Novel Hybrid Microbial Electrochemical System for Efficient Hydrogen Generation from Biomass

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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) 2019 Objectives

- Continue evaluating the fermentation and microbial electrolysis cell (F-MEC) reactor using biomass hydrolysate and wastewater to demonstrate the ability to produce 30 L H_2/L-reactor/day on average from lignocellulosic hydrolysate feedstock using a 10-L F-MEC reactor operating for at least 24 hours continuously.
- Develop a cost performance model to demonstrate the techno-economic feasibility of the F-MEC system.

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[1]:

- (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 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 2019 Accomplishments

- Demonstrated the effectiveness of chloroform against the hydrogen scavengers in the scaled-up F-MEC operated in continuous flow mode.
- Hydrogen yield has increased from 8.5 mol H_2/mol glucose to 10.8 mol H_2/mol glucose in the scaled-up F-MEC operated in continuous flow mode, which is 20% higher than the target of 9 mol H_2/mol glucose.
- Hydrogen production rate has increased from 20 L/L/day to more than 30 L/L/day using glucose in the scaled-up F-MEC operated in 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 Microbial Electrolysis Cells (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	10.8
MEC cost of electrodes	$/m^2	300	50	70

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 microbial electrolysis cell (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 are also developed. A cost-performance model is used to supplement the H2A analysis tool throughout the project to prioritize the critical factors and demonstrate potential to meet DOE cost goals.

In FY 2016, we identified suitable bacterial cultures for the hybrid system. In FY 2017, we determined the optimal operational conditions using small lab reactors, developed low-cost and low-overpotential cathode catalyst, and conducted cost and performance analysis. In FY 2018, we designed and fabricated a scaled-up F-MEC reactor (10 L) based on the results obtained in 2017. Since January 2019, we have been evaluating the scaled-up F-MEC using glucose, biomass hydrolysate, and brewery wastewater.

RESULTS

Effectiveness of Chloroform against Hydrogen Scavengers in the Scaled-Up F-MEC

In our previous studies, we discovered that hydrogen production was greatly affected by the hydrogen scavengers (methanogens and homoacetogens) during long-term operation. To reduce the hydrogen consumption by the scavengers, we investigated the feasibility of using chloroform to inhibit both methanogens and homoacetogens in the 10-L reactor operated in continuous flow mode. The addition of 0.02% chloroform resulted in over 90% cathodic hydrogen recovery with no methane produced, suggesting that low concentration of chloroform can successfully inhibit both methanogens and homoacetogens. The higher current density generated in the presence of chloroform suggests that 0.02% chloroform does not inhibit the exolectrogens (Figure 1). These results demonstrate the great potential of this method to be used in F-MEC operation.

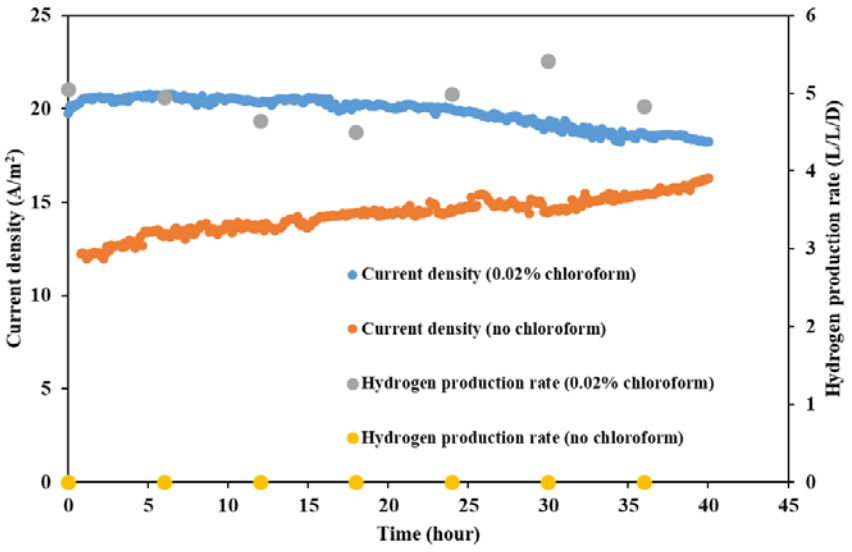

Figure 1. Impacts of 0.02% of chloroform on the current density and hydrogen production rate of the 10-L F-MEC reactor operated in continuous flow mode

Hydrogen Yield Achieved in the Scaled-Up F-MEC

We evaluated the 10-L F-MEC at various organic loading rates to maximize the hydrogen yield. The reactor was initially operated using glucose as feedstock and switched to biomass hydrolysate after high hydrogen yield was achieved. Hydrogen yield gradually increased with the decrease of organic loading rate and reached over 80% with 0.45 g/day of glucose. After switching to the biomass hydrolysate with a loading of 0.4 g/day, the hydrogen yield increased to 90% (Figure 2).

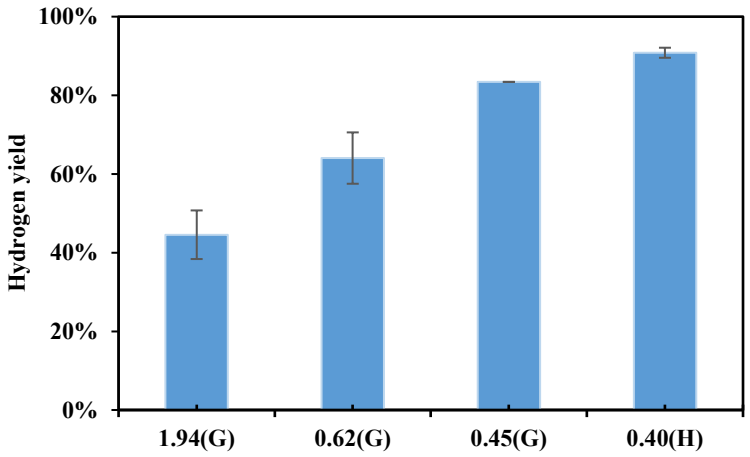

Figure 2. Hydrogen yield based on the dosed substrates at various organic loading rates (g/day) using glucose (G) or hydrolysate (H)

Hydrogen Production Rate at High Organic Loading Rates

To maximize the hydrogen production rate, high organic loading rates over 100 g/day were investigated using both glucose and biomass hydrolysate. The hydrogen production rate increased from 10 L/L/day to 33 L/L/day when the organic loading rate increased from 104 g/day to 208 g/day (Figure 3). After switching to biomass hydrolysate, the hydrogen production rate decreased to about 23 L/L/day at the same organic loading rate. The decreased hydrogen production rate was possible due to the complex compositions in the hydrolysates.

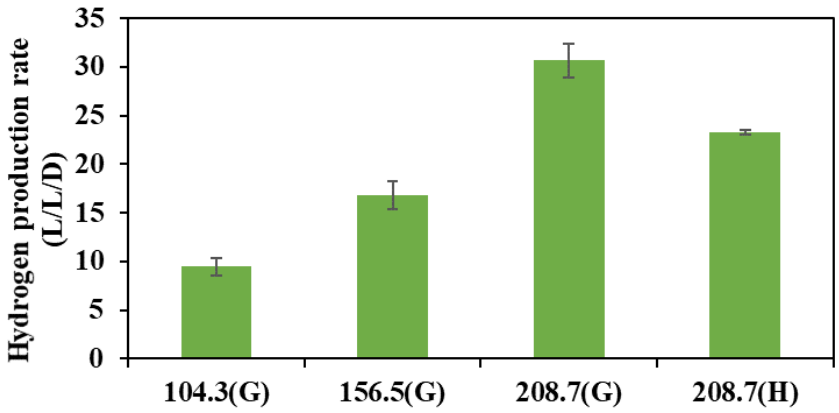

Figure 3. Hydrogen production rate at various organic loading rates using glucose (G) or hydrolysate (H) as substrate

CONCLUSIONS AND UPCOMING ACTIVITIES

We have made significant progress toward reaching our project target. We have demonstrated the effectiveness of chloroform in inhibiting the hydrogen scavengers, which has greatly increased the hydrogen yield and production rate in the scaled-up reactor. We have evaluated the scaled-up F-MEC reactor using glucose and biomass hydrolysate as feedstock and demonstrated that our targeted hydrogen yield and production rate are achievable.

Future work includes:

- Finish the evaluation of the 10-L F-MEC reactor using wastewater as feedstock.
- Finalize the cost performance model.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. Luguang Wang, Stephanie Trujillo, and Hong Liu, "Selective Inhibition of Methanogenesis by Acetylene in Single Chamber Microbial Electrolysis Cells," *Bioresource Technology* 274 (2019): 557–560.
2. Andrew Miller, Lakhveer Singh, Luguang Wang, and Hong Liu, "Linking Internal Resistance with Design and Operation Decisions in Microbial Electrolysis Cells," *Environment International* 126 (2019): 611–618
3. Xiaohong Xie, Miao Song, Luguang Wang, Mark H. Engelhard, Langli Luo, Andrew Miller, Yayun Zhang, Lei Du, Huilin Pan, Zimin Nie, Yuanyuan Chu, Luis Estevez, Zidong Wei, Hong Liu, Chongmin Wang, Dongsheng Li, and Yuyan Shao, "Electrocatalytic Hydrogen Evolution in Neutral pH Solutions: Dual-Phase Synergy," *ACS Catal.* 9 (2019): 8712–8718.
4. Luguang Wang, Ye Chen, Fei Long, Lakhveer Singh, Stephanie Trujillo, Xiang Xiao, and Hong Liu, "Breaking the Hydrogen Production-Consumption Loop: Tackling Homoacetogenesis by Chloroform in Single Chamber Microbial Electrolysis Cells," *Chemical Engineering Journal*, 389 (2019):124436.
5. Hong Liu, Yuyan Shao, and Vilayanur Viswanathan, "Novel Hybrid Microbial Electrochemical System for Efficient Hydrogen Generation from Biomass," presented at the DOE Hydrogen and Fuel Cells Program 2019 Annual Merit Review and Peer Evaluation Meeting, Washington, D.C., April 30, 2019.
6. Hong Liu, "Microbial Electrochemical Cells for Hydrogen Generation from Biomass and Waste Streams," presented at the 7th Conference of the International Society of Microbial Electrochemical Technology (ISMET 7), Okinawa, Japan, October 7–11, 2019.