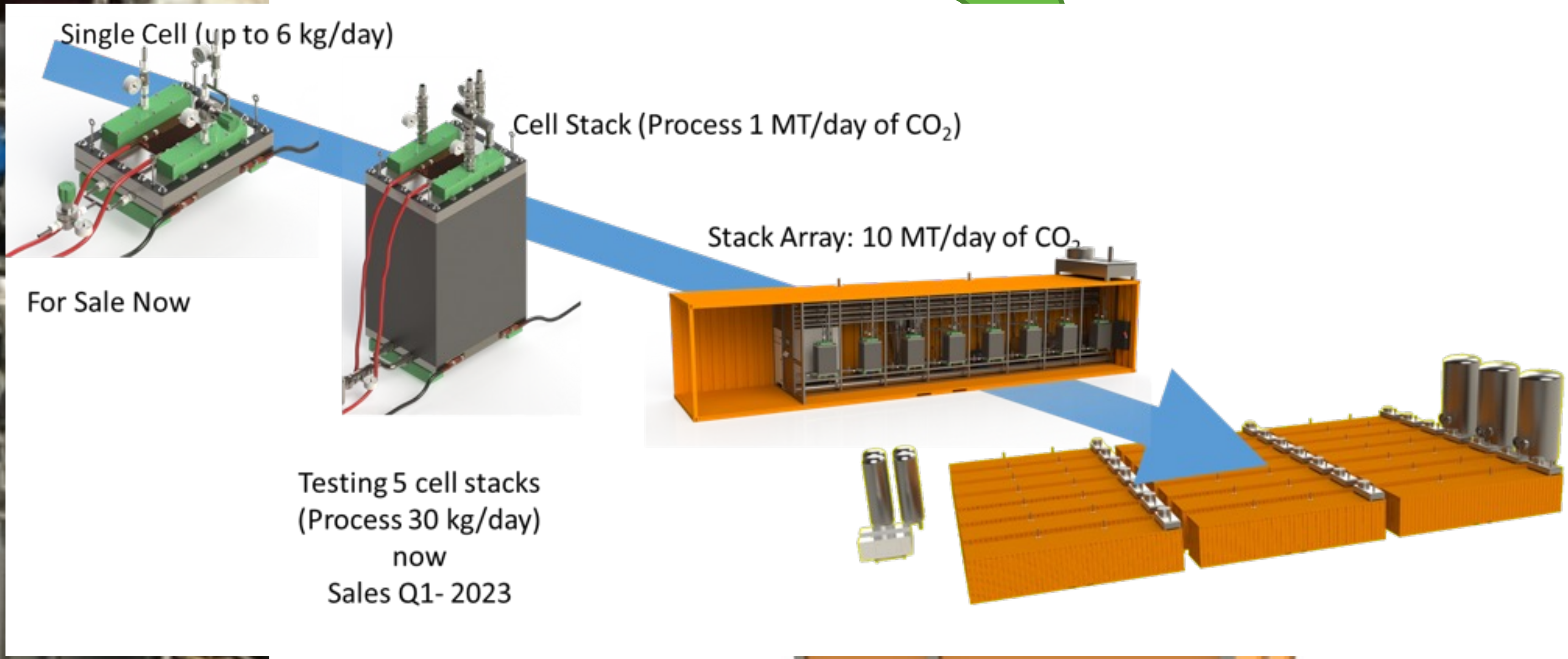
CI of ethanol using renewable electricity is magnitudes lower than using U.S. average grid electricity

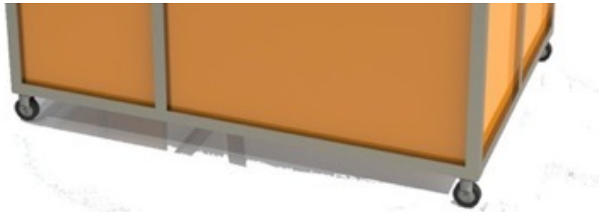
3. Impact - Industrial CO_2 Flue Gas Feedstocks

3. Integration and Scaling

1000L EtOH Fermenter

$CO:H_2$





10kW 2x 5–Cell Stacks of 1000 cm^2 Electrolyzers

Summary

- Integrated 250 cm^2 CO_2 electrolyzer with CSTR
- Improved MEA membranes
- Successfully ran CO_2 electrolyzers with 3 ppm H_2S for 3000 hours
- Demonstrated transformation and gene expression in *C. auto*
- Adapted *C. auto* using ALE to improve growth on high and low CO gas mixtures
- Identified key genes responsible for enhanced growth phenotype
- Identified process parameters to optimize usage of low-cost renewable electricity to power electrolysis

Team Members

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CO_2 Fuel Dioxide Materials™

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Thank You

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

NREL/PR-5100-85326

Quad Chart Overview

Timeline
- **Start Date:** 1/1/2022
- **End Date:** 9/30/2024

	FY22 Costed	Total Award
DOE Funding	$925,000	$1,750,000
Project Cost Share*	*N/A*	

TRL at Project Start:
TRL at Project End:

Funding Mechanism
CO_2 Lab Call FY22

Project Goal

Incentivize CO_2 Utilization via integration of downstream electrolytic and biocatalytic upgrading of flue gases into fuels and chemical intermediates.

End of Project Milestone

1) Reduce CO_2 membrane crossover by 20% in a MEA CO_2 electrolyzer.

2) Identify at least 3 near term sites with low carbon electricity and low-cost CO_2 feedstocks to identify opportunities to integrate this technology at scale.

3) Increase the carbon conversion efficiency from CO_2 to ethanol and isoprene by at least 20%. (9/30/2024)

Project Partners

- Dioxide Materials
- LanzaTech
- Oak Ridge National Lab

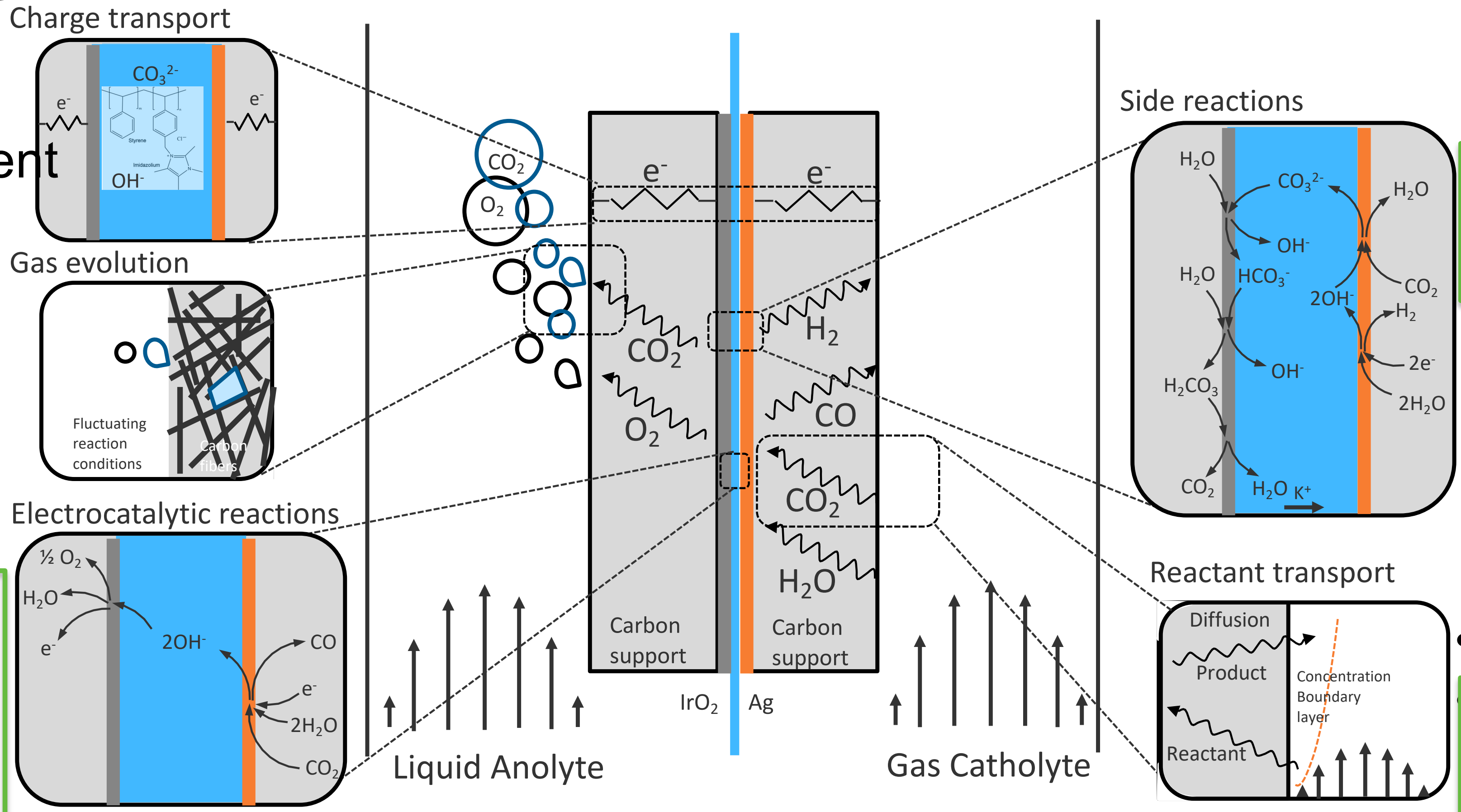
Electrochemical CO_2 Reduction Gaps

Technology gaps

- Carbon support stability
- Heat management
- Mass Transport

- Carbon support chemistry
- Channel design

- Catalyst stability
- Contaminant tolerance

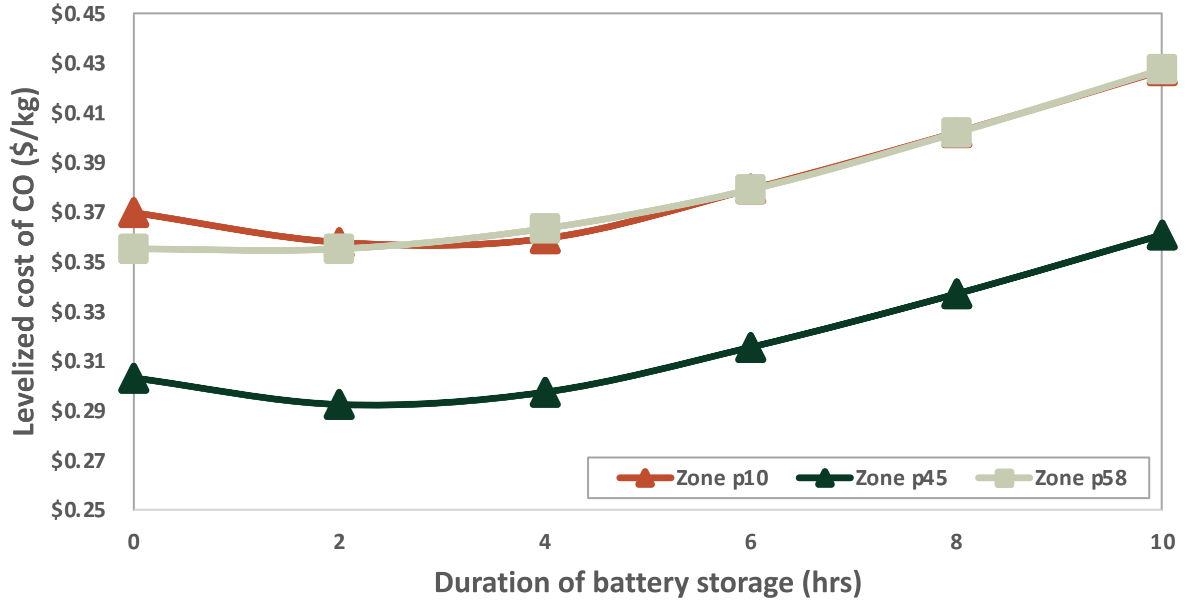


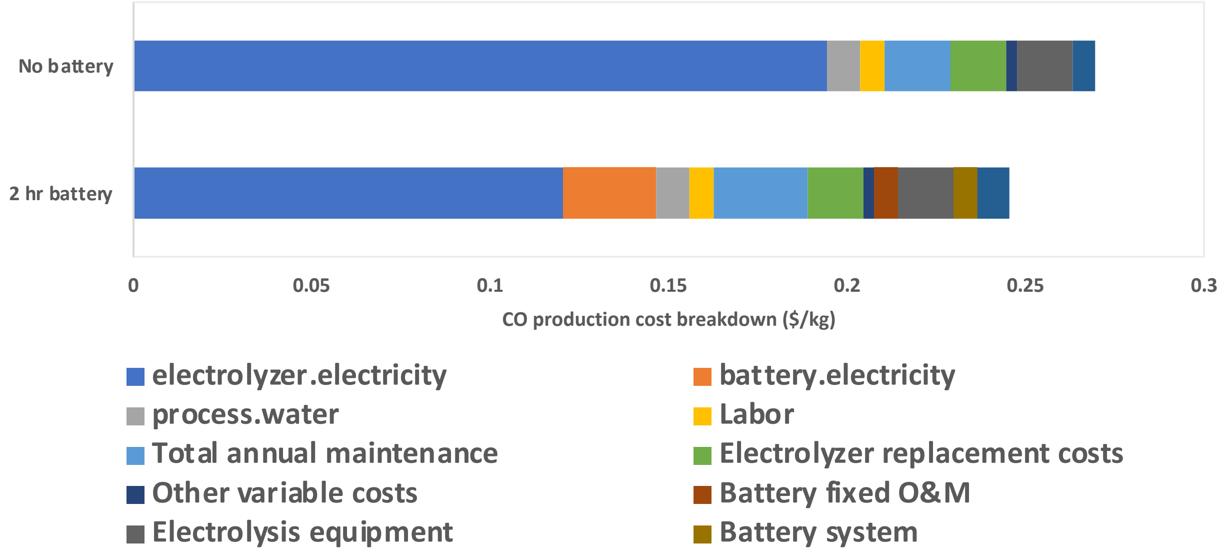
Technology gaps

- Mechanisms
- pH effects

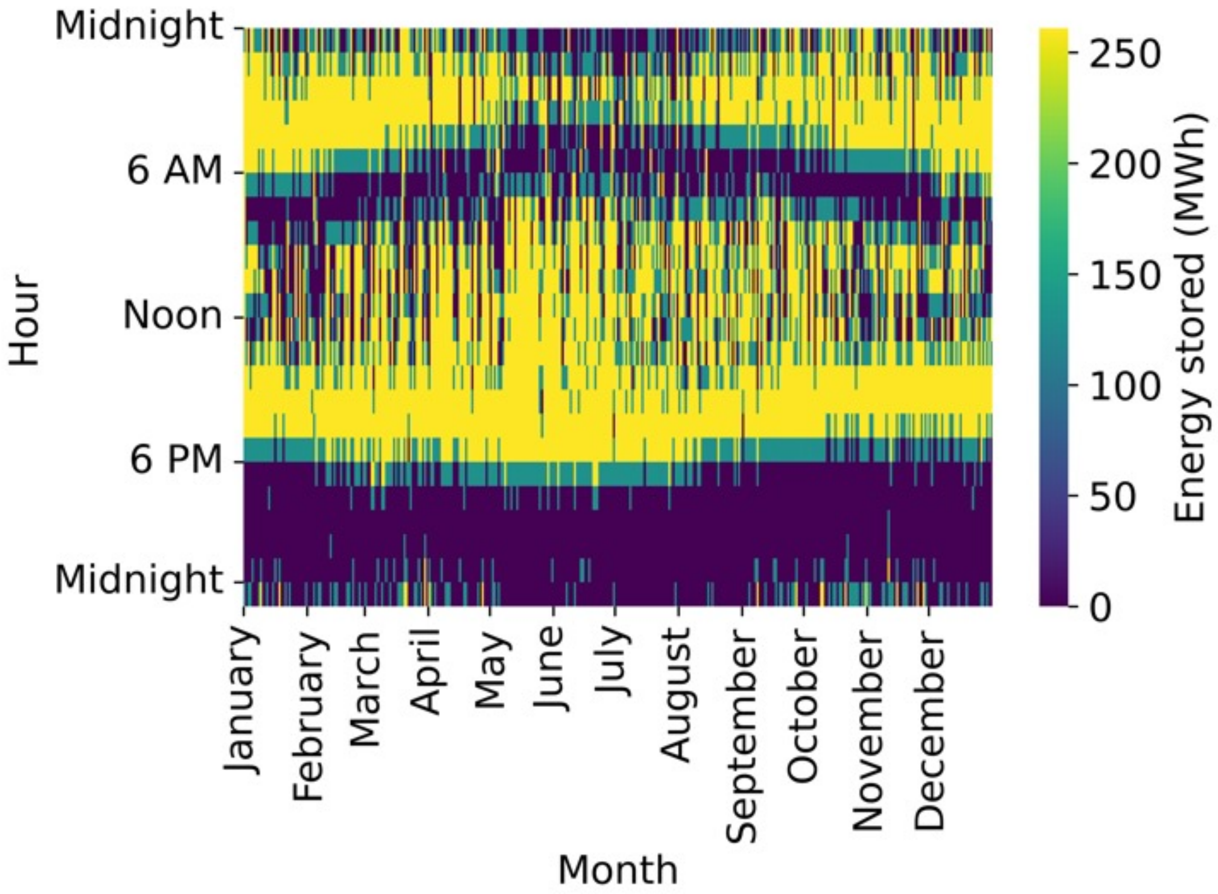
- Channel desig
- Humidification requirement

2. CO production cost benefits from 2 hr battery storage





Avoid peak prices during morning and evening demand spikes, charging overnight and midday



Project milestones	Due date	Percent complete	Date Completed	On track?
Establish Material Transfer Agreement for the Transfer of proprietary strains and sequences from LT to ORNL and NREL	03/31/2022	100%	03/31/22	Y
Run electrolyzer on H_2S. No more than 10% increase in electrolyzer voltage at 200mA/cm² when fed with ~3 ppm of H2S for 250 hours	06/30/2022	100%	06/30/2022	Y
Demonstrate at least 2X increase in maximum expression level of a reporter gene by promoter, RBS, mRNA stability, or plasmid copy number engineering.	9/30/2022	100%	12/31/22	Y
Generate functional mevalonate biosensor. Demonstrate mevalonate-mediated activation of an anaerobic fluorescent reporter cassette in response to exogenously supplemented mevalonate. Strains harboring a functional biosensor will be screened and selected via fluorometry to establish a background chassis for C. autoethanogenum variants with enhanced mevalonate co-production capacity.	12/31/22	50%		N
Quantify H_2S effects on electrolyzer performance. No more than 5% increase in electrolyzer voltage when fed with 3 ppm of H_2S for 500 hours at 100 mA/cm^2.	3/30/23	75%		Y
Draft technoeconomic analysis report. Draft report summarizing methodologies and assumptions for modeling of a CO2 -> CO electrolyzer system integrated into an existing biorefinery. Report optimal operating strategies and system designs for electrolyzers operating in wholesale power markets in regions with existing biorefineries under current and future market conditions. Report will also summarize spatial analysis of low-cost electricity and high-concentration CO2 resources. Key performance metrics include the levelized production cost of CO in $/kg CO	6/30/23	50%		Y
Electrolyzer regeneration. Demonstrate membrane regeneration strategies to recover performance within 90% of initial performance.	9/30/23	25%		Y

Milestone Name/Description	Criteria	End Date	Type
Moving to an industrial process	1. Reduce CO_2 membrane crossover by 20% in a MEA CO_2 electrolyzer. 2. Identify at least 3 near term sites with low carbon electricity and low cost CO_2 feedstocks to identify opportunities to integrate this technology at scale. 3. Increase the carbon conversion efficiency from CO_2 to ethanol and melonic acid by at least 20%.	9/30/24	End of Project Milestone

Publications, Patents, Presentations, Awards, and Commercialization

Provisional Patent "*Clostridium autoethanogenum* with enhanced growth rate" Prov/22-91, Patent Application No. 63/412,137

Publications / Presentations:

1. Resch, Michael "Increasing Carbon Efficiencies of Biorefineries" Aug 2022 SIMB Annual Meeting, San Francisco, CA
2. Adam Guss. "Using synthetic biology to solve challenges in plastic waste and renewable chemical production". Biological Sciences Departmental Seminar, Missouri S&T, Rolla, MO. September 27, 2022.
3. R. Gary Grim, Dwarak Ravikumar, Eric Tan, Zhe Huang, Jack Ferrell, Michael Resch, Zhenglong Li, Chirag Mevawala, Steven D. Phillips, Lesley Snowden-Swan, Ling Tao, and Joshua A. Schaidle. "Electrifying the Production of Sustainable Aviation Fuel: The Risks, Economics, and Environmental Benefits of Emerging Pathways Including CO_2" *Energy & Environmental Science*, 2022, DOI: 10.1039/D2EE02439J

Market Trends

Product
- Gasoline/ethanol demand decreasing, 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

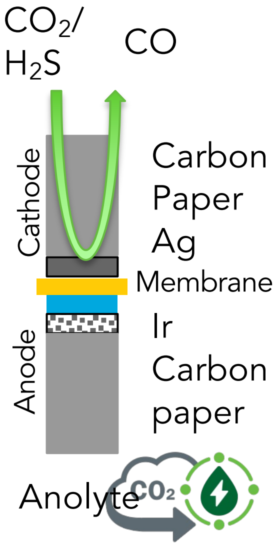
- By producing valuable products from waste CO_2 this project will incentivize CCU to realize carbon circular economy opportunities

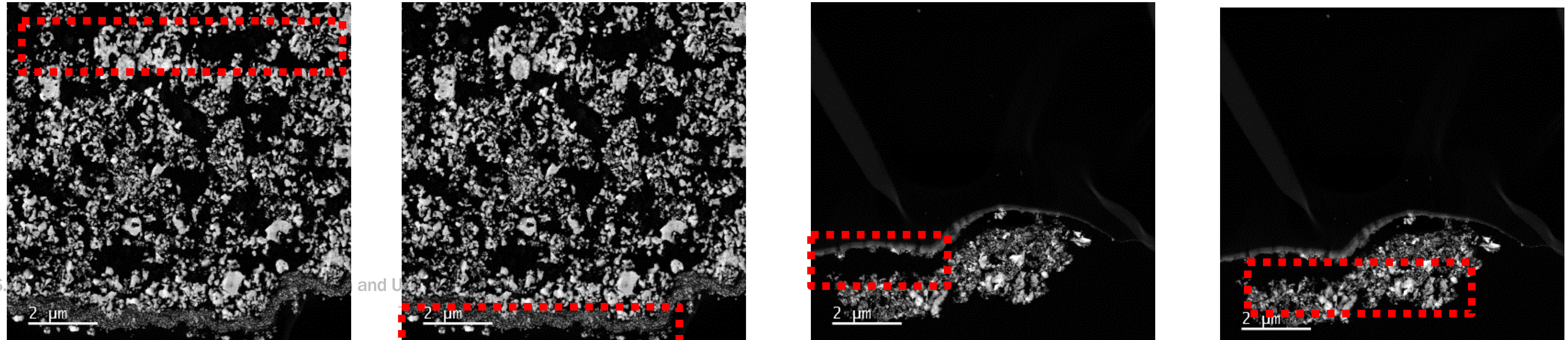
Key Differentiators

- Utilization of inexpensive feedstocks to produce products with low carbon intensity
- Process integration to link concepts
- Core national lab capability
- Market drive to low carbon fuels and chemicals
- Industrial partners
- Best in class technology

2. STEM-EDS Element Quantification

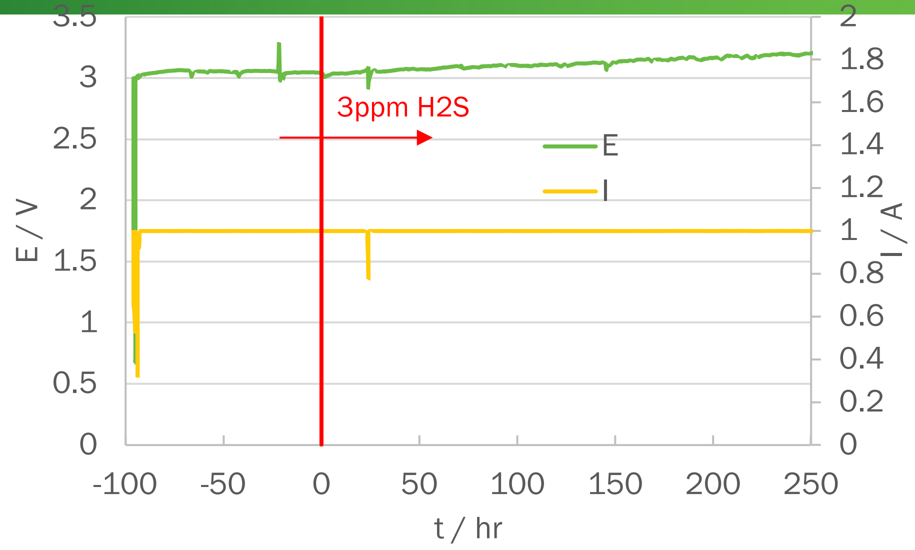
	Cathode			Cathode/Membrane Interface			Anode/Membrane Interface			Anode		
	50 mA/cm^2	100 mA/cm^2	200 mA/cm^2	50 mA/cm^2	100 mA/cm^2	200 mA/cm^2	50 mA/cm^2	100 mA/cm^2	200 mA/cm^2	50 mA/cm^2	100 mA/cm^2	200 mA/cm^2
C	84.47	81.72	79.96	82.12	67.91	89.46	85.99	80.45	78.73	79.69	76.01	79.27
O	4.17	2.41	3.46	1.11	0.59	2.27	10.40	1.91	16.65	14.15	15.06	17.06
S	0.46	0.31	0.61	1.01	6.45	2.06	0.01	4.43	0.66	0.12	0.61	0.20
Ag	10.86	15.51	15.91	12.69	24.78	6.08	0.02	12.73	0.14	0.52	1.13	0.24
Ir	0.01	0.00	0.01	0.02	0.03	0.05	3.55	0.21	3.78	5.47	7.15	3.23

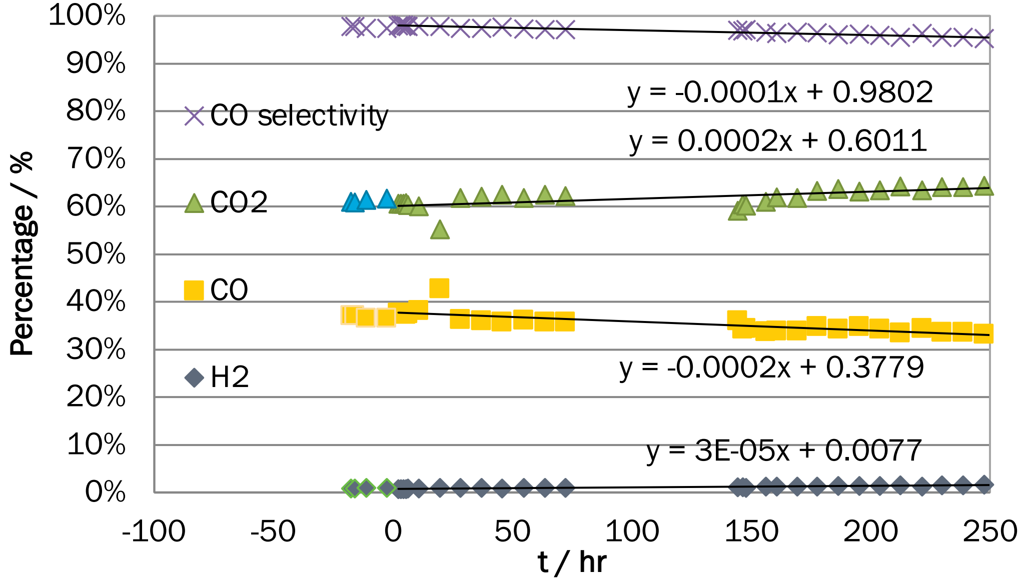




2. H_2S effect over 250 hours

- Q4 FY22 Milestone Met
  - no more than 10% increase in electrolyzer voltage at 200 mA/cm^2 when fed 3ppm H_2S for 250 hours
  - Cell voltage increased from 3.04 to 3.20V, by 5.3%
- Cell conditions
  - Membrane thickness 70um
  - 200mA/cm2
  - 3ppm H2S

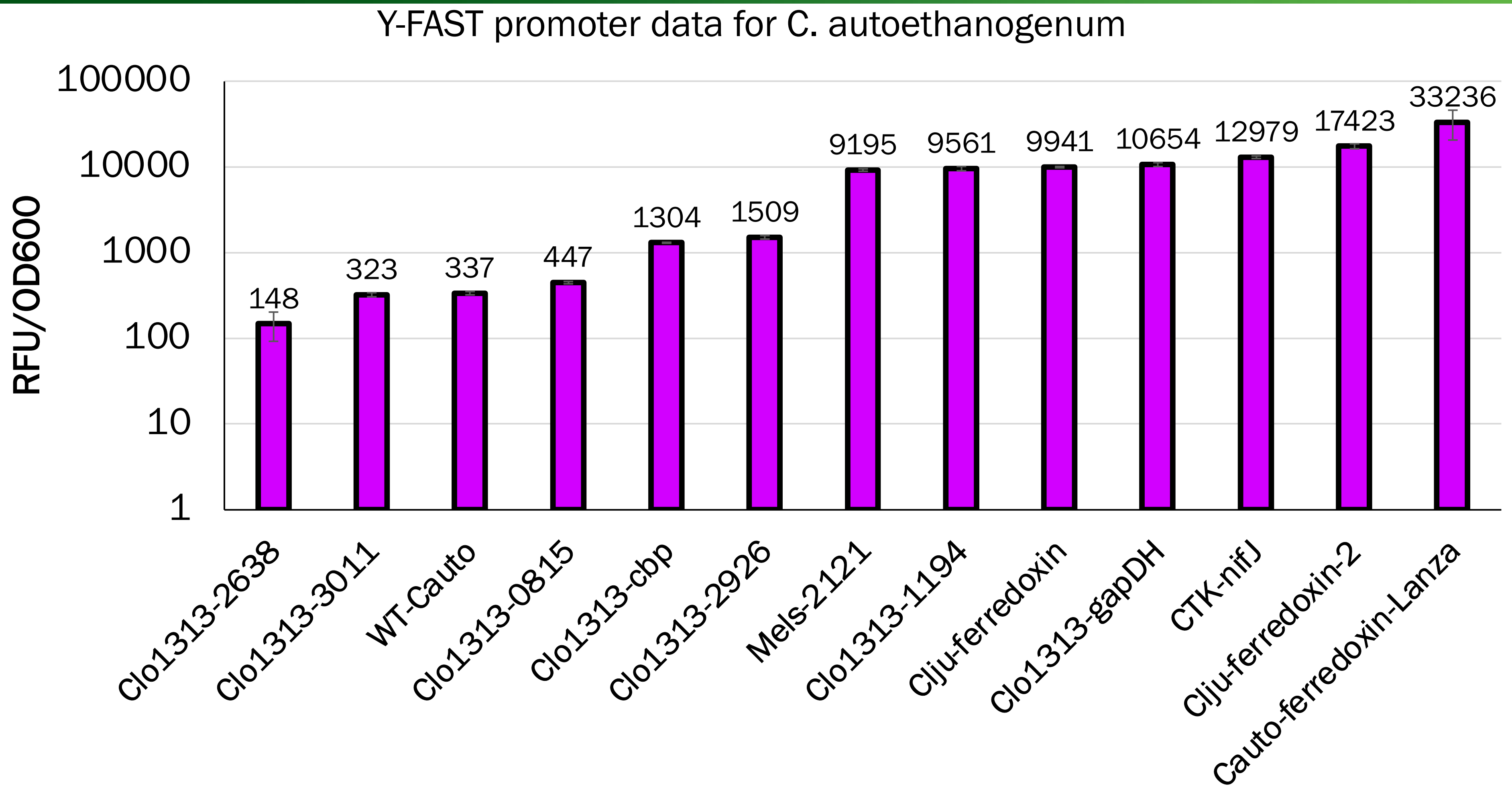




Electrolyzer Regeneration/elimination strategies

- Noticeable degradation in the presence of H_2S
  - Cell voltage increased with time
  - Conversion of CO_2 to CO Decreased over time.
    - Leakage current developed at higher current of 200mA/cm^2
- Possible reasons
  - Chemical effects
    - H_2S interaction with Ag
    - Switching to pure CO_2
      - Cell voltage decreased/ performance returned
  - Physical effects
    - Improve membrane properties
  - Anolyte
    - pH and conductivity decrease due to migration of HS^- (from cathode to anode) and K^+ (from anode to cathode)
  - carbon corrosion in anode
    - Plan to replace carbon substrate

2. Development of Genetic Tools in *C. auto*



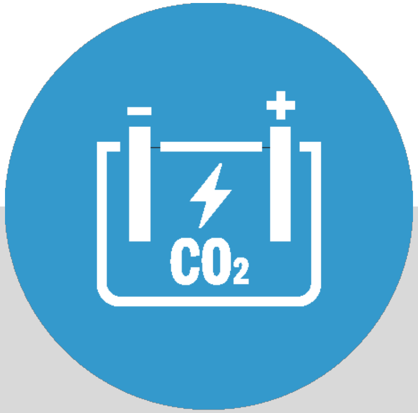
Milestone met FY22 Q4: Demonstrate at least 2X increase in maximum expression level of a reporter gene

Next steps for analysis

- Continued collaboration with other CO_2RUe analysis projects and teams:
  - Low carbon electricity price datasets (current and future) with Markets-EEJ project
  - Insights from TEA/LCA project for cost drivers that are beyond the scope of this work but could impact electrolyzer integration and operation with fermenter
- Analysis of key cost drivers for CO_2 -> CO electrolyzer
- Identify two biorefinery locations and model bolt on conversion technology

Slide Title

- Analysis and Modeling



- CO_2 Electrolysis

- Biological Upgrading