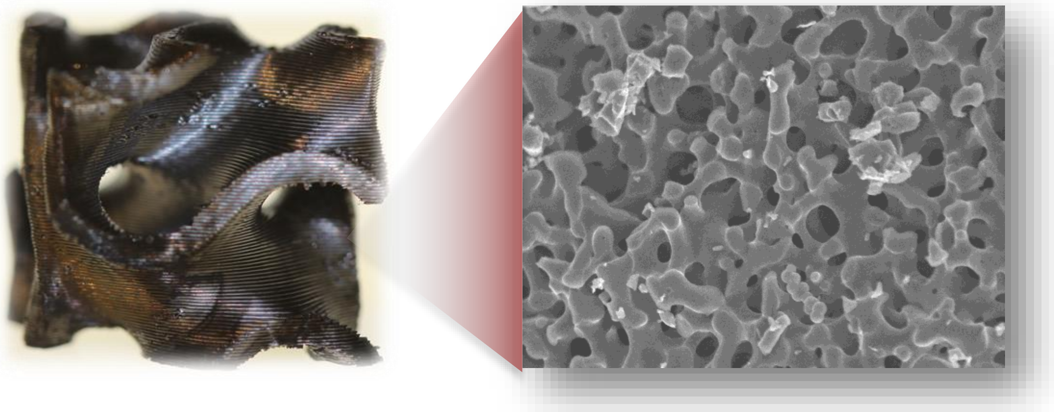
DOE Bioenergy Technologies Office (BETO) 2019 Project Peer Review

Modular Microbial Electromethanogenesis Flow Reactors for Biogas Upgrading

March 4-8, 2019

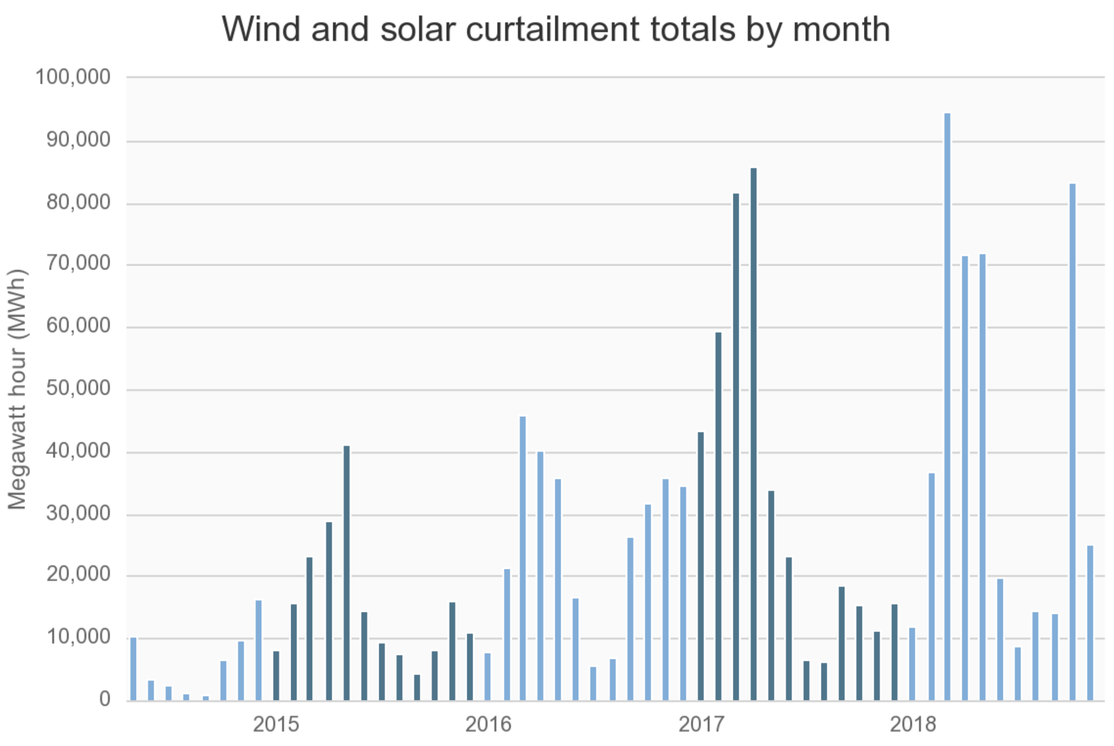


Waste to Energy Technology Session Area

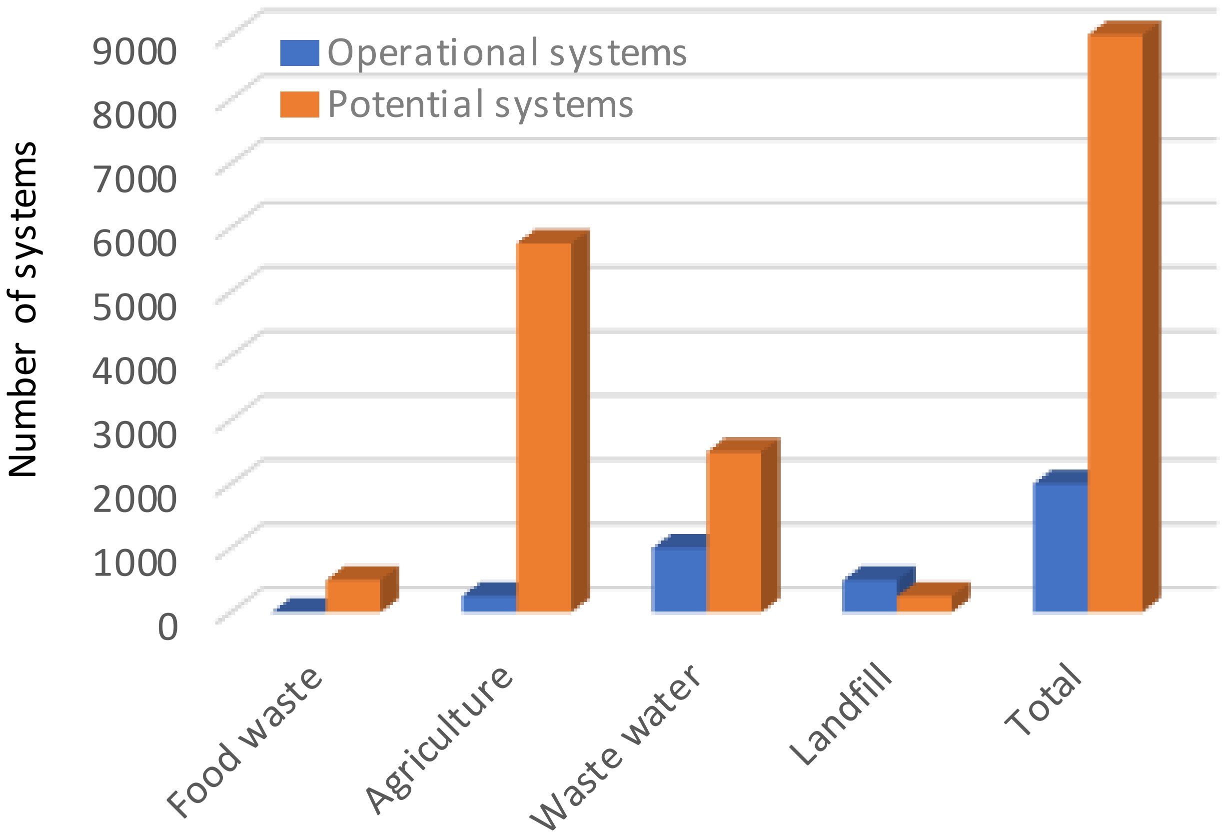
Sarah E. Baker, Lawrence Livermore National Laboratory

Lawrence Livermore National Laboratory
Stanford University
SoCalGas

We Need to Better Utilize Carbon-Neutral Energy Sources



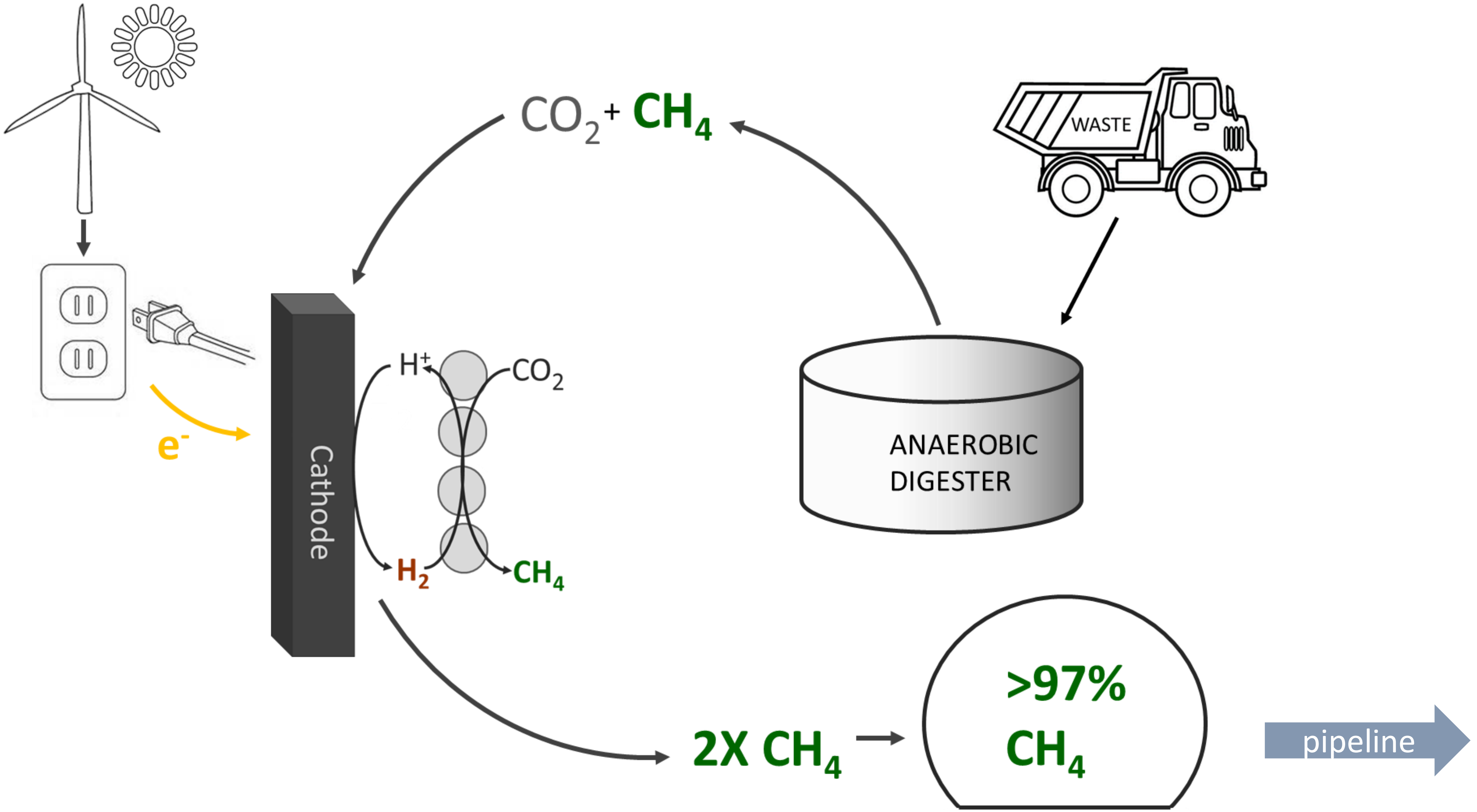
California renewable curtailments are rising; 452,507 MWh in 2018 (which could power 45,000 homes for a year)



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**

Goal: Renewable Energy Stored in Biogas CO_2



•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

Challenges

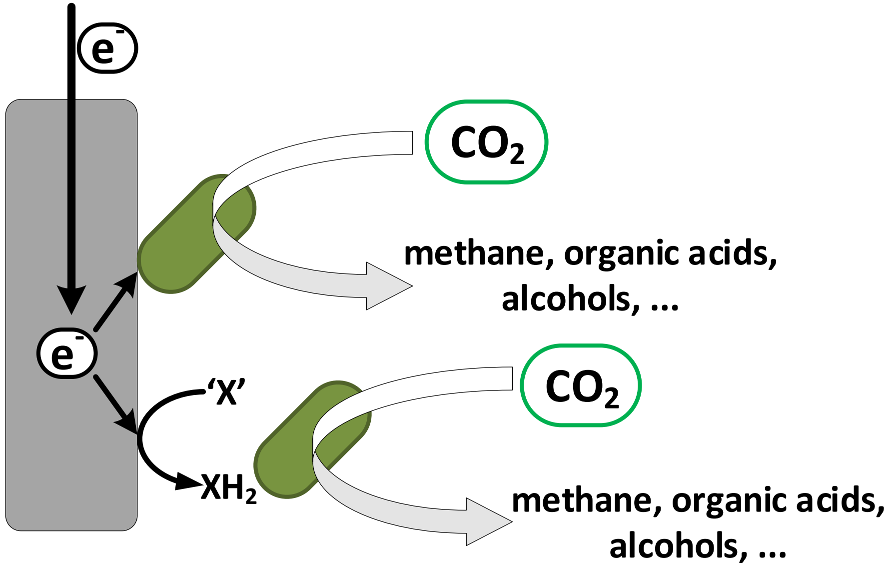
*"The challenge is to harness the [microbial electrochemical cells] into techo-economically viable systems"** Key issues: scaling, cost-effective mass production of cathodes, attaining and sustaining economically viable current density.

- Materials, Reactor, Microbe *Compatibility*: efficient methanogens that flourish in non-fouling media with high conductivity. Compatibility of temperatures with membranes.
- Materials, Reactor, Microbe *Stability*: maintaining cultures under high current density conditions in continuous reactors. Eliminating pH fluctuations. Maintaining electrocatalyst activity in microbial media
- Materials, Reactor *Costs*: ensuring all materials are scalable and mass manufacturable. Eliminating precious metals if possible.

**Biofuels and Bioproducts from Wet and Gaseous Waste Streams: Challenges and Opportunities. BETO, 2017*

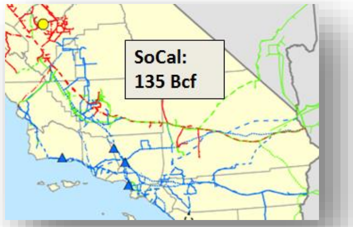
Project Genesis

Microbial Electrosynthesis (Stanford)

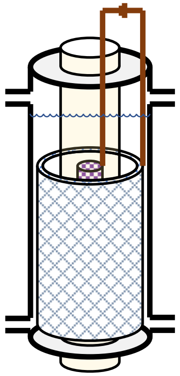


Spormann Lab at Stanford brings world-leading expertise in anaerobic microbes and their application in bioenergy and remediation

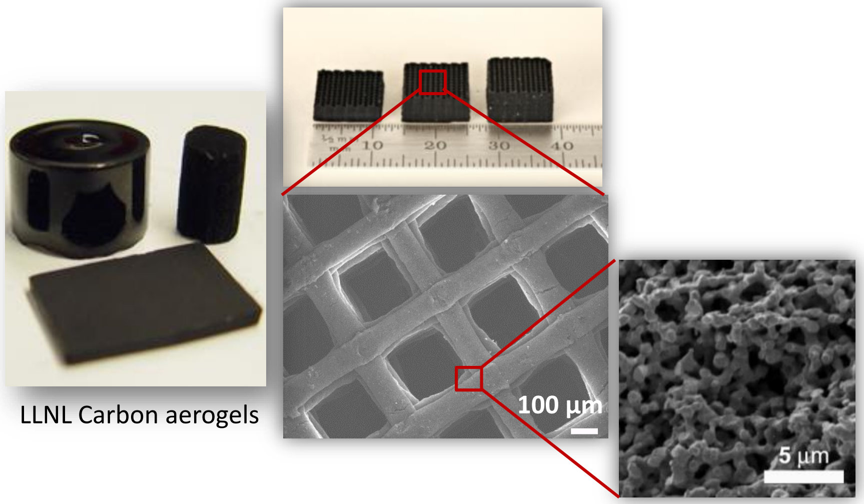
Industrial Insights (SoCalGas)



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)
- HER and CO_2R

Project Goal:

Improve the performance, scalability, and economics of microbial electromethanogenesis for biogas upgrading and energy storage at <1 L scale for multiple days.

Outcome:

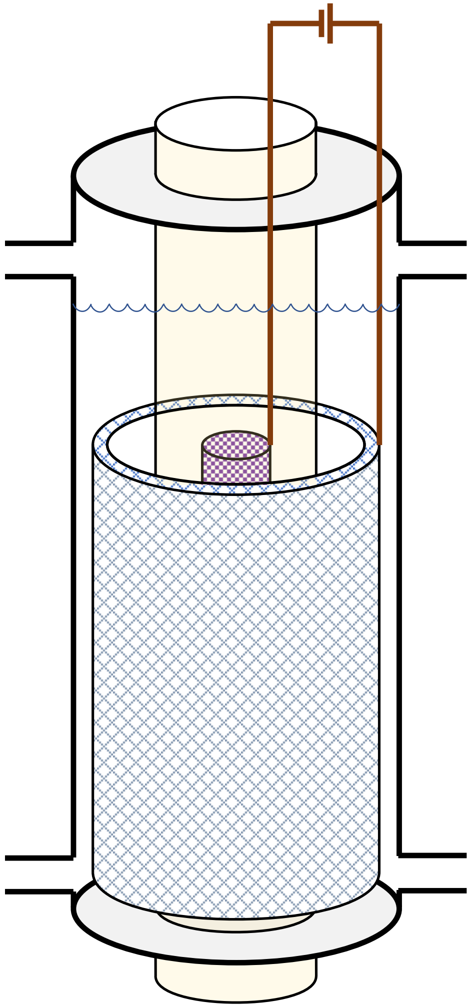
Bench scale device that upgrades biogas to pipeline quality biomethane at 0.03g/Whr for more than 2 days. Sufficient data for informed TEA.

Relevance:

Enable long term storage of renewable energy using existing natural gas infrastructure; increase capture and utilization of biogas by decreasing process costs of upgrading. Eliminate *both* CO_2 and methane emissions.

Using Advanced Materials to Integrate Biological and Electrochemical Processes:

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



We will construct proof-of-concept reactor with scalable low cost components that demonstrates materials, reactor, and process requirements for 1) upgrading biogas to pipeline quality 2) at target energy efficiency metric for > 3 days 3) suitable for preliminary TEA.

- *Advanced manufactured, hierarchical materials allow scalable surface area and modular design.*
- *In situ H_2 generation at high surface area catalysts in vicinity of microbes may increase rates and reduce energy of H_2 dissolution;*
- *Demonstrating on Biogas: good CO_2 point source and ready revenue stream through RIN and LCFS;*
- *Microbes may manage H_2S thus further reducing costs of upgrading*
- *No biofilm → utilize bulk electrolyte, higher current density and less concern about fouling.*

Approach: Management

DOE/BETO: Beau Hoffman and Mark Philbrick

LLNL/Sarah Baker: Overall Project Management

NREL/ANL: TEA

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. Anna Ivanovskaya: Electrochemistry and Electrode Characterization

Lawrence Livermore National Laboratory

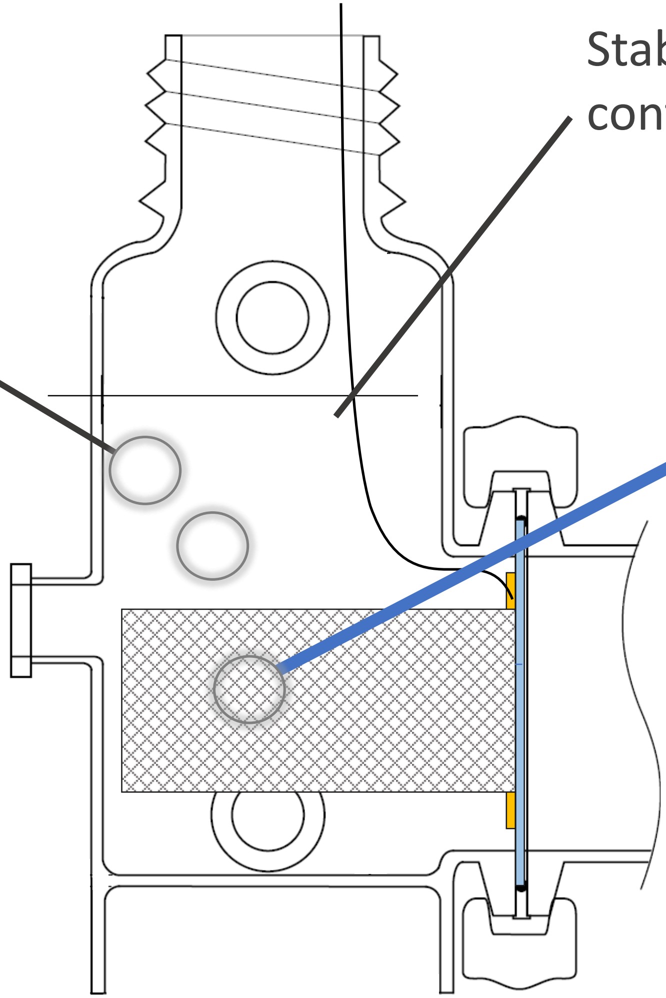
Stanford University

SoCalGas

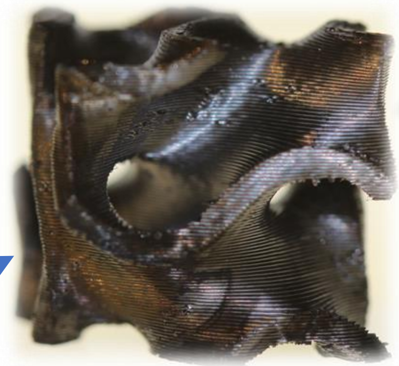
Technical Approach Year 1: Identify Components, Evaluate Stability & Demonstrate Energy Efficiency

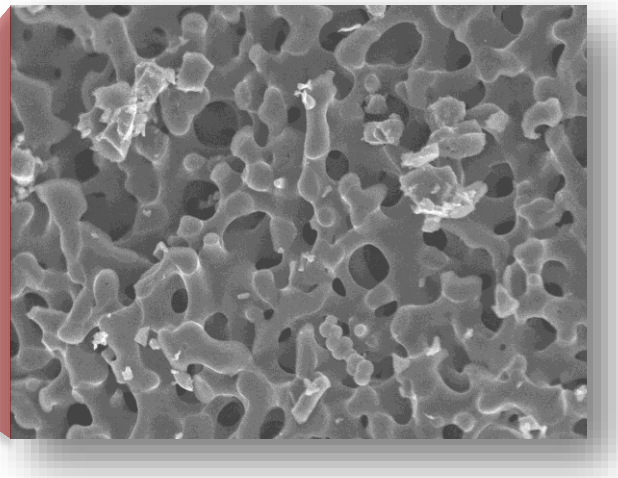
4 Strains
Tested for
tolerance to >5
mA/cm^2,

>80% FE for CH_4



Stable and low resistance
contacts





Test two cathode materials to determine
contaminate tolerance

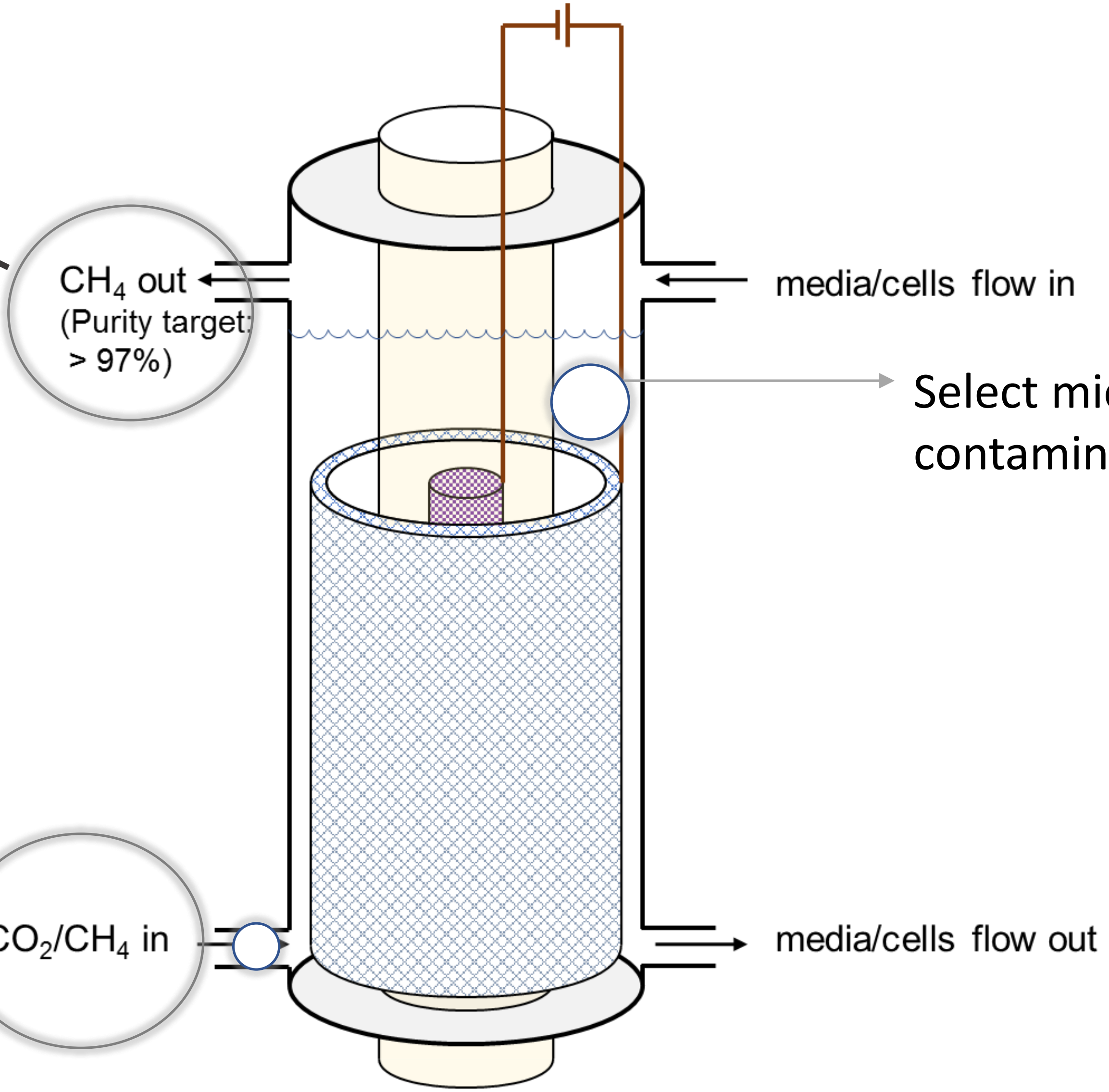
Go/No Go: Demonstrate Methane from Biogas for > 2 days at > 0.03 g/Whr

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

Demonstrate pipeline quality biogas

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

Select biogas treatment

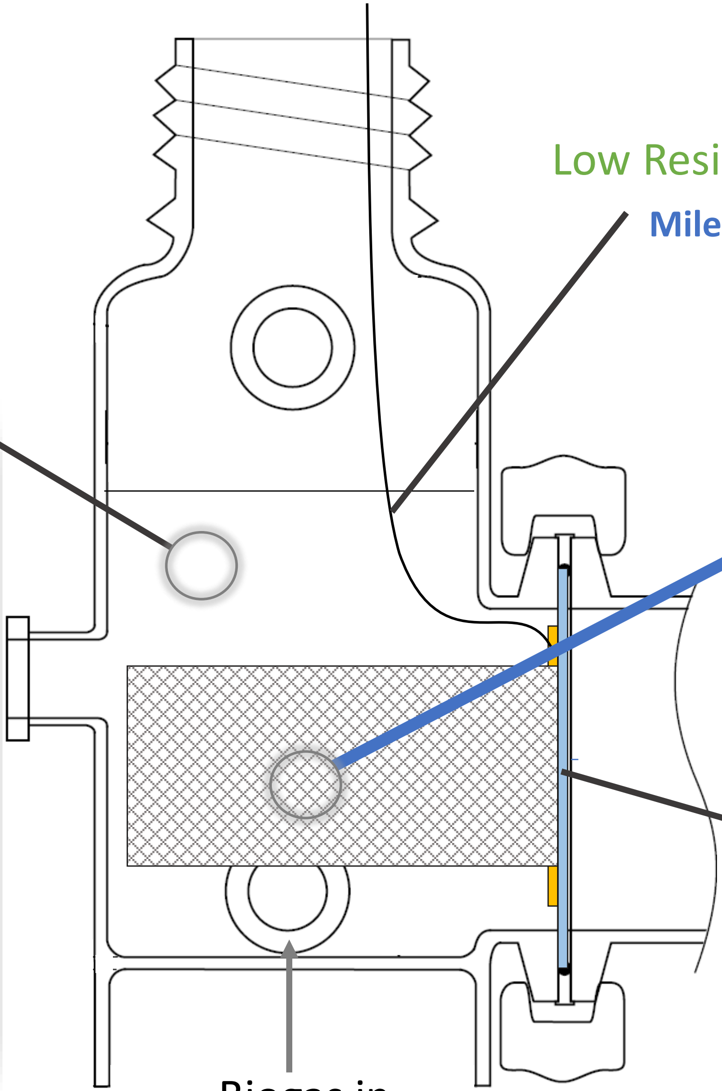


Select microbe and document contaminant tolerance

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

Designed New Electrochemical Cells for Component Testing

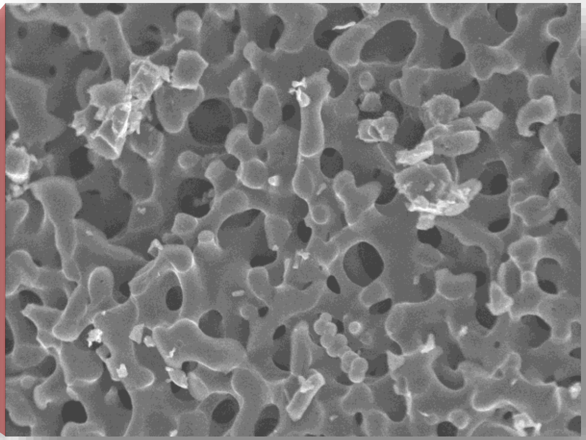
Microbes with good load following, non-fouling media, salt and pH tolerance, tolerance to H_2S



Biogas in

Low Resistance Contacts for > 1Day

Milestone #1 Completed



Inexpensive, hierarchical conductive cathodes with scalable surface area for high current density HER; large pores for active transport

Large area membrane proximal to cathode to minimize pH instability at high current density

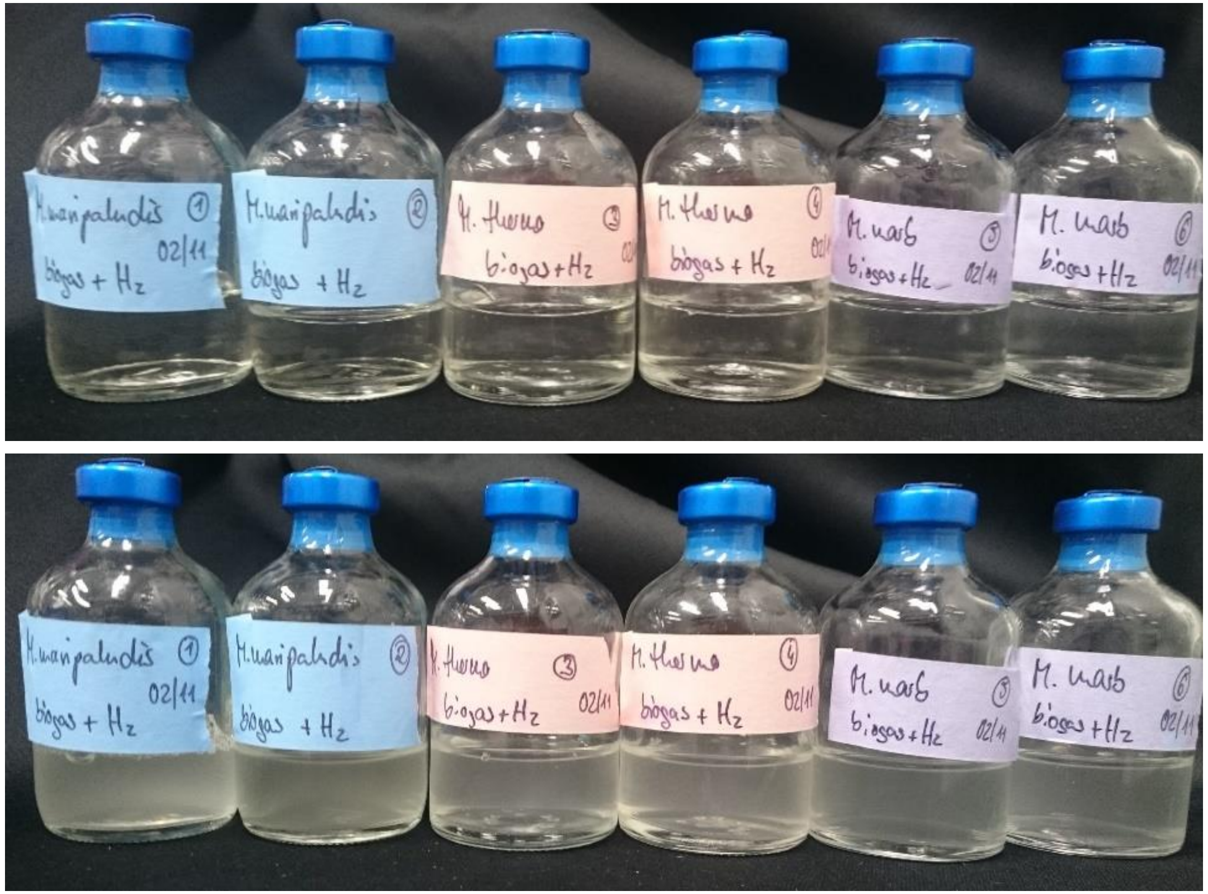
Milestone 2 Completed: 3 Strains Viable on Raw Biogas

Sampling raw-biogas from Delta Diablo treatment plant.

Strain #1 Strain #2 Strain #3

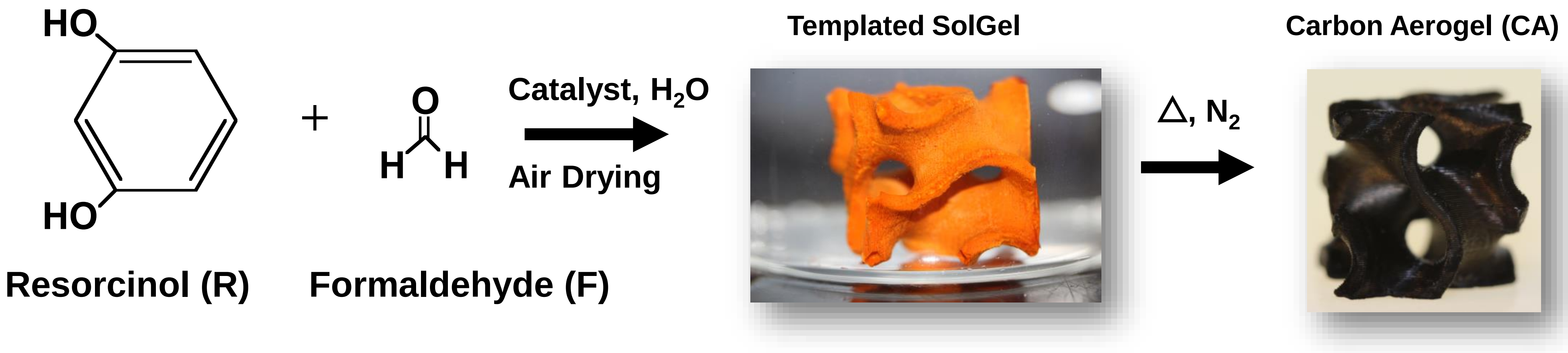
t = 0 h

t = 48 h



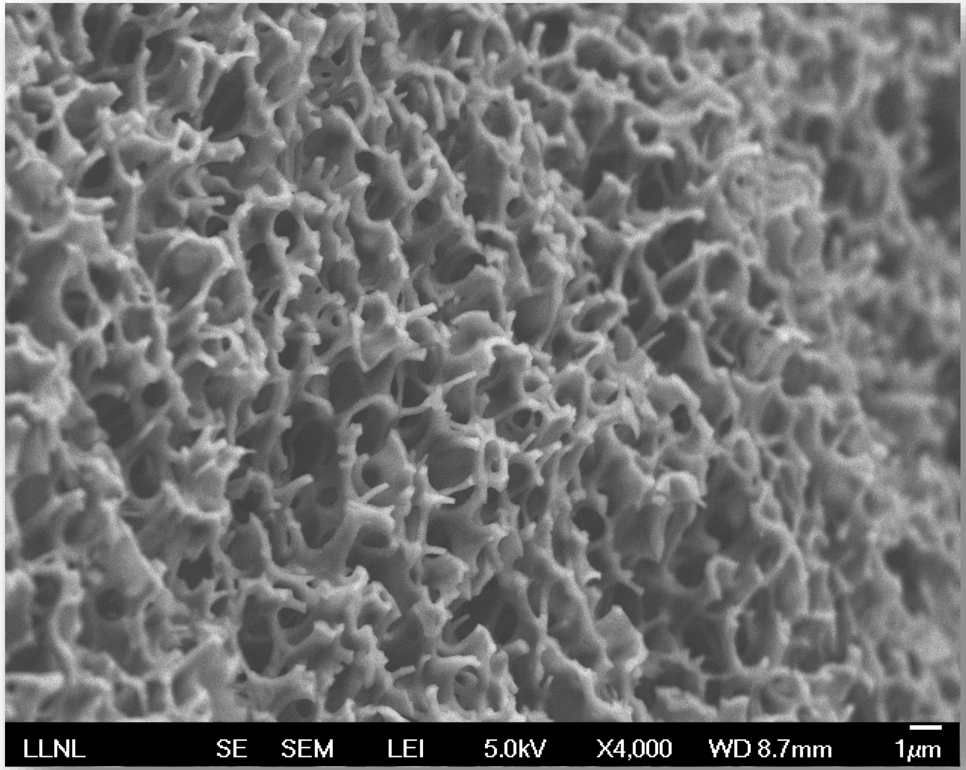
Serum vials containing methanogenic archaea, raw biogas as the only carbon source, and hydrogen as the sole electron source.

Developed New Low Cost Molding Method for Patterned Aerogel Synthesis



High 3D conductivity, mechanically robust, limitless geometries w/ high surface area

Conformal Electrodeposition of Hydrogen Evolution Catalyst



NiMo Coated Aerogel.

Hydrogen Evolution

Ongoing /Future Work

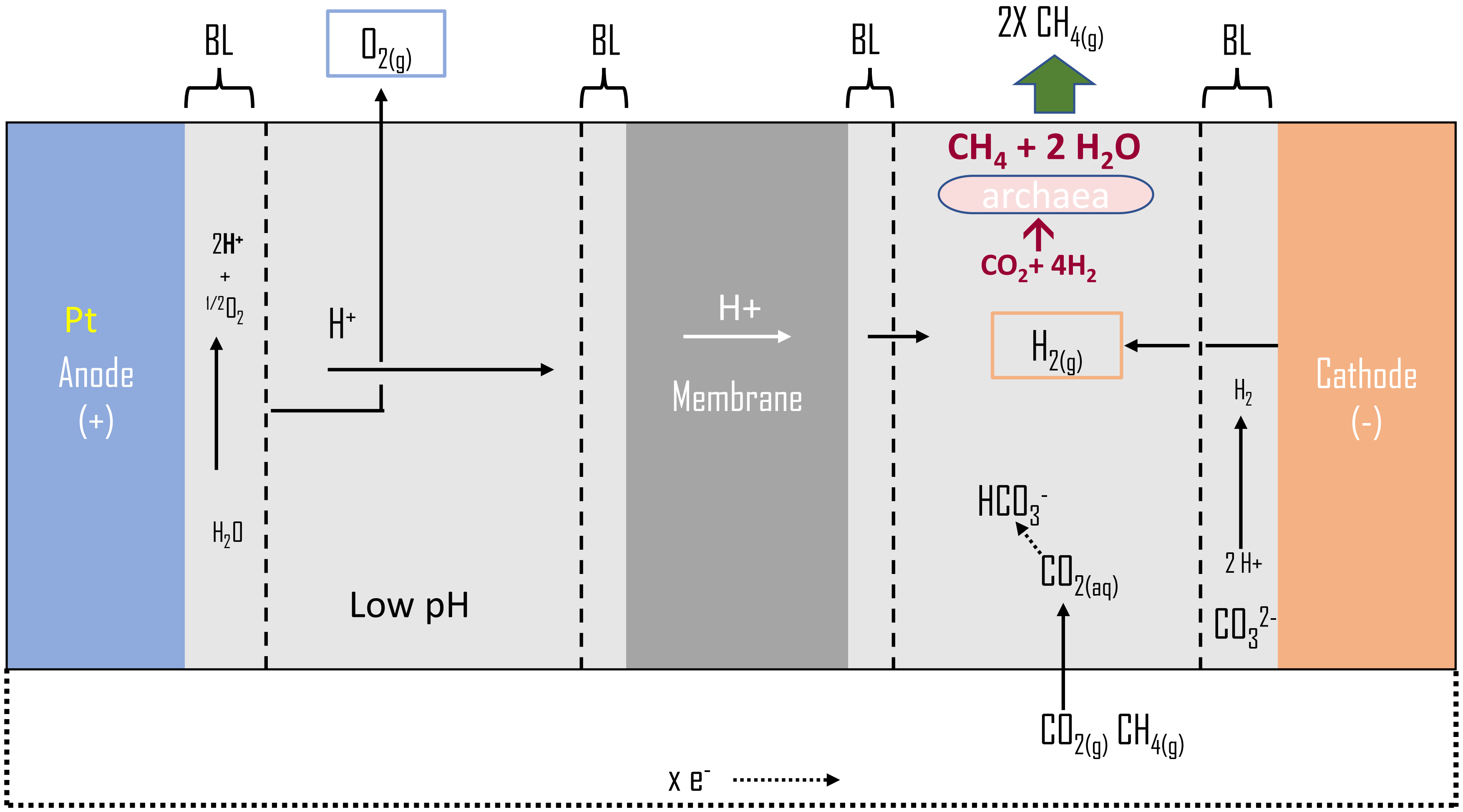
Testing systems under continuous gas flow for first time

Bubble bottle culture of *M. marburgensis* on H_2/CO_2 (80/20)
Optical density: about 1 (~10^9 cell/ml).

- Hydrogen limited (gas recirculation and stirring increase methanogenesis rates)
- Methanogenesis rates of up to 2 ml/min/L
- corresponding to 1 A L^{-1} current if H_2 supplied via electricity

***Electrochemical* reactors with the same strain as bubble bottle: Only stable < 1 day**

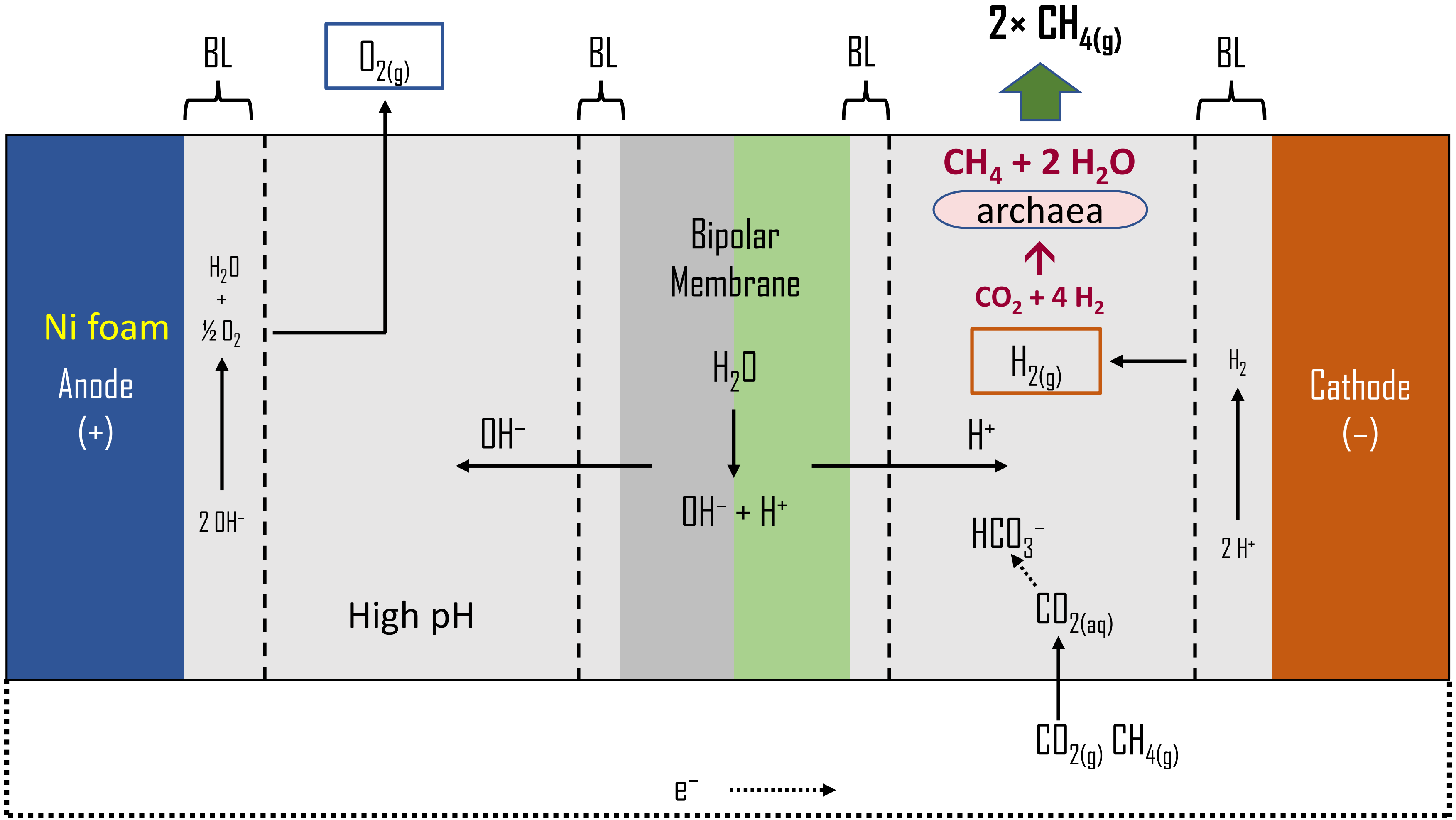
pH instabilities arising from proton exchange membrane



Adapted from Singh, M. R., et. al. *PCCP.* **2015**

Tolerates high temperatures (more productive organisms), but requires Pt and pH unstable

Target system with biopolar membrane and alkaline anode



Adapted from Singh, M. R., et. al. *PCCP.* **2015**

Stable pH and lower cost materials

Integration of Microbes in Productive Electrochemical Reactors

Microbial strains tested:

Strains tested	Temp.	Salinity	Density and turnover rates	medium
Methanothermobacter thermautotrophicus	65°C	low	High	Freshwater (DSMZ medium 119)
Methanothermobacter marburgensis	65°C	low	high	Freshwater (DSMZ medium 119)
Methanococcus maripaludis	30°C	high	medium	Sea water (Artificial sea water or DSMZ medium 141)

Delamination of bipolar membrane at elevated temperatures.

Scaling of NiMo coated graphite rod in marine media.

- Most productive pure strain needs high temp and low salt→ *membrane breakdown, high IR*
- Lower temp strain allows for high salt but needs Mg → *cathode scaling*

Overcoming integration challenge : finding “goldilocks” strain *(in progress)*

- **Adaptation/acclimation of freshwater strains for higher salt**

  Successful with Methanothermobacter strains, but requires Nafion membrane because of higher temperature

- **Isolation of strains in media suitable for electrosynthesis**

  (low Mg/Ca concentrations, high salinity)

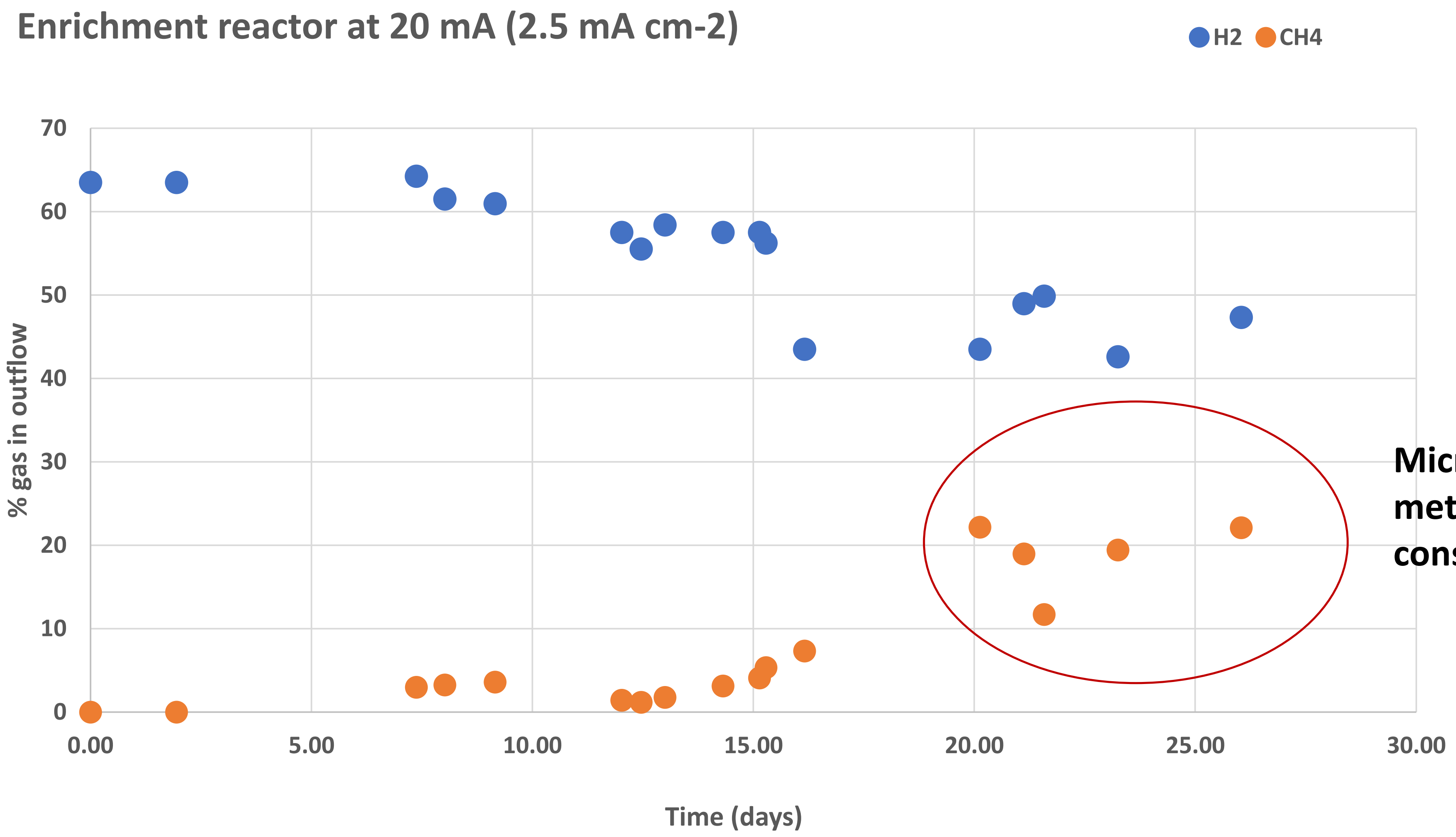
  In progress

- **Isolation of strains in electrochemical cell while running high current density**

  In preparation

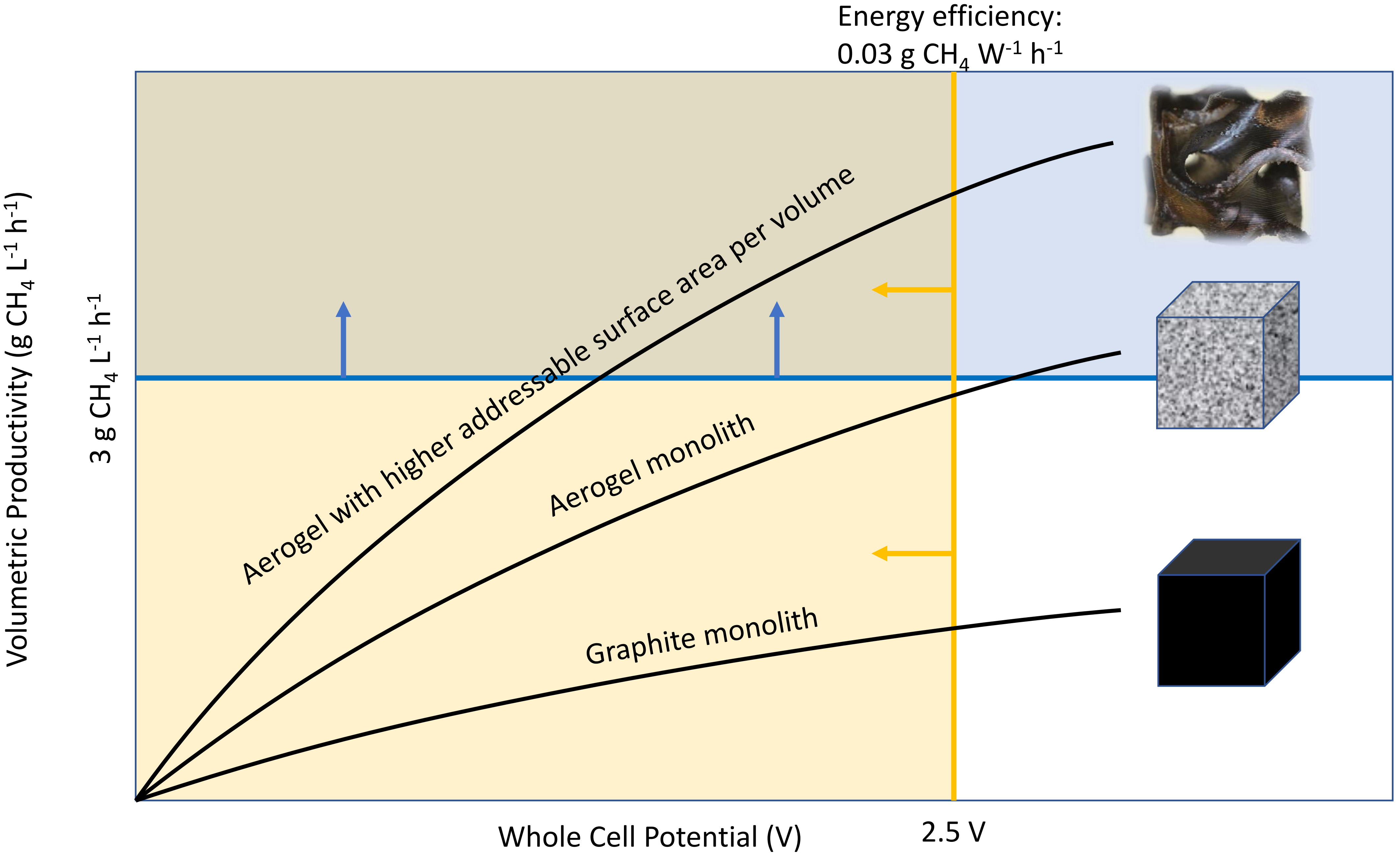
→**Key Milestones:** Testing of new isolates of 1-3 strains for tolerance to current density >5 mA/cm^2 (Q5); selection of strain (Q6)

Finding “goldilocks strain” from Delta Diablo Sludge



Microbes evolving methane under constant current

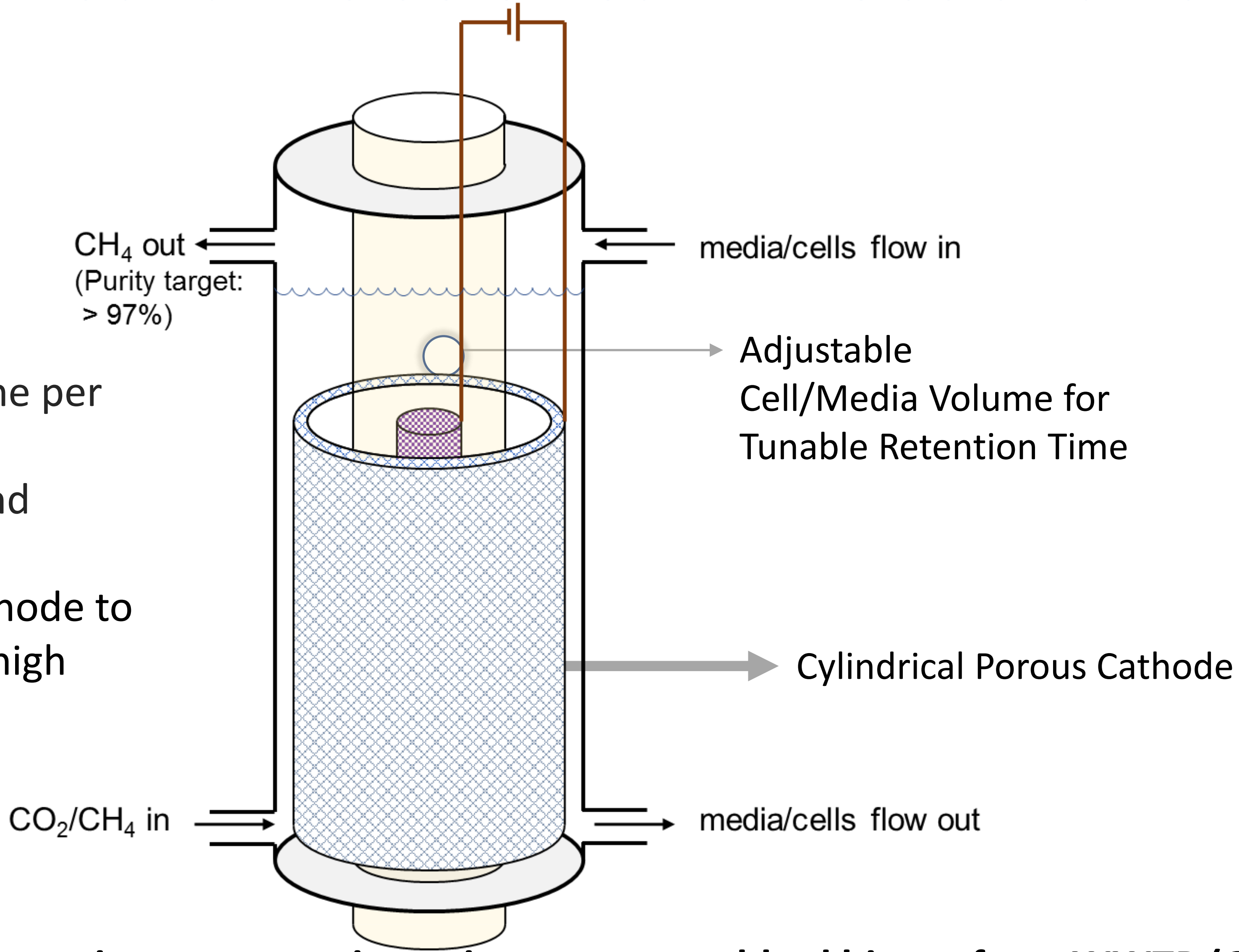
Selecting cathode material and geometry (key milestone Q6)



Building Reactor Around the Selected Microbe and Cathode

Desired Features:

- Maximize cell/media volume per reactor volume
- All components low cost and scalable
- Membrane proximal to cathode to minimize pH instability at high current density



Key Milestones: Construction and continuous operation using raw or scrubbed biogas from WWTP (Q7) Demonstrate outlet gas purity of 97% CH4, <3% CO_2, <0.2% O_2, <4 ppm H_2S, <0.1 mg/m³ siloxanes at 0.03g/Whr in continuous reactor (Q8)

Strategic Importance

- *We aim to **improve the performance** (to reach target energy efficiency, biogas purity) and TRL of Electromethanogensis by constructing a prototype continuous reactor*

- *This project will, for the first time, integrate in situ H_2 generation with biogas purification to pipeline quality in a continuous, modular device*

- *Electromethanogenesis provides a pathway for increased utilization of biomass carbon and renewable energy*

- *SoCalGas will be integral in advising on technical direction, identifying next step, partners, and potential pilot sites.*

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

Summary

- Our goal is to upgrade biogas to pipeline quality by coupling (renewable) electricity to methanogenesis.
- Success factors include energy efficiency (0.03 g/Wh) biogas purity (97%) and stability (days)
- We have shown feasibility with individual components and need to focus on isolating suitable microbe and integration with reactor

Quad Chart Overview

Timeline

- Project start date 10/01/18
- Project end date 10/01/20
- Percent complete: 20%

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

EXTRA

To beat Electrochaea-rates we need about 40 mA/cm³ cathode volume

Quick update:
Bubble bottle culture of *M. marburgensis* on H_2/CO_2 (80/20) successful after changing medium composition

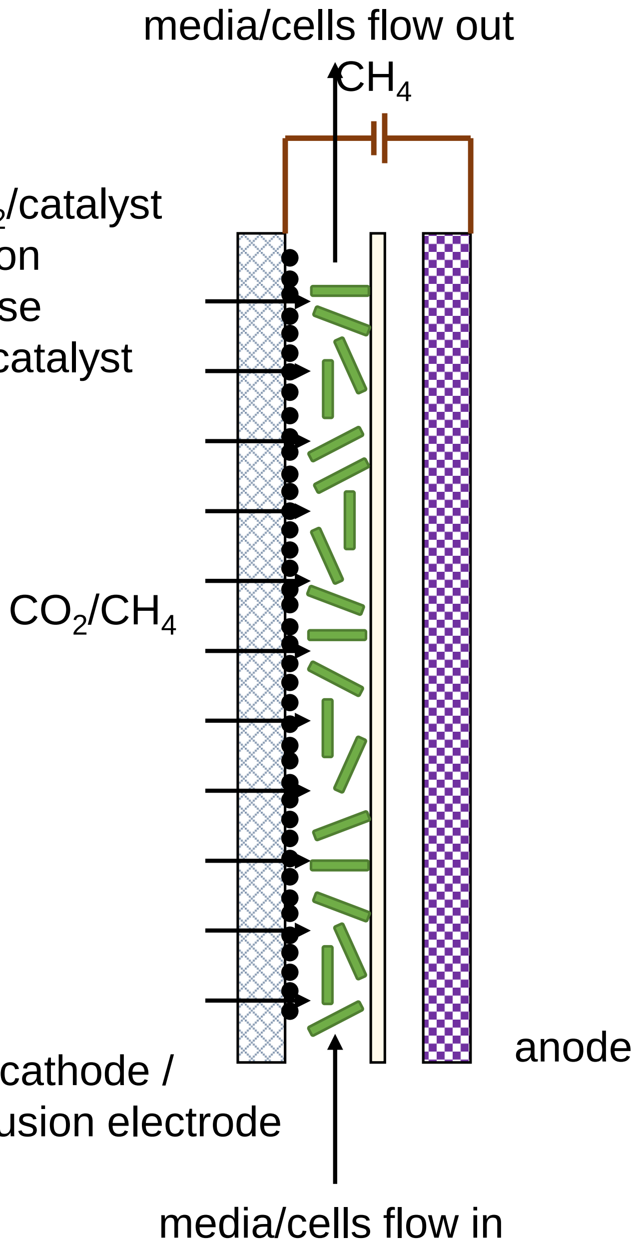
- Optical density: about 1 (~10^9 cell/ml).
- Hydrogen limited (gas recirculation and stirring increase methanogenesis rates)
- Methanogenesis rates of up to 2 ml/min/L
- corresponding to 1 A L^{-1} current if H_2 supplied via electricity

Electrochemical reactors with the same strain as bubble bottle:
→ not working for more than a few hours

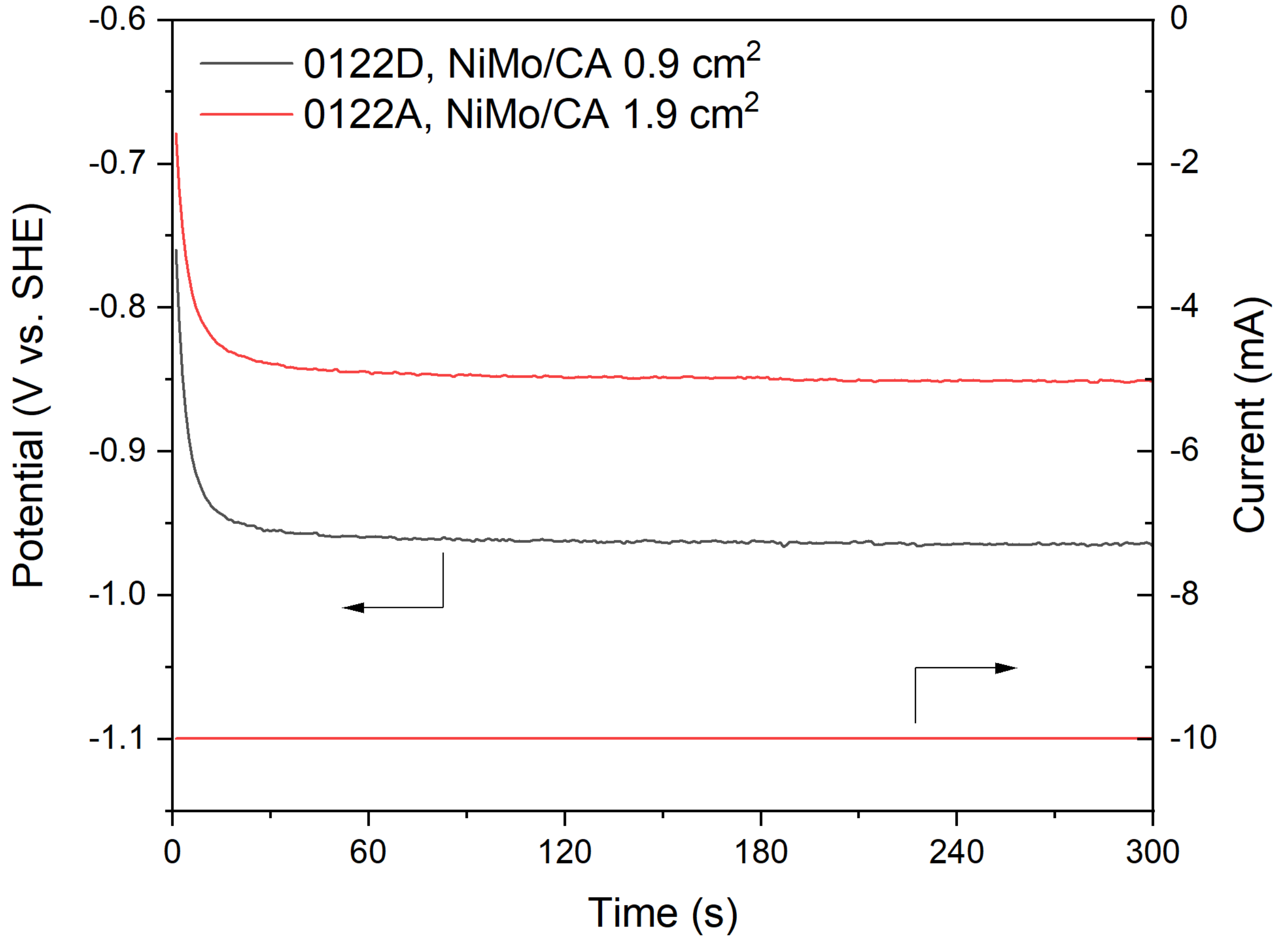
Electrochemical reactor with mixed enrichment from Delta Diablo:

- 30°C
- bipolar membrane
- fed with 200 µl CO_2/min (lowest our MFC is doing right now)
- 20 mA constant current (ca. 18 mmol e^-/H^+ d^{-1} = ca. 150 µL H_2 min^{-1})
- running for >1.5 months (two medium exchanges)
- hydrogen limited (increased stirring increased methane concentration)
- Slow growing?
- Outflowing gas: 50% H_2, **11% CH_4**

Good for maximizing CO_2/catalyst interaction, but our reaction happens in the liquid phase where the cells are! Our catalyst is just a source of H_2.



Higher Surface Area Cathodes Require Less Energy



Potential required to achieve the same current is less negative for higher surface area materials – high surface area electrodes reduce the energy required to supply H_2 *in situ*

Task	Milestone Description	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8
1	LLNL demonstrates method for stable (>1 day) and low resistance (< 10 ohms) electrical contacts to porous or printed electrodes	X							
2	Test raw biogas with small scale cultures or electrosynthesis to determine microbial tolerance to contaminants H_2S and siloxanes.		X						
3	4 pure methanogenic strains tested for tolerance to increasing current density in the reactor (> 5 mA/cm^2)		X						
4	Test two cathode materials with raw or scrubbed biogas to determine contaminant tolerance; Demonstration of >80% Faradaic Efficiency for methane			X					
5	Operation of ME reactor that produces methane from biogas CO2 for >2 days at greater than 0.03g/Whr				X				
6	Testing of new isolates of 1-3 electromethanogenic strains for tolerance to H_2S and siloxanes and current density >5 mA/cm^2					X			
7	Selection of reactor configuration and anode and membrane material. Selection criteria are activity, cost, compatibility with system, and stability over >2 days					X			
8	Microbe downselect and contaminant tolerance documented. Biogas treatment (raw or scrubbed) selected. Cathode material selected.						X		
9	Construction and continuous operation of flow-through electromethanogenesis reactor module using raw or scrubbed biogas from WWTP							X	
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								X
11	Reactor, process, system design and operating strategies for TEA.							X	
12	Completion of TEA (Joint Milestone with NREL/ANL)								X