II.E.3 Novel Hybrid Microbial Electrochemical System for Efficient Hydrogen Generation from Biomass

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Project End Date: January 31, 2019

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) 2017 Objectives

- Evaluate fermentative H_2 production.
- Evaluate H_2 production from liquid fermentation products in microbial electrolysis cells (MEC).
- Develop robust and low-cost cathode materials.
- 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 Plan.

(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.

TABLE 1. Progress towards Meeting Technical Targets for Dark Fermentative Hydrogen Production and MECs

Characteristic	Units	DOE 2015 Targets	DOE 2020 Targets	Project Status
Yield of H_2 production from glucose by integrated MEC–fermentation	mol H_2 /mol glucose	6	9	8
MEC cost of electrodes	$\$/m^2$	300	50	120

The overall goal of this project is to develop and scale-up our novel hybrid fermentation and 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 H_2.

FY 2017 Accomplishments

- Developed an immobilization method that can increase the fermentative bacteria density in reactors with stable H_2 production. The hydrogen production rate reached over 10 L/L-reactor/d.
- Determined the suitable design and operational conditions for MECs.
- Discovered a low-cost chemical that can effectively inhibit methanogens in MECs. The estimated chemical cost for using this inhibitor is less than 5¢/kg H_2.
- Synthesized molybdenum phosphide (MoP) hydrogen evolution reaction (HER) catalysts with high activity (comparable to Pt) and high durability. The MoP catalyst shows a stable polarization curve after 2,000 potential cycles.

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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 over potential, 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 fermentation and microbial electrolysis cell for hydrogen generation from lignocellulosic biomass hydrolysates and sugar-rich wastewater through maximizing the hydrogen production rate and yield of both processes. Since MEC cathode material is a key factor affecting both capital and operational costs of the system, robust and low-cost cathode materials with low over-potentials 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 had identified suitable bacterial cultures for the hybrid system in FY 2016. In FY 2017, we have been focusing on determining the optimal operational conditions using small lab reactors, developing a low-cost and low-overpotential cathode catalyst, and conducting cost and performance analysis. Based on the results, a scaled-up reactor will be designed, fabricated, and evaluated in the fiscal year of 2018.

RESULTS

Continuous hydrogen production by immobilized fermentative culture. Bacterial cell density in continuous-flow reactors can be increased significantly through immobilizing the bacterial culture with immobilization agents. Stability is a major concern when using immobilized bacterial culture. Our batch experiments demonstrated that acrylic latex silicone beads containing immobilized fermentative bacterial culture could maintain their original shapes with reliable hydrogen production over 80 days of operation. Continuous hydrogen production from mixed sugars was investigated under different hydraulic retention times, sugar concentrations, and biomass content. A hydrogen production rate of over 10 L/L/day was achieved at 40 g/L, 8 h hydraulic retention time (HRT), and 15% biomass content (Figure 1).

Identification of the limiting factors in MECs. To provide better design and operational parameters for the continuous flow reactor, we investigated the impacts of four parameters on hydrogen production, including electrode distance, buffer concentration, mixing condition, and electrode surface area ratio. The mixing condition far outweighs the effect of other parameters on current density, suggesting that MECs should be designed to facilitate mixing. The maximum current density possible for the anode is around 33 A/m^2. The cathode current density can reach 50 A/m^2 (Figure 2).

Determination of suitable inhibitor concentration and frequency for inhibiting methanogenesis in MECs. Methanogens can utilize H_2 produced and reduce hydrogen yield in MECs. We discovered that periodically adding a low-cost chemical to the reactor can effectively inhibit methane production. This discovery is critical for the operation of our continuous flow reactor, particularly using wastewater as feedstock. We have determined that the injected concentration can be as low as 1% with less than two injections per month (Figure 3), which corresponds to a few cents per kilogram H_2 produced, indicating its feasibility for practical application.

MEC cathode development. We developed a new MoP cathode catalyst, which has demonstrated comparable activity to Pt catalyst. The catalyst shows stable performance after 2,000 potential cycles (Figure 4). The MoP|P material appear as quasi-spherical nanoparticles with an average diameter of ~100 nm. High-resolution transmission electron microscopy image showed that the MoP|P nanoparticles were

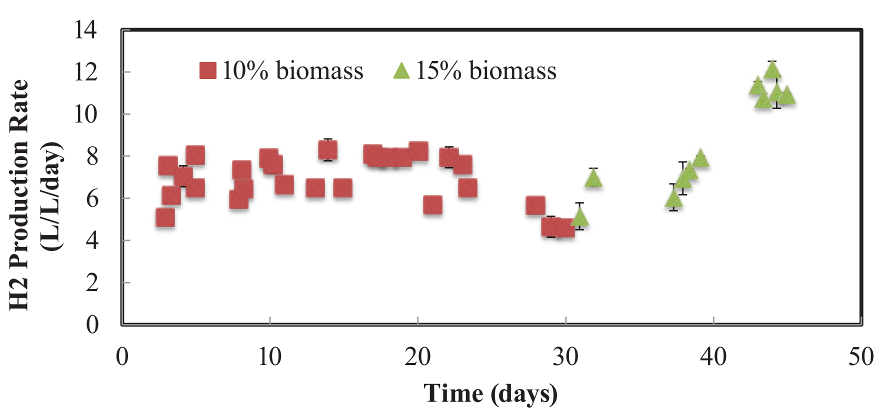


FIGURE 1. Continuous hydrogen production using immobilized fermentative culture

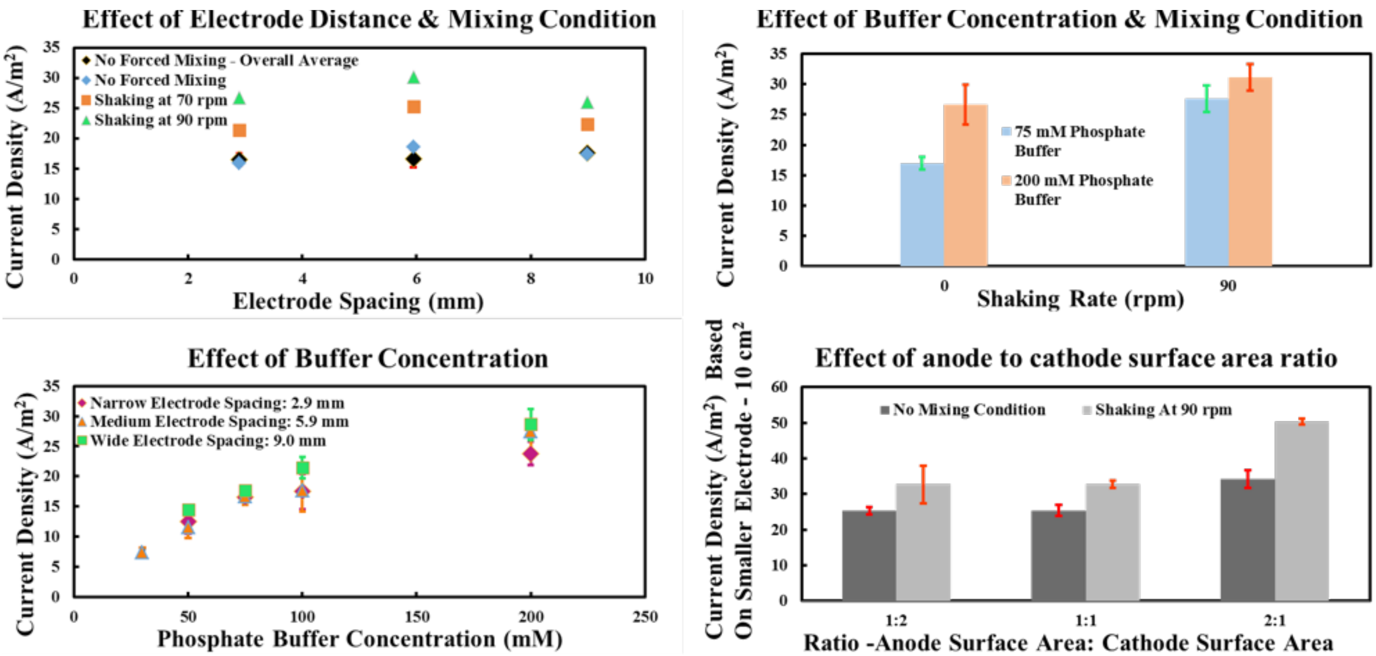


FIGURE 2. Effect of electrode spacing, buffer concentration, mixing condition, and electrode surface area ratio on current density of MECs

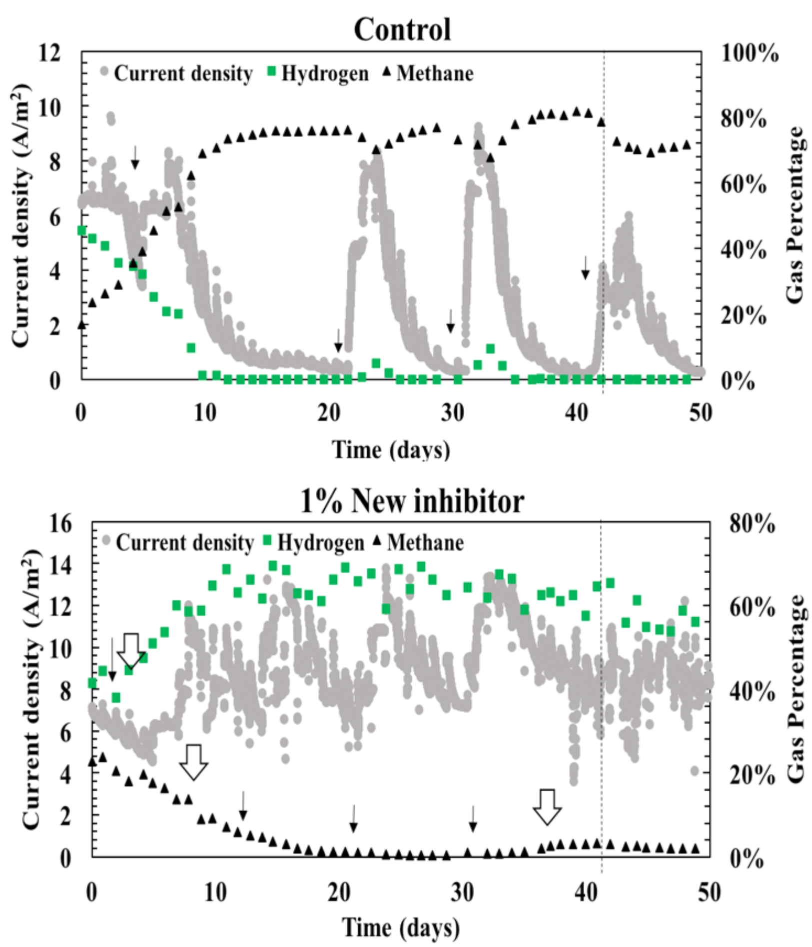
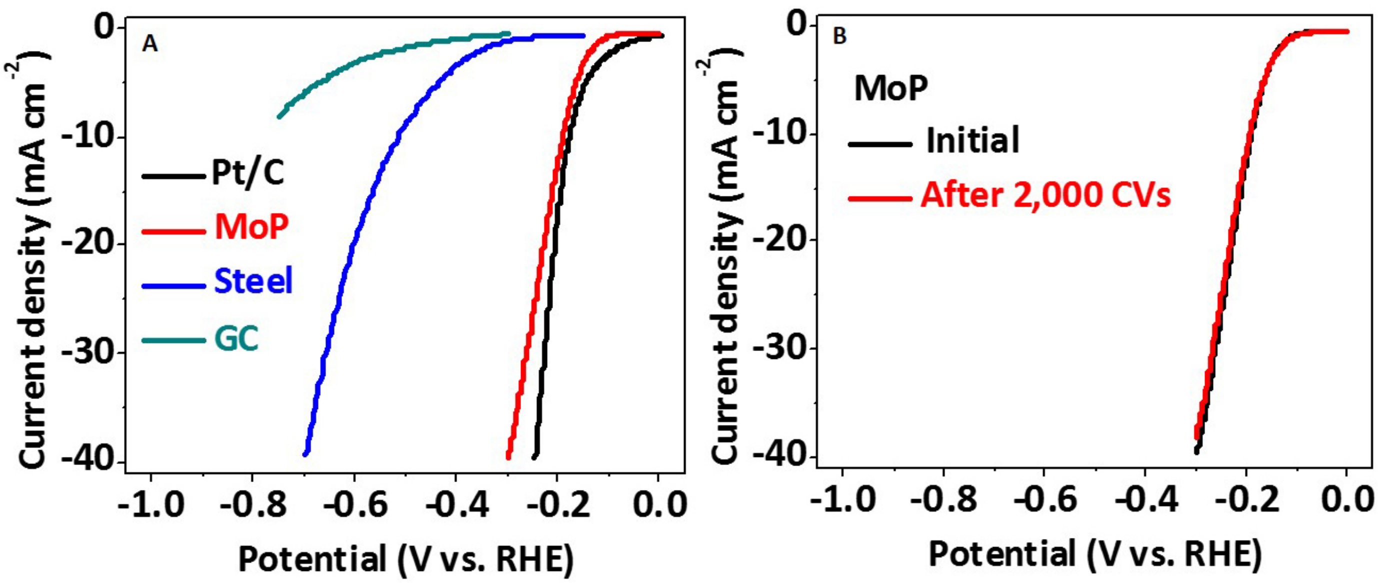


FIGURE 3. Inhibiting methane production in MECs using a low-cost chemical



RHE – reference hydrogen electrode; GC – glass carbon; CV – cyclic voltammogram

FIGURE 4. (A) HER on MoP catalyst in comparison with other catalysts/electrode materials. MoP shows comparable activity to Pt; (B) MoP catalyst durability test.

single crystalline and faceted. The observed lattice fringes correspond to the (001) P-terminated plane of MoP, indicating that the nanoparticle surfaces exposed, among other facets, the (001) MoP|P crystal planes that have been predicted to have the highest activity for the HER.

Cost performance model. We developed an H2A model based on some of the experimental results and drew the following general conclusions: (1) increasing the overall hydrogen yield is critical when using biomass hydrolysate since the feedstock cost contributes about half of the targeted H_2 production cost; (2) increasing the current density is critical, which significantly affect the capital cost, especially for using wastewater as feedstock; (3) using wastewater as feedstock is more promising than biomass hydrolysate in term of meeting DOE's cost target even we use a more conservative cost inputs (high reactor cost, low current density).

CONCLUSIONS AND UPCOMING ACTIVITIES

We have made significant progress towards reaching our project target. We have determined the design and operational conditions for our scaled-up reactors, including the method for immobilizing the fermentative culture, the critical factors affecting fermentative and microbial electrochemical hydrogen production, the low-cost chemical for inhibiting methanogens, the low-cost and low-over potential cathode catalyst, and the anode and cathode surface area ratio. Our cost and performance analysis demonstrated that increasing current density is critical and using waste streams is more promising than biomass hydrolysate.

Future work includes:

- Stability test of the cathode catalyst
- Hybrid reactor design and fabrication
- Lab and on-site evaluation of the hybrid reactor

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Filed an invention disclosure report on "A PGM-free catalyst for hydrogen evolution in neutral electrolytes," by Yuyan Shao at PNNL.

FY 2017 PUBLICATIONS/PRESENTATIONS

1. Luguang Wang, Ningshengjie Gao, Cameron Platner, Cheng Li, and Hong Liu, "Hybrid Microbial Electrochemical System for Efficient Hydrogen Generation from Lignocellulosic Hydrolysate," presented at the 2016 NA ISMET Meeting, Stanford University, CA, October 2016.

2. Hong Liu, Yuyan Shao, and Vilayanur Viswanathan, "Novel Hybrid Microbial Electrochemical System for Efficient Hydrogen Generation from Biomass," presented at the DOE Annual Merit Review and Peer Evaluation Meeting, Washington, D.C., June 2017.

3. Stephanie Trujillo, Luguang Wang, and Hong Liu, "Using Acetylene as a Low-cost and Effective Methanogenesis Inhibitor in Single Chamber Microbial Electrolysis Cells," Submitted to *International Journal of Hydrogen Energy*.