Novel Hybrid Microbial Electrochemical System for Efficient Hydrogen Generation from Biomass

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Project ID PD129

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Overview

Timeline

- Project Start Date: 02/01/16
- Project End Date: 01/31/19*

* Project continuation and direction determined annually by DOE

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*: $583K

* As of 3/31/17

Partners

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

Relevance

Project Objective:

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	1.29/0	0.98/0	0.98/0
Capital cost contribution	\$/kg H_2	0.82/2.77	0.80/1.51	0.44/0.78
Electricity cost + other operational cost	\$/kg H_2	1.19/2.00	0.75/1.05	0.60/0.75
Total cost	**\$/kg H_2**	**3.31/4.80**	**2.55/2.58**	**2.03/1.54**
Credits	\$/kg H_2	0/-10	0/-10	0/-10
Final cost	**\$/kg H_2**	**3.26/-7.04**	**2.55/-7.42**	**2.03/-8.46**

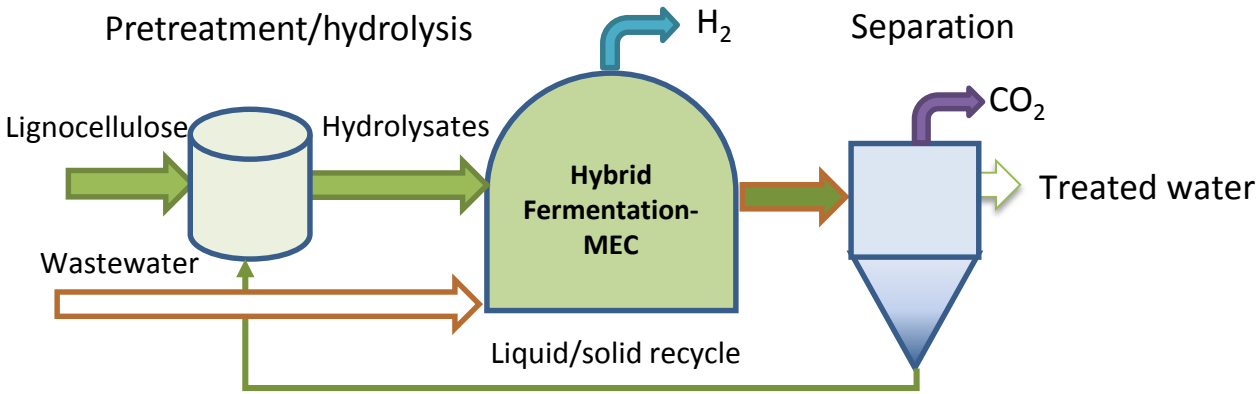
Using wastewater as feedstock can generate a credit as much as -\$10/kg H_2 assuming:

- 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

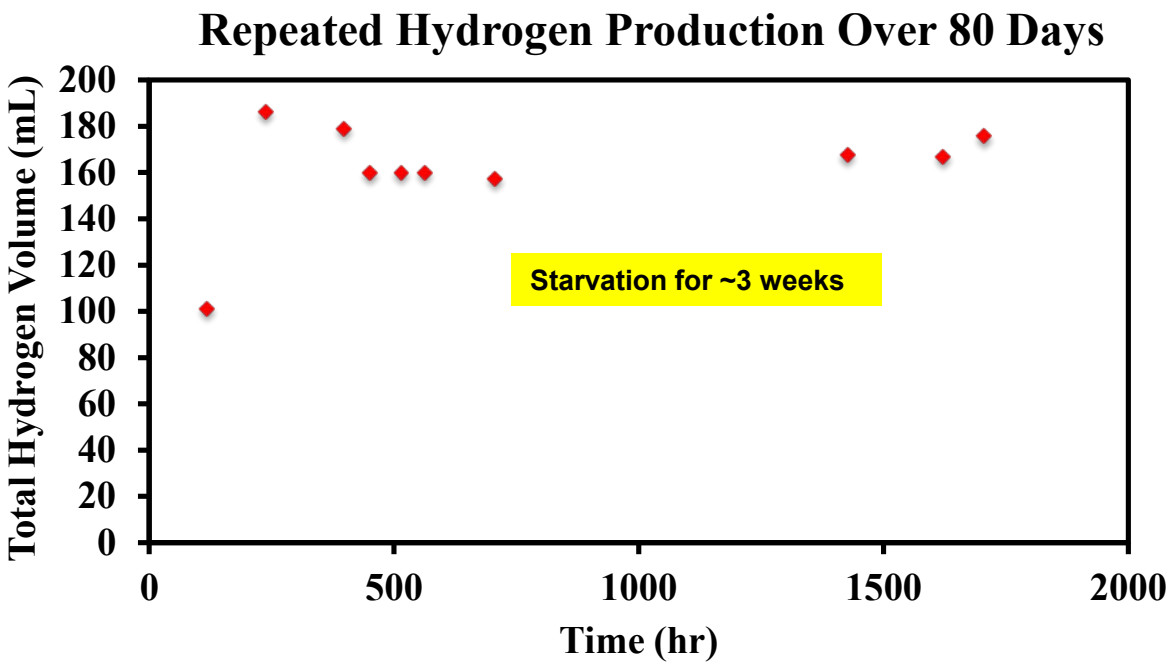
Approach/Milestone

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 (Jan. 31 2017)**
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	90%
Milestone 2: The stability of hybrid nonprecious metal electrocatalyst higher than or equal to Pt	60%
Milestone 3: Finish the design of the hybrid reactor	30%
Go/NoGo: Reaching hydrogen production rate of 24 L $H_2/L_{reactor}$/day using the hybrid reactor	20%

Accomplishments and Progress

Task 1: Fermentative hydrogen production

- Immobilization of bacterial culture
- Stability of the immobilized culture
  - Increase cell density in continuous-flow reactors
  - Increase H_2 production rate

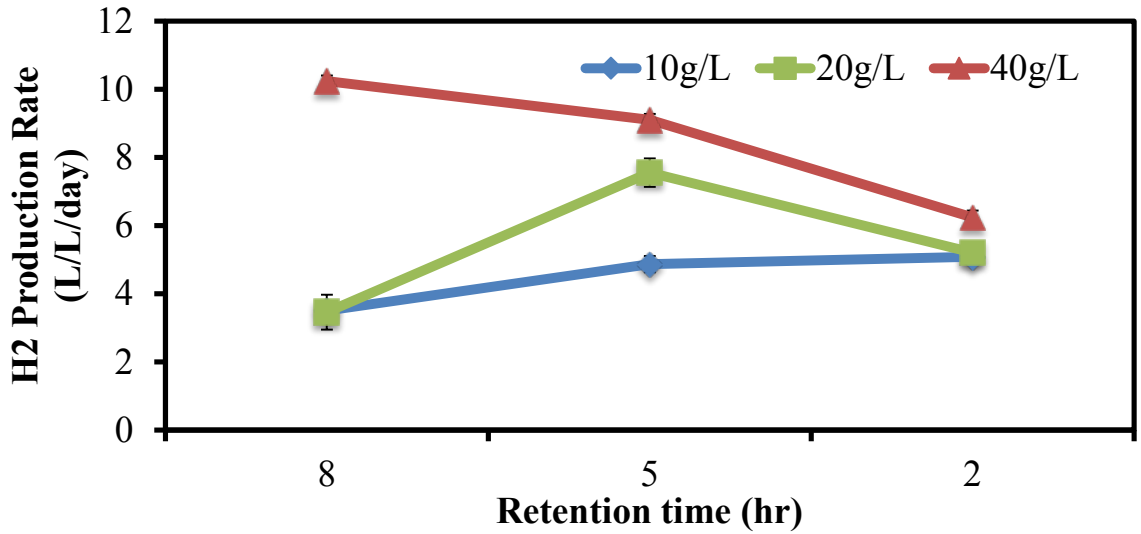


Summary: The beads containing the immobilized cells can maintain their original shapes with reliable H_2 production over 80 days of batch operation.

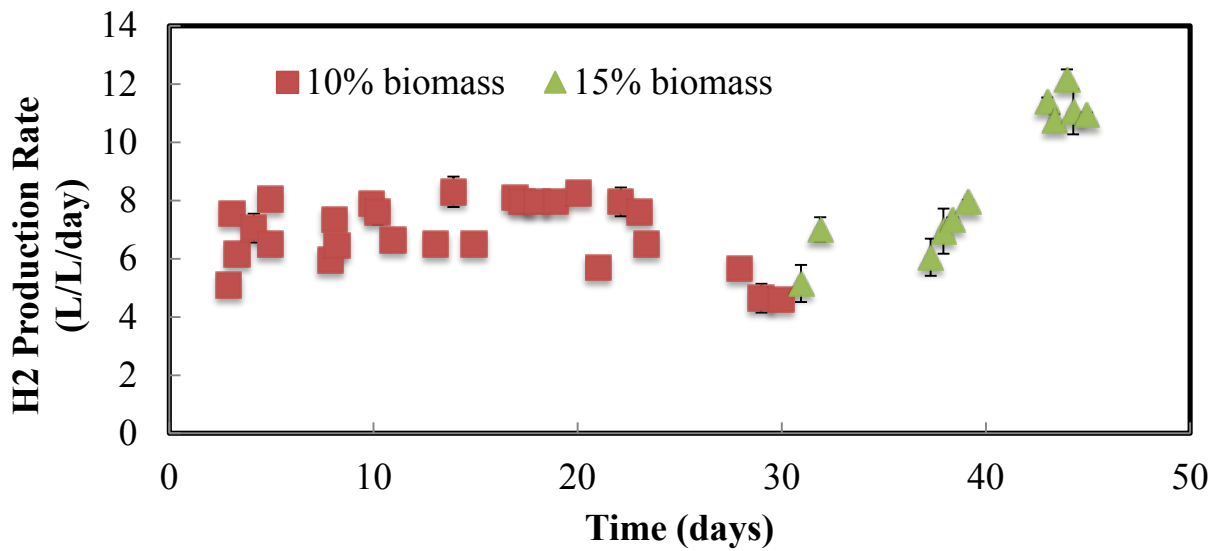
Accomplishments and Progress (cont.)

Task 1: Fermentative hydrogen production

– Continuous H_2 production using the immobilized culture



Fermentative hydrogen production rate is affected by mixed sugar concentrations and HRTs (upper figure) and the immobilized biomass concentration (bottom figure)

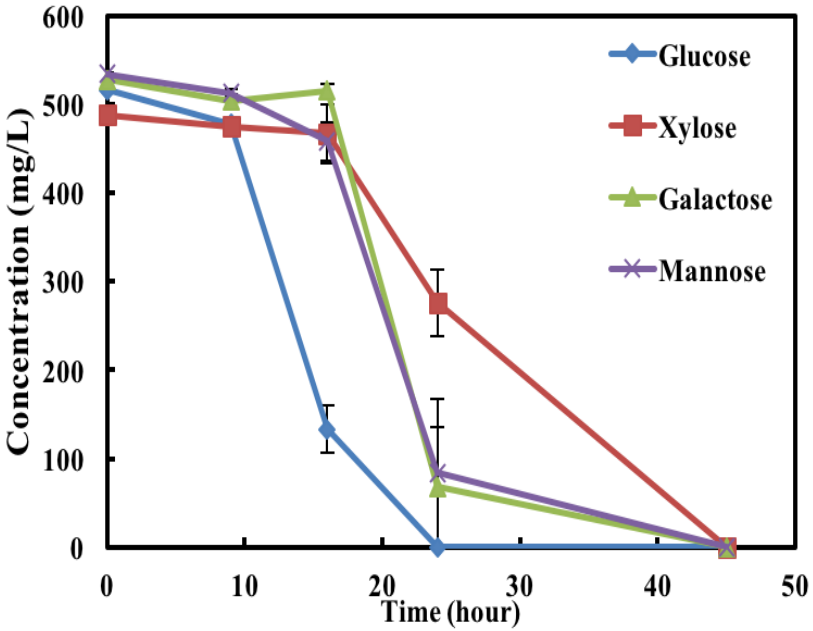


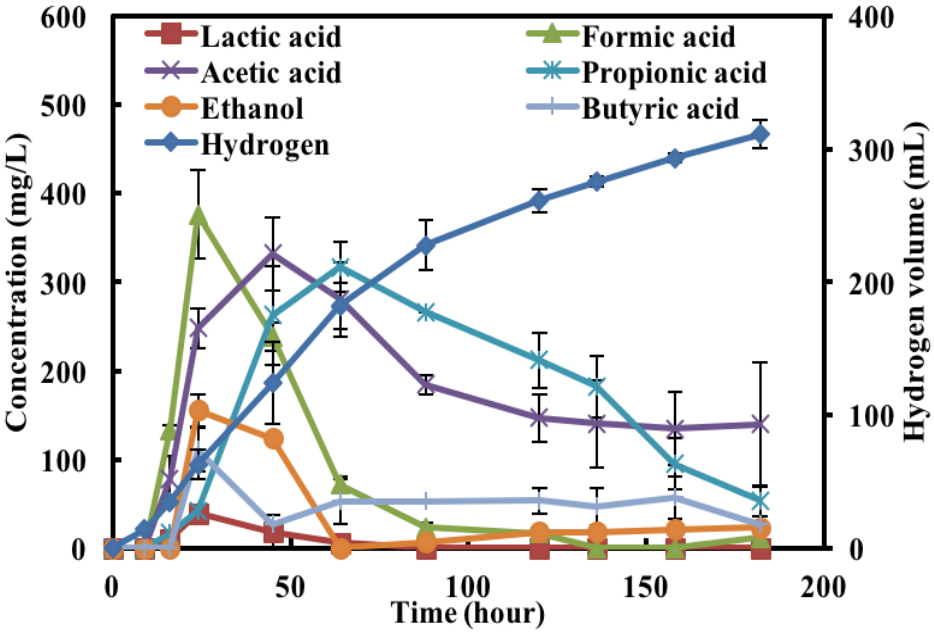
Summary: Hydrogen production can reach over 10 L/L/day in a continuous flow reactor with immobilized fermentative bacteria using mixed sugars as feedstock.

Accomplishments and Progress (cont.)

Task 2: Hydrogen production in MECs

- **Identification of a microbial electrochemical culture capable of producing H_2 from liquid fermentation products**



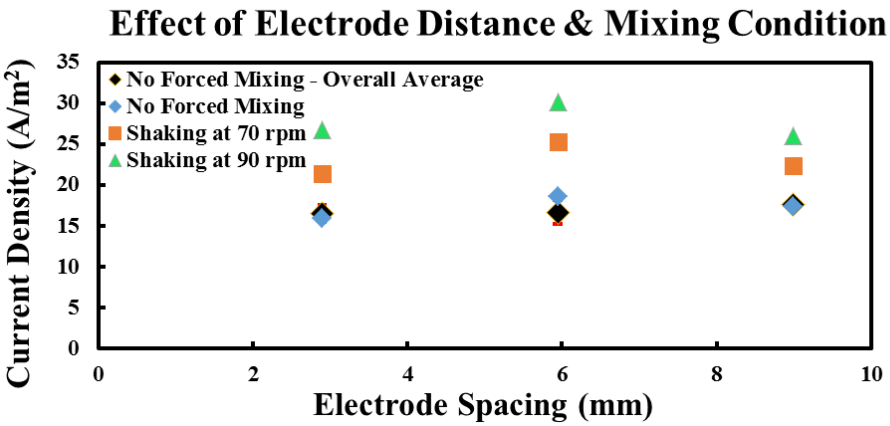


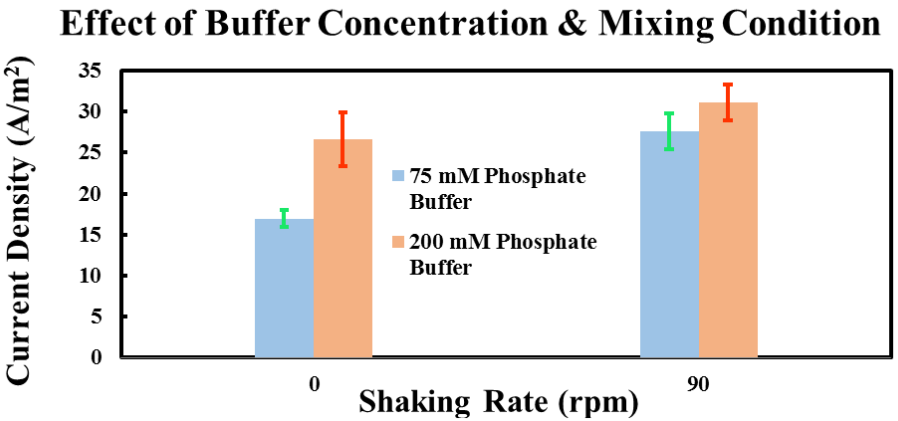
Summary: Our lab exoelectrogenic culture enriched with acetate is capable of utilizing all fermentative products for hydrogen production.

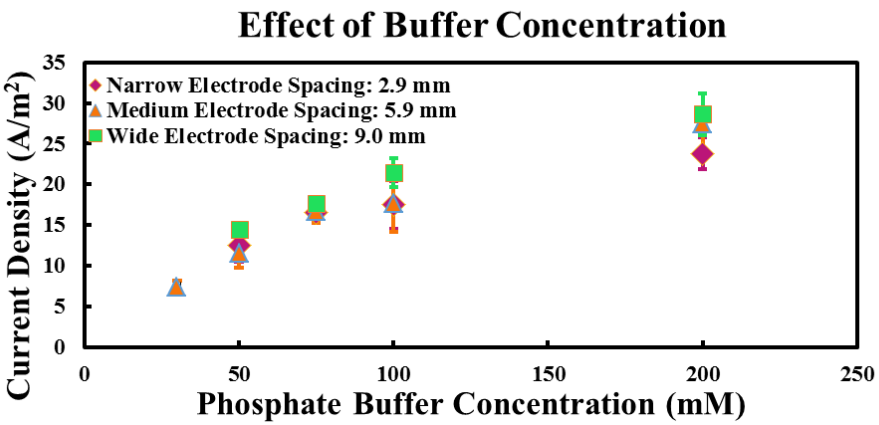
Accomplishments and Progress (cont.)

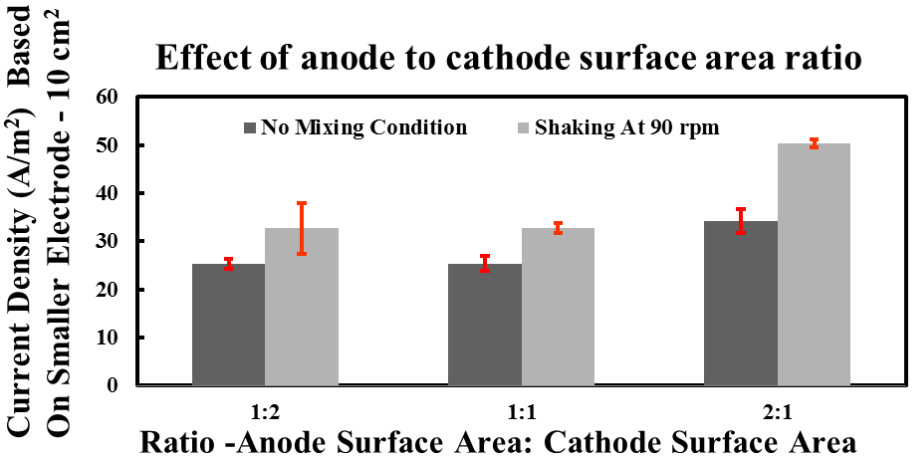
Task 2: Hydrogen production by MECs:

- **Optimization of MECs: provide design and operational parameters for the continuous flow reactor**









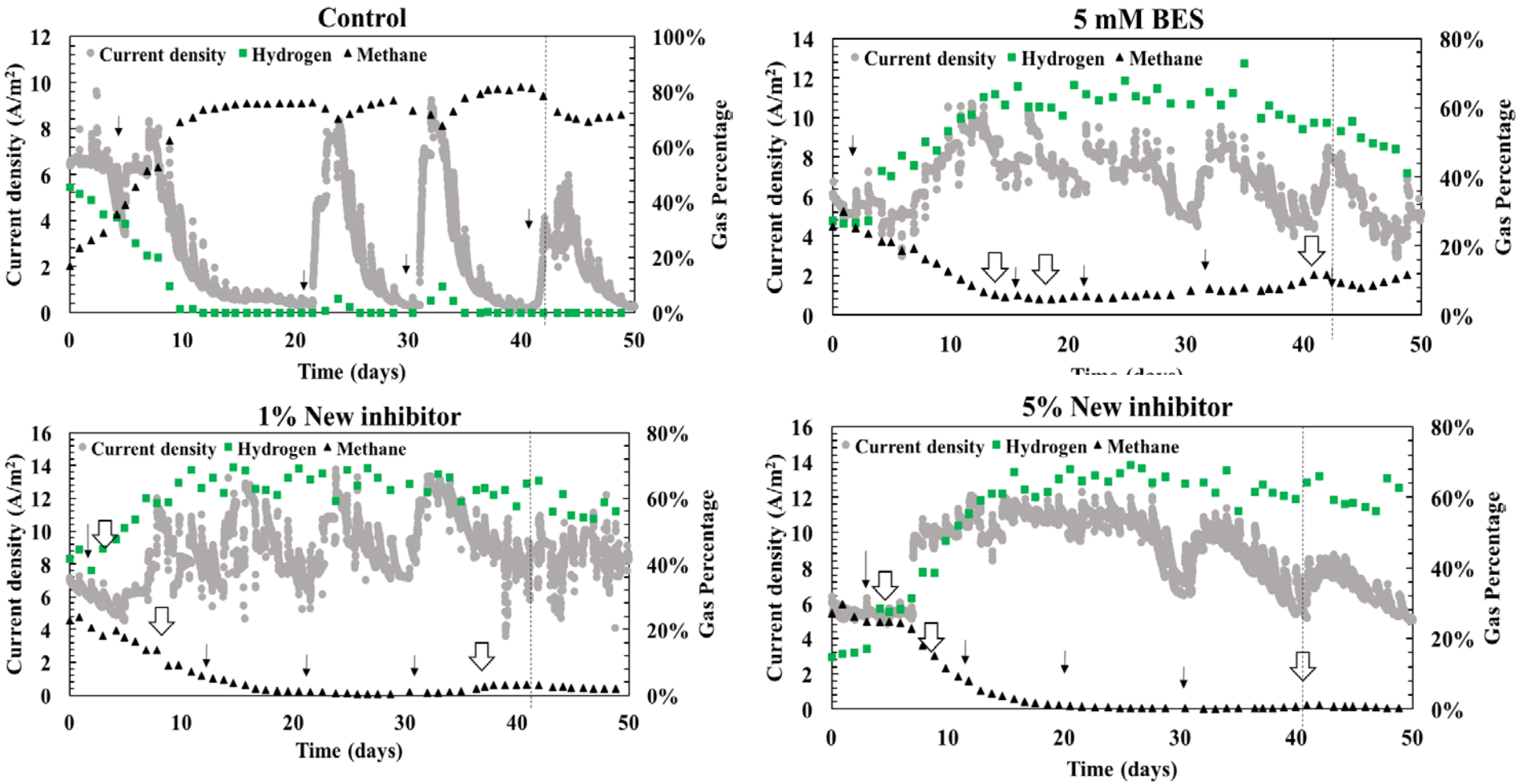
Summary: Mixing condition outweighs electrode spacing and buffer concentration, suggesting that the continuous reactor should be designed to facilitate mixing.

Accomplishments and Progress (cont.)

Task 2: Evaluate hydrogen production by MEC

- **Inhibition of methanogens**

H_2 loss due to methanogens: $H_2 + CO_2 \rightarrow CH_4 + H_2O$

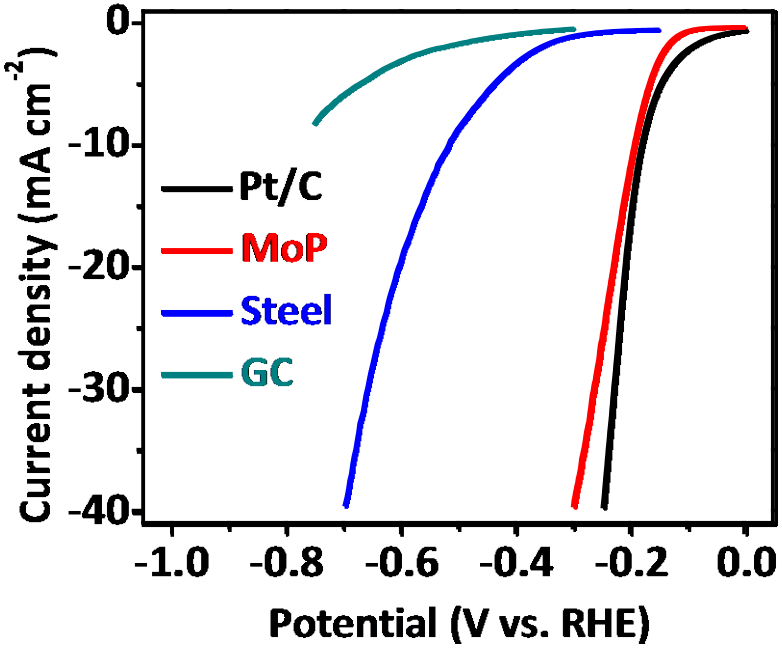


Summary: Periodically injecting low cost chemical inhibitor (<1 cent/kg H_2) to the headspace of the reactor can effectively inhibit methane production without affecting exoelectrogens.

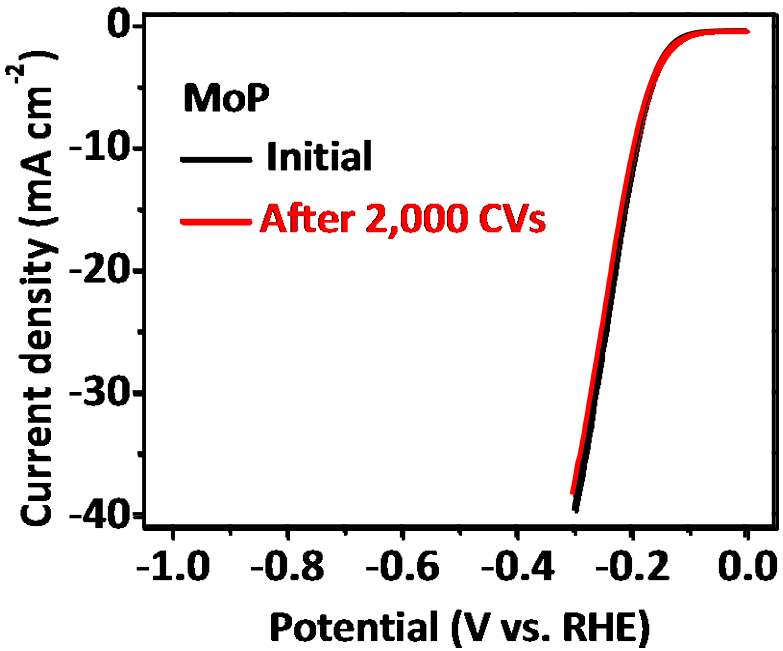
Accomplishments and Progress (cont.)

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

- Catalyst synthesis and test



HER on MoP catalyst in comparison with other catalysts/electrode materials. MoP shows comparable activity to Pt.



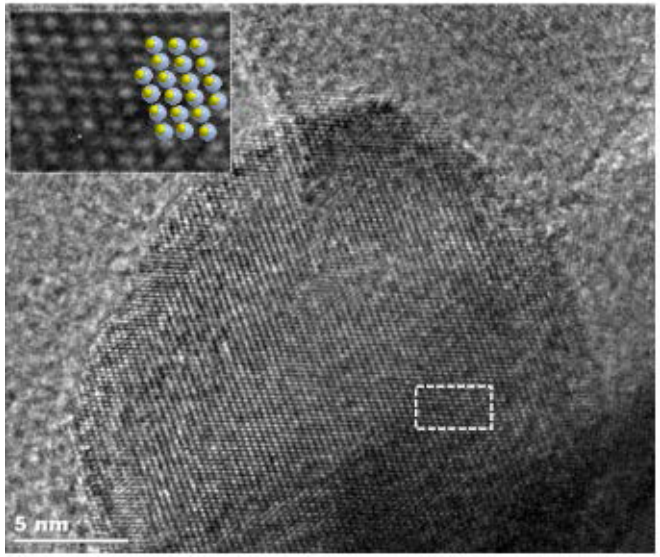
MoP catalyst durability test. MoP shows stable polarization curve after 2000 potential cycles (-0.3~0.3V RHE, 50 mV/s).

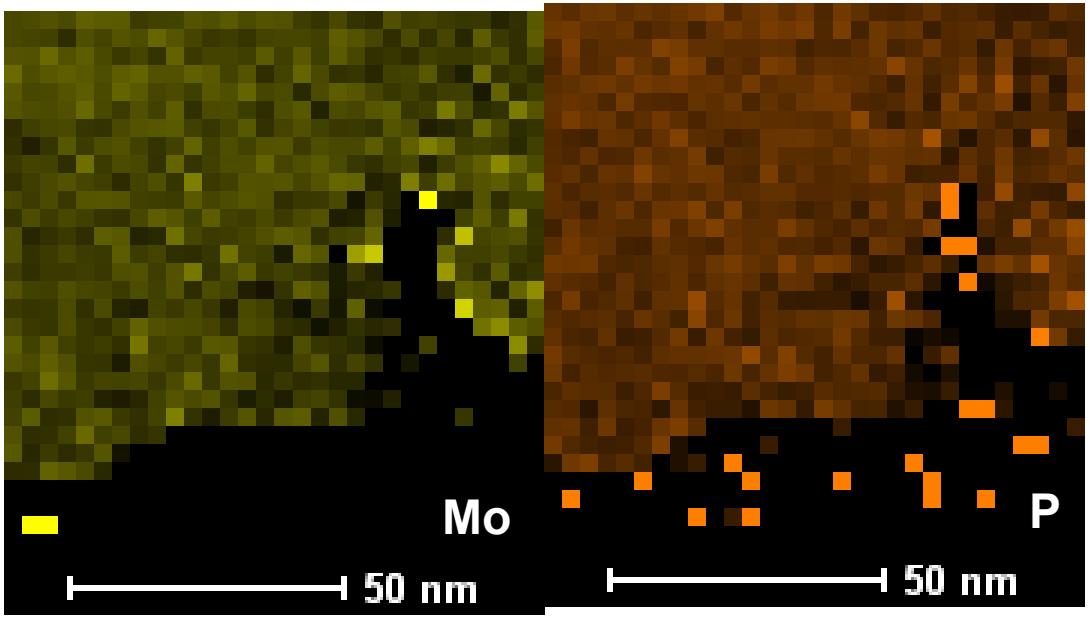
Summary: Synthesized MoP HER catalysts with high activity (comparable to Pt) and high durability under ex-situ test.

Accomplishments and Progress (cont.)

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

- **Understanding structure-property relationship**





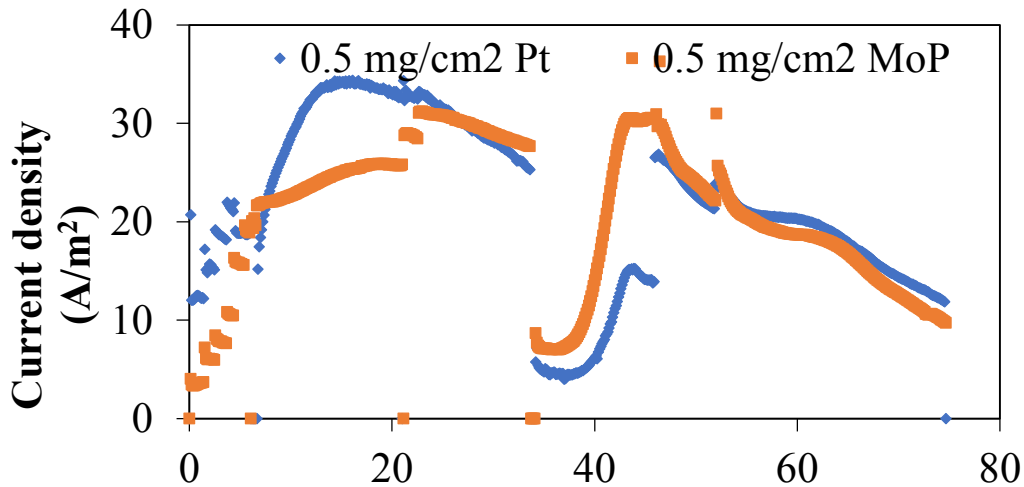
P-terminated surface

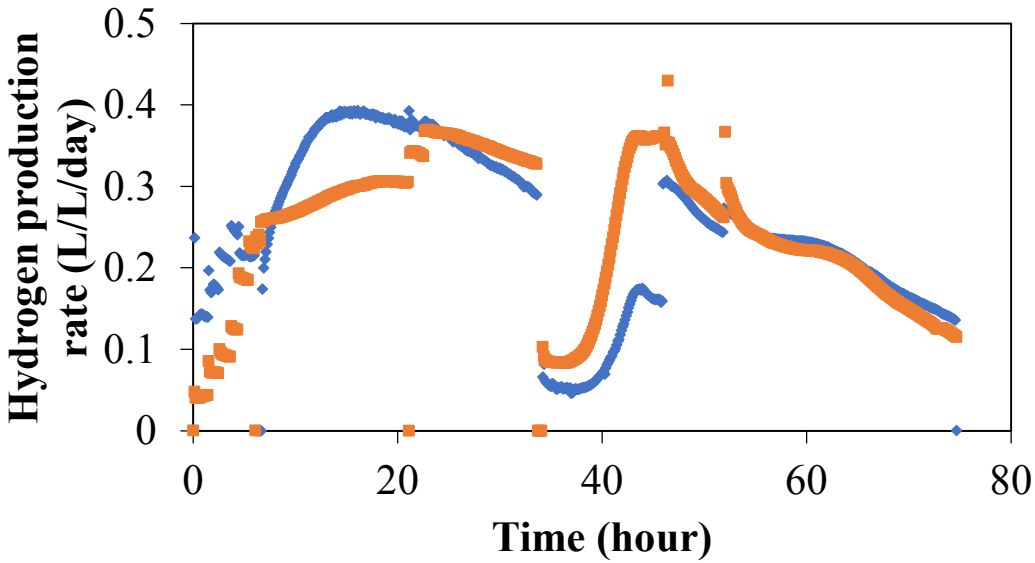
Summary: Atomic structure characterization and surface chemistry analysis points to a P-terminated surface of MoP catalysts that facilitates HER.

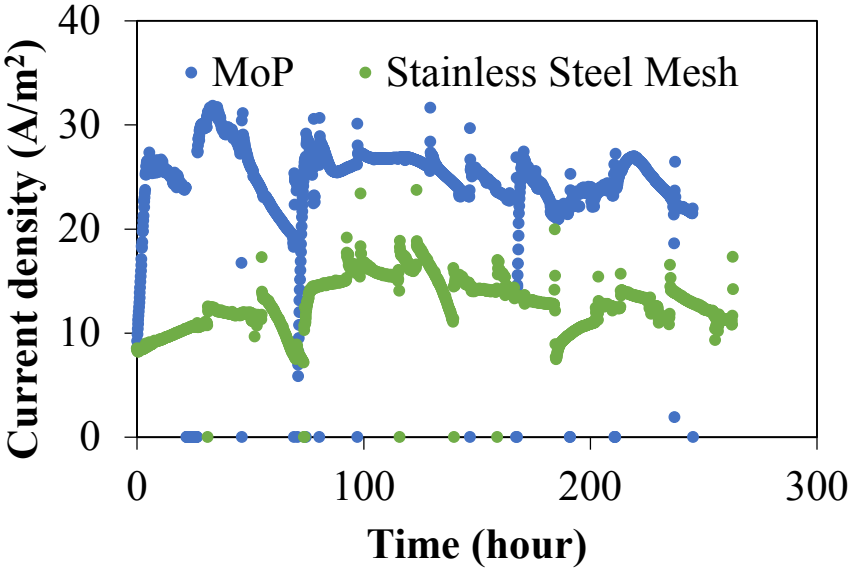
Accomplishments and Progress (cont.)

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

- **Performance of the catalyst in MECs**



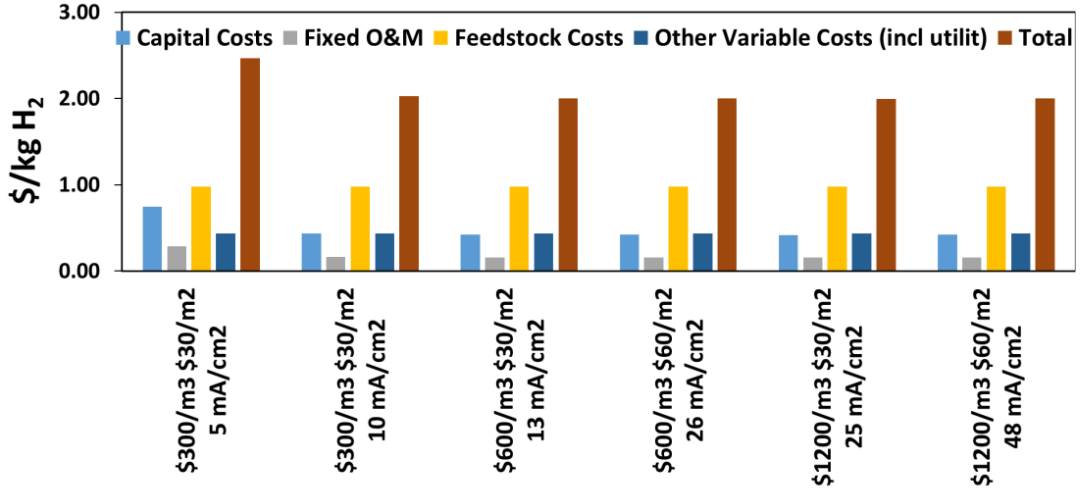




Summary: The newly developed MoP catalyst can perform similarly to Pt catalyst (at the same loading) and much better than stainless steel mesh in MECs and stable over 10 batches of operation.

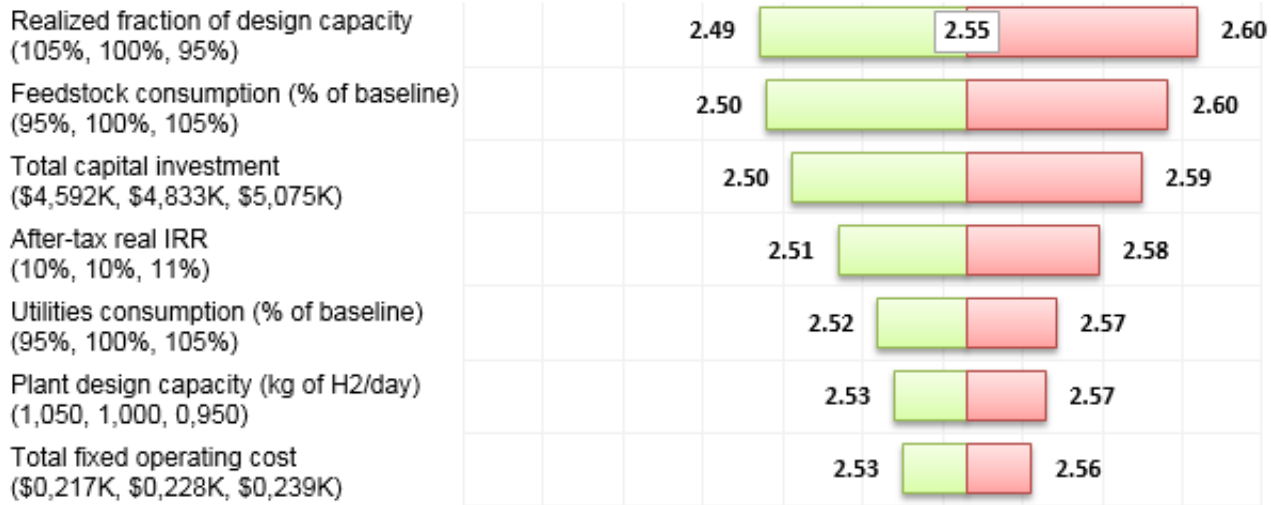
Accomplishments and Progress (cont.)

Task 6: Cost performance modeling – biomass hydrolysate



Tornado chart assumptions :

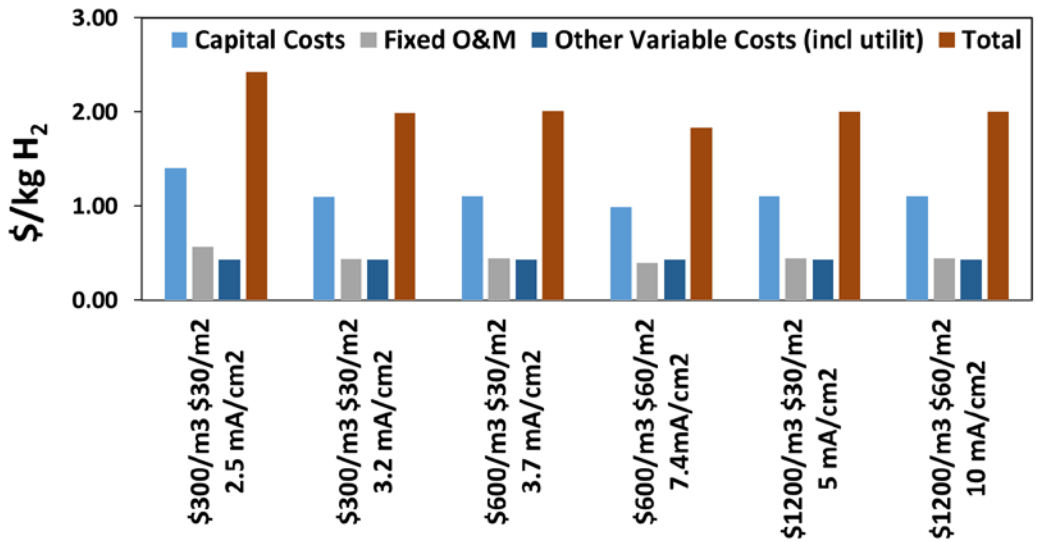
- **$600/m³**
- **$60/m²**
- **10 mA/cm²**



Summary: Project costs based on measured I_d (5 mA/cm²)/low capital cost (bar chart $2.47/kg H2) and 2X measured I_d/quoted capital costs (tornado) are higher than the target. Multiple pathways to meet the target are identified.

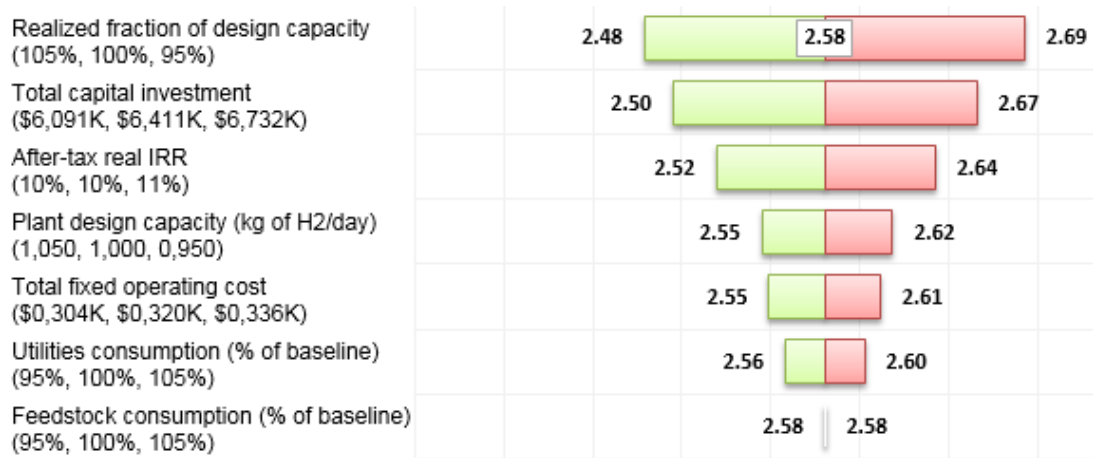
Accomplishments and Progress (cont.)

Task 6: Cost performance modeling - wastewater



Tornado chart assumptions:

- **$600/m³**
- **$60/m²**
- **5 mA/cm²**



Summary: Project costs based on measured I_d/low capital cost (bar chart $2.42/kg H2) and 2X measured I_d/quoted capital costs (tornado $2.58/kg H2) are higher than the target. Multiple pathways to meet the target are identified.

Responses to Previous Year Reviewers' Comments

- This project was not reviewed last year.

Collaborations

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

Remaining Challenges and Barriers

- **Hydrogen uptake by other bacteria in the mixed culture**
  - Have identified a few low-cost chemicals and operational conditions to inhibit the hydrogen uptake
- **Wastewater quality variation**
  - Add a buffer tank
- **Cathode**
  - Catalyst scale up and robust catalyst coating

Proposed Future Work

- **Remainder of the year**:
  - Stability test of the cathode catalyst
  - Determine the design and operational parameters of the hybrid reactor
  - Hybrid reactor design and fabrication
  - Cost performance modeling

- **FY 2018-2019:**
  - Lab and on-site evaluation of the hybrid reactor
  - Cost performance modeling

Technology Transfer Activities

- **Technology-to-market or technology transfer plans or strategies**
  - IP related to reactor design and operation
    - Communicated with OSU technology transfer office on the method for methane inhibition in MECs
  - IP related to cathode catalyst/material
    - Filed an IDR related to cathode catalyst.
  - Scale up the system
  - Identify industry partners for commercialization

- **Plans for future funding**
  - Seeking support from industry partners

Summary

Objective: Demonstrate a novel microbial system for efficient H_2 production from low-cost biomass.

Relevance: Provide a green and renewable approach for H_2 production at a cost less than $2/kg.

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.

Accomplishments:

- Identified microbial communities that are capable of utilizing all major components in lignocellulosic biomass hydrolysates and food/beverage wastewater and their fermentative products for H_2 production;
- Developed an immobilization method that can increase the fermentative bacteria density in reactors with stable H_2 production;
- Discovered a low-cost chemical that can effectively inhibit methanogens and reduce the H_2 uptake in MECs;
- Synthesized MoP HER catalysts with high activity (comparable to Pt) and high durability.