Novel Hybrid Microbial Electrochemical System for Efficient Hydrogen Generation from Biomass

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Project ID PD129

Overview

Timeline

- Project Start Date: 02/01/16
- Project End Date: 04/30/19

Barriers

- Low hydrogen molar yield (AX)
- High electrode (cathode) cost (AAA)
- Low hydrogen production rate (AAB)

Budget

- Total Project Budget: $1,670K
  - Total Recipient Share: $167K
  - Total Federal Share: $1,500K
  - Total DOE Funds Spent*: $1,010K

* As of 3/31/18

Partners

- **US DOE**: project sponsor and funding
- **OSU**: project lead; cost-share funding
- **PNNL**: co-project lead
- **ONAMI**: cost-share funding

Relevance

Project goal:

Develop a microbial electrochemical system for H_2 production from low-cost feedstock (lignocellulosic biomass and wastewater) at a cost close to or less than \$2/kg H_2.

Approach/Strategy to Achieving DOE's target:

Characteristics	**Units**	**Current Status**	**Project Target**	**Commercial Target**
Feedstock		hydrolysate/ wastewater	hydrolysate/ wastewater	hydrolysate/ wastewater
Feedstock cost contribution	\$/kg H_2	1.21/0	0.98/0	0.98/0
Capital cost contribution	\$/kg H_2	0.98/0.98	0.81/0.85	0.46/0.63
Electricity cost + other operational cost	\$/kg H_2	0.75/0.86	0.75/0.76	0.40/0.75
Fixed O&M cost	\$/kg H_2	0.38/0.38	0.31/0.33	0.17/0.25
Total cost	**\$/kg H_2**	**3.32/2.22**	**2.86/1.94**	**2.03/1.63**
Credits	\$/kg H_2	0/-10	0/-10	0/-10
Final cost	**\$/kg H_2**	**3.32/-7.78**	**2.86/-8.06**	**2.03/-8.46**

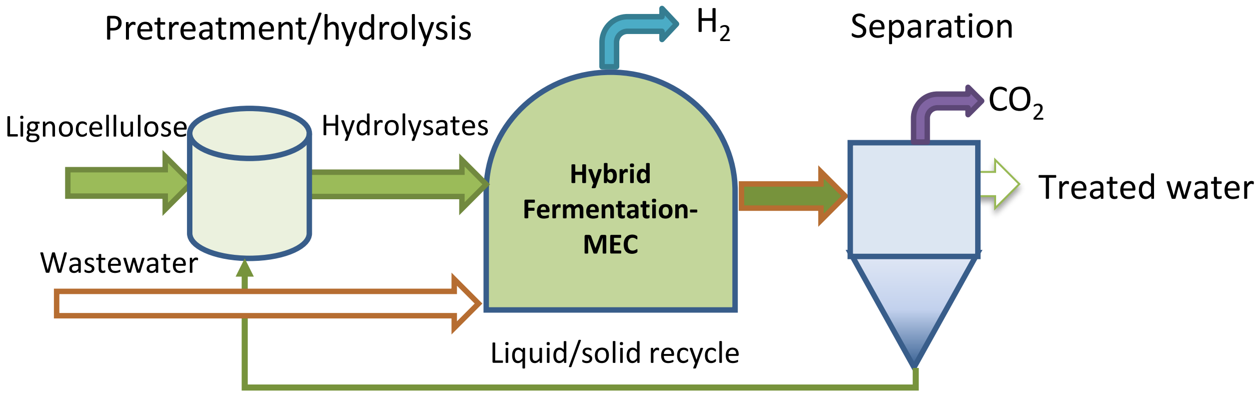
Using wastewater as feedstock can generate a credit as much as -\$10/kg H_2 assuming:

- A surcharge of \$0.6 per pound of BOD discharged
- Generating 1 kg H_2 corresponding to 17.6 pounds of BOD reduction
- Sewage system available on site

Approach

Overall approach:

Develop a hybrid fermentation and microbial electrolysis cell (F-MEC) system that can be integrated with lignocellulose pretreatment/hydrolysis or wastewater treatment processes for H_2 production.



Uniqueness of the approach:

- Use low-cost feedstock
- Combine strengths of dark fermentation and MEC processes
- Reduce capital/operational costs with low-cost and low-overpotential cathode
- Reduce operational cost with novel reactor design and operational conditions
- Apply cost performance model throughout the project to prioritize development

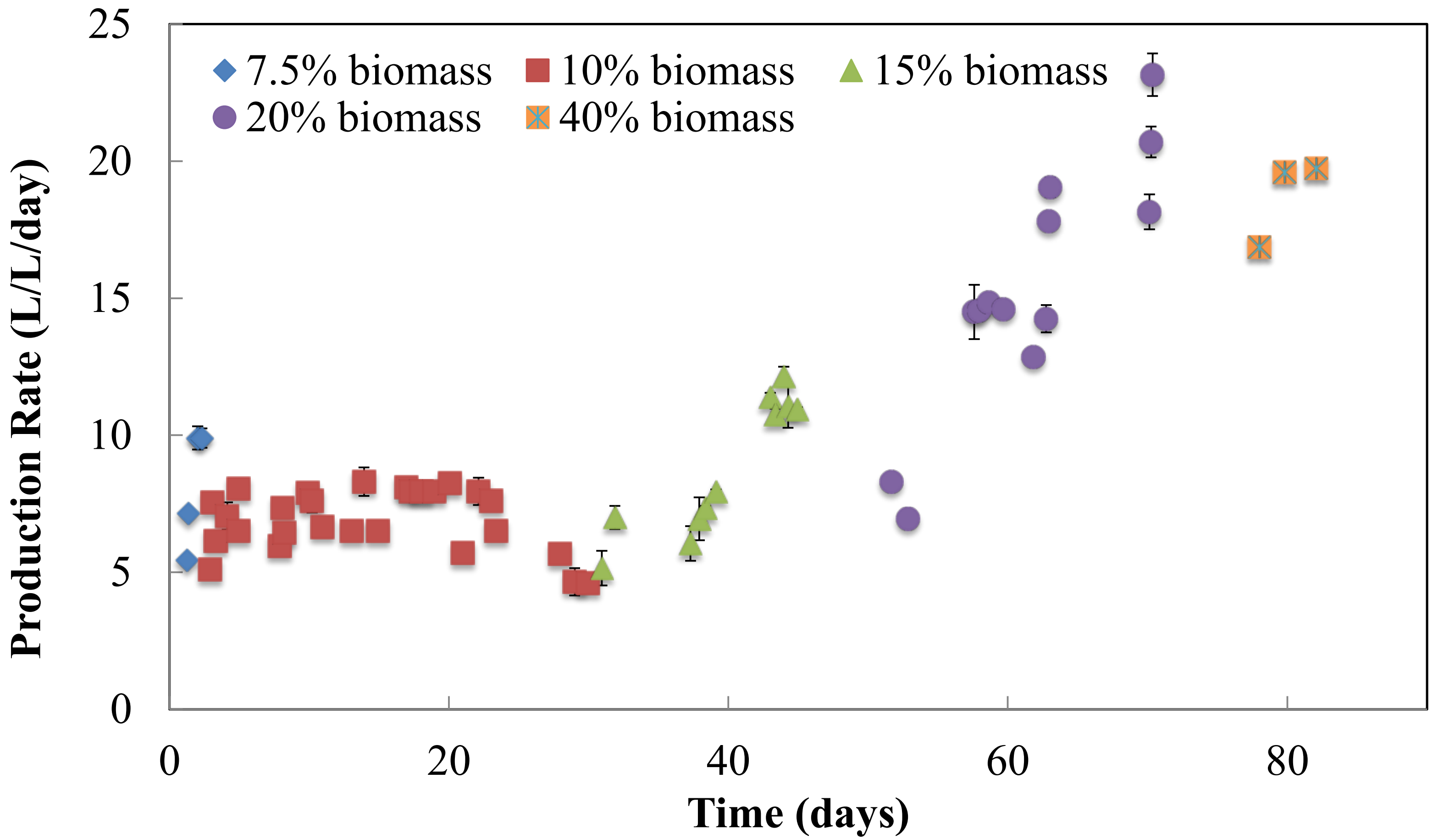
Approach/Milestone

Phase I Fermentation and MEC optimization (FY 16-17)	**Accomplished**
Milestone 1: Identify a bacterial culture capable of producing H2 from all major sugars with > 10% yield	100%
Milestone 2: The activity of hybrid nonprecious metal electrocatalyst higher than or equal to Pt.	100%
Milestone 3: H_2 production rate >0.2 m^3 H_2/m^2 cathode/day using a cathode surface area of >20 cm^2	100%
Go/NoGo: Reaching a fermentative hydrogen production rate of 8 $L_{H2}/L_{reactor}$/day	**Met**
Phase II Hybrid F-MFC system design/fabrication (FY 17-18)	
Milestone 1: H2 production rate >0.3 m^3 H_2/m^2cathode/day using a cathode surface are of > 100 cm^2	100%
Milestone 2: The stability of hybrid nonprecious metal electrocatalyst higher than or equal to Pt	100%
Milestone 3: Finish the design of the 10 L hybrid reactor	100%
Go/NoGo: Finish the fabrication of the reactor and demonstrate or show significant progress towards reaching an overall hydrogen production rate of 24 L $H_2/L_{reactor}$/day	**Met**

Accomplishments and Progress

Task 1: Fermentative hydrogen production

- Continuous H_2 production using the immobilized culture



H_2 production can reach over 20 $L/L_{reactor}$/day in a continuous flow reactor with immobilized fermentative bacteria, which met our targeted 8 $L/L_{reactor}$/day by fermentation.

Accomplishments and Progress (con.)

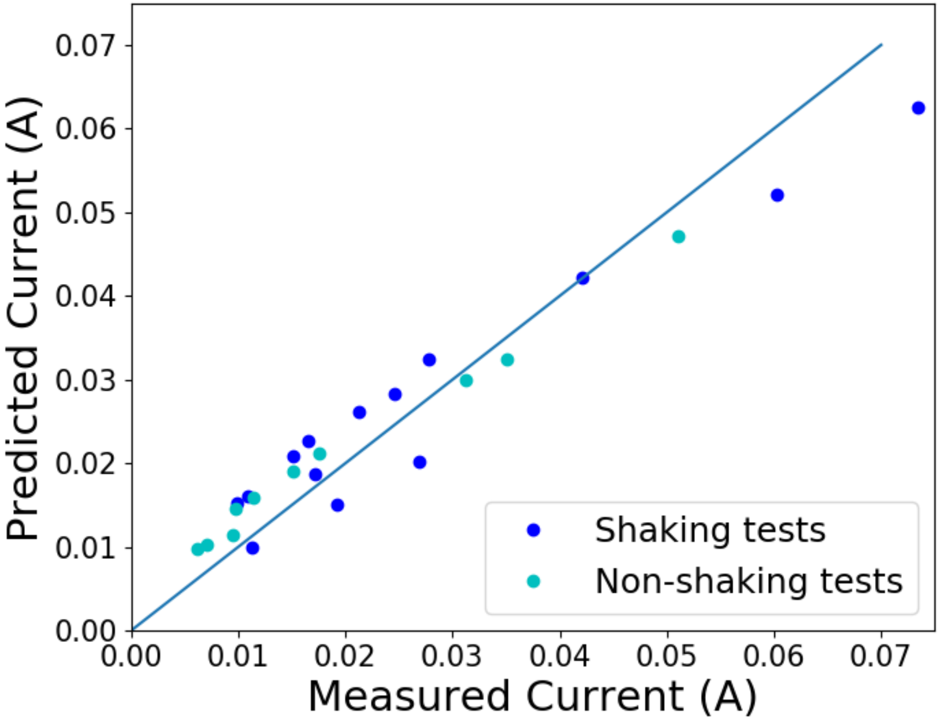
Task 2: Hydrogen production by MECs: Quantifying Limiting Factors

$$V_{Input} = R_{Internal} * I_{Electrical} + V_{Zero-Current}$$

$$R_{Internal} = R_{An} + R_{Cat} + R_{Sol}$$

$$R_{Internal} = \frac{r_{An}}{S_{An}} + \frac{r_{Cat}}{S_{Cat}} + \frac{\alpha_{Sol}}{S_{sol} * C_{Buffer}}$$

Term [units]	Non-Shaking	Shaking
r_{An} [Ω m^2]	0.014	0.010
r_{Cat} [Ω m^2]	0.0052	0.0032
α_{Sol} [Ω m^2 mol/m^3]	0.77 200 mM → 0.0039 Ω m^2 75 mM → 0.010 Ω m^2	0.36 200 mM → 0.0018 Ω m^2 75 mM → 0.0050 Ω m^2



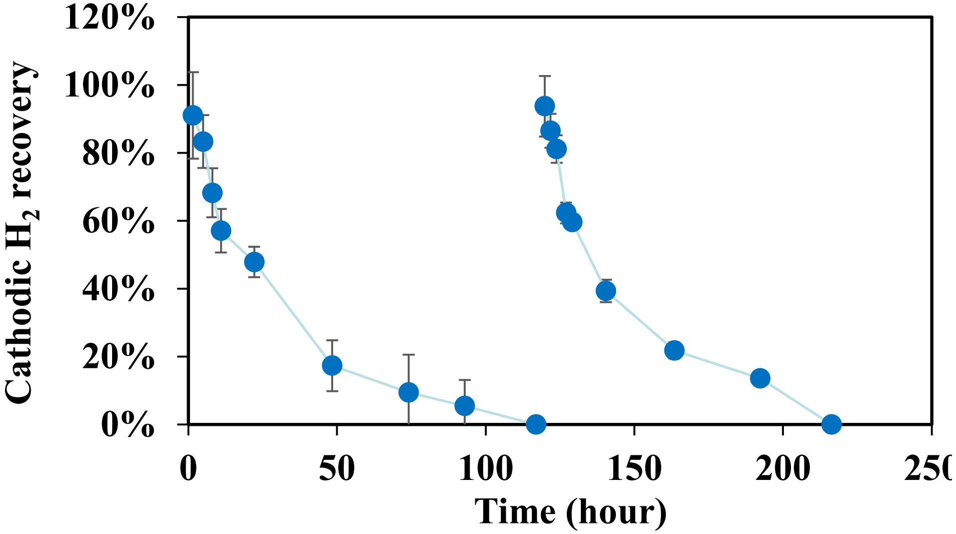
An MEC with an anode: cathode surface area ratio of about 3:1, with shaking, and with a phosphate buffer concentration of about 120 mM would have well-balanced internal resistance.

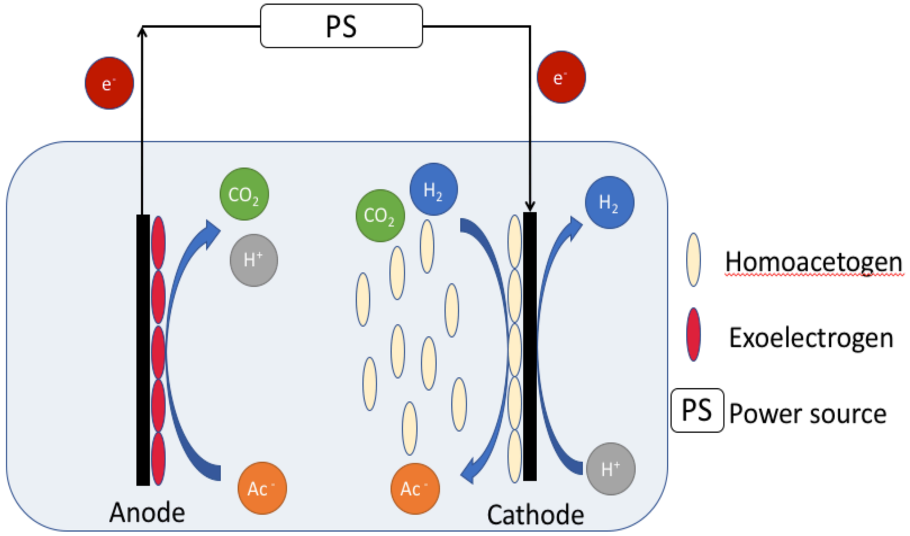
The model developed is reliable to predict the performance of the MECs.

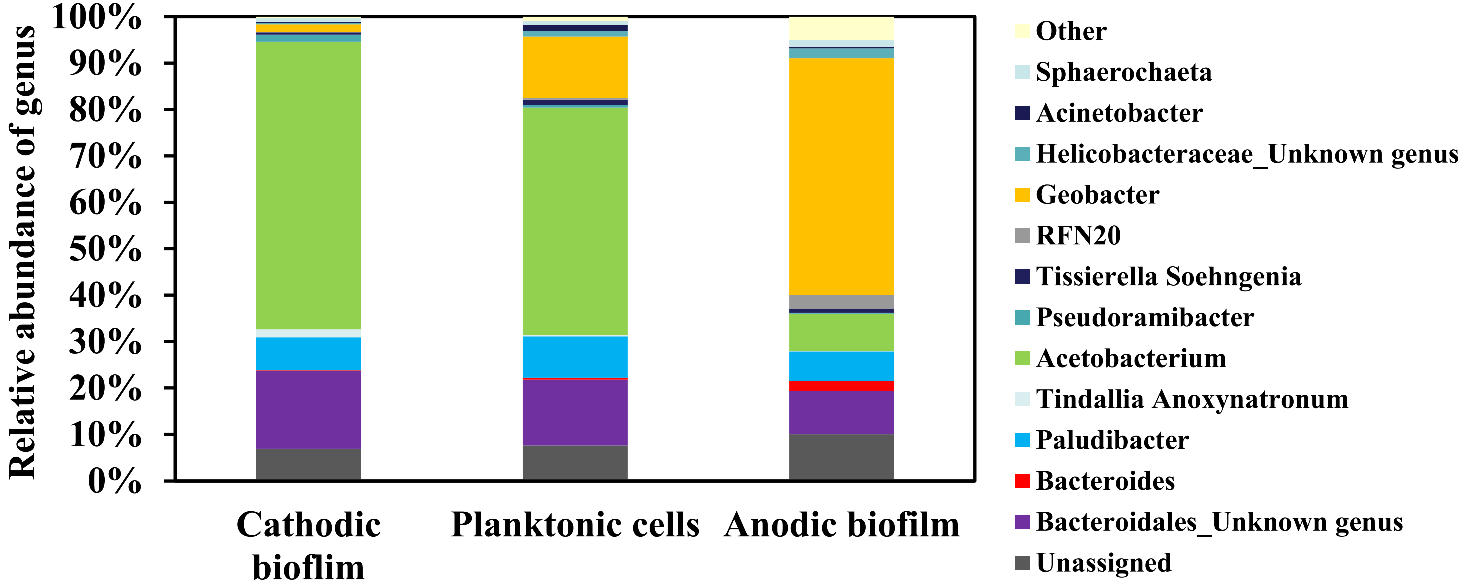
Accomplishments and Progress (con.)

Task 2: Hydrogen production by MECs:

- Hydrogen uptake by homoacetogens in MEC





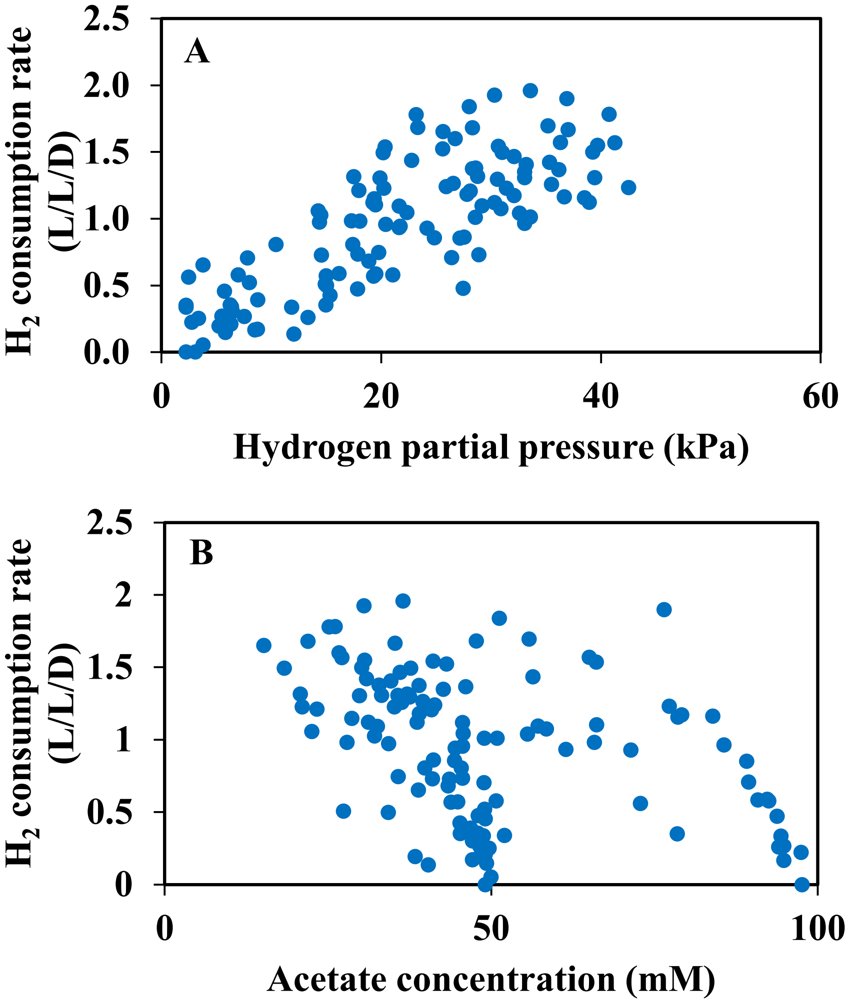


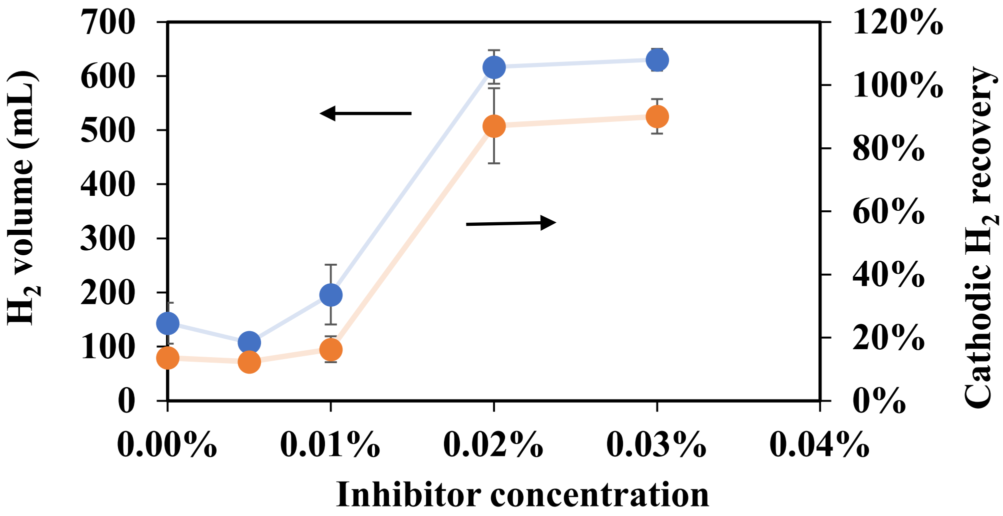
Cathodic H_2 recovery decreased due to the growth of homoacetogens (acetobacterium) on the cathode during long term operation.

Accomplishments and Progress

Task 2: Hydrogen production by MECs:

- Reducing hydrogen uptake by homoacetogens in MECs





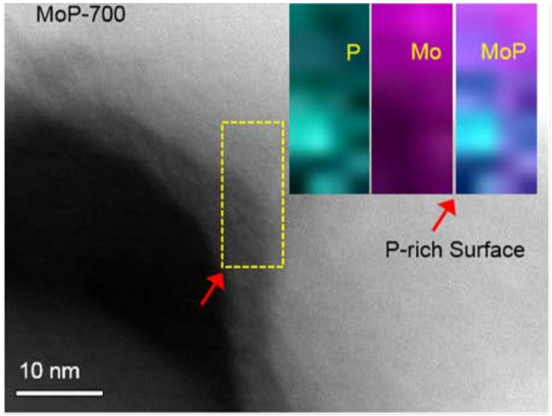
- **Hydrogen consumption rate** is more affected by hydrogen partial pressure than acetate concentration in the presence of homoactogens
- **Addition of a low-cost inhibitor:**
  - effectively inhibits H_2 consumption by homoacetogens and methanogens
- **Cost for the inhibitor < 1 cent per kg H_2**

Accomplishments and Progress (con.)

Task 3: Develop low-cost cathode materials with low overpotential

- **Understanding synthesis-structure-property relationship**

a)



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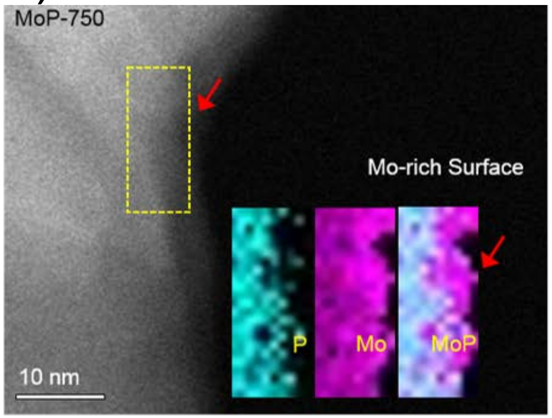

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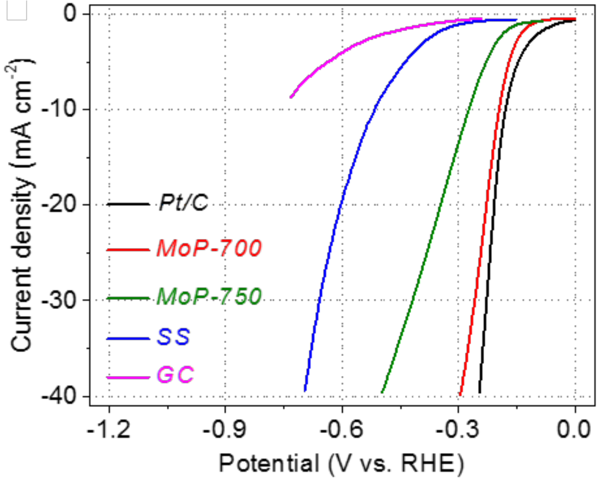

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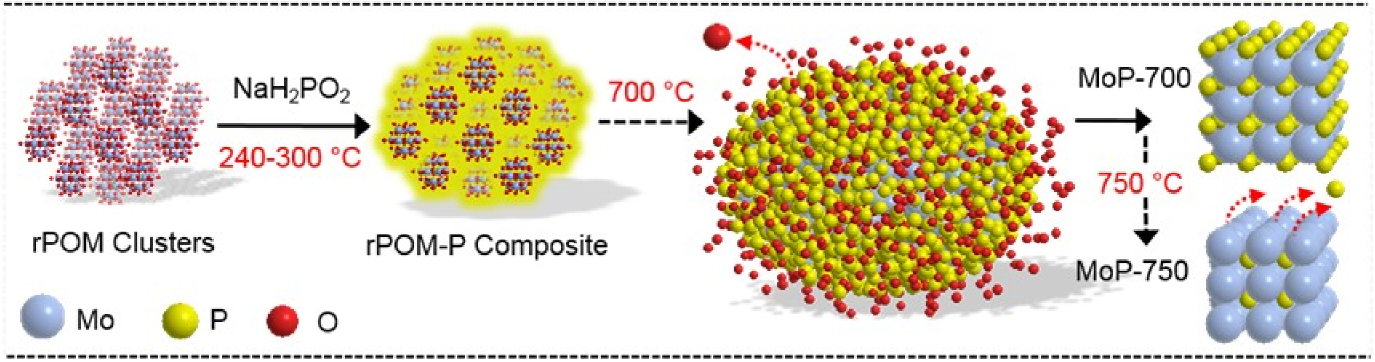
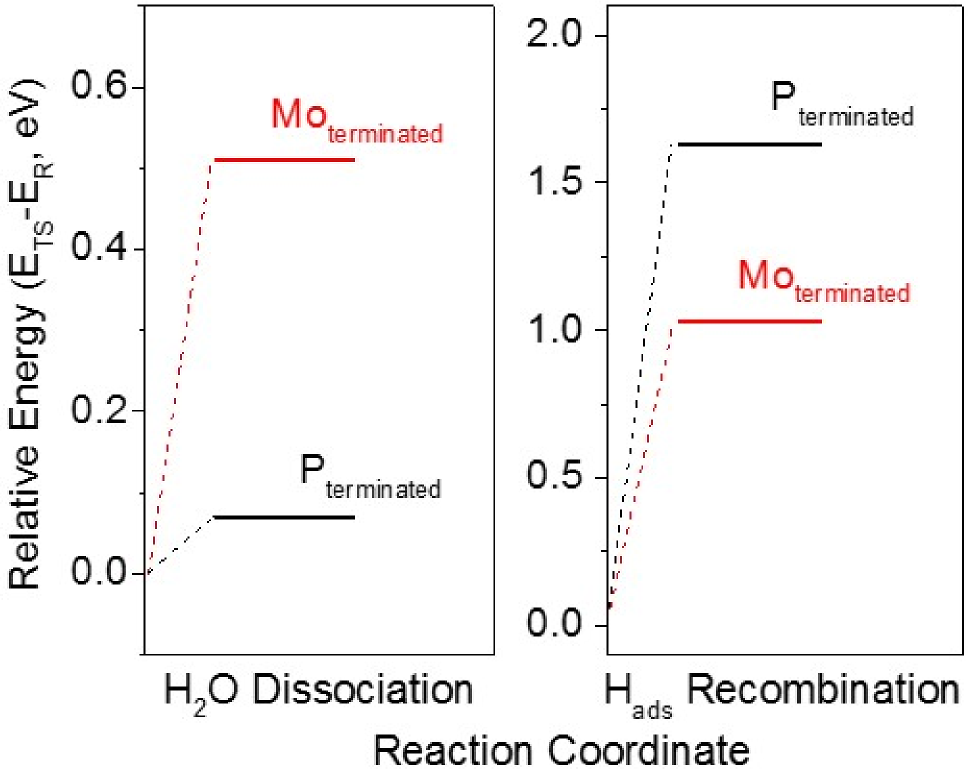


Surface-determined HER activity: P-rich surface → high activity

Accomplishments and Progress (con.)

Task 3: Develop low-cost cathode materials with low overpotential

- **Understanding mechanisms using density functional theory (DFT) calculation**

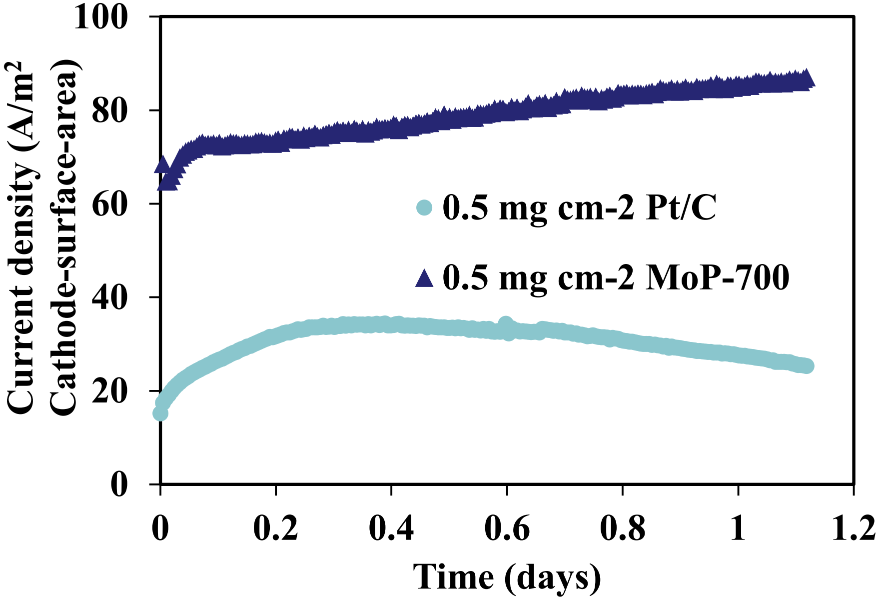


P facilitates H_2O dissociation while Mo promotes H recombination to H_2
→ Surface atom synergy of Mo and P leads to high HER activity.

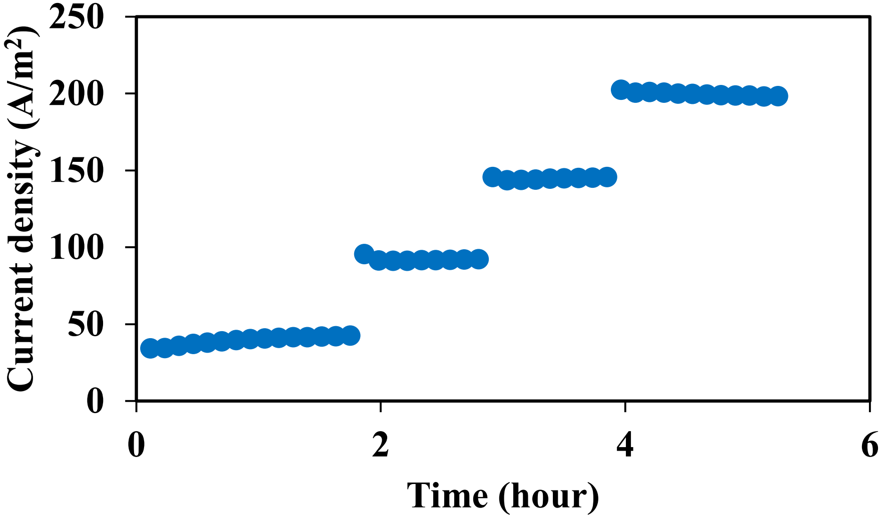
Accomplishments and Progress (con.)

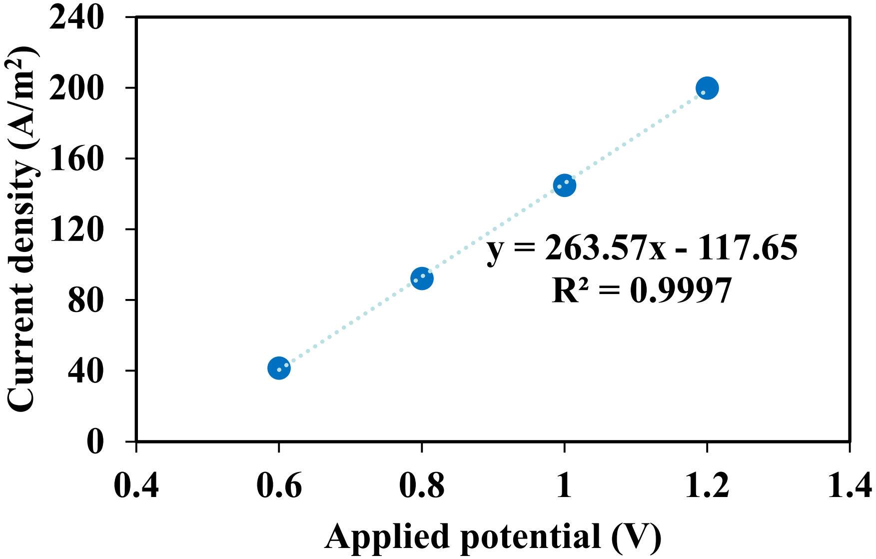
Task 3: Develop low-cost cathode materials with low overpotential

- Performance of the P-rich surface catalyst in MECs



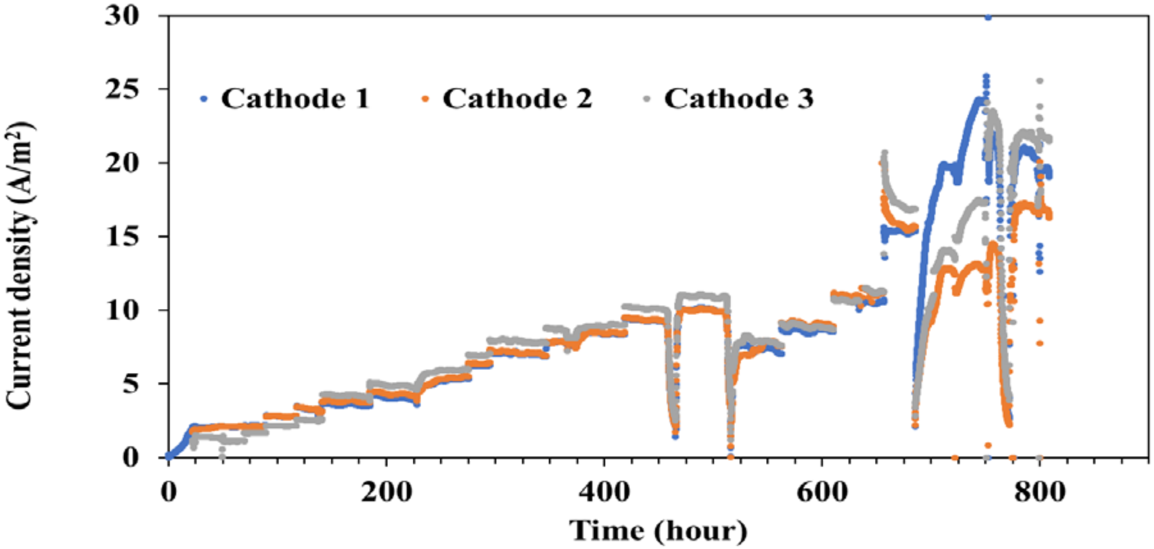
The P-rich surface MoP catalyst can perform much better than the Pt/C catalyst at 0.5 mg/cm^2 loading, reaching a current density over 100 A/m^2 at 0.8 V, higher than any reported current density in MECs.



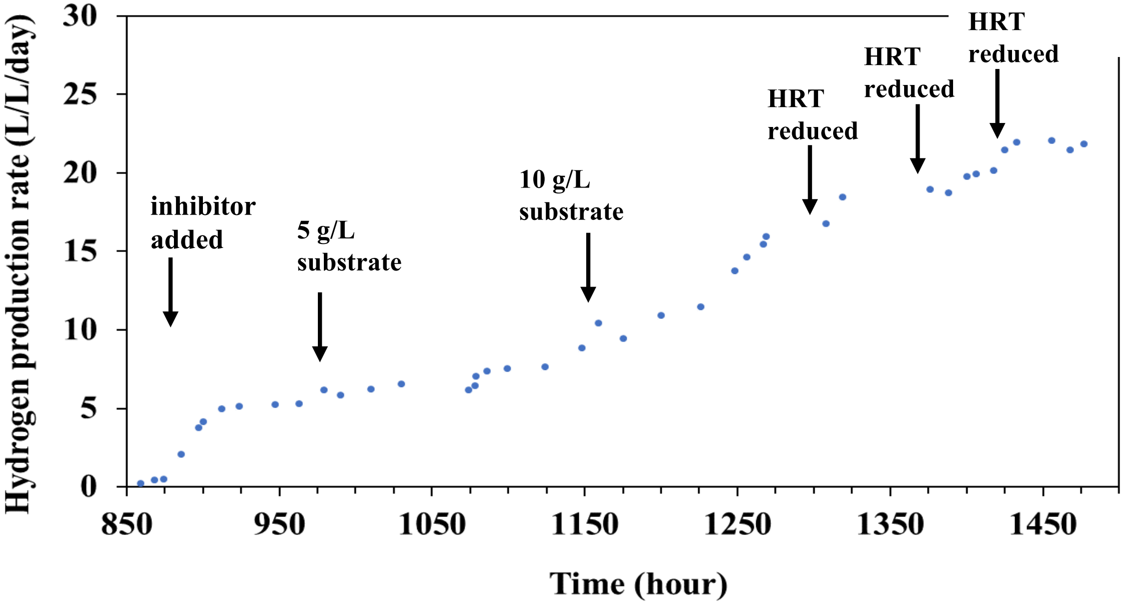


Accomplishments and Progress (con.)

Task 4: 10L reactor design/fabrication and preliminary evaluation

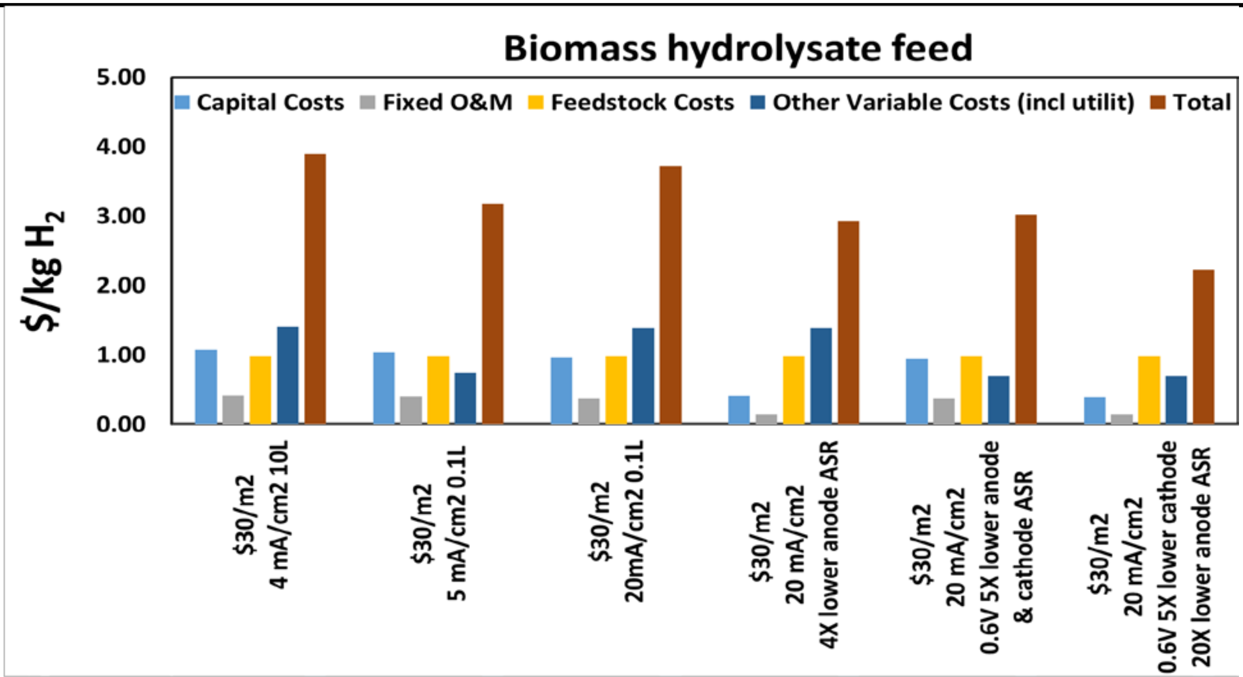


10 L reactor startup took longer than expected possibly due to the large anode surface area and configuration.

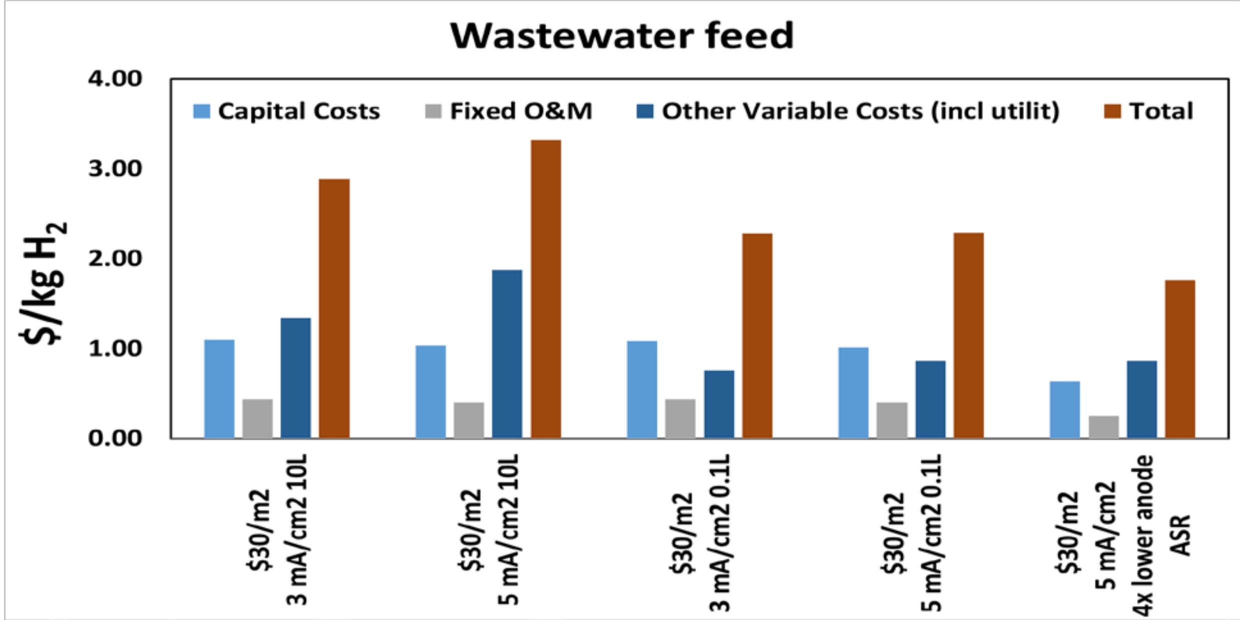


Over 20 L/L/day H_2 production can be achieved in the 10L reactor under continuous flow mode using glucose

Cost Performance Modeling


Biomass hydrolysate feed

Feedstock cost and current density (affecting capital cost) and ASR (affecting utility costs) are the three key parameters affecting the H_2 production cost.


Wastewater feed

Note1: ASR: Area Specific Resistance

Note 2: Wastewater treatment credit (~$10/kg H_2) is not included.

Responses to Previous Year Reviewers' Comments

"The project approach is excellent, despite the fact that it was not clear how the F-MEC system will be designed."

- The F-MEC design details can be found in the reviewer-only slides (Slides 21- 22).

"The MEC culture work was also successful, with hydrogen production from liquid fermentation products. However, it was possible to observe an increase in acetic acid concentration. The strategy to inhibit homoacetogenesis in the system is unclear.

- We have identified a low-cost chemical to effectively inhibit homoacetogensis.

"It would be beneficial at some point to have industry input on the commercial feasibility of the technology."

- We have interviewed several food and beverage industries in the US. Mid-size and small food and beverage plants have the most critical need for a similar technology. A local startup is also interested in our technology.

"There is a strong recommendation: to obtain experimental data of continuous hydrogen production using the actual feedstocks"

- We are in the process of evaluating and optimizing the hydrogen production using two actual feedstocks: 1) Napier grass hydrolysate; and 2) brewery wastewater

Collaborations

Partner	**Project Roles**
Oregon State University	Project lead, management and coordination
Prof. Liu research group	Bioreactor design and operation
Prof. Murthy’s group	Lignocellulosic feedstock selection and treatment
Center for Genome Research and Biocomputing	Microbial community characterization
Pacific Northwest National Laboratory	
Dr. Shao’s group	Cathode catalyst and catalyst layer coating
Dr. Viswanathan group	Cost performance modeling
Oregon Nanoscience and Microtechnologies Institute	Supplemental funding to support a graduate student to work on this project

Remaining Challenges and Barriers

- **Wastewater**
  - Low conductivity and buffer capacity may affect hydrogen production
  - Composition and concentration change over time may affect the stability
- **Hydrolysate**
  - Sugar concentration higher than 100 g/L might require dilution before feeding to the reactor
  - Low concentration of phenolic compounds may affect hydrogen production

Proposed Future Work

- **Remainder of the year**:
  - Evaluation of the 10 L reactor using actual biomass hydrolysate and wastewater
  - Evaluation of the stability of the cathode catalyst over long term
  - Cost performance modeling

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

Technology Transfer Activities

- **Technology-to-market or technology transfer plans or strategies**
  - IP related to reactor design and operation
    - In the process of filing patents related to
      - 1) hybrid reactor design
      - 2) method for inhibiting homoacetogens in MECs
  - IP related to cathode catalyst/material
    - Filed a U.S. Provisional Patent Application related to cathode catalyst.
  - Scale up the system
  - Identify industry partners for commercialization

- **Plans for future funding**
  - Seeking support from industry partners or SBIR grants

Summary - progress and accomplishment

- Immobilized fermentative culture is capable of generating hydrogen at high production rates (20 $L/L_{reactor}$/day);
- Cathodic H_2 recovery may decrease under long term operation due to the growth of homoacetogens on cathode;
- Discovered low-cost chemicals that can effectively inhibit methanogens and homoacetogens and reduce the H_2 uptake in MECs;
- Synthesized an MoP metal catalyst with P-rich surface that can perform better than the Pt/C catalyst in MEC;
- Quantified resistance distribution provided guidance for the design and operation of the larger reactor;
- Designed, fabricated, and preliminarily evaluated a 10 L F-MEC reactor;
- Feedstock cost, current density, area specific resistance are the key parameters affecting the hydrogen production cost.