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

Hong Liu (Primary Contact), Yuyan Shao, Vilayanur Viswanathan, Murthy Ganti
Oregon State University/Pacific Northwest National Laboratory
116 Gilmore Hall
Oregon State University
Corvallis, OR 97331
Phone: (541) 737-6309
Email: liuh@engr.orst.edu

DOE Manager: Katie Randolph
Phone: (240) 562-1759
Email: Katie.Randolph@ee.doe.gov

Project Start Date: February 1, 2016
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) 2016 Objectives

- Identify a bacterial culture capable of producing hydrogen from all major sugars in biomass hydrolysate.
- Investigate hydrogen producing capability of lab culture from various liquid fermentation products in microbial electrolysis cell (MEC).
- Develop efficient and low-cost cathode materials.

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 Microbial Electrolysis Cells (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	7.6
MEC cost of electrodes	$\$/m^2$	300	50	150

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. This project was initiated in February 2016 and is still in the early stages.

FY 2016 Accomplishments

- Identified fermentative bacterial cultures capable of producing hydrogen from major sugars in lignocellulosic biomass hydrolysate. The hydrogen yield reached 40% of theoretical yield, which is defined as the maximum for known metabolic pathways.
- Identified an exoelectrogenic bacterial culture capable of utilizing all liquid fermentation products and generating a current density up to 15 A/m^2 of anode surface area.
- Discovered that fermentative hydrogen production is a much faster process compared to the MEC process in a hybrid system and determined that further optimization should focus on the MEC process.
- Synthesized nonprecious metal catalyst with an intrinsic activity very close to Pt/C electrocatalyst. Synthesized nitrogen doped porous carbon (N-C) with surface area tunable between 1,000–2,500 m^2/g, which will be integrated with the synthesized metal catalyst for MEC cathode fabrication.

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 (F-MEC) 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.

For the first phase of this project, we have been focusing on identifying suitable fermentative and exoelectrogenic bacterial cultures for the hybrid system and determining the optimal operational conditions using small lab hybrid reactors. Non-precious metal catalyst and nitrogen doped porous carbon were also synthesized and are being integrated for fabricating low-cost MEC cathode materials.

RESULTS

H_2-producing capability of bacterial cultures from major sugars in lignocellulosic biomass hydrolysates. We investigated the capability of three mixed bacterial cultures in generating H_2 from major sugars in hydrolysates, including glucose, xylose, mannose, and galactose, and a mixture of the sugars using serum bottle reactors operated in batch mode. Our results demonstrate that all three tested cultures are capable of producing hydrogen from all tested sugars. The lab culture enriched from wastewater with glucose as carbon source demonstrated the highest hydrogen yield (Figure 1).

Direct H_2 production from mixed sugars in F-MECs. We also investigated direct mixed sugar fermentation by our lab exoelectrogenic culture enriched from acetate in microbial fuel cells (MFCs). Figure 2A demonstrates that the lab culture is capable of fermenting all tested sugars without the addition of a fermentative bacterial inoculum. Figure 2B illustrates the liquid fermentation products distribution and

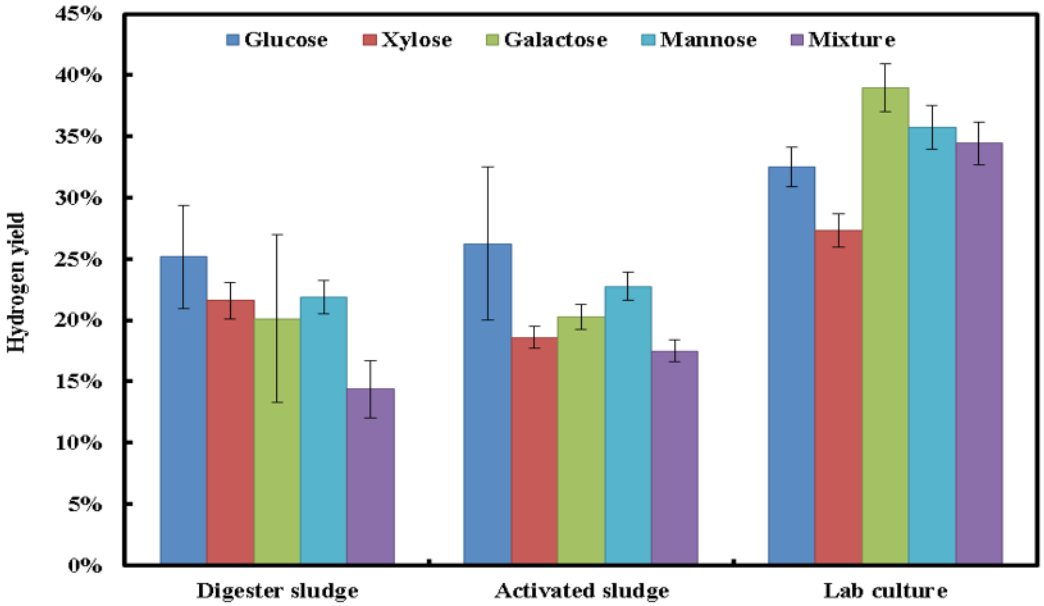


FIGURE 1. Hydrogen yields (defined as the maximum for known metabolic pathways) of three tested bacterial cultures (n = 3, error bars represent standard deviation)

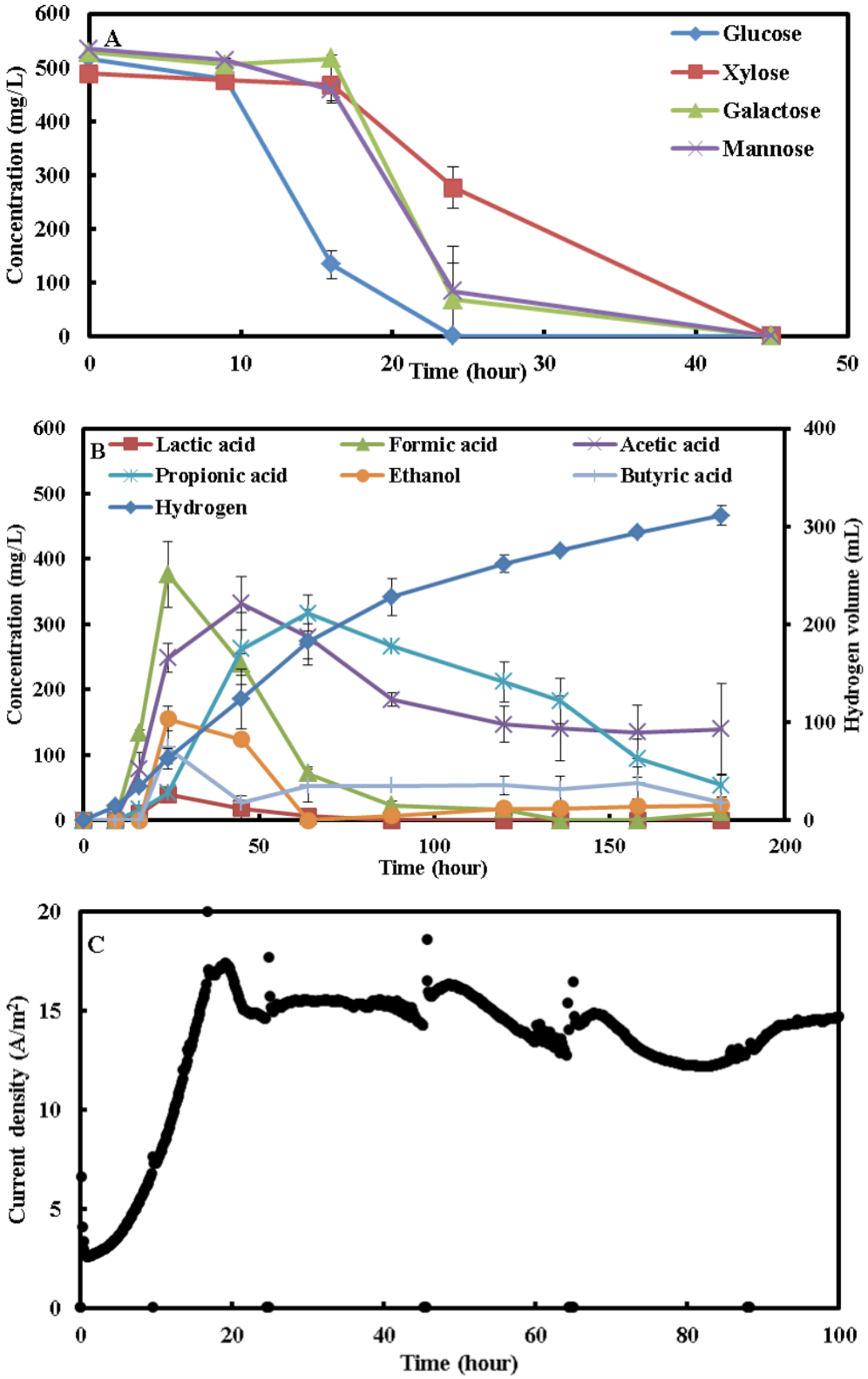
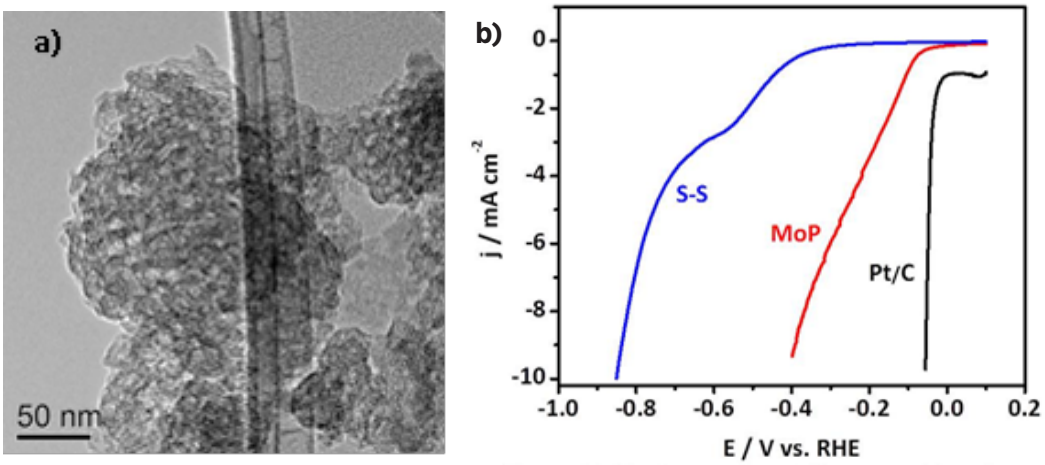


FIGURE 2. (A) Sugar utilization by the lab exoelectrogenic culture enriched with acetate in F-MECs; (B) liquid fermentation products distribution and hydrogen production in F-MECs; (C) current generation in MEC process (n = 3, error bars represent standard deviation in Figures 2A and 2B)



RHE – Reference hydrogen electrode

FIGURE 3. (a) TEM image of nitrogen-doped high surface area carbon; (b) Hydrogen evolution reaction linear sweep voltammongrams on different electrodes (0.1 M PBS, 10 mV/s)

hydrogen production in the F-MECs and Figure 2C shows current generation from the liquid fermentation products in the MEC process. The relatively long operational time for fully utilizing the fermentation liquid products suggests that the MEC process in the tested batch reactor is much slower than the fermentation process. Further optimization will focus on MEC process.

MEC cathode development. We have synthesized nitrogen doped high surface area carbon (N-C) using sucrose as a precursor (Figure 3a). The surface area of N-C is tunable between 1,000-2,500 m^2/g using various activation protocols. We have also synthesized and tested nonprecious metal catalysts. Figure 3b shows the hydrogen evolution reaction (HER) linear sweep voltammograms on different electrocatalysts (0.1 M PBS, 10 mV/s). Stainless steel (S-S) is the most commonly used electrode in today's MECs. Our electrocatalyst MoP shows much higher activity than S-S, with an onset HER potential close to Pt/C electrocatalyst, indicating its intrinsic activity is close to Pt/C. But the current density at higher overpotentials is still lower than Pt/C, probably due to the less active sites. Through optimization of the structure and composition of the nonprecious metal electrocatalysts and integration with nitrogen doped porous carbon, we expect to increase the active sites and the overall catalytic activity significantly.

CONCLUSIONS AND FUTURE DIRECTIONS

Although the project is still in early stages several conclusions can be drawn:

- Mixed bacterial cultures enriched from digester sludge, active sludge, and wastewater are capable of producing hydrogen from all major sugars in lignocellulosic biomass hydrolysate.
- Our lab's exoelectrogenic bacterial culture is capable of fermenting all major sugars and generating current from fermentation products in the MEC.
- MoP, a nonprecious metal catalyst, has demonstrated an intrinsic activity close to Pt/C electrocatalyst for hydrogen evolution in solution chemistry of the MEC.

Future work includes:

- Further MEC development through integrating the newly developed cathode materials.
- Optimization of fermentative and MEC processes in continuous-flow reactors.
- Hybrid system design, fabrication, and evaluation
- Cost performance modeling.

FY 2016 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*, 2016 NA ISMET Meeting. Accepted.