

Novel Microbial Electrolysis Cell Design for Efficient Hydrogen Generation from Wastewaters

Bruce E. Logan (PI)

Penn State University

DOE Project Award #: DE-EE0009623

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DOE Hydrogen Program

2022 Annual Merit Review and Peer Evaluation Meeting

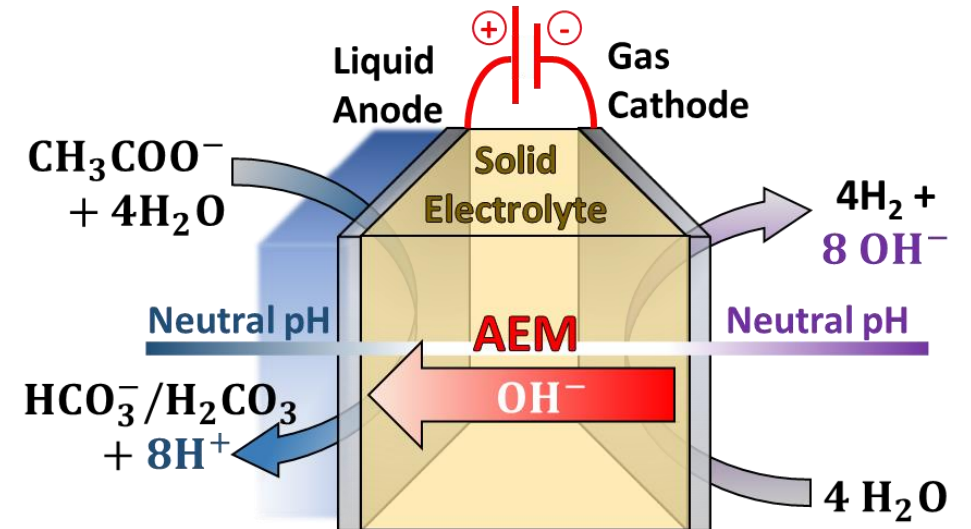
Project ID: P202

PROJECT GOALS – project just started

- The final project goal is to develop a bench-scale MEC (100 cm²) for H₂ production at high rate and low applied potentials from waste streams using a zero-gap configuration with an anion exchange membrane (AEM) and vapor-fed cathode to limit bioanode acidification.

Tasks for current year

1. Electrode preparation. Acclimation and operation of the bioanode and assembly of the cathode – AEM membrane electrode assembly (MEA). (PSU)
2. Start-up of the lab-scale zero-gap MEC fed vapor at the cathode. (PSU)
3. Ramping up biomass fermentation stage and investigation of the fermentation effluent composition (organic content, suspended solids, buffer capacity)



OVERVIEW

Timeline and Budget

- Project Start Date: 09/01/2021
- Project End Date: 09/30/2024
- Total Project Budget: \$ 1.2M
- DOE Share: \$ 1M
- Cost Share: \$ 0.2M
- DOE Funds Spent*: \$ 108K (PSU)
- Cost Share Funds Spent*: \$ 0
- DOE Funds Spent*: \$ 42K (NREL)
- * As of ~ 03/01/2022

Barriers

- Current density
- Suspended solid content
- H₂ productivity

Partners

- Project lead: Bruce E. Logan (Penn State)
- Co-PI: Dr. Katherine Chou (NREL)
 - NREL will provide fermentation effluent from *Clostridium thermocellum* having neutral pH, with ethanol and acetate as the primary fermentation byproducts to be fed in the MEC.
- Partner organization: Dr. Patrick Kiely (Island Water Technologies)
 - Island Water Technologies (IWT) will connect with waste producers that can provide the waste feedstock for the project and will be the primary distribution channel of our technology

RELEVANCE

Our team addresses major limitations in H₂ production from waste streams and waste feedstock toward practical applications. We will optimize and operate a bench scale microbial electrolysis cell (MEC) enabling hydrogen production from the oxidation of the organic matter in wastewaters via exoelectrogenic microorganisms.

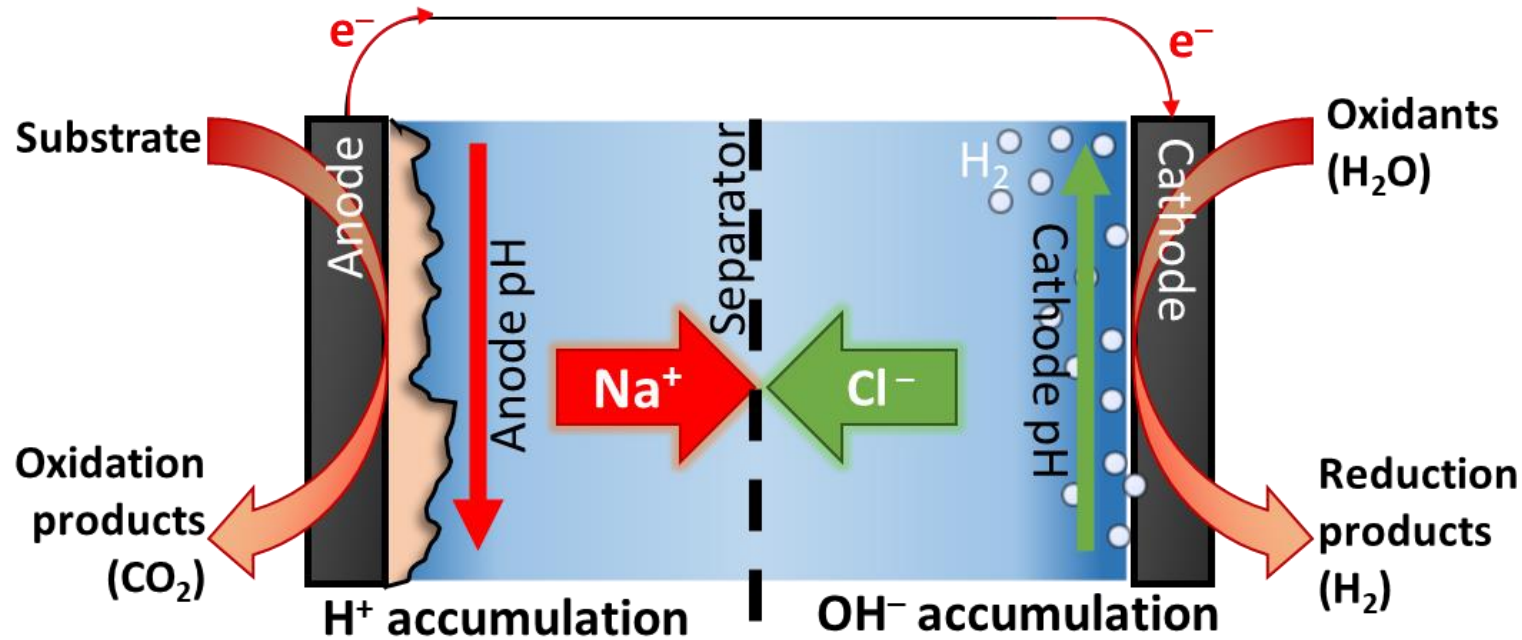
Milestone Schedule							
Milestone #	Project Milestones	Type	Task Completion Date (Project Quarter)				Progress Notes
			Original Planned	Revised Planned	Actual	Percent Complete	
1.0	Impact of reactor configuration on the MEC performance						
1.1	Electrodes preparation	1.1.1	Q1	Q1	Q1	100%	Completed
1.2	MEC assembly and acclimation	1.2.1	Q2	Q2	Q2	80%	In completion
1.2	Biomass fermentation effluent production and characterization	1.2.2	Q2	Q2	Q2	100%	Completed.
1.3	Impact of MEC operational parameters on performance	1.3.1	Q3	Q3	Q3	0%	Not started.
1.4	Development of Pt-group metal free cathode	1.4.1	Q4	Q4	Q4	30%	Started.
1.5	MEC performance with synthetic media	1.5.1 Go/no-go	Q4	Q4	Q4	0%	Not started.

We will develop a novel MEC design producing unprecedented current densities and H₂ production rates by addressing mass-transport limitations in the cell, enabling a more stable pH across the reactor and larger bioanode performance.

Our project is relevant to DOE goal to achieve the Hydrogen Shot goal of \$1 for 1 kg hydrogen in 1 decade

NOVELTY

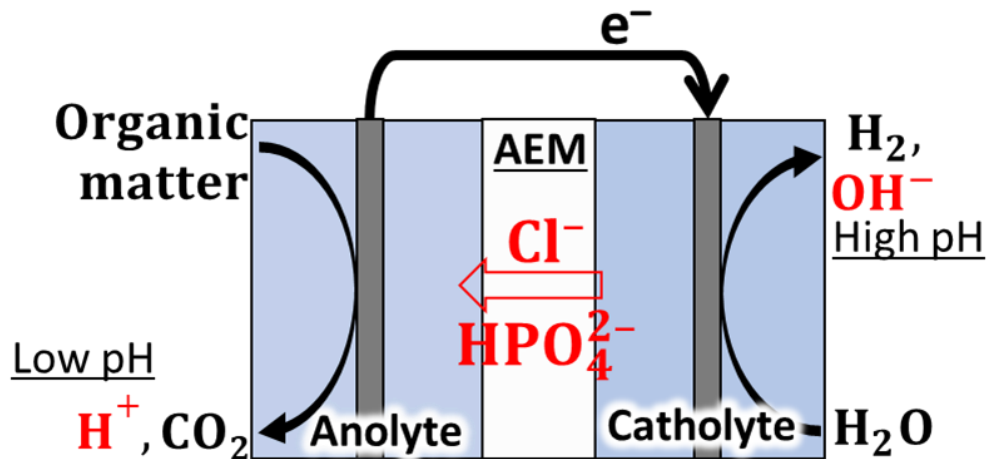
Ion transport in **previous MEC designs that have a liquid electrolyte** between anode and cathode.



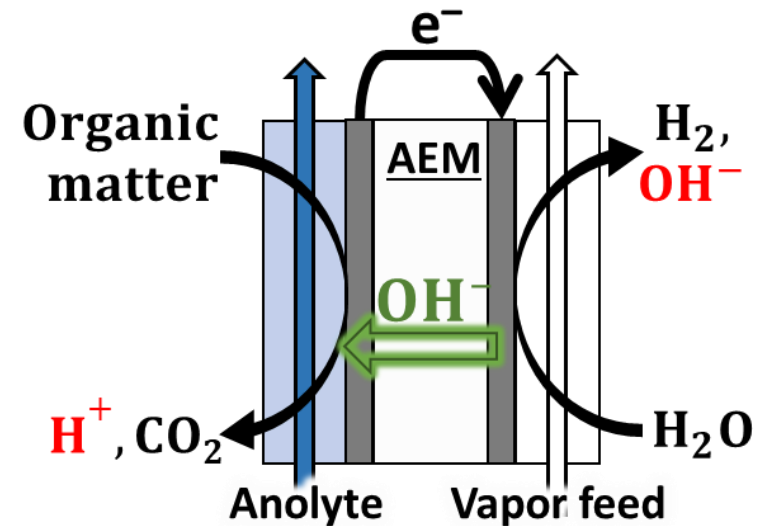
The large pH difference between anode and cathode increases the applied voltage due to the Nernst equation while the anode acidification limits the maximum current density.

APPROACH

Microbial electrolysis cells (MECs) enable hydrogen production from wastewaters via microbial biomass conversion through a smaller applied voltage than that needed to split water.



Current MEC technologies use a liquid catholyte containing a buffer or salts. The anions in these catholytes result in charge being balanced predominantly by ions other than hydroxide or protons, leading to anode acidification and low current density.



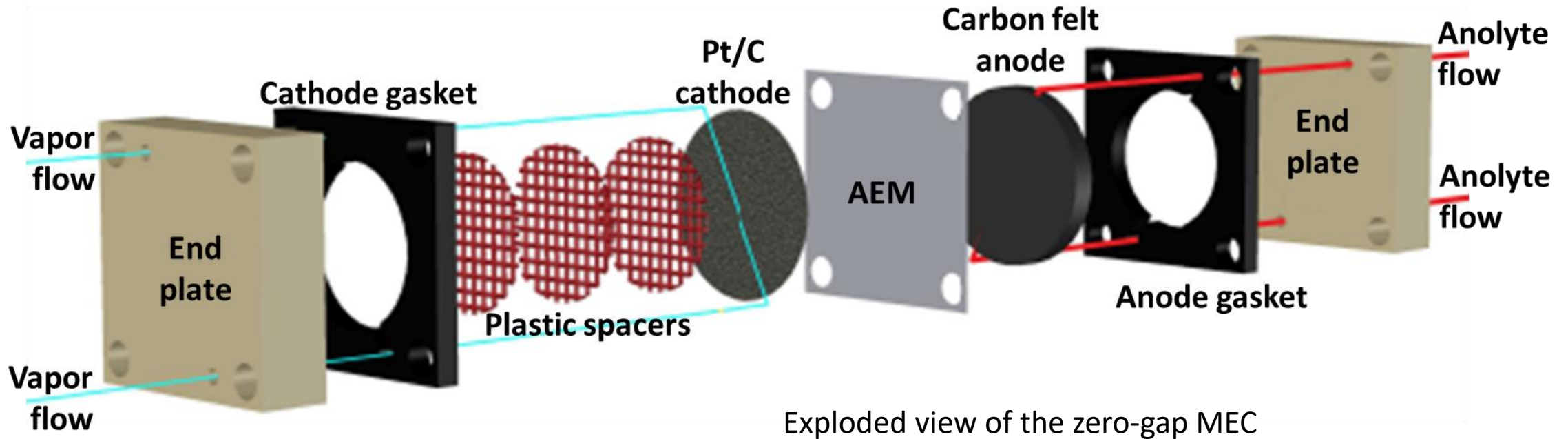
To enhance only hydroxide ion transport to the anode and boost current density and hydrogen production rates, we developed a novel vapor-fed MEC configuration lacking a catholyte with closely spaced electrodes and an anion exchange membrane to limit the acidification.

APPROACH

The vapor-fed MEC design advances the existing reactor configuration by

- (1) removing the solution separating anode and cathode and
- (2) allowing only the hydroxide ions generated at the cathode to be transported to the anode.

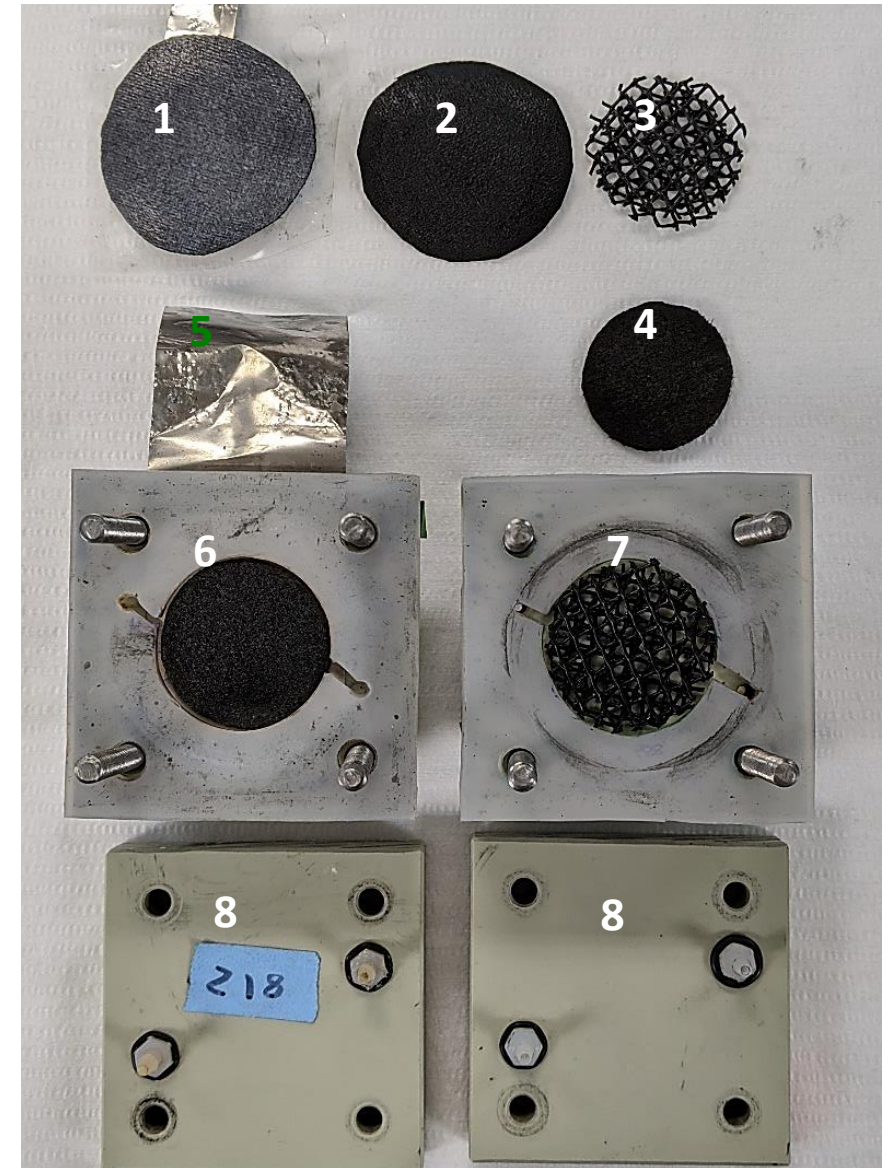
The absence of a liquid catholyte in our system will exclude the transport of any anion except the hydroxide ions generated by the HER, which will ensure sufficient neutralization of protons generated by the bioanode next to the membrane.



APPROACH (PSU) – project just started

- (1) Acclimation of the bioanode;
- (2) Synthesis and preparation of the cathode
- (3) Assembly of the zero-gap MEC fed vapor at the cathode

Milestone Schedule							
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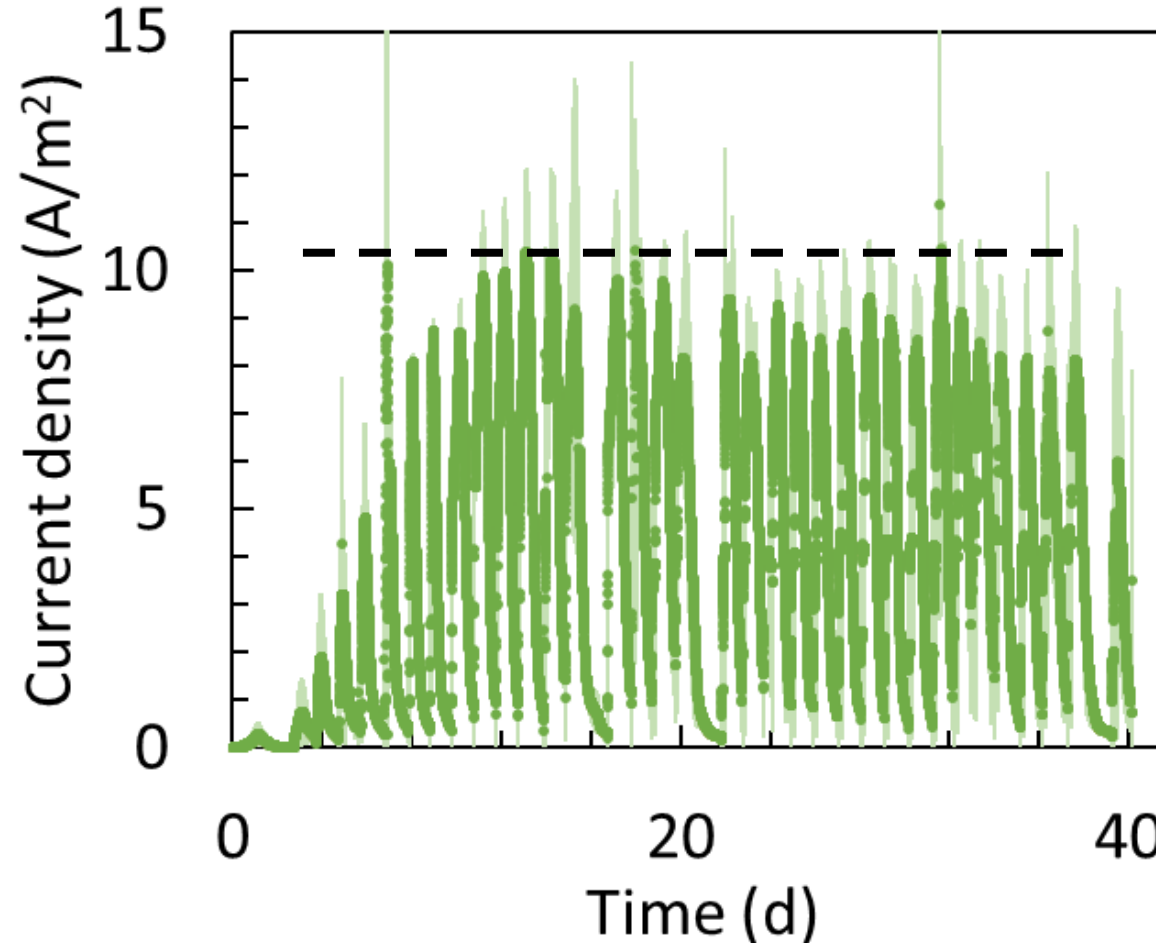
MEC materials: (1) Cathode MEA, gas-side; (2) cathode, solution side; (3) spacers; (4) carbon felt bioanode; (5) anode current collector; (6) anode chamber; (7) cathode chamber; (8) end-plates.

Accomplishments – Task 1 (PSU)

Acclimation of the bioanode

Bioanode was successfully acclimated in conventional cubic cells producing stable current density over time

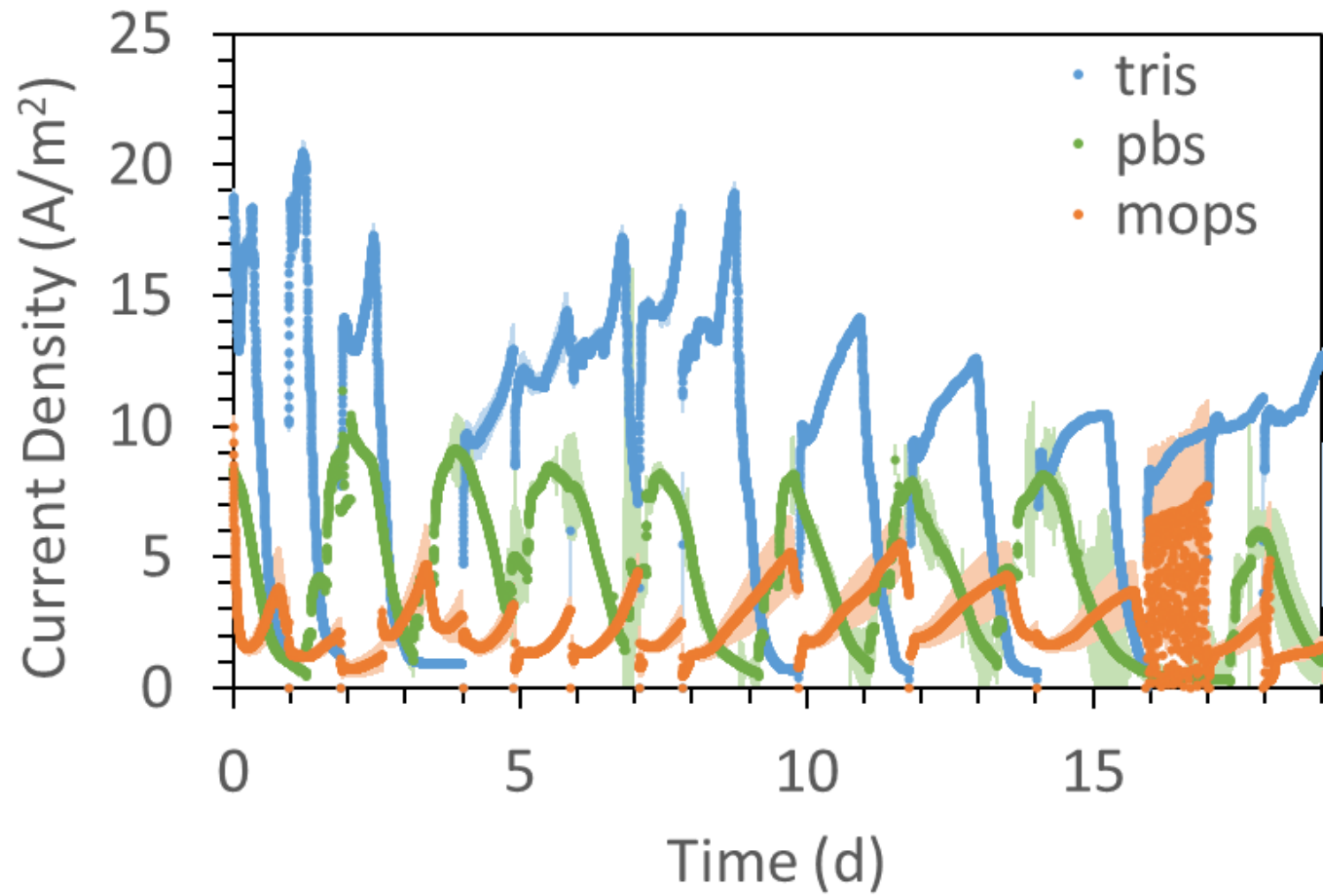
- The bioanode was fed daily with a solution containing acetate as a substrate for the bacteria.
- Bacteria oxidized the acetate, generating current.
- Once the substrate concentration decreased, the current generated diminished, resulting in the spikes visible in the figure..



Average current density of 9 A/m^2

Accomplishments – Task 1 (PSU)

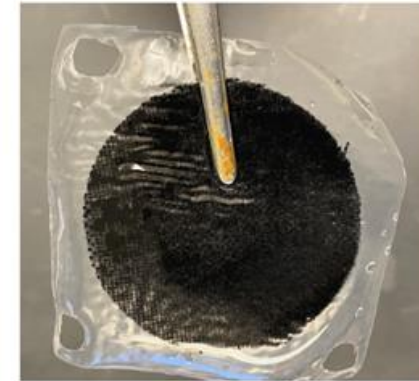
- We investigated the impact of the buffer type (organic; mops or tris) vs inorganic (pbs) on the bioanode performance.
- Using pbs increased the performance compared to mops and tris
- NREL will run biomass fermentations using inorganic buffers



Accomplishments – Task 1 (PSU)

Cathode preparation

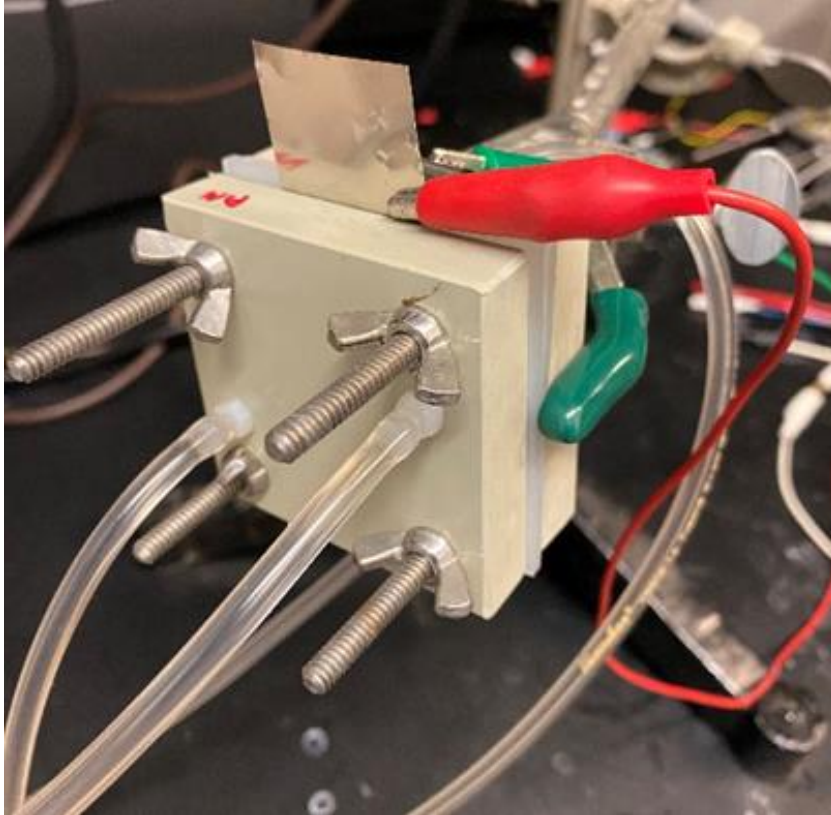
We prepared the cathode (Pt/C) for the H₂ evolution reaction and optimized the membrane electrode assembly using an anion exchange membrane.



Accomplishments – Task 1 (PSU)

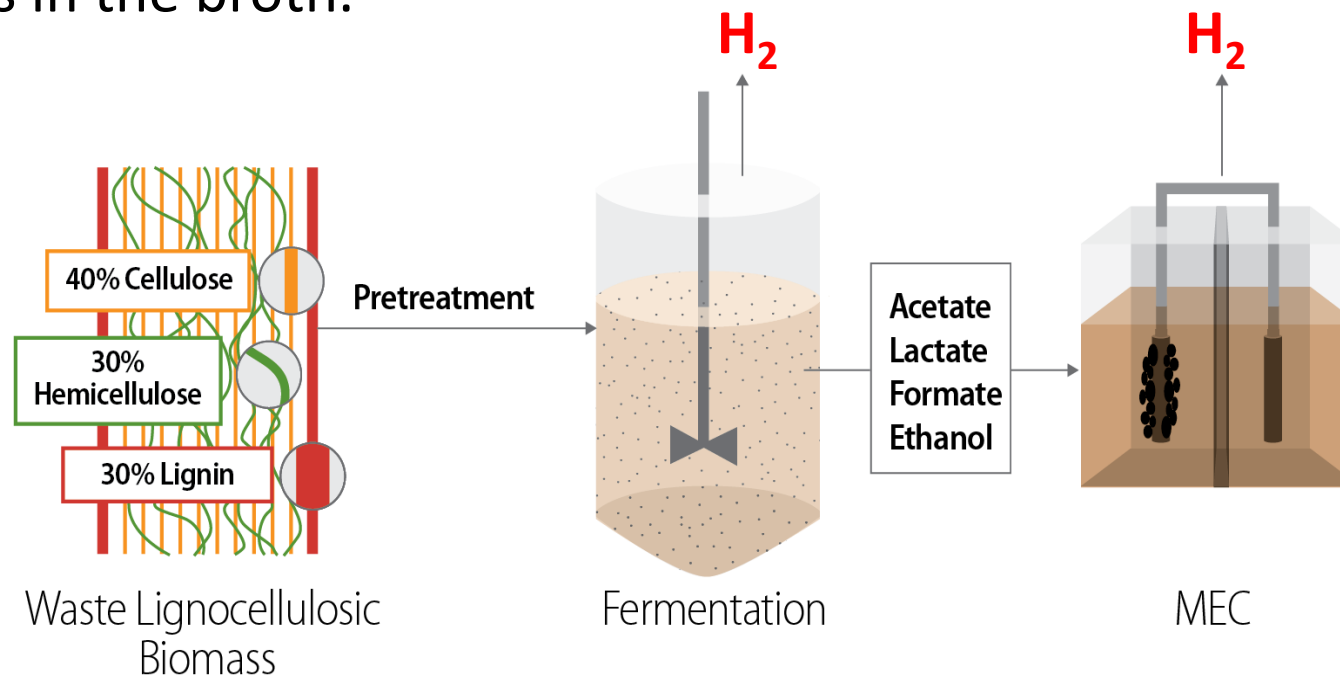
Assembly and testing the MEC

(The assembled zero-gap MEC is currently being tested and we will report the results in the next quarter)



Approach (NREL): Analyze fermentation effluent and investigate methods to remove particles

- Microbial fermentation of lignocellulosic biomass produces H_2 and wastewater that is rich in organic acids and a suitable model feedstock for MEC optimization for H_2 production
- NREL performs fermentation of crystalline cellulose (Avicel) by *Clostridium thermocellum* and provides the fermentation effluent to Penn State for MEC optimization.
- As solids may interfere with MEC performance, NREL investigates methods to effectively remove particles in the broth.



Accomplishments (NREL): Identification of relatively more effective parameters to remove suspended solids in fermentation wastewater

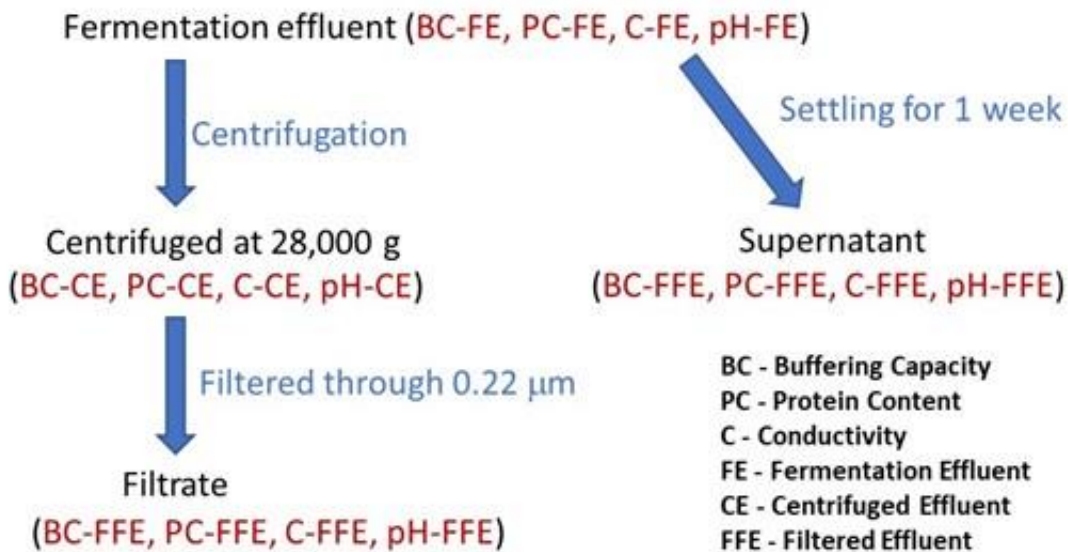
FY22 Q2 Milestone

Q2: Investigation of methods for removal of particles from fermentation effluent (centrifugation, filtration, settling). Provide preliminary samples to PSU for their own analyses and MEC tests.

Mar 2022

Complete

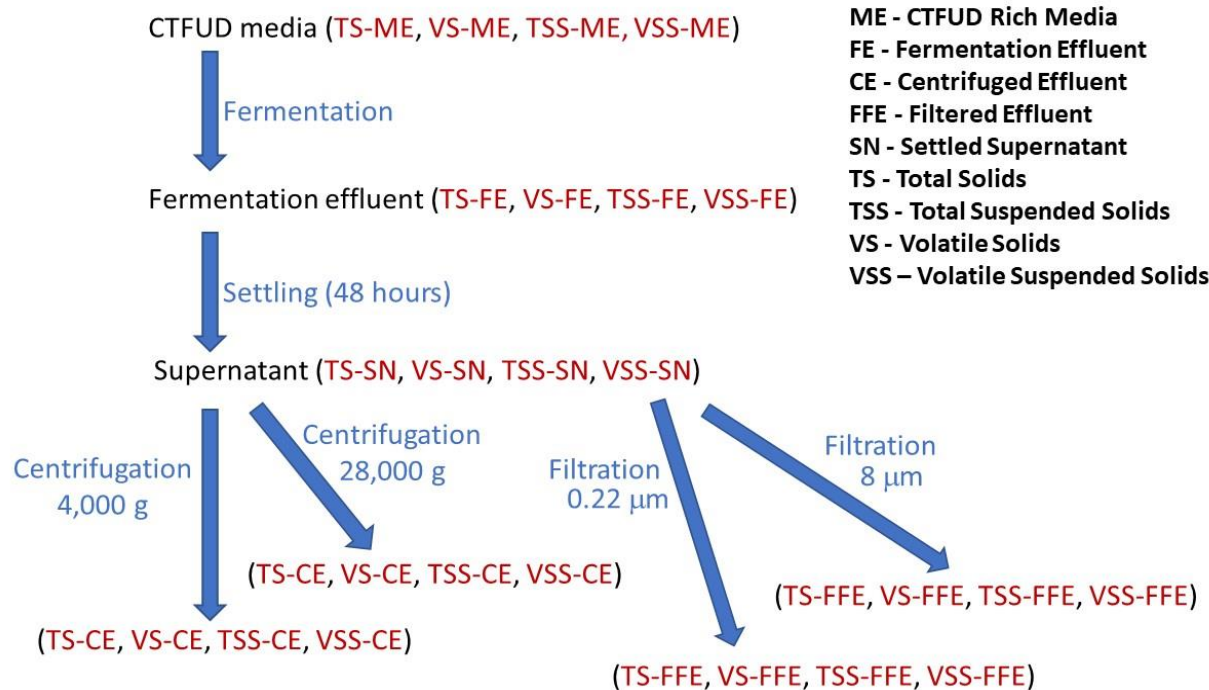
Fermentation effluent post settling, centrifugation, and filtration as methods to remove particles were analyzed for buffer capacity, conductivity, pH, and protein content.



Property	Settling	Centrifugation	Filtration
Buffering capacity (mM/pH-1)	11.2	10.4	10.4
Conductivity (mS/cm)	10.6 ± 0.92%	10.5 ± 1.18%	10.2 ± 1.24%
pH	7.35	7.65	7.77
Protein (mg/L)	207 ± 6.28% (in supernatant)	49.6 ± 3.87%	37.9 ± 8.71% (post Filtration)
Protein (mg/L)	275 ± 4.9% (in pellet from settlement)		
Total Protein in supernatant and pellet combined (mg/L)	482 ± 5.39%	49.6 ± 3.87%	37.9 ± 8.71%

Accomplishments (NREL): Identification of relatively more effective parameters to remove suspended solids in fermentation wastewater

- Settling (48 h) removes 67% of total suspended solids (TSS)
- Centrifugation at 28000 g further removes 76% of TSS but was not substantially more effective than centrifugation at 4000 g which removes 73% of the TSS.
- Filtration through 0.22 μm removed 75% of the total suspended solids vs. 20% TSS removal from the supernatant through an 8 μm filter.



Condition	Total Suspended Solids (mg/L)	Volatile Suspended Solids (mg/L)	Total Solids (g/L)	Volatile Solids (g/L)
CTFUD Rich media	73 \pm 13%	53 \pm 35%	24.2 \pm 0.4%	20 \pm 0.2%
Fermentation effluent	4620 \pm 6%	3127 \pm 11%	26 \pm 1%	15 \pm 0.8%
Supernatant	1507 \pm 4%	1367 \pm 3%	23 \pm 0.6%	13. \pm 0.8%
Centrifuged @ 28000 g	360 \pm 11%	407 \pm 8%	22 \pm 0.7%	12 \pm 1%
Centrifuged @ 4000 g	407 \pm 24%	400 \pm 8%	22 \pm 0.9%	12 \pm 1%
Filtered @ 0.22 mm	380 \pm 22%	367 \pm 10%	23 \pm 1%	12 \pm 0.6%
Filtered @ 8 mm	1200 \pm 4%	1120 \pm 3%	23.9 \pm 0.3%	13 \pm 0.4%

Accomplishments and Progress: Responses to Previous Year Reviewers' Comments

- The project was just started and was not reviewed last year

Collaboration and Coordination

- PSU leads the project by assembly and operate the zero-gap MEC.
- NREL works with Penn State to investigate methods to remove solids in fermentation wastewater and provide the processed fermentation broth to PSU.
- Island Water Technologies (IWT) operates with waste producers that can provide the waste feedstock for the project and will be the primary distribution channel of our technology

Remaining Challenges and Barriers

- Effective removal of suspended solids from the anolyte to avoid clogging of the zero-gap MEC;
- Identify potential wastewaters for the MEC containing sufficient biodegradable substrate and minimal solid content;

Proposed Future Work

- PSU will operate the flow-through MEC and investigate the optimal operational parameters to maximize H₂ productivity and current density.
- PSU will synthesize Pt-group metal free cathodes to replace Pt/C in the MEC.
- NREL will investigate the impact of different biological buffering systems (sodium bicarbonate, Tris, phosphate-buffer) on the buffering capacity of the wastewater.
- NREL will work with a select feedstock (Penn State provides) for fermentation and provide the fermentation effluent for Penn State to test on MEC.
- IWT will identify different wastewater producers and organize shipment of the wastewater to PSU, where the wastewater will be fed to the MEC.

Any proposed future work is subject to change based on funding levels

Summary

1. Successful acclimation and operation of the MEC in cubic reactors fed organic matter for H₂ production from wastewater sources (PSU).
2. Synthesis of high performance Pt/C cathode (PSU).
3. Assembly of the cathode and AEM in a MEA enabling a gas-cathode chamber in the zero gap MEC (PSU).
4. Complete cellulose fermentation achieved by NREL producing effluent with primary acetate and ethanol as a feed for the MEC (NREL).
5. Large suspended solids removal with filtration and centrifugation from the cellulose fermentation effluent to avoid clogging the MEC (NREL).
6. Outreach to large companies for wastewater sample requests and technology transfer (IWT)

Technical Backup and Additional Information

Technology Transfer Activities

- IWT is advancing the market transformation plan by advocating for our MEC with industry partners to identify wastewaters appealing for the MEC design we are proposing and increase company awareness on energy recovery from waste feedbacks.
 - IWT Activities:
 - Advising and reviewing communications documentation required to present the technology to industry partners;
 - Industry outreach;
 - Hosting remote technical presentation and introduction with large private company.

Publications and Presentations

Presentations:

- Logan, B.E.; Rossi, R. Novel microbial electrolysis cell design with asymmetric feed to manage the ion transport across the membrane, NA-ISMET, Nov.2021.
- Logan, B.E. 2021. Pathways to green hydrogen using water electrolyzers and microbial electrolysis cells. Invited seminar, King Abdullah University of Science and Technology (KAUST), Thuwal, Saudi Arabia. September 2021.