
Novel Hybrid Microbial Electrochemical System for Efficient Hydrogen Generation from Biomass

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Project End Date: April 30, 2020

Overall Objectives

- Design and fabricate a low-cost, robust, and highly efficient fermentation and microbial electrochemical system.
- Determine the techno-economic feasibility of the system using biomass hydrolysates and wastewater.

Fiscal Year (FY) 2018 Objectives

- Continue the investigation on hydrogen production through the fermentation and microbial electrolysis cell (F-MEC) process.
- Design and fabricate a 10-liter F-MEC reactor.
- Evaluate the F-MEC reactor.
- Develop cost performance model.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan¹:

(AX) Hydrogen Molar Yield

(AAA) Electrode Cost

(AAB) Solution Density (Production Rate).

Technical Targets

Progress has been made in achieving the DOE targets listed in the Multi-Year Research, Development, and Demonstration Plan. Table 1 lists DOE's technical targets and where our research and development efforts stand to date.

The overall goal of this project is to develop and scale-up our novel hybrid F-MEC system that can be integrated with well-developed lignocellulose pretreatment/hydrolysis or wastewater treatment processes for efficient hydrogen production at a cost less than \$2/kg H₂.

FY 2018 Accomplishments

- Optimized fermentative hydrogen production conditions using immobilized fermentative bacteria. The hydrogen production rate reached over 20 L/L-reactor/day by fermentation alone.
- Identified the key reason causing the decrease of hydrogen production efficiency in microbial electrolysis cells (MECs) during long-term operation.
- Developed a method to effectively inhibit homoacetogenesis in MECs.
- Revealed the synthesis-structure-property relationship of molybdenum phosphide (MoP) hydrogen evolution reaction (HER) catalysts with high activity (comparable to platinum).
- Designed and fabricated a 10-liter F-MEC reactor.
- Evaluated the F-MEC with glucose. More than 20 L/L-reactor/day hydrogen production was achieved in the 10-L reactor operated under continuous-flow mode.

¹ <https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

Table 1. Progress Toward Meeting Technical Targets for Dark Fermentative Hydrogen Production and MECs

Characteristic	Units	DOE 2015 Targets	DOE 2020 Targets	Project Status
Yield of hydrogen production from glucose by integrated MEC-fermentation	mol H ₂ /mol glucose	6	9	8.5
MEC cost of electrodes	\$/m ²	300	50	90

INTRODUCTION

The global interest in hydrogen production has been stimulated by the promise of the clean operation and high efficiencies of hydrogen fuel cells. Currently, almost all the hydrogen produced is from non-renewable fossil sources. Hydrogen can be produced from renewable biomass by biological dark fermentation. Unfortunately, the hydrogen yields using current fermentation techniques are low. Hydrogen can also be produced by MEC, which can overcome the fermentation barrier and achieve higher hydrogen yield. However, the key challenges for realizing the practical applications of MECs include (1) difficulty in utilizing biomass directly and in utilizing certain biomass components, such as sugars; (2) low hydrogen production rate or high energy input due to inefficient reactor designs, high cathode overpotential, and high solution resistance; and (3) high capital cost due to high electrode and membrane or separator costs. In this project, we will develop a hybrid system that integrates the dark fermentation and MEC processes and overcomes the challenges identified above.

APPROACH

The overall approach of this project is to develop an efficient F-MEC for hydrogen generation from lignocellulosic biomass hydrolysates and sugar-rich wastewater through maximizing the hydrogen production rate and yield of both processes. Because MEC cathode material is a key factor affecting both capital and operational costs of the system, robust and low-cost cathode materials with low overpotentials will also be developed. A cost-performance model will be used to supplement the H2A analysis tool throughout the project to prioritize the critical factors and demonstrate potential to meet DOE cost goals.

We identified suitable bacterial cultures for the hybrid system in FY 2016. In FY 2017, we focused on determining the optimal operational conditions using small lab reactors, developing low-cost and low-overpotential cathode catalyst, and conducting cost and performance analysis. In FY 2018, we have continued the investigation on fermentation and MEC process and designed, fabricated, and evaluated a scaled-up F-MEC reactor.

RESULTS

Continuous Hydrogen Production by Fermentation

We investigated the effect of immobilized bacterial biomass content in reactor on hydrogen production. We found that increasing the biomass content to 20%–40% can result in more than 20 L/L-reactor/day of hydrogen production through fermentation alone using simulated hydrolysate solution, which contained mixed sugars at a ratio of 58.9% glucose, 35.6% xylose, 7.4% mannose, 5.2% galactose, and 2.9% arabinose (Figure 1).

Reducing Hydrogen Uptake by Homoacetogens in MECs

We observed that hydrogen recovery decreased while the coulombic efficiency was over 100% during long-term operation. Our liquid sample analysis and microbial community characterization revealed that the growth of homoacetogens (acetobacterium) caused the low cathodic recovery (Figure 2a). We also found that the hydrogen consumption rate was more affected by hydrogen partial pressure than acetate concentration in the presence of homoacetogens. We further demonstrated that chloroform (0.02%) can be used as an effective homoacetogen inhibitor to reduce hydrogen uptake by homoacetogens (Figure 2b).

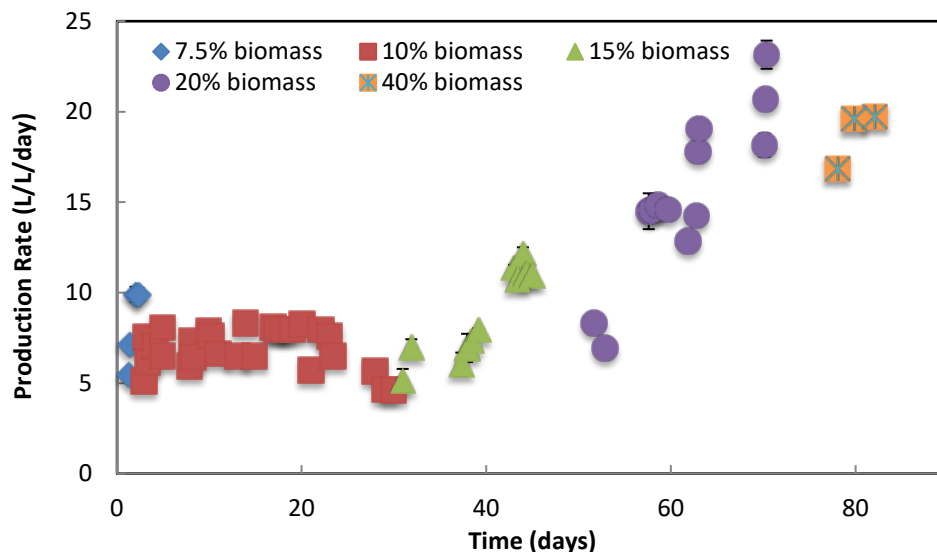


Figure 1. Continuous hydrogen production with immobilized sludge beads at 7.5%–40% (v/v) ratio of beads to media

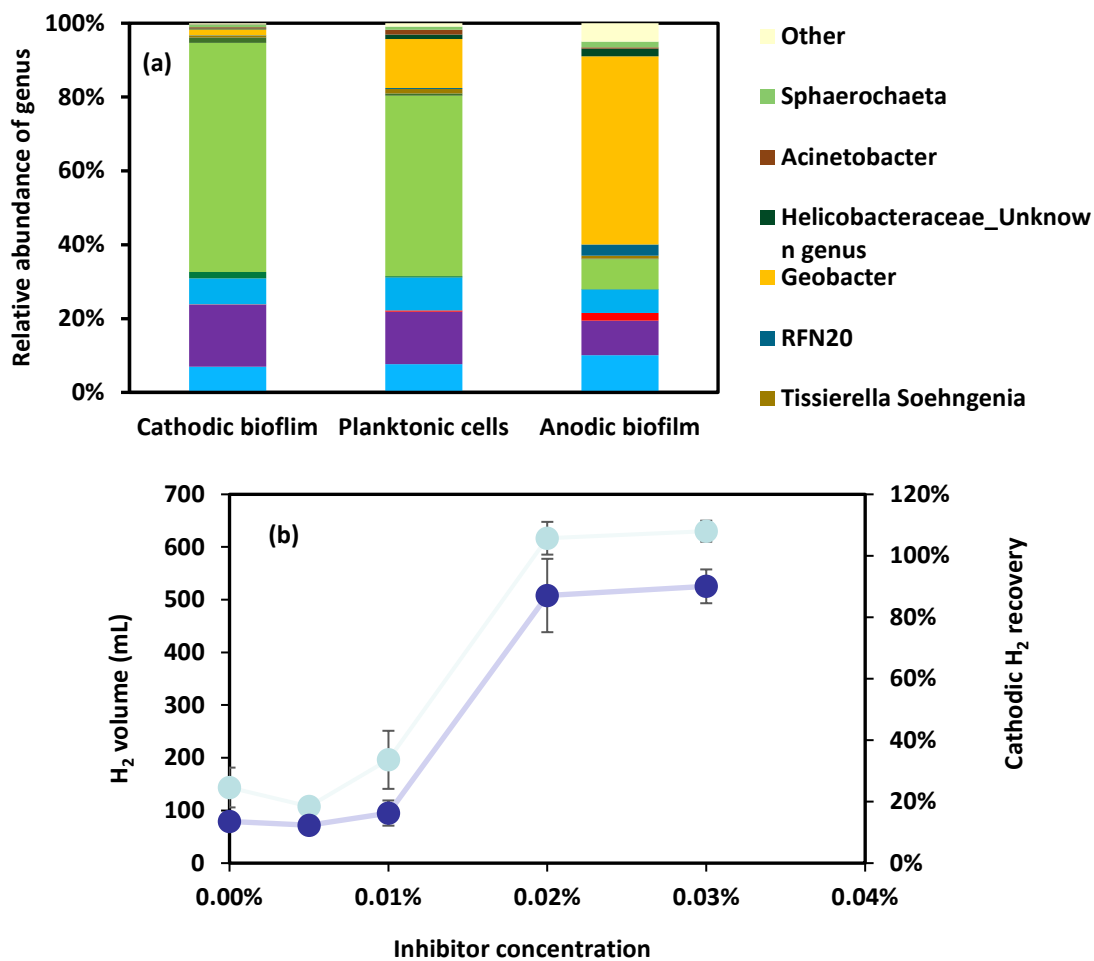


Figure 2. Relative abundance of genus in cathodic, planktonic, and anodic microbial communities. Genus with less than 1% of relative abundance were classified into others (a); and effect of chloroform concentration on hydrogen production (b).

MEC Cathode Development

We investigated the structure-property relationship of MoP electrocatalysts that demonstrate comparable performance to platinum catalyst. The higher catalytic activity for MoP-700 with P-rich surface is possible because the P-terminated surface allows Mo to be exposed, because P atom size is only half that of Mo, and there is synergy between Mo and P, which promotes HER in neutral solution (Figure 3). We also found the reversible transformation of MoP structure (i.e., heat treatment of MoP-700 at 750°C leads to its dephosphorization with the formation of MoP-750, which can be transformed back to MoP-700). This indicates a proper post-treatment of commercial MoP may achieve the desired surface structure that enables high performance—a more scalable, cost-effective method for production of this material.

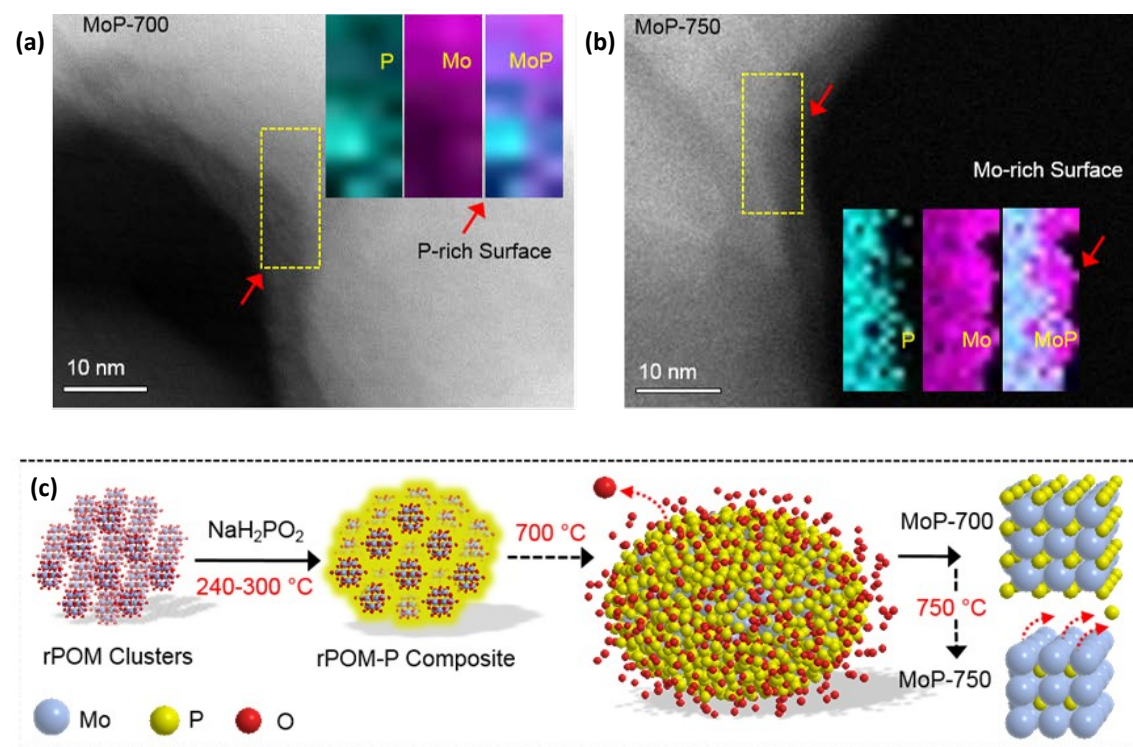


Figure 3. Micrographs of materials and schematic illustration of the synthesis of MoP. STEM images and corresponding EELS mapping of (a) MoP-700 and (b) MoP-750. (c) Schematic diagram illustrates the synthesis process of MoP-700 and MoP-750.

Scaled-Up (10-L) F-MEC Reactor Design and Fabrication

We designed the reactor based on the performance of small lab-scale fermentative reactors and MECs and developed a procedure to fabricate the cathodes. The assembled reactor has a fermentation volume of 0.8 L and an MEC portion of 9.3 L. Five pieces of cathode each with a surface area of 563 cm² and six pieces of anode each with 1,689 cm² area were installed in the MEC portion. The electrodes were arranged in the direction of the flow so that high fluid speeds could be achieved with recirculation (Figure 4).

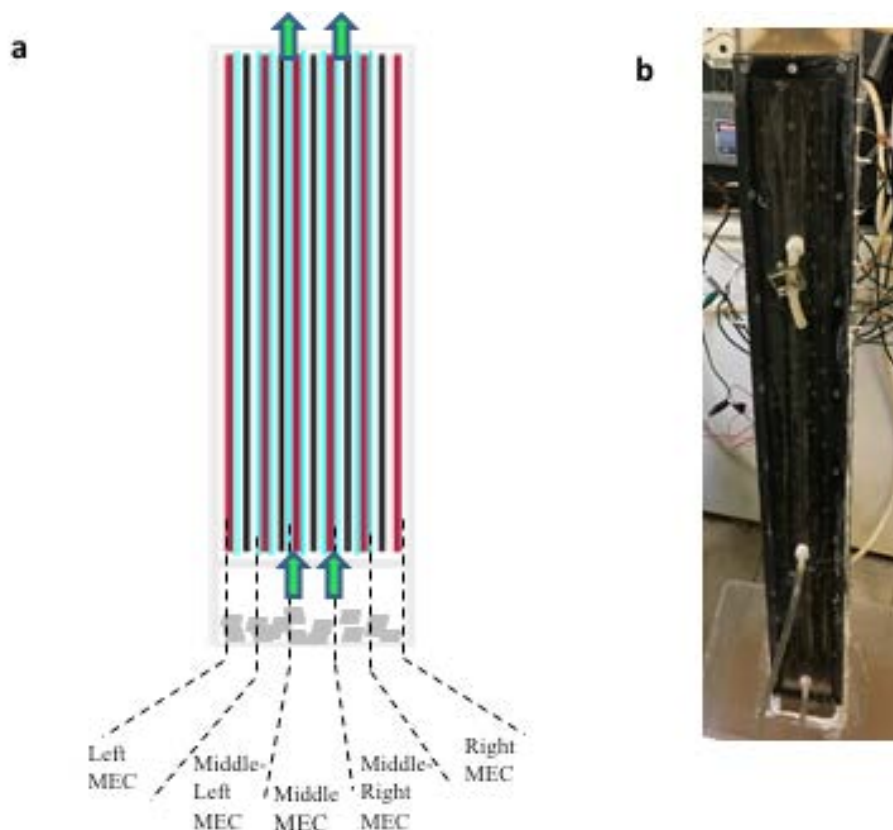


Figure 4. (a) Diagram of reactor electrode configurations with recirculation inlets and outlets—green arrows; anode set—red; cathode—black; separator—blue; and fermentative beads in bottom—gray. (b) Photo of the F-MEC reactor.

F-MEC Evaluation in Continuous Flow Mode

After about one month of startup period, the reactor was switched to continuous flow mode using acetate. We observed that the cathode can reach a current density of 35–40 A/m² at an applied voltage of 1.0 V. Fermentation beads containing immobilized fermentative bacteria were then added to the fermentation zone of the reactor and glucose was added to the feeding solution. Our preliminary testing demonstrates that a hydrogen production rate over 20 L/L-reactor/day can be achieved with glucose in the scaled-up F-MEC reactor (Figure 5).

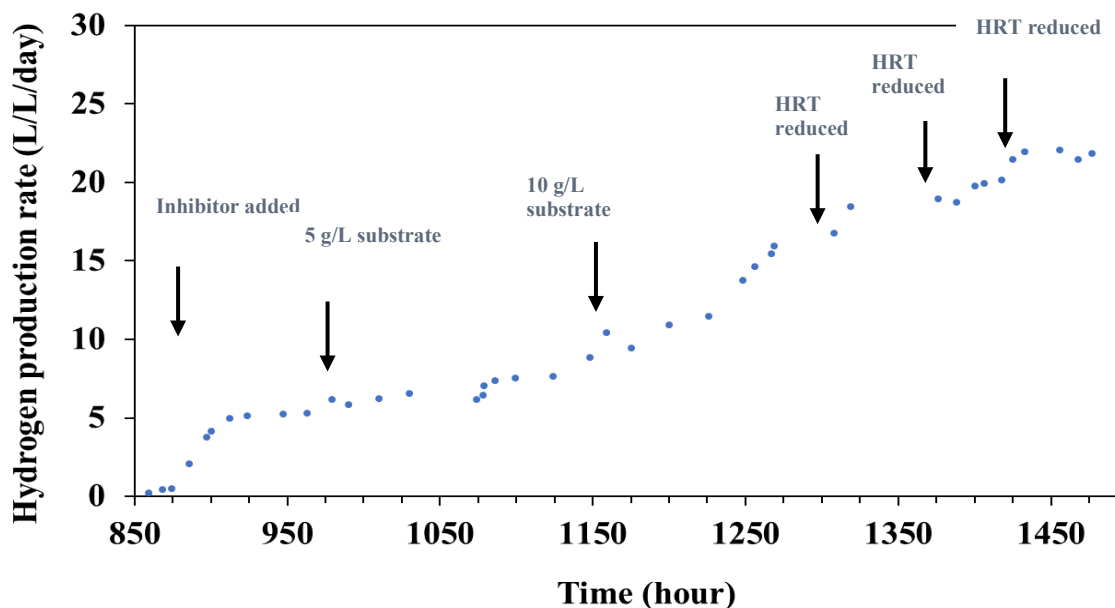


Figure 5. Continuous hydrogen production in 10-liter F-MEC

CONCLUSIONS AND UPCOMING ACTIVITIES

We have made significant progress toward reaching our project target. We have identified an issue (homoacetogenesis) associated with the MEC process for long-term operation and developed a solution. We have revealed the structure-property relationship of MoP electrocatalysts that demonstrate comparable performance to platinum catalyst. We have designed, fabricated, and preliminarily evaluated a scaled-up 10-liter F-MEC reactor.

Future work includes the following.

- Identify the reasons causing the instability of the large reactor.
- Finish the evaluation of the large reactor with wastewater and biomass hydrolysate.

SPECIAL RECOGNITIONS AND AWARDS/PATENTS ISSUED

1. Patent filed on “Modified transition metal-phosphide catalysts with enhanced catalytic activity in neutral media and process of making,” by Yuyan Shao at Pacific Northwest National Laboratory.

FY 2018 PUBLICATIONS/PRESENTATIONS

1. Luguang Wang, Lakhveer Singh, and Hong Liu. “Revealing the Hydrogen Consumption-Production Loop in Single Chamber Microbial electrolysis cells (MECs).” *International Journal of Hydrogen Energy*. 43, no. 29 (19 July 2018): 13064–13071.
2. Cheng Li, Luguang Wang, Hong Liu. “Enhanced Redox Conductivity and Enriched Geobacteraceae of Exoelectrogenic Biofilms in Response to Static Magnetic Field.” *Appl. Microbiol. Biotechnol.* (2018 Jun 20). doi: 10.1007/s00253-018-9158-3.
3. Luguang Wang, Stephanie Trujillo, and Hong Liu. “Using Acetylene as a Low-cost and Effective Methanogenesis Inhibitor in Single Chamber Microbial Electrolysis Cells.” Submitted to *Bioresource Technology*.
4. Andrew Miller, Lakhveer Singh, and Hong Liu. “Quantifying the International Resistances in Single Chamber (MECs).” Submitted to *Environment International*.

5. Luguang Wang, Lakhveer Singh, and Hong Liu. “Chloroform as an Effective Homoacetogen Inhibitor to Enhance Hydrogen Recovery in Single Chamber Microbial Electrolysis Cells (MECs).” Submitted to *Chemical Engineering Journal*.
6. Andrew Miller. Master thesis: “Microbial Electrolysis Cells for the Production of Hydrogen Gas: Evaluation of Internal Resistance and Design for Scale-Up.”
7. Hong Liu, Yuyan Shao, and Vilayanur Viswanathan. “Novel Hybrid Microbial Electrochemical System for Efficient Hydrogen Generation from Biomass,” presented at the DOE AMR meeting, Washington, D.C., June 2018.
8. Hong Liu. “Microbial Electrochemical System for Hydrogen Generation from Biomass and Waste Streams,” 22nd World Hydrogen Energy Conference, June 17–22, 2018, Rio, Brazil.
9. Hong Liu. “Energy Recovery from Waste Streams Using Microbial Electrochemical Systems,” Separation Technology Event at Lappeenranta University in Finland, August 22, 2018 (Invited talk).
10. Yuyan Shao. “Surface Atom Synergy in Electrocatalysis on Precious Metal Free Catalysts,” Nature Conference on Materials Electrochemistry: Fundamentals and Applications, January 15, 2018, Shenzhen, China (Invited talk).
11. Yuyan Shao. “Materials Electrochemistry for Energy Conversion and Storage @Scale,” UC Riverside Seminar, April 2, 2018, Riverside, CA, United States.