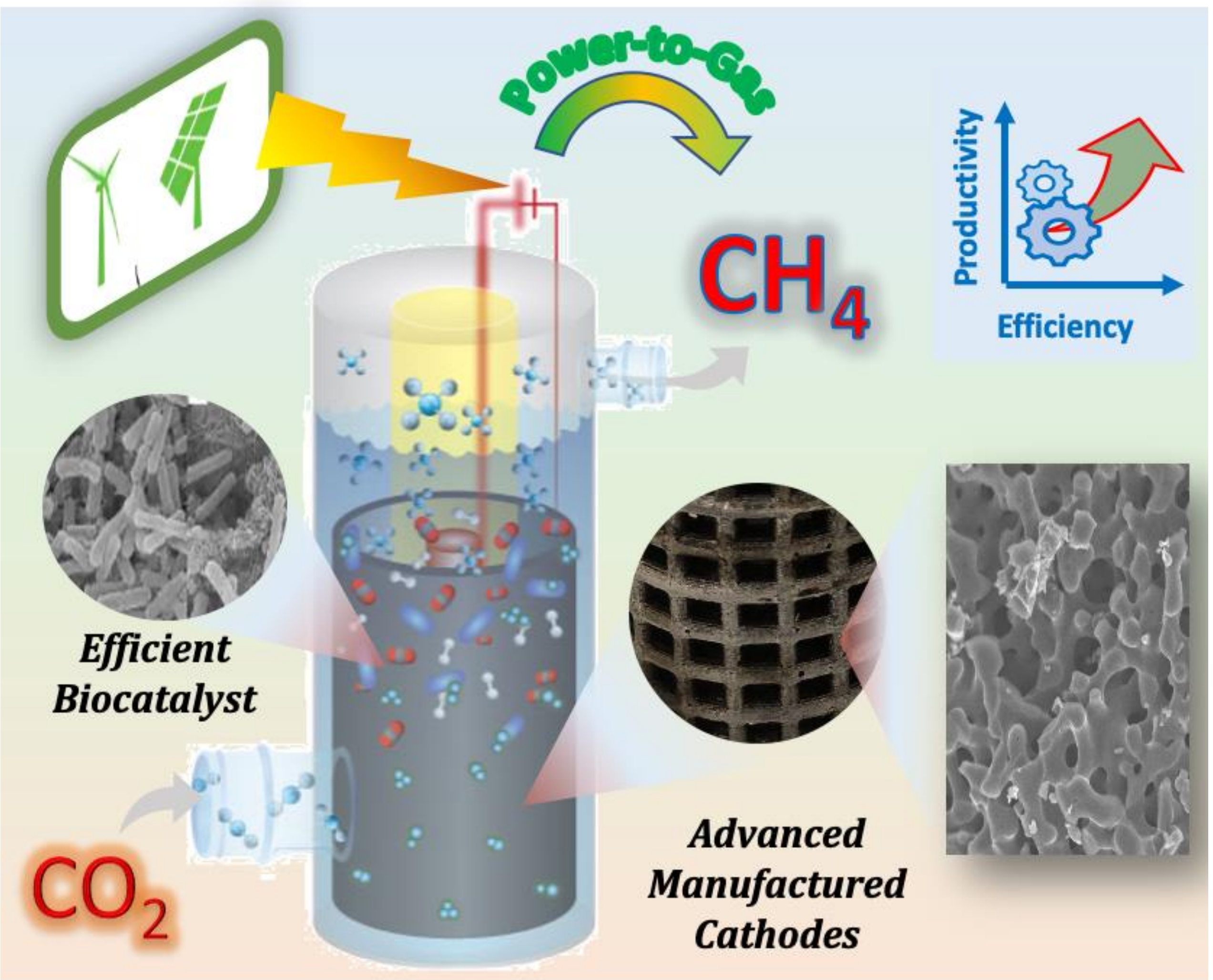
# Modular Microbial Electromethanogenesis Flow Reactors for Energy Storage and Biogas Upgrading



Project Team: Sarah Baker, Swetha Chandrasekaran, Megan Freyman, Buddhinie Jayathilake, Simon Pang, Ron Kent, Paul Ghougassian, Joerg Deutzmann, Frauke Kracke, Alfred Spormann

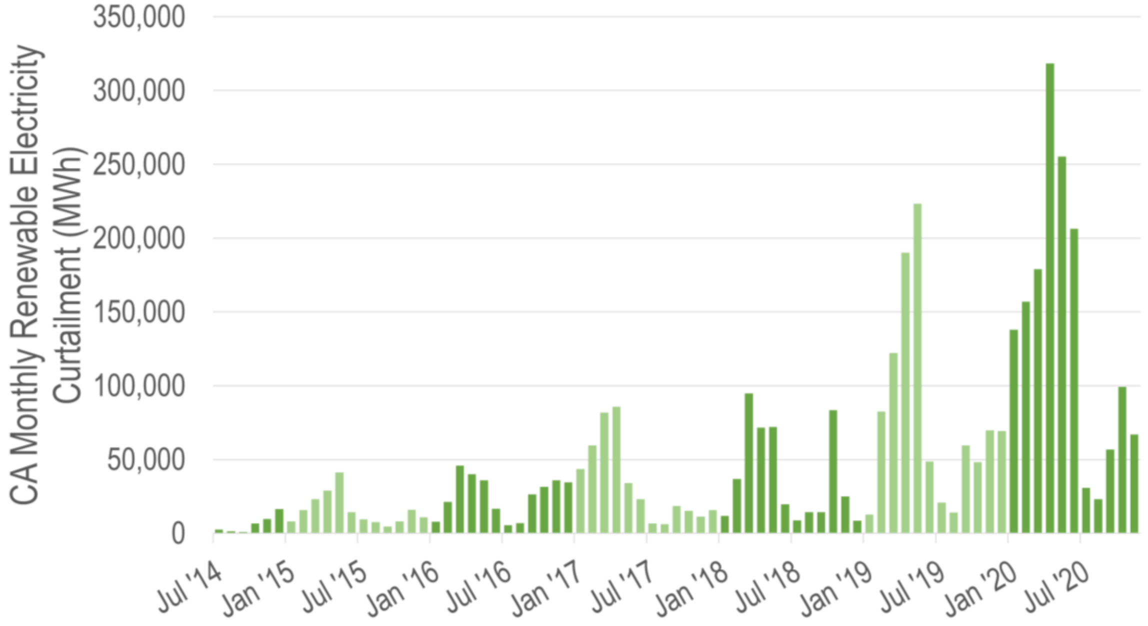
BETO Peer Review March, 2021

Lawrence Livermore National Laboratory

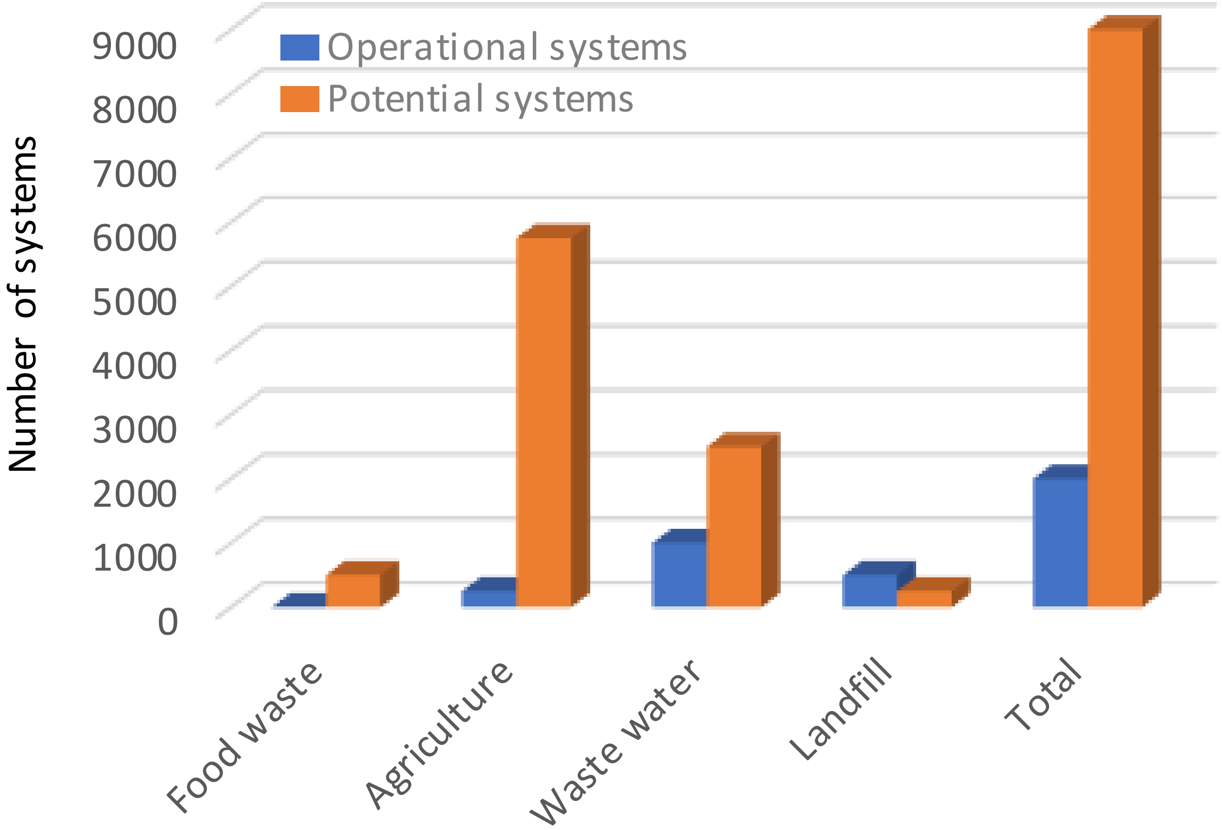
Stanford University

SoCalGas

# We Need to Better Utilize Carbon-Neutral Energy Sources



California renewable curtailments are rising; 1,588,000 MWh in 2020 (which could power 100,000 homes for a year).



Biogas is underutilized, responsible for 25% of US methane emissions, and could replace 46% of grid natural gas or 3% of transportation fuel

Sources: http://www.caiso.com/informed/Pages/ManagingOversupply.aspx, American Biogas Council, **Biofuels and Bioproducts from Wet and Gaseous Waste Streams: Challenges and Opportunities**

# Strategic Importance and Impact

Biogas producers need small-scale solutions for upgrading; Seasonal energy storage is critical need as we transition to 100% renewable.

*Our project realizes both of these goals in a single continuous, modular device for the first time.*

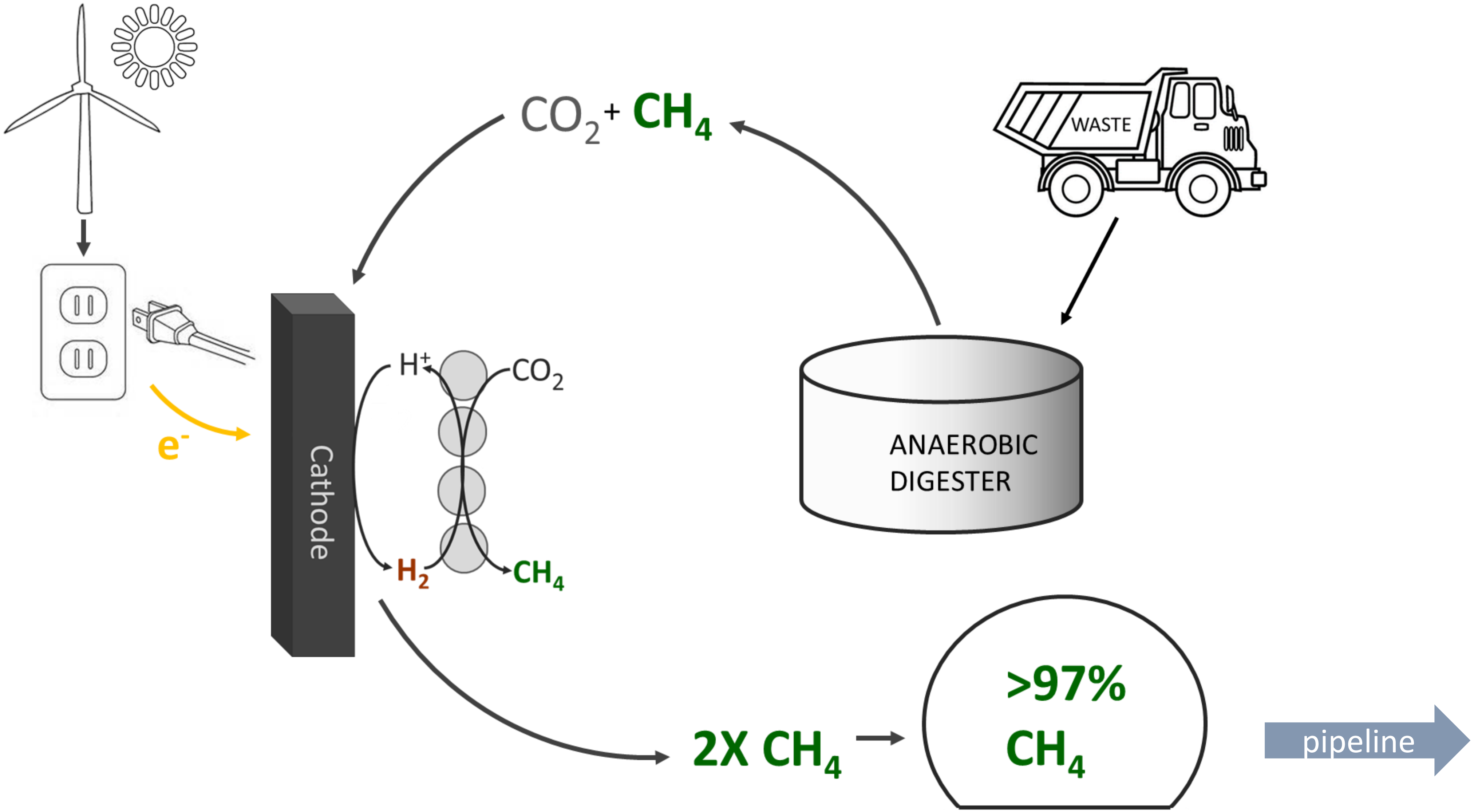
**This project directly supports the BETO mission: to develop and transform domestic renewable biomass into commercially viable biofuels & biopower**

**-Compatible with today's infrastructure (natural gas pipelines and abundant storage capacity)**
**-Reduce GHGs by displacing petroleum fuels**
**-Supports domestic bioenergy industry**

# Power to Gas Provides a Route to Store Renewable Energy in Waste $CO_2$-as $CH_4$-and Utilizes Existing Infrastructure for Transport and Utilization

| Power to Gas Technology | Operating Conditions/Energy Efficiency | Performance Notes |
|---|---|---|
| Sabatier | 250-550 °C, 1-100 bar<br>54-80% Energy Efficiency | Commercial. Sensitive to Biogas contaminants. High temperatures required. |
| Electrocatalytic Methanation-abiotic | 25-75 °C, ~1 bar<br>2-25% Energy Efficiency | Bench scale, TRL 2. Low single pass conversion and selectivity to methane. |
| Biomethanation-2 stage (electrolyzer + stirred tank reactor) | 25-70 °C, 1-20 bar<br>46-62% Energy Efficiency | Pilot scale. 100% Single pass conversion, 100% selectivity to methane.<br>**High capital costs due to electrolyzer+fermentation.**<br>**Mass transfer of $H_2$ limits productivity**. |

# Our solution: Single Stage Biomethanation.



•$H_2$ generated *in situ:* no need for separate $H_2$ production, storage, compression • Low temperature and pressure • Complete $H_2S$ utilization is possible • Microbes are selective

## Project Goal:

Demonstrate single stage electromethanogenesis for biogas upgrading: Realize conversion of biogas to pipeline quality biomethane at steady state, in one reactor, at viable energy efficiency.

## Outcome:

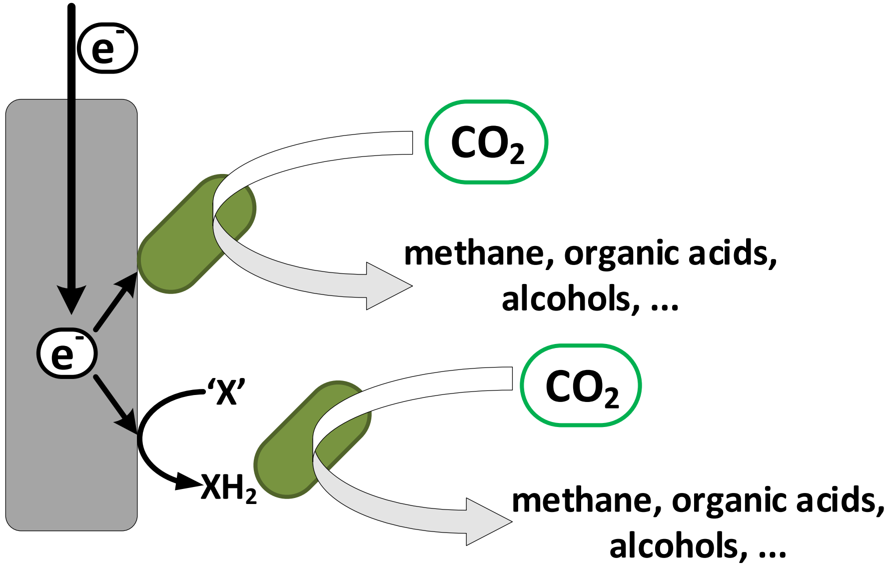
First rigorous demonstration of electromethanogenesis for biogas upgrading: can it be done? How much will it cost? What activities are needed to demonstrate scaleup and viability?

## Relevance:

Economical technologies for seasonal renewable energy storage are urgently needed; converting $CO_2$ to methane leverages our vast natural gas infrastructure for energy storage. Biogas upgrading provides an underutilized waste $CO_2$ stream with the additional benefit of expanding biogas utilization (and reducing methane emissions)

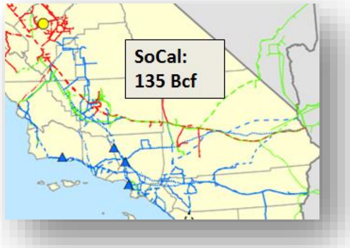
# Project Genesis

## Microbial Electrosynthesis (Stanford)

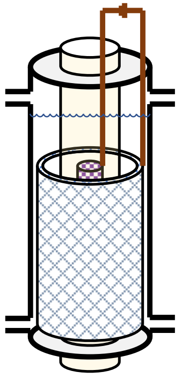


Spormann Lab at Stanford brings world-leading expertise in anaerobic microbes and their application in bioenergy and remediation

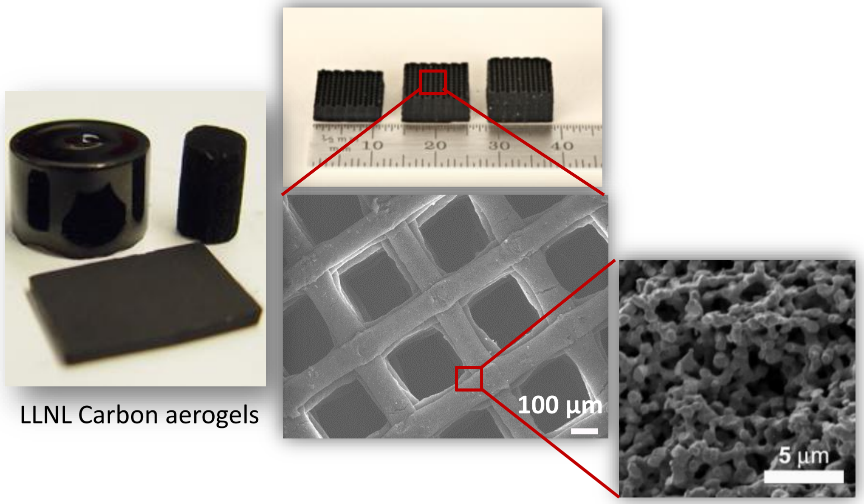
## Industrial Insights (SoCalGas)



## Biogas Upgrading Reactors



## Advanced Materials (LLNL)



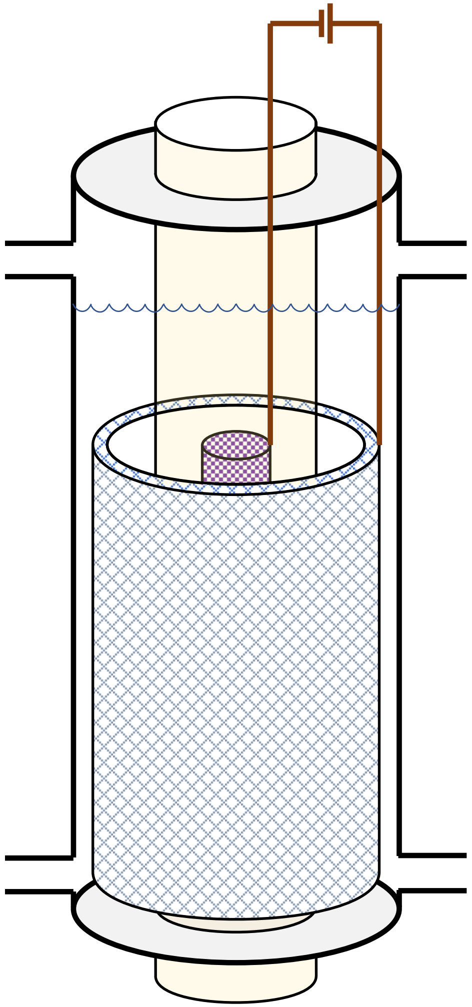
LLNL Carbon aerogels

LLNL has been a world leader in synthesis of porous carbon electrodes for over 30 years:

- Capacitive Desalination (pilot scale)
- Supercapacitors (highest power density)
- Electrochemical Reactors

# Technical Approach: Use Advanced Materials to Integrate Biological and Electrochemical Processes:

*Toward Scalable Conversion Reactors that are Limited Only by the Kinetics of the Microbes*



- *Advanced manufactured, hierarchical materials allow scalable surface area and modular design.*
- *Advanced manufacturing allows rapid prototyping and designing components around microbial requirements*

# Approach: Management

DOE/BETO: Beau Hoffman and Mark Philbrick

LLNL/Sarah Baker: Overall Project Management

NREL/ANL: TEA and LCA

SoCalGas/Ron Kent: Project Advisor

Stanford/Prof. Spormann: Lead of Stanford Team & Microbial Electrosynthesis Tasks

Dr. Joerg Deutzmann: Microbial Enrichment at Cathodes

Dr. Frauke Kracke: Reactor Design and Biotic Testing

LLNL/Sarah Baker: Lead of LLNL Team & Reactor Tasks

Dr. Simon Pang: Reactor Design and Abiotic Testing

Dr. Swetha Chandrasekaran: Materials Design and Synthesis

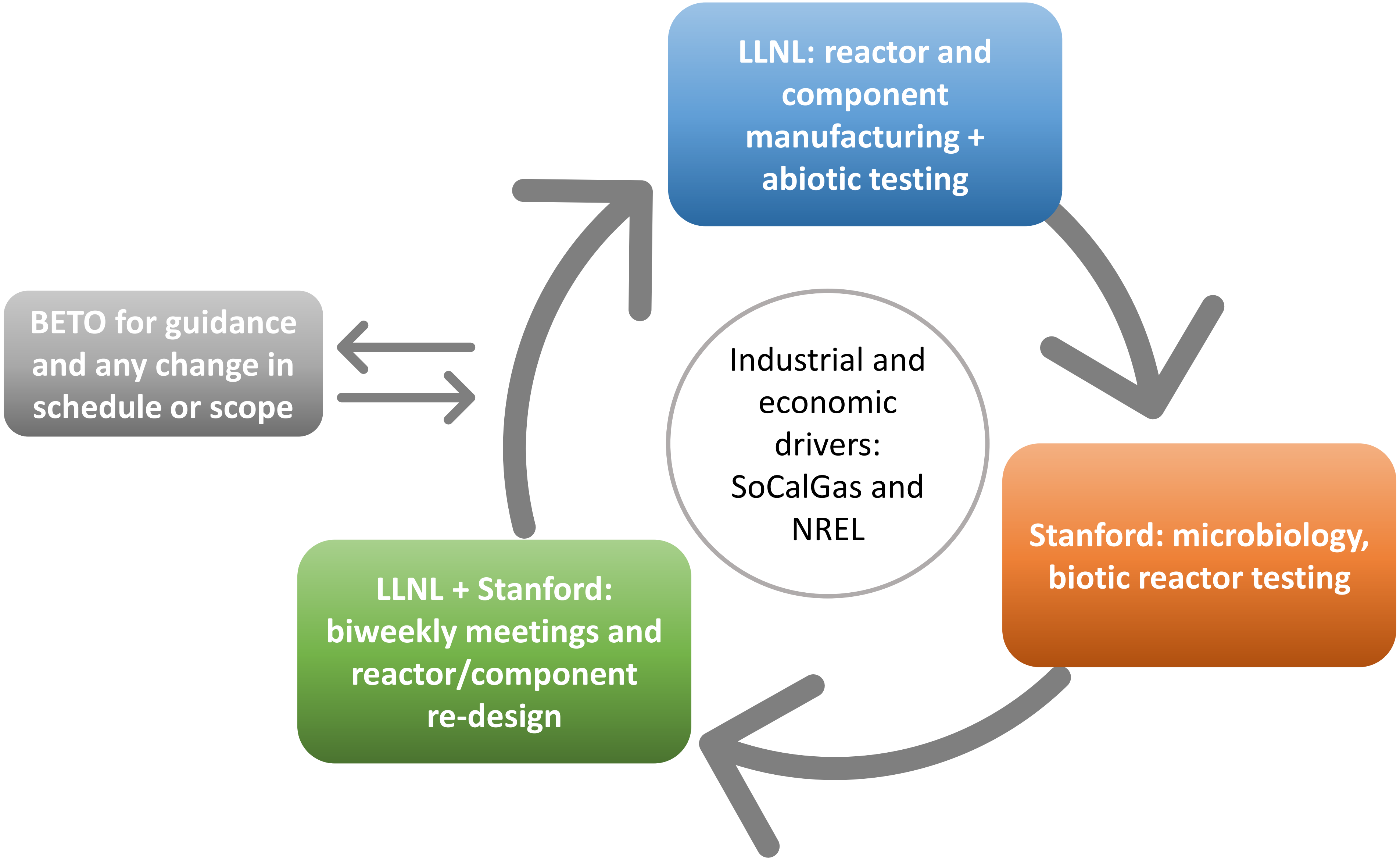
Dr. Buddhinie Jayathilake: Electrochemistry and Electrode Characterization

Lawrence Livermore National Laboratory

Stanford University

SoCalGas

# Management: communication, workflow, and risk mitigation



LLNL: reactor and component manufacturing + abiotic testing

Stanford: microbiology, biotic reactor testing

LLNL + Stanford: biweekly meetings and reactor/component re-design

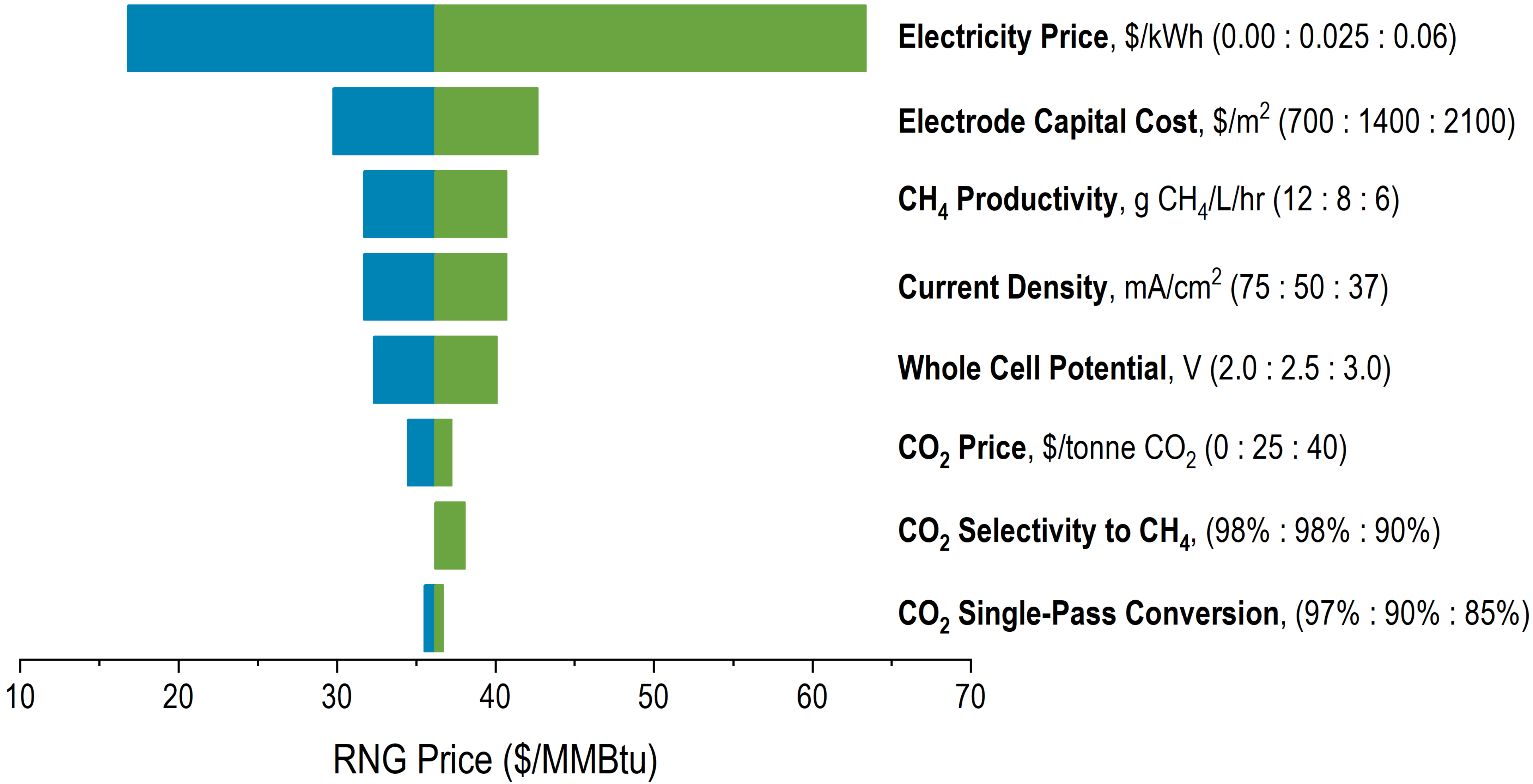
BETO for guidance and any change in schedule or scope

Industrial and economic drivers: SoCalGas and NREL

# Previous Reviewer Comments:

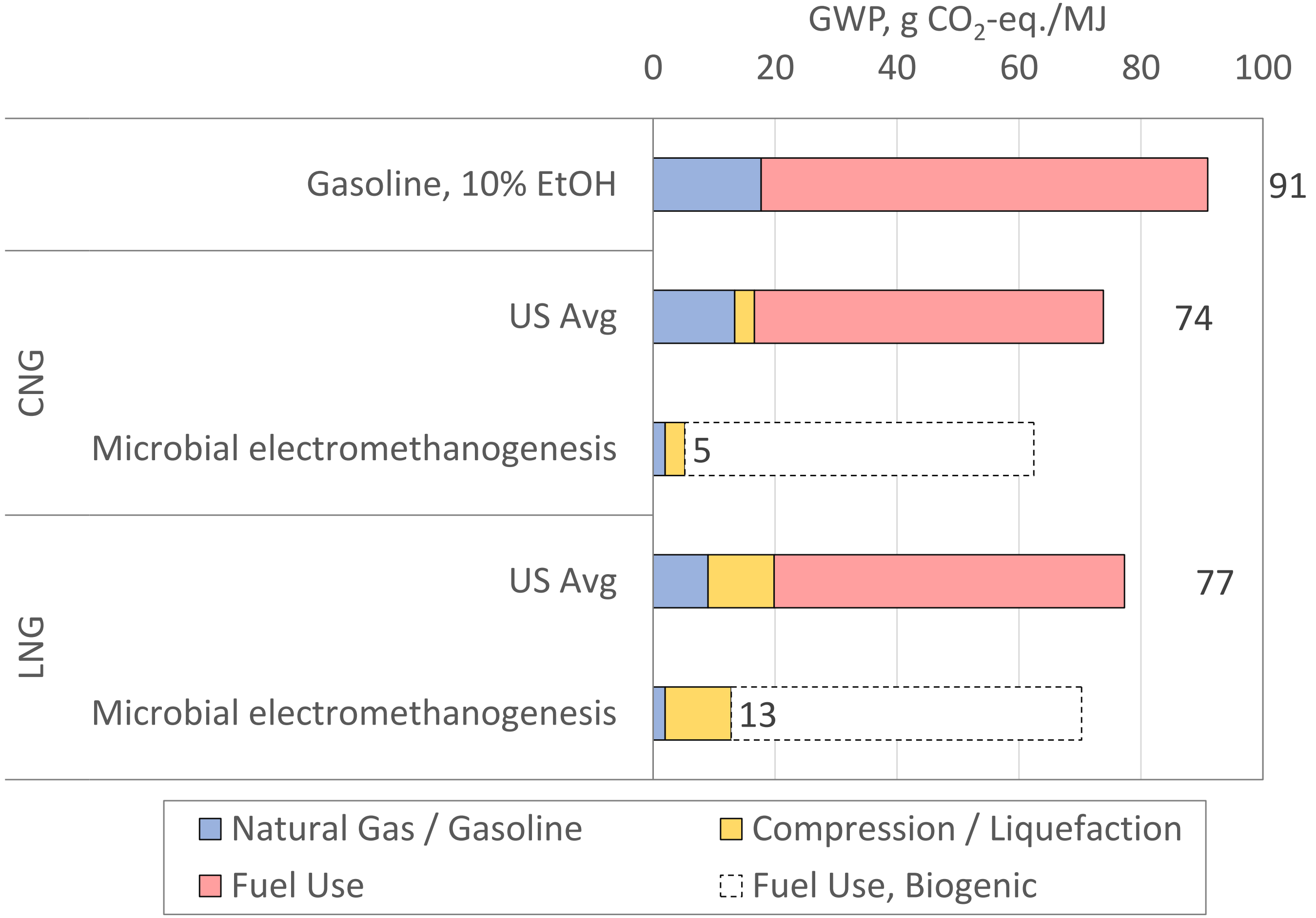
- Perform preliminary TEA prior to project end to inform reactor design/metrics
- If project progresses, need to demonstrate with renewable/intermittent electricity

# Preliminary TEA: Electricity cost, electrode cost, productivity strongest cost drivers (Courtesy Ling Tao and Jenny Huang, NREL)



# Preliminary Carbon Intensity: (Courtesy Troy Hawkins, ANL)

- GWP of renewable methane considering renewable energy
- Significant reductions in GWP in the microbial electromethanogenesis pathway
- Cases shown for the baseline $CO_2$ target case



**CI of renewable methane is ~2 g $CO_{2e}$/MJ when using renewable electricity (solar, wind); orders of magnitude lower than U.S. grid average electricity (~332 g $CO_{2e}$/MJ)**

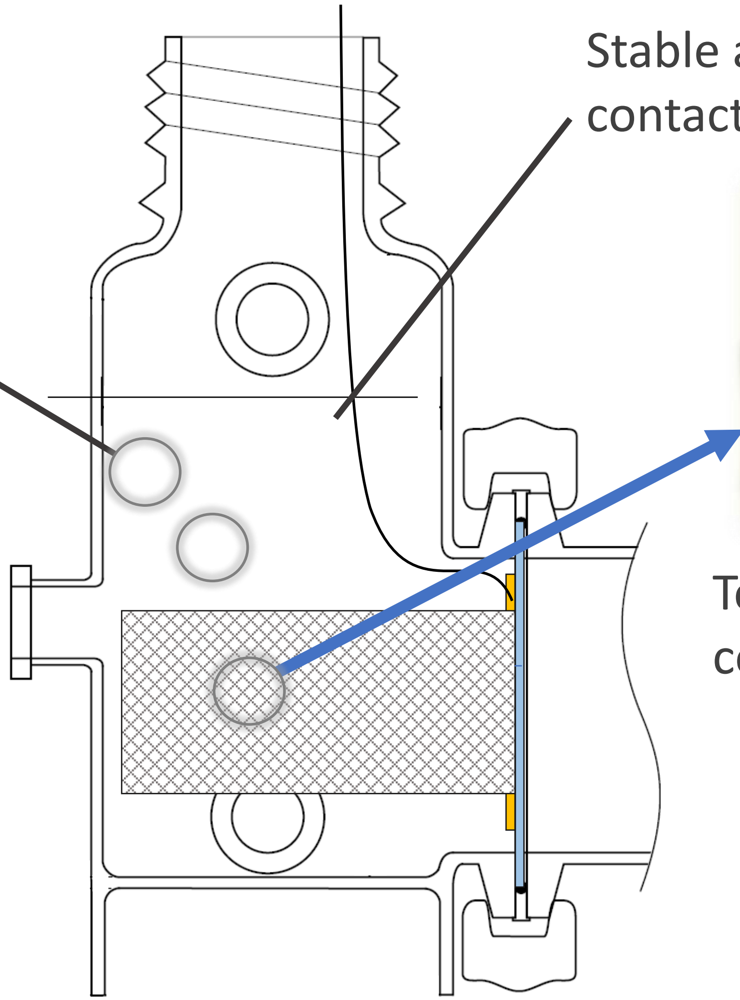
# Project Progress

| | | |
|---|---|---|
| 1 | Stable (>1 day) and low resistance (< 10 ohms) electrical contacts to porous or printed electrodes | ✓ |
| 2 | Test raw biogas with small scale cultures or electrosynthesis to determine microbial tolerance to contaminants $H_2S$ and siloxanes. | ✓ |
| 3 | 4 pure methanogenic strains tested for tolerance to increasing current density in the reactor (> 5 mA/cm^2) | ✓ |
| 4 | Test two cathode materials with raw or scrubbed biogas to determine contaminant tolerance; Demonstration of >80% Faradaic Efficiency for methane | ✓ |
| 5 | **Go No Go: Operation of ME reactor that produces methane from biogas $CO_2$ for >2 days at greater than 30g/kWhr** | ✓ |
| 6 | Testing of new isolates for tolerance to $H_2S$ and siloxanes and current density >5 mA/$cm^2$ | ✓ |
| 7 | Selection of reactor configuration and anode and membrane material. | ✓ |
| 8 | Microbe downselect and contaminant tolerance documented. Biogas treatment (raw or scrubbed) selected. Cathode material selected. | ✓ |
| 9 | Construction and continuous operation of flow-through electromethanogenesis reactor module using raw or scrubbed biogas from WWTP | ✓ |
| 10 | Demonstrate outlet gas purity of 97% CH4, <3% $CO_2$, <0.2% $O_2$, <4 ppm $H_2S$, <0.1 mg/$m^3$ siloxanes at 0.03g/Whr in continuous reactor (Due June, 2021) | |
| 11 | Reactor, process, system design and operating strategies for TEA. (Due June, 2021) | |
| 12 | Completion of LCA/TEA (Joint Milestone with NREL/ANL) (Due June, 2021) | |

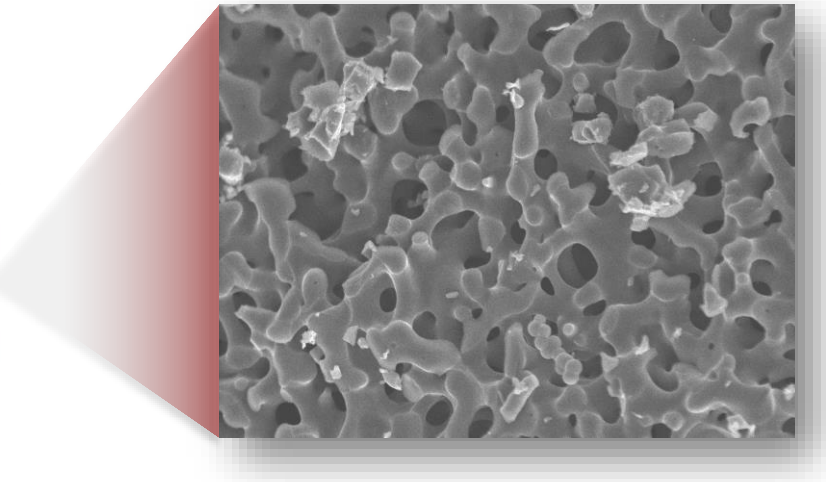
# Technical Approach Year 1: Identify Components, Evaluate Stability & Demonstrate Energy Efficiency

4 Strains
Tested for
tolerance to >5
mA/cm$^2$,

>80% FE for $CH_4$



Stable and low resistance contacts



Test two cathode materials to determine contaminate tolerance

**Go/No Go: Demonstrate Methane from Biogas for > 2 days at > 30 g/kWhr**

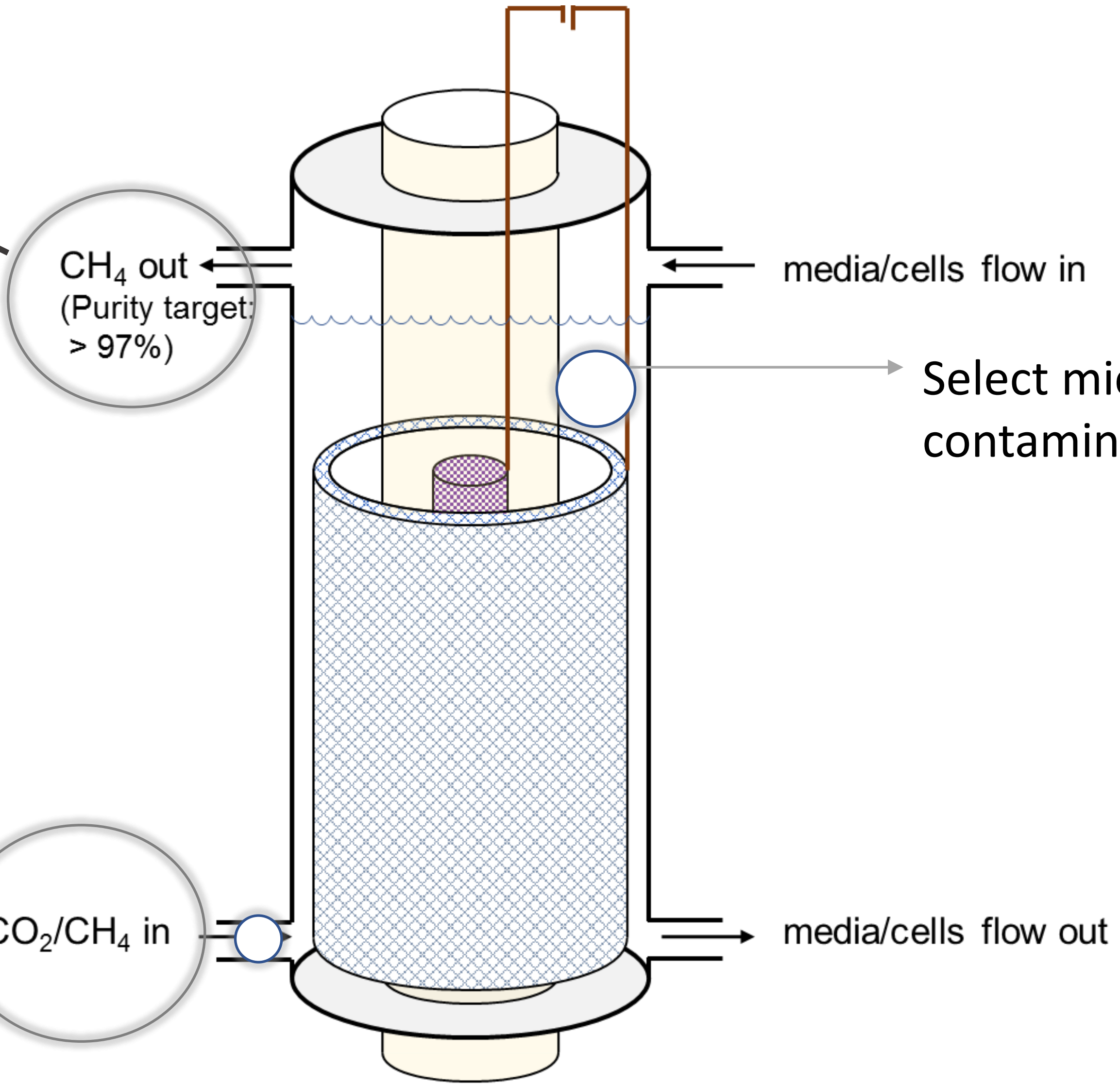
# Technical Approach Year 2: Continuous system, Biogas purity, TEA

Reactor, process system design and operating strategies for TEA. Completion of TEA

Demonstrate pipeline quality biogas

- Select reactor configuration, anode, and membrane material.
- Construct continuous reactor

Select biogas treatment



Select microbe and document contaminant tolerance

End of Project Goal: >97% CH4, <3%CO2 at 30 g/kWhr in a continuous reactor

# Technical Results Outline:

1. Selection of Microbe: tolerance to biogas contaminants and conditions in electrochemical reactors (Milestones 2, 3, 6 and 8)

2. Energy efficiency target: Go/No Go Milestone reached using selected microbe (Milestone 5)

3. Electrode and reactor design: achieving target energy efficiency *and* gas purity requires rapid prototyping of electrodes and reactor design for continuous flow and improved mass transport (Milestones 7,8,9)

4. Gas purity target: >97% methane achieved in continuous reactor

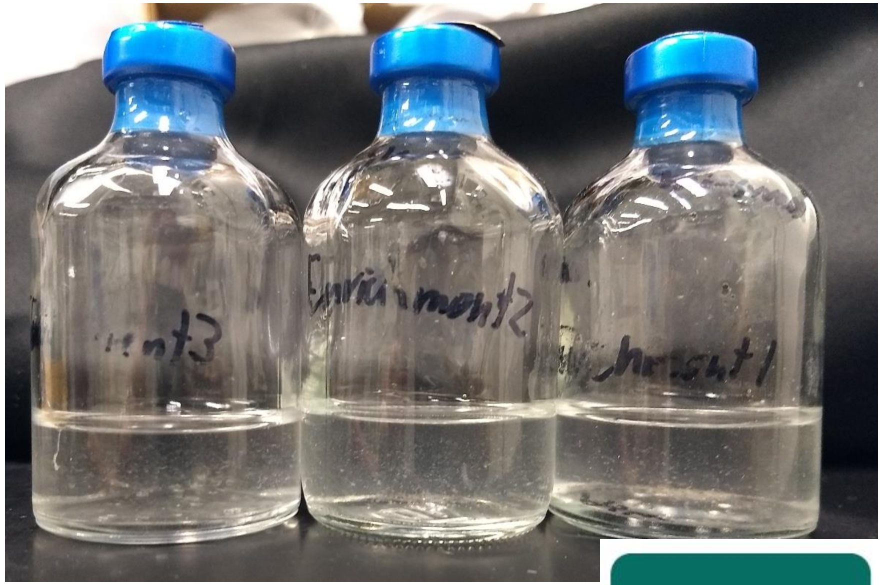
5. Scaleup of cathodes to reach gas purity target at energy efficiency target (Milestone 10-*pending*)

# Microbe selection: All Tested Microbes Grow on Raw Biogas

**Incubation of different microbial strains with raw biogas**

*M. maripaludis* *M. thermolithotrophicus* *M. marburgensis*

Enrichment culture



Growth indicated by turbidity or cell clumps in liquid phase; All strains used $CO_2$ from raw Biogas when additional $H_2$ was added. Also collected enrichment culture for milestone 6, “testing of new isolates”

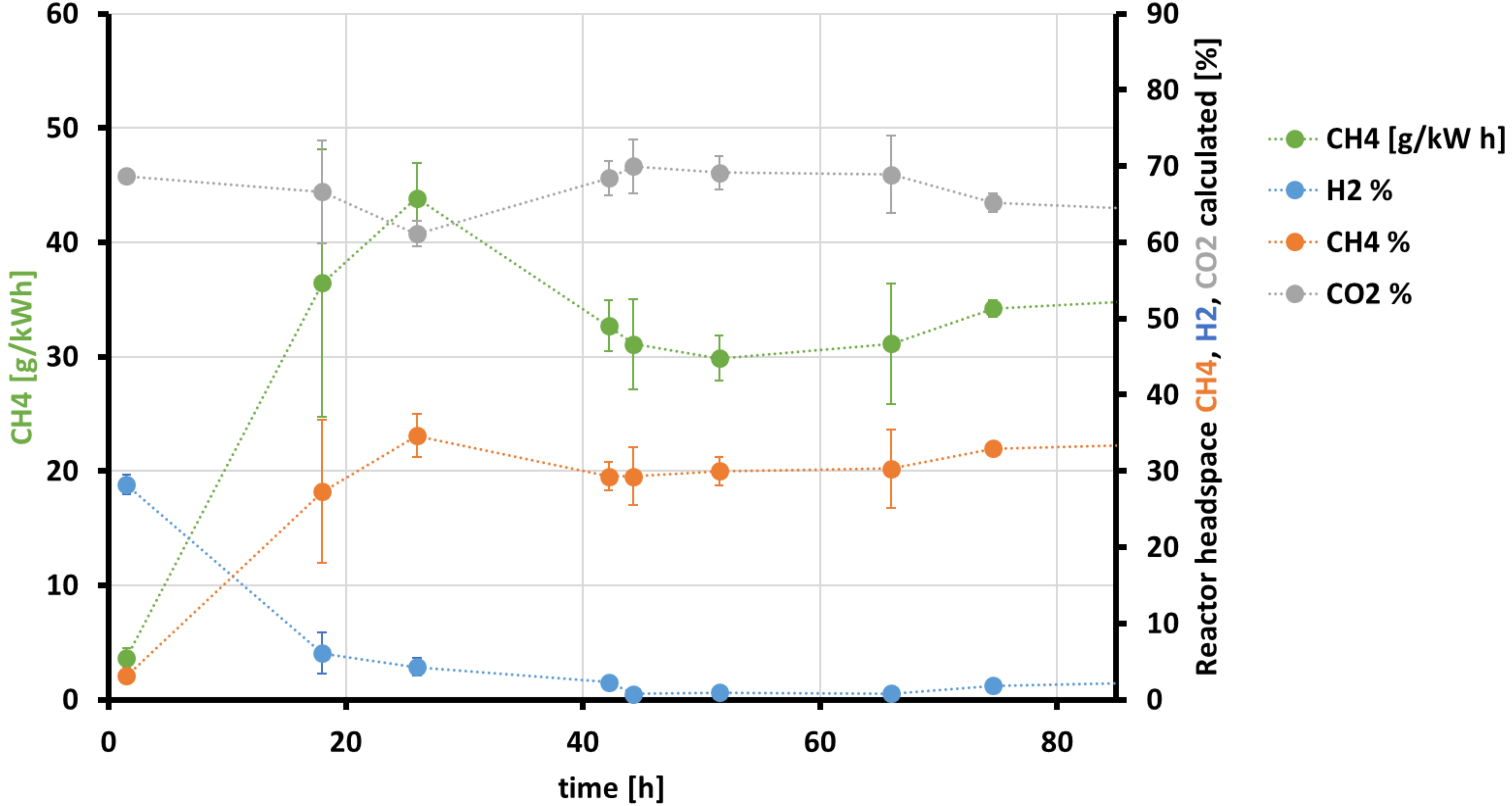
Delta Diablo

# Microbe Selection: *Which microbes tolerate electrochemical conditions and have predictable performance ?*

| **M. maripaludis** | **M. marburgensis** | **Enrichment culture (M. subterraneum dominated)** |
|---|---|---|
| Pure, defined culture | Pure, defined culture | Undefined mixed culture |
| Comparable biological agent between experiment | Comparable biological agent between experiment | Unpredictable change in community possible |
| Reproducible performance in E-chem systems | Erratic performance in pure E-chem systems so far | Reproducible performance in E-chem systems |
| 30-37°C | 60-70°C | 30-37°C |
| No biofilms, solution based process | No biofilms, solution based process | Thick biofilms, electrode attached process |
| $< 1$ mA $cm^{-2}$ | $< 40$ mA $cm^{-2}$ | $< 2.5$ mA $cm^{-2}$ |

**While other strains tolerate higher current density and have high productivity, based on reliability in purely electrochemical systems we selected *M. maripaludis*.**

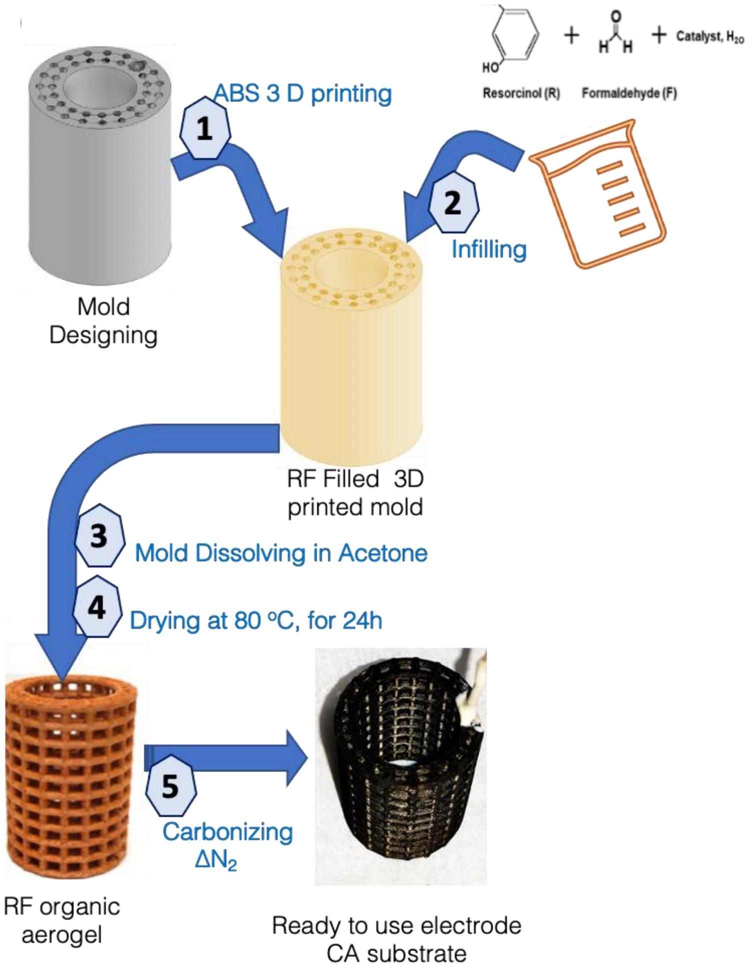
# Achieved Go/No Go Milestone: methane production > 30 g/kWh



Proof of concept that energy efficiency of two stage system can be achieved in single stage-with *in situ* $H_2$ generation

# We Have Developed Printable Carbon and Stainless Steel Electrodes *for rapid prototyping and to increase accessible surface area in continuous flow reactors*

## Carbon Aerogel Electrodes



\+ \+ Catalyst, $H_{20}$

Resorcinol (R)

Formaldehyde (F)

Mold Designing

1 ABS 3 D printing

2 Infilling

RF Filled 3D printed mold

3 Mold Dissolving in Acetone

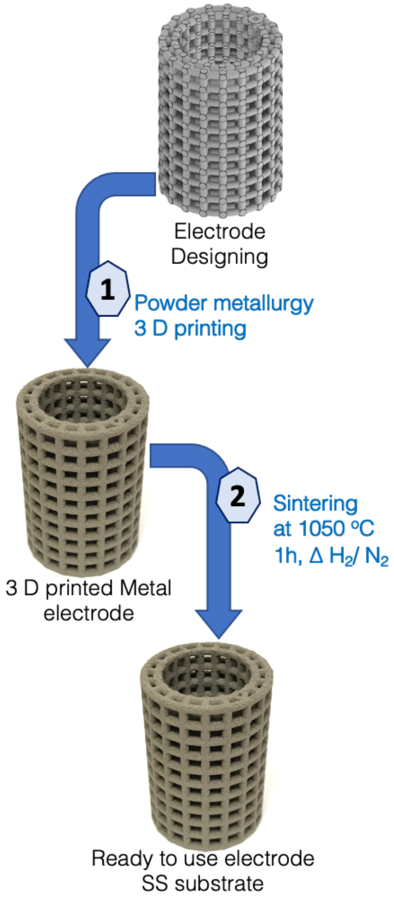
4 Drying at 80 °C, for 24h

RF organic aerogel

5 Carbonizing $\Delta N_2$

Ready to use electrode CA substrate

## Printed Steel Electrodes



Electrode Designing

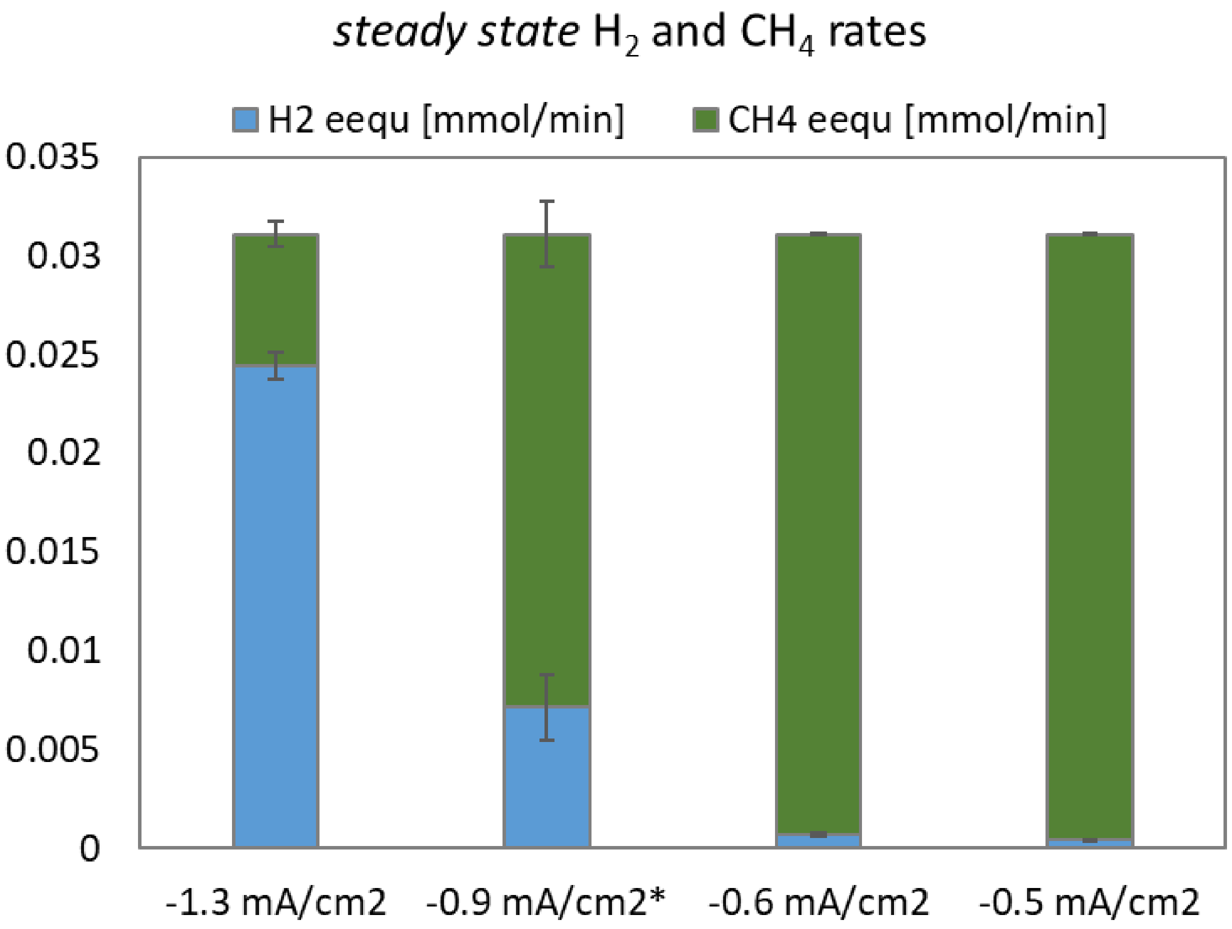
1 Powder metallurgy 3 D printing

3 D printed Metal electrode

2 Sintering at 1050 °C 1h, $\Delta H_2/ N_2$

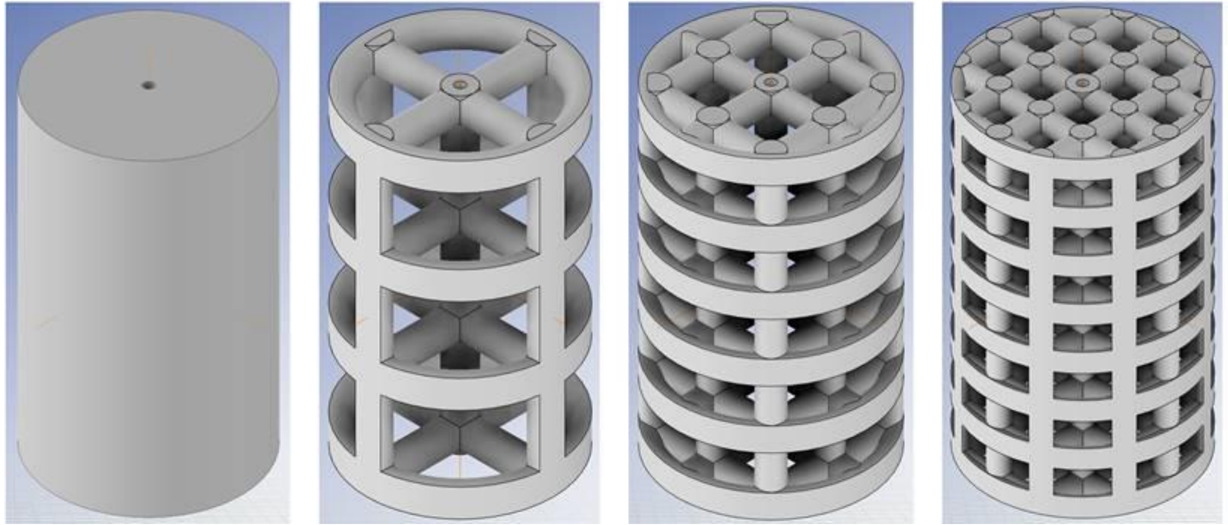
Ready to use electrode SS substrate

# Printed Electrodes Enable Higher Steady State Methane Concentration

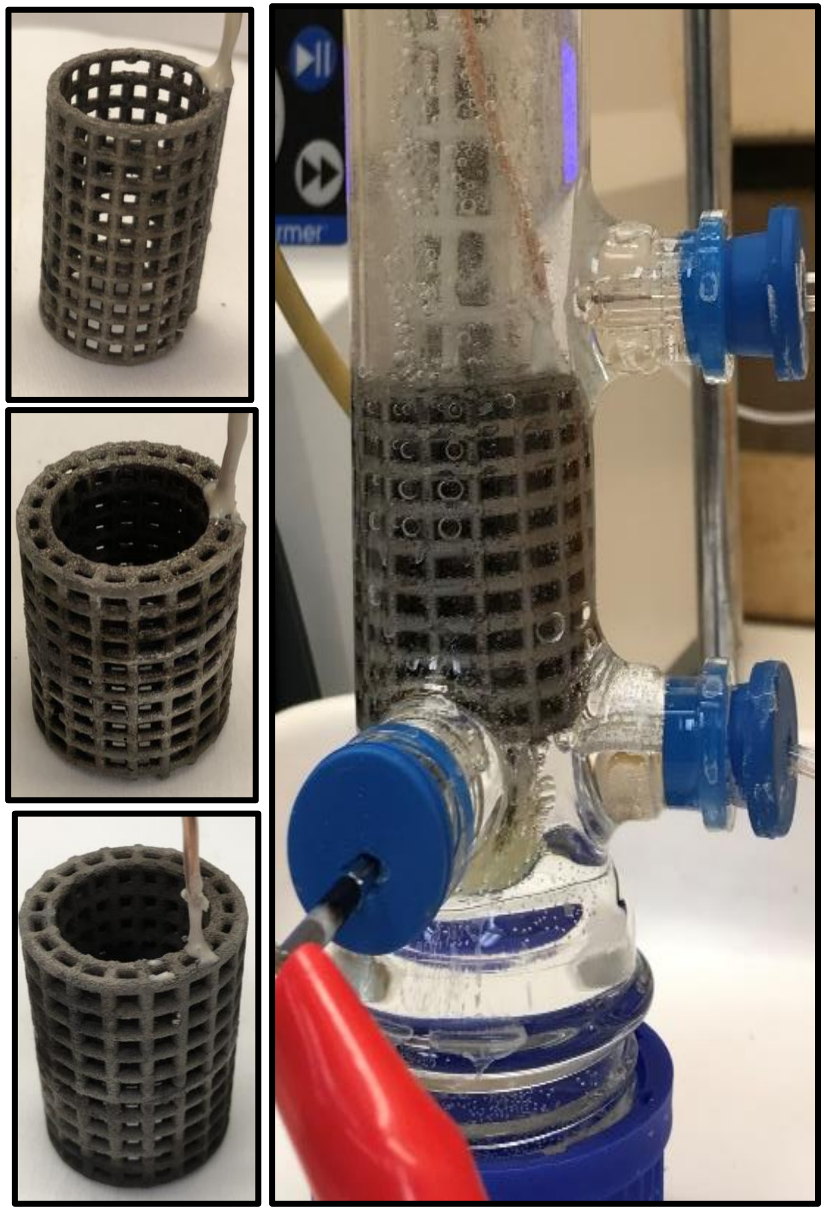


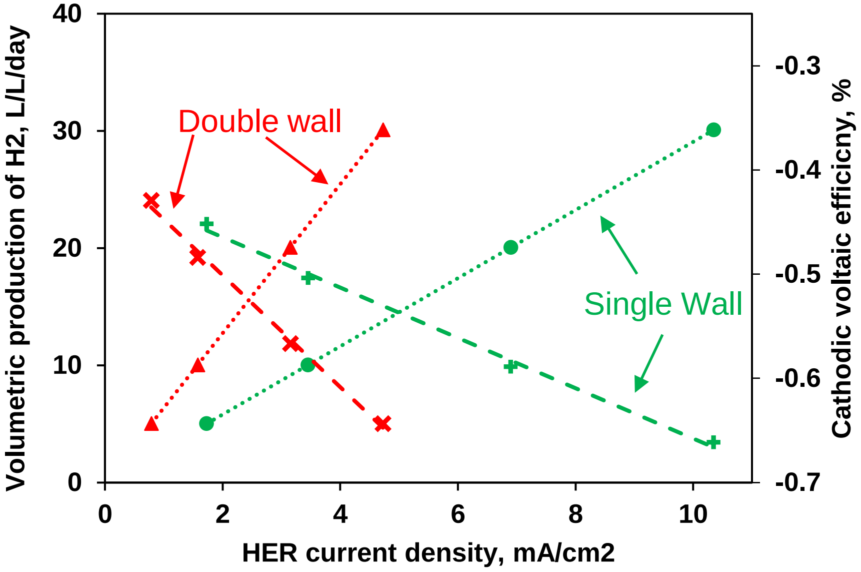
Increasing Surface Area

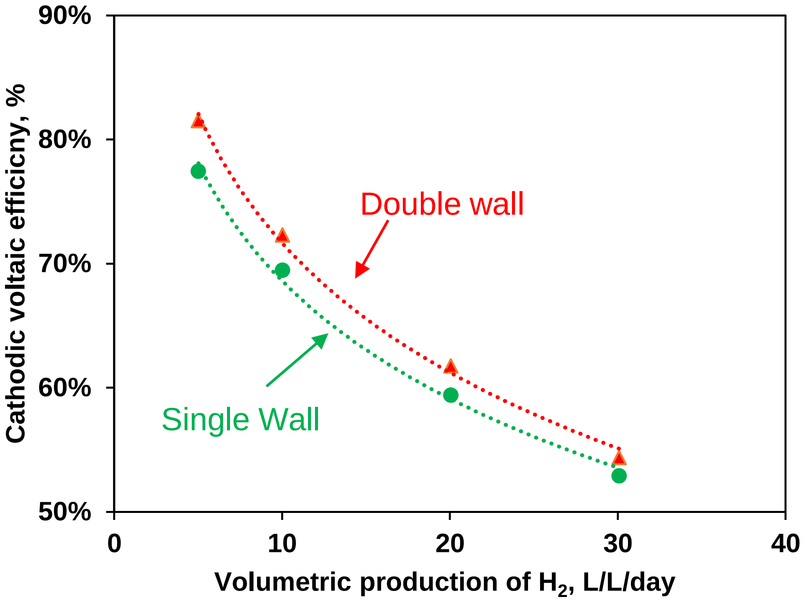
Increasing Surface Area



# Electrochemical Analysis of Electrode Geometries in Continuous Reactors

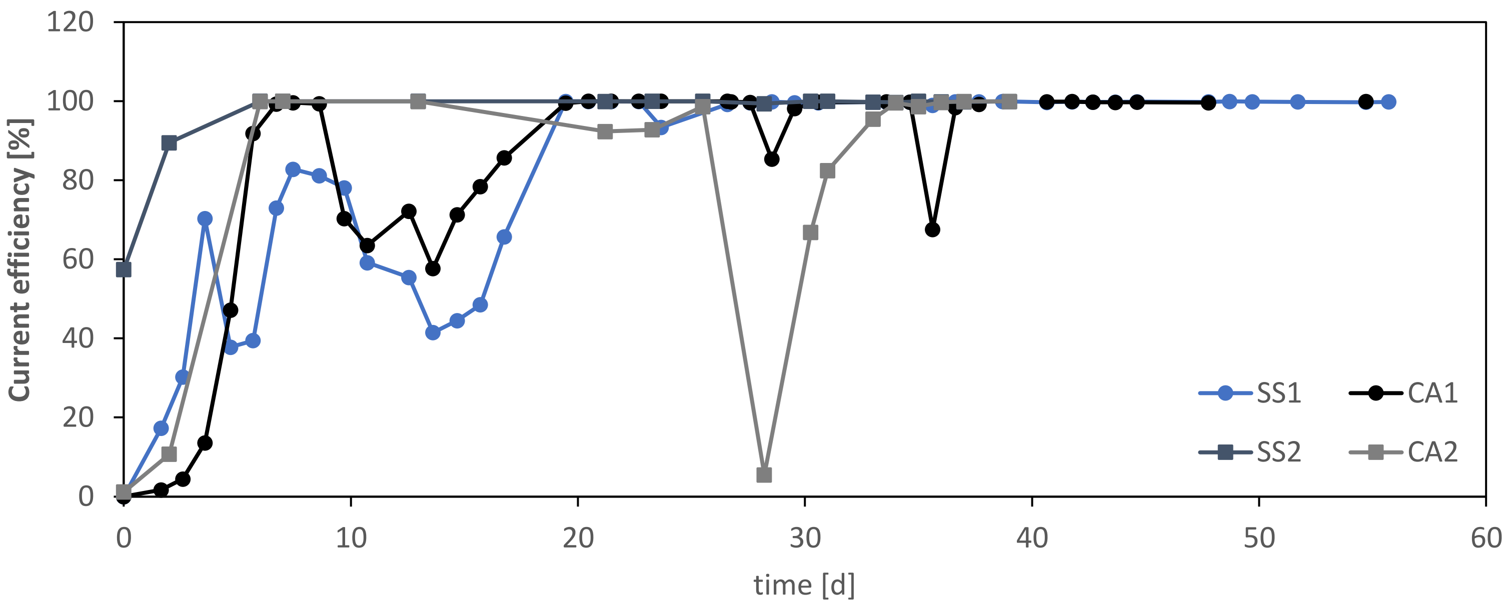






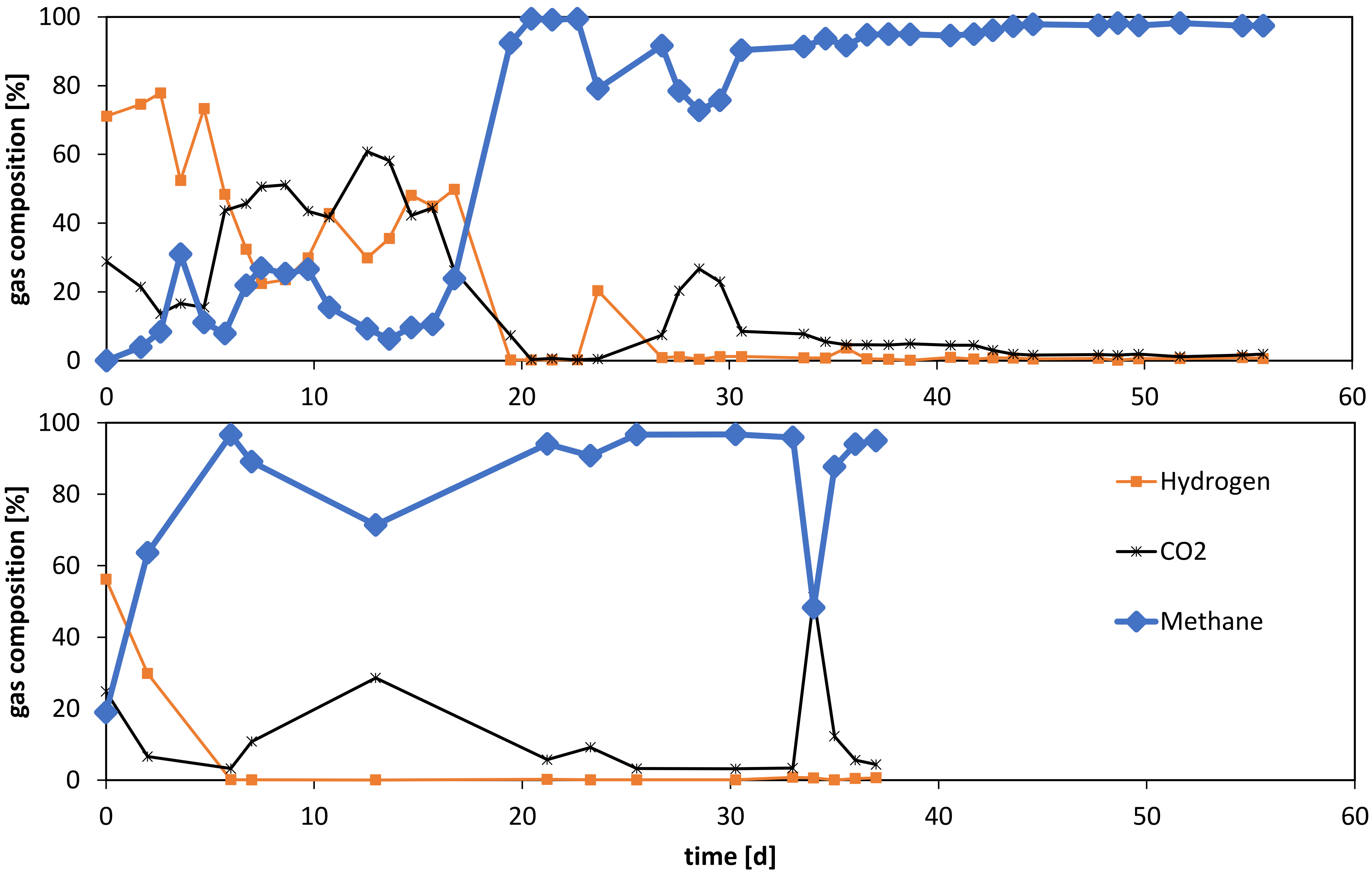
**Tuning cathode geometry using additive manufacturing allows us to <u>increase volumetric productivity and energy efficiency</u>**

# Printed Electrodes Enable Stable, High Performance *In Situ* Biomethanation



- >99% coulombic (electrons-to-methane) efficiency (Milestone 8 > 80%)
- Constant methane production rates
- Both carbon and steel perform well over 30 days
- Stable cell potential over 60 days

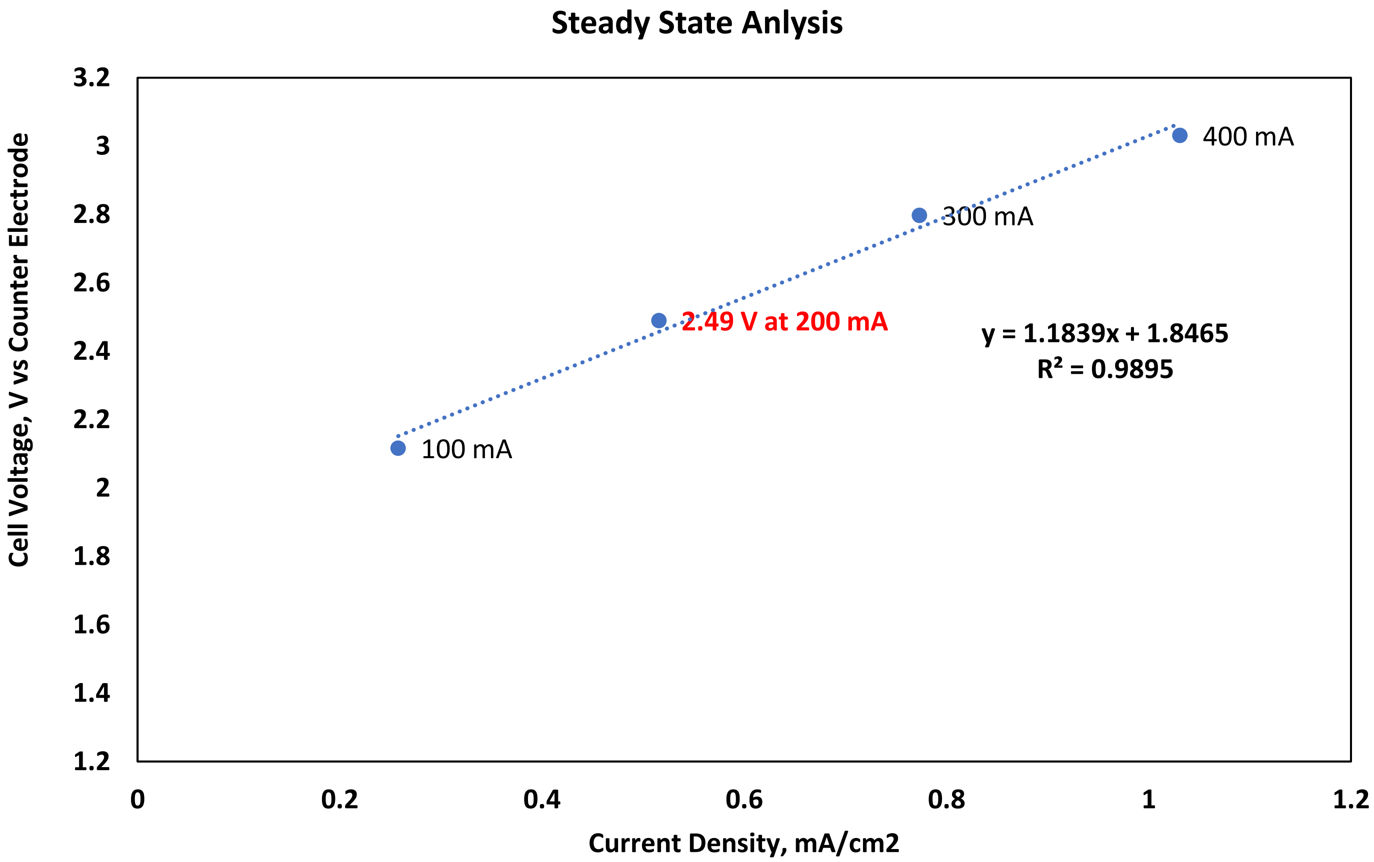
# Methane Purity of >97% achieved in single pass using *in situ* generated $H_2$ and 100% $CO_2$, can be replicated and sustained



Experiment 1

Experiment 2

# Scaleup to 0.25L -to reach target gas purity at required energy efficiency



**Abiotic testing: At required current, required cell voltage of 2.5 V can be achieved. *Final step is putting it all together: demonstrate target gas purity from simulated biogas, @ target energy efficiency.***

# Summary of Progress

- We have printed/designed/selected every component of modular, continuous reactors + microbes to demonstrate 97% methane from electricity and $CO_2$ in a single pass and in one unit for >30 days for first time.

- We have shown that a range of pure strains and enrichments are stable to raw biogas contaminants-offering a promising path to economical biogas upgrading. In addition, we have reached energy efficiency and selectivity targets for economic viability

- Our approach of using advanced manufacturing to realize the potential of microbial electrosynthesis was successful; demonstrated rapid performance improvements and gained insights into what is required to electrify bioreactors for power to gas-4 joint publications pending on this topic.

# Next Steps

- Demonstrate on simulated biogas stream containing 40% $CO_2$, 1000 ppm $H_2S$ and balance $N_2$

- We have demonstrated target gas purity and energy efficiency *separately*- we will meet both targets by increasing the surface area of our printed electrodes within the reactor volume.

- Analysis needed for understanding energy storage markets, customer needs and competition. Further de-risking of technology by demonstrating promising performance with intermittent electricity and at increasing scales is needed.

# Quad Chart Overview

**Timeline**

- Project start date 10/01/18
- Project end date 06/01/21
- Percent complete: 90%

**Barriers addressed**

Ct-H. Gas Fermentation Development

Ct-D. Advanced Bioprocess Development

**Total Planned Funding (FY 19-Project End Date)**

| | |
|---|---|
| **DOE Funded** | 800K |
| **Project Cost Share*** | 400K |
| **Partners: SoCalGas and Stanford (400K subcontract from LLNL)** | |

**Objective**

Demonstrate Microbial Electrosynthesis flow reactors feasible for biogas upgrading and grid storage

**End of Project Goal**

Production of pipeline quality biogas and Informed TEA of Microbial Electrosynthesis Flow Reactors

# Publications, Patents, Presentations, Awards, and Commercialization

**Presentations**:

- Biogas Upgrading Reactor Development For Microbial Electro-methanogenesis; Buddhinie S. Jayathilake, Simon H. Pang, Swetha Chandrasekaran, Megan C. Freyman, Jörg S. Deutzmann, Frauke Kracke, Alfred M. Spormann and Sarah Baker: ACS Fall 2020 Virtual Meeting & Expo, August 2020
- Microbial Electro-Methanogenesis Coupled with in-Situ Hydrogen Generation for Biogas Upgrading; Buddhinie S. Jayathilake, Simon H. Pang, Swetha Chandrasekaran, Megan C. Freyman, Jörg S. Deutzmann, Frauke Kracke, Alfred M. Spormann and Sarah Baker: 2020 AIChE Annual Meeting, November 2020
- Single Stage Reactors for Electrifying Bio-methanation; Buddhinie S. Jayathilake, Swetha Chandrasekaran, Megan C. Freyman, Jörg S. Deutzmann, Frauke Kracke, Alfred M. Spormann, Simon H. Pang and Sarah E. Baker: 239th ECS Meeting, June 2021, Abstract Submission December 2020

**Patents:** Electromethanogenesis Reactor (LLNL, **US20190309242A1** United States)

**Publications in progress:** 4

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