Novel Microbial Electrolysis Cell Design for Efficient Hydrogen Generation from Wastewaters

Bruce E. Logan (PI)
Ruggero Rossi (co-PI - presenter)
Penn State University, Johns Hopkins, NREL, Sentry
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2024 Annual Merit Review and Peer Evaluation Meeting

This presentation does not contain any proprietary, confidential, or otherwise restricted information
• High rate (20 $L_{H_2}/L_{reactor}$-day) hydrogen production from real wastewater in a zero-gap bench-scale (100 cm$^2$) microbial electrolysis cell (MEC).

Key Innovation: The novel MEC design combines an AEM and no catholyte for driving electrochemical H$_2$ production from real waste streams. This compact MEC with no catholyte minimizes mass-transfer limitations and pH imbalances in the cell, boosting the overall current density and hydrogen production rates, while lowering the applied potential.

Outcome: Results from this work will accelerate toward the DOE goal of $1 per one kilogram of hydrogen in one decade.
OVERVIEW

Timeline and Budget

- Project Start Date: 09/01/2021
- Project End Date: 05/31/2024
- Total Project Budget: $ 1.2M
- DOE Share: $ 1M
- Cost Share: $ 0.2M
- DOE Funds Spent*: $ 400K
- Cost Share Funds Spent*: $ 80K
  - * As of ~ 02/28/2024

Barriers

- Low electrochemical cell efficiency due to high internal resistance
- Small current density
- High cathode cost and poor H₂ production

Partners

- Project lead: Bruce E. Logan (Penn State);
- Co-PI: Ruggero Rossi (Johns Hopkins)
- Co-PI: Dr. Katherine Chou (NREL)
  - Production of wastewaters from lignocellulosic fermentations.
- Partner organization: Dr. Patrick Kiely (Island Water Technologies)
  - Sourcing the waste feedstock for the project and distribute our technology.
RELEVANCE AND IMPACT

DOE goals:
- Hydrogen Shot goal of $1 for 1 kg hydrogen in 1 decade.
- Lower greenhouse gas emissions
- Build clean energy infrastructure
- Support and improve energy, environmental, or social justice

Project goals:
- Hydrogen production via microbial biomass conversion utilizing diverse feedstocks.
- $\text{H}_2$ production at scale, focusing on cost, performance, durability, and scale-up challenges for hydrogen from wastewaters.
- Eliminating the feedstock cost and avoiding disposal and clean-up costs.

Strategies to achieve DOE targets:
1) Optimizing cell architecture by reducing internal resistance and mass-transfer limitations
2) Maximize hydrogen production efficiency by using a gas-phase cathode
3) Increase anodic current density and coulombic efficiency in a flow-through zero-gap reactor
4) Develop non-Pt group metal cathodes and scale up
RELEVANCE AND IMPACT

Tasks for current year (project was delayed due to transfer from PSU to JHU)

1. Start-up and operation of the lab-scale zero-gap MEC. (PSU-JHU)
2. Determine impact of wastewater composition on MEC performance (current density and applied voltage). (PSU-JHU)
3. Optimize cell architecture and influent pretreatment to minimize clogging with wastewaters with large suspended solids concentrations (PSU-JHU)
4. Identify performance limitations over long-term operation. (PSU-JHU)
5. Optimize lignocellulose fermentation step to achieve maximum performance in MEC. (NREL)
6. Identify wastewater sources other than lignocellulosic fermentation effluent for MEC (Sentry)

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<th>2.0 MEC performance with biomass fermentation effluent</th>
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Ion transport in previous MEC designs that have a liquid catholyte.

**Asymmetric-fed MEC vs Conventional MEC w/ liquid catholyte**

**NEW Approach: Asymmetric-fed MEC**
- No catholyte = no anions other than $\text{OH}^-$
- AEM facilitates only $\text{OH}^-$ transport from catholyte to anolyte
- pH of anode is stabilized $\rightarrow$ current is increased

**OLD Approach**
- AEM facilitates anion transport from catholyte to anolyte
- pH imbalance, anode acidified, cathode basified $\rightarrow$ low current, high applied voltage
The vapor-fed MEC design advances the existing reactor configuration by (1) removing the solution separating anode and cathode and (2) allowing only the hydroxide ions generated at the cathode to be transported to the anode.

The absence of a liquid catholyte in our system will exclude the transport of any anion except the hydroxide ions generated by the HER, which will ensure sufficient neutralization of protons generated by the bioanode next to the membrane.
(1) Validation and optimization of MEC performance with REAL waste streams;
(2) Optimization of MEC architecture for scale up;
(3) Optimization of fermentation step by NREL;

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<thead>
<tr>
<th>Milestone #</th>
<th>Project Milestones</th>
<th>Type</th>
<th>Task Completion Date (Project Quarter)</th>
<th>Progress Notes</th>
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<tr>
<td>1.0</td>
<td>Impact of reactor configuration on the MEC performance</td>
<td>1.1.1</td>
<td>Q1</td>
<td>Q1</td>
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<td>MEC assembly and acclimation</td>
<td>1.2.1</td>
<td>Q2</td>
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<td>1.3</td>
<td>Biomass fermentation effluent production and characterization</td>
<td>1.2.2</td>
<td>Q2</td>
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<td>1.4</td>
<td>Impact of MEC operational parameters on performance</td>
<td>1.3.1</td>
<td>Q3</td>
<td>Q3</td>
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<td>Development of Pt-group metal free cathode</td>
<td>1.4.1</td>
<td>Q4</td>
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<td>1.6</td>
<td>MEC performance with synthetic media</td>
<td>1.5.1</td>
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2.0 MEC performance with biomass fermentation effluent

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<th>Milestone #</th>
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<tr>
<td>2.1</td>
<td>Impact of solids and void volume on MEC</td>
<td>2.1.1</td>
<td>Q5</td>
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<td>2.2</td>
<td>H2 production using fermentation effluent</td>
<td>2.2.1</td>
<td>Q7</td>
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<tr>
<td>2.3</td>
<td>Long term MEC performance with biomass fermentation effluent</td>
<td>2.3.1</td>
<td>Q8</td>
<td>0%</td>
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</tbody>
</table>

2.2 H2 production using real wastewater streams | 2.4.1 | Q8 | 0% | Started |

3.0 Stability and performance using different waste sources
APPROACH (NREL): Optimize and Improve Fermentation Effluent Compatibility with MEC

- Microbial fermentation of lignocellulosic biomass produces H₂ and wastewater that is rich in organic acids and would require further treatment.

- MEC is a competitive technology to recover the energy content of the remaining organic acids to produce hydrogen gas in a bioelectrochemical reactor.

- NREL performs fermentation by *Clostridium thermocellum* in various conditions and with different strains and provides the fermentation effluent for MEC operation.

- Explored different biological buffering system and provided PSU MEC compatible effluent composition.
A safety plan was not required for this project.
Development and operation with non-precious metal cathode catalyst

- MEC with NiMo can produce performance similar to Pt MEC with slightly higher cell voltage
- **Highest H₂ production rate ever recorded of 81 ± 3 L_H₂/L-d**
- Cathode resistance (5.3 ± 0.5 mΩ m²) dominates (70%) MEC internal resistance
ACCOMPLISHMENTS AND PROGRESS

Probing ion transport to quantify superiority of asymmetric-fed MECs

- Asymmetric-fed electrochemical reactors allow to minimize pH gradients across the AEM.
- No vapor feed is needed up to 500 A/m²

Using a saline anolyte and no catholyte result in minimal anion crossover (due to electric field) and small cation crossover (due to membrane charge—controlled by diffusion).

Reducing cation transport by minimizing salinity in the cathode allow to minimize pH gradients across AEM.

Using saline catholyte results in large pH gradients across the membrane, driven by the migration of anions from cathode to anode.
ACCOMPLISHMENTS AND PROGRESS

Zero-gap MEC vs other conventional reactor architecture

• Comparison with previous work indicate that zero-gap MECs with AEM is the most efficient reactor configuration for hydrogen production from liquid waste.

• The zero-gap MECs with AEM produced the largest hydrogen production rate in a reactor with the lowest internal resistance, even when compared with other systems using much larger buffer capacity (> 200 mM vs 50 mM here).
• Current production in the MEC is strictly connected to the wastewater composition. Acetate is the preferred substrate and the presence of biodegradable chemicals other than acetate can decrease performance.

Problem: large concentration of ethanol or lactate in solution can decrease MEC performance.
Solution: Optimize fermentation step to increase acetate ratio vs other biodegradable substrate

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<tr>
<th></th>
<th>Acetate (mM)</th>
<th>Ethanol (mM)</th>
<th>Formate (mM)</th>
<th>Lactate (mM)</th>
<th>pH</th>
<th>Total Soluble Protein (mg/L)</th>
<th>Glucose (mg/L)</th>
<th>Gluco-oligomers (mg/L)</th>
<th>Xylose (mg/L)</th>
<th>Xylo-oligomers (mg/L)</th>
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<tbody>
<tr>
<td>Δldh 22h</td>
<td>14.9 ± 0.16</td>
<td>15.1 ± 0.05</td>
<td>13.4 ± 0.73</td>
<td>0.4 ± 0.08</td>
<td>6.83</td>
<td>87.8 ± 27.6</td>
<td>17.1 ± 4.8</td>
<td>65.6 ± 3.2</td>
<td>20 ± 4.8</td>
<td>19.8 ± 2.8</td>
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<td>Δldh 190h</td>
<td>25.9 ± 0.07</td>
<td>13.1 ± 0.02</td>
<td>18.5 ± 0.03</td>
<td>0.5 ± 0.001</td>
<td>6.79</td>
<td>103 ± 1.1</td>
<td>145 ± 0.3</td>
<td>48.7 ± 17.5</td>
<td>40.2 ± 0.2</td>
<td>12.7 ± 3.2</td>
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<tr>
<td>Δhpt 190h</td>
<td>20 ± 0.04</td>
<td>13.4 ± 0.1</td>
<td>14.8 ± 0.1</td>
<td>4.6 ± 0.04</td>
<td>6.8</td>
<td>96.1 ± 8</td>
<td>41.1 ± 0.8</td>
<td>24.8 ± 0.7</td>
<td>31.7 ± 0.3</td>
<td>5.2 ± 0.2</td>
</tr>
</tbody>
</table>

NREL utilized process engineering and engineered *C. thermocellum* strains to produce fermentation effluent with organic substrate concentrations targeting the optimal ranges established by PSU.
Further optimization of the fermentation step allowed to produce an effluent with almost 100% acetate.

- An engineered strain (\(\Delta pfl \Delta ldh\)) allowed to produce an effluent with >15 mM acetate and only 5 mM ethanol with traces of formate and lactate.
- When tested in the zero-gap MEC, similar performance were obtained with the real fermentation effluent compared to only acetate.
ACCOMPLISHMENTS AND PROGRESS

Optimization of the reactor architecture to facilitate scale-up

- Optimizing flow path allows to operate with effluents containing larger concentrations of suspended solids
- Using a square rather than circular electrode area will simplify the scale up
- Similar performance was obtained between the two flow paths
• **Separation of chemicals in anode or cathode streams:** Only one reviewer indicated that the project economics can be limited by a separation step. In this project, there is **NO SEPARATION** of chemicals at any point in any phase. We believe that operation in our cell could be more cost effective compared to conventional systems as hydrogen gas can be compressed in the gas chamber, which could not be done in liquid-catholyte MECs. We **DID NOT** observe reactant crossover in the AEM.

• **Impact of biodegradable organic matter composition:** Investigated and addressed in this budget period. We are developing a model to quantify the impact of the media composition on performance.

• **Stability of AEM and performance:** in the following budget period, the MEC will be operated for > 1 month using real waste streams. Our previous work did not indicate a decrease in performance for up to 3 months of operation. The cell architecture limits oxygen intrusion and large biomass formation.

• **Small scale of current work:** Scaling up will be addressed in current and following budget period.

• **One reviewer suggested H₂A analysis:** a cost analysis was not required and could be misleading given the low TRL.

• **Vapor gas generation and condensation:** We removed the vapor feed, simplifying operations while maintaining similar performance. The water diffusing through the AEM was sufficient to maintain hydrogen production at the cathode.

• **Carbon felt degradation:** In all the previous experiments with MECs and MFCs we did never observe carbon felt degradation given the low applied voltage. Carbon oxidation is problematic in conventional water electrolysis but here the applied voltages are lower.

• **IWT role:** IWT is not only focusing on the commercialization approach but is also connecting other members of the team with treatment facilities which can provide REAL waste streams.
• **PSU/JHU** leads the project by assembly and operate the zero-gap MEC.

• **NREL** works with PSU/JHU to:
  1. Reduce solid content in fermentation wastewater
  2. Identify alternative feedstocks for fermentation
  3. Optimize effluent composition to maximize MEC performance

• **IWT** (Island Water Technologies):
  1. Connects with waste producers to source optimal waste feedstock
  2. Work with industry to publicize our technology
Challenges

- Variability in wastewater composition can impact performance (buffer capacity, biodegradable fraction and composition).
- Focusing on only acetate production during fermentation while limiting other organic compounds (ethanol, formic acid, lactic acid) can increase complexity. (no separation)
- Maintaining our high performance during scale up.

Planned solution

- Modelling approach to correlate performance to substrate composition
- Simplify approach and fermentation architecture to optimize substrate composition of the produced effluent.
- Optimization of flow path and architecture to facilitate scale up.
1. Long-term (>1 month) operation of the zero-gap MEC with fermentation effluent from NREL.
2. Long-term (>1 month) operation with other effluents provided by IWT.
3. Develop of a correlation between media composition and MEC performance.
4. Optimization of flow path.
5. Scaling up through 25 cm² up to 100 cm². Quantification of impact of scale on performance.
6. Provide real corn stover fermentation effluent for MEC testing (NREL)
7. Further optimize oligomeric sugar concentrations in the fermentation effluent for MEC operation (NREL)

Any proposed future work is subject to change based on funding levels
SUMMARY

**MEC operation**
1. Best MEC performance to date – smallest internal resistance and largest hydrogen production rate to date.
2. Use of non-precious metal catalysts minimize cost.
3. Simplification of MEC performance to avoid vapor feed. Hydrogen gas is accumulated in the gas chamber.
4. Identification of critical reactor architecture element to facilitate scale up.

**Feedstock fermentation**
5. Fermentation effluent using genetically engineered strains demonstrated compatibility with MEC operation (NREL)
6. Real biomass fermentation generates effluent with greater complexity (than sugar fermentation) and will need further optimization

**Industry collaboration**
7. Outreach to large companies for wastewater sample requests and technology transfer (ongoing discussion with Shell, Bishop Water, Catalyst Power) (IWT)