Technology-Enabling Materials and Cell Designs for Reversible PEM Fuel Cells

Nemanja Danilovic
Lawrence Berkeley National Laboratory
6/13/18

Project ID #: FC183

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Overview

Timeline
• Project Start Date: 01/01/2018
• Project End Date: 12/23/2020
• Percent complete: 12.5%

Budget
• Total Project Budget: $400K
  • Total Recipient Share: $0K
  • Total Federal Share: $400K
  • Total DOE Funds Spent*: $33K
* As of 3/31/18

Partners
• Project lead: Danilovic, Weber (LBNL)
• Co-PI: Debbie Myers (ANL)
• Interactions/collaborations:
  – 3M
  – Proton OnSite
  – Molecular Foundry @ LBNL

Barriers
• Barriers addressed
  • No regenerative fuel cell specific barriers, optimization between fuel cell and electrolyzer barriers:
  • Fuel cells
    • Catalyst, Catalyst support and Membrane electrode assembly:
      A: Durability; B: Cost; C: Performance
  • Hydrogen Production
    • Catalyst, Catalyst support and Membrane electrode assembly:
      F: Capital cost; G: System efficiency and electricity cost
Relevance - Objectives

- The main focus of this project is to demonstrate a highly efficient and stable unitized regenerative fuel (URFC) achieved through novel cell operation and engineered supported catalysts.

**DOE Targets from MYRD&D**

<table>
<thead>
<tr>
<th>Specified Parameter</th>
<th>Baseline FC</th>
<th>Baseline Electrolyzer</th>
<th>Baseline URFC</th>
<th>Proposed URFC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane thickness</td>
<td>25</td>
<td>125</td>
<td>125-175</td>
<td>50-60</td>
</tr>
<tr>
<td>Total cell Pt catalyst loading (mg/cm²)</td>
<td>0.4</td>
<td>1</td>
<td>6</td>
<td>0.8</td>
</tr>
<tr>
<td>Ir catalyst loading (mg/cm²)</td>
<td>n/a</td>
<td>2</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>Fuel cell stack efficiency</td>
<td>&gt;50%</td>
<td>n/a</td>
<td>&lt;40%</td>
<td>&gt;60%</td>
</tr>
<tr>
<td>Electrolysis stack efficiency</td>
<td>n/a</td>
<td>~65%</td>
<td>&lt;55%</td>
<td>&gt;75%</td>
</tr>
<tr>
<td>Round trip electrical efficiency (%)</td>
<td>n/a</td>
<td>n/a</td>
<td>&lt;25%</td>
<td>&gt;45%</td>
</tr>
</tbody>
</table>

**LBNL/ANL Targets**

<table>
<thead>
<tr>
<th>Specification</th>
<th>Baseline FC</th>
<th>Baseline Electrolyzer</th>
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<tr>
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<td>n/a</td>
<td>&lt;25%</td>
<td>&gt;45%</td>
</tr>
</tbody>
</table>
Relevance - Project Goal

- Show feasibility of fixed polarity unitized regenerative fuel cell (URFC) and engineered bifunctional OER/HOR catalyst

### Electrode Fuel Cell Mode Electrolyzer mode

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Fuel Cell Mode</th>
<th>Electrolyzer mode</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Anode</strong></td>
<td>Hydrogen oxidation reaction (HOR) ( \text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- )</td>
<td>Oxygen evolution reaction (OER) ( \text{H}_2\text{O} \rightarrow 2\text{H}^+ + \frac{1}{2} \text{O}_2 + 2\text{e}^- )</td>
</tr>
<tr>
<td><strong>Cathode</strong></td>
<td>Oxygen reduction reaction (ORR) ( \frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O} )</td>
<td>Hydrogen evolution reaction (HER) ( 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 )</td>
</tr>
</tbody>
</table>

Traditional URFC

- **Anode**: Hydrogen oxidation reaction (HOR) \( \text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- \)
- **Cathode**: Oxygen evolution reaction (OER) \( \text{H}_2\text{O} \rightarrow 2\text{H}^+ + \frac{1}{2} \text{O}_2 + 2\text{e}^- \)

Proposed URFC

- **Anode**: Hydrogen oxidation reaction (HOR) \( \text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- \)
- **Cathode**: Oxygen evolution reaction (OER) \( \text{H}_2\text{O} \rightarrow 2\text{H}^+ + \frac{1}{2} \text{O}_2 + 2\text{e}^- \)

**1-2 nm ALD Pt & Ir**

**20-40nm Transition metal carbide/nitride nanoparticle**
Relevance – Energy Storage

• An URFC is an energy storage device which stores electricity in the form of H$_2$ & O$_2$ gas and producing electricity

• Advantages:
  • Combine balance of plant and cell, and MEA materials of discrete systems
  • Energy density (>400 kWh/kg)
  • Scalable storage (H$_2$, w/ or w/o O$_2$)
  • High current density (up to 2A/cm$^2$)
  • No corrosive or toxic substances

• Disadvantages:
  • Durability
  • Performance and cost
  • Technical maturity vs discrete counterparts
  • Switching time
## Approach

### LBNL

Show feasibility of URFC approach in MEA testing

- Use state of the art PEM fuel cell and electrolysis materials
  - N212 <-> N117
  - Pt/C: HER/ORR
  - Pt and Ir black: HOR/OER
- Develop application relevant cycling protocol
- Track technoconomics of device

### ANL

Show feasibility of engineered supported catalyst approach

- Develop ALD deposition process
- Characterize *activity* and *stability* of supported bifunctional catalyst vs baseline materials for HOR, OER and cycling
Approach - Tasks

- Task 1: Oxygen evolution reaction/ Hydrogen oxidation reaction catalyst development

- Task 2: Membrane electrode assembly development and testing

- Task 3: Cyclability and durability (Phase 2)

- Task 4: Cost analysis (Phase 2)

<table>
<thead>
<tr>
<th>Task</th>
<th>Lead</th>
<th>Y1 Q1</th>
<th>Y1 Q2</th>
<th>Y1 Q3</th>
<th>Y1 Q4</th>
<th>Y2 Q1</th>
<th>Y2 Q2</th>
<th>Y2 Q3</th>
<th>Y2 Q4</th>
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<tbody>
<tr>
<td>Task 1</td>
<td>ANL</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Task 2</td>
<td>LBL</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Task 3</td>
<td>LBL</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Task 4</td>
<td>LBL/ANL</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>
Approach - Milestones

• Phase 1 Milestones

<table>
<thead>
<tr>
<th>Progress measures</th>
<th>Type</th>
<th>Deliverable</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q1-3/31/2018</td>
<td>Progress measure</td>
<td>Definition of technical targets, and parameters for techno-economic tracking</td>
<td>Complete</td>
</tr>
<tr>
<td>Q2-6/31/2018</td>
<td>Progress measure</td>
<td>Flow battery station modified to operate between fuel cell and electrolysis modes using LabView software</td>
<td>On track</td>
</tr>
<tr>
<td>Q3-9/30/2018</td>
<td>Progress measure</td>
<td>Pt, IrO₂ and Pt-IrO₂ coatings on high-surface-area carbide or nitride supports evaluated for OER and HOR activity in aqueous electrolyte testing</td>
<td>On track</td>
</tr>
<tr>
<td>Q4-12/30/2018</td>
<td>Milestone</td>
<td>Pt, Ir and Pt-Ir alloy catalysts baselined under RDE and MEA experimental conditions in discrete fuel cell (HOR) and electrolysis (OER) modes</td>
<td>On track</td>
</tr>
<tr>
<td></td>
<td>Go/No-Go</td>
<td>Pt-IrO₂ on high-surface-area carbide or nitride support exhibits OER and HOR overpotentials at 10 mA/cm² within 100 mV of state-of-the-art unsupported IrO₂ and Pt/C OER and HOR electocatalysts and &lt;50 mV increase in overpotential after 5,000 cycles between OER and HOR modes.</td>
<td>On track</td>
</tr>
</tbody>
</table>
Task 1 – HOR/OER Catalyst Development

Approach:

- Bifunctional HOR and OER catalyst needs to withstand cycles between 0.1 and 1.7 V while it undergoes HOR and OER, respectively.

- Lower limit of loading in MEA will be limited by activity and distribution of unsupported catalysts, need:
  - Stable electrocatalyst supports
  - Low loading, active and stable Pt and IrO₂ catalyst

Pre-project result: RDE testing of physical mixtures of Pt and IrO₂ or RuO₂.
Task 1-HOR/OER Catalyst Development

Approach:

• ANL collaborators Debbie Myers and Jeff Elam will engineer a supported bifunctional electrocatalyst using ALD

• Proposed catalysts: Thin Films of Pt-IrO$_x$ on corrosion resistant high-surface-area support
  • Supports are transition metal carbides and/or nitrides chosen to have high electronic conductivity, corrosion resistance, and strong and favorable interactions with Pt and Ir and stability in the catalytic environment
  • Preferred method for forming thin film of catalytic metals is atomic layer deposition (ALD) which can result in thin conformal films and strong interactions with support
  • ALD system at Argonne can coat powders at kilogram scale

Accomplishment
Test matrix for baseline catalysts

<table>
<thead>
<tr>
<th>Material</th>
<th>Fuel Cell</th>
<th>Electrolyzer</th>
<th>URFC</th>
</tr>
</thead>
<tbody>
<tr>
<td>ORR catalyst</td>
<td>Pt46wt% /C</td>
<td>n/a</td>
<td>Pt46wt%/C</td>
</tr>
<tr>
<td>HOR catalyst</td>
<td>Pt46wt% /C</td>
<td>n/a</td>
<td>Pt black</td>
</tr>
<tr>
<td>OER catalyst</td>
<td>n/a</td>
<td>Ir black, IrO$_2$/TiO$_2$</td>
<td>Ir black, IrO$_2$/TiO$_2$</td>
</tr>
<tr>
<td>HER catalyst</td>
<td>n/a</td>
<td>Pt46wt%/C</td>
<td>Pt46wt%/C</td>
</tr>
</tbody>
</table>
Task 2 – MEA development and testing

Approach:

• URFC membrane electrode assembly (MEA) and gas diffusion layers (GDLs) need to allow for efficient feed of reactants and removal of products within discrete modes and cyclic operation

• Fixed polarity electrodes optimize for gas and water management on ORR electrode

• Proposed URFC cell shown with baseline bifunctional catalysts:
Task 2: MEA development and testing

Approach:
- In cell water management as important as catalyst selection
- Determine target cell catalyst and diffusion layers
- Cell optimization to start with baseline materials and flowfields in discrete modes of operation, before cycling operation

Accomplishment
Identified baseline MEA and cell components

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Fuel Cell Mode</th>
<th>Electrolyzer mode</th>
<th>Catalyst support and loading</th>
<th>Diffusion layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode</td>
<td>HOR: H₂ → 2H⁺ + 2e⁻</td>
<td>OER: H₂O → 2H⁺ + ½ O₂ + 2e⁻</td>
<td>Baseline: Pt-IrO₂ blacks, BP2: ANL catalyst</td>
<td>0.4 mg/cm² Pt, 1 mg/cm² Ir, Sintered titanium porous transport layer</td>
</tr>
<tr>
<td>Cathode</td>
<td>ORR: ½ O₂ + 2H⁺ + 2e⁻ → H₂O</td>
<td>HER: 2H⁺ + 2e⁻ → H₂</td>
<td>Pt 46wt% @ C</td>
<td>0.4 mg/cm² Pt, Carbon paper with microporous layer</td>
</tr>
</tbody>
</table>
Task 3 (BP2) – Cyclability and Durability

Approach

• Preliminary data on physical mixtures of Pt-IrO$_2$ shows good stability between HOR/OER cycles

Pre-project result: RDE cycling of Pt-IrO$_2$ between HOR and OER

• Cycling and durability ASTs to be defined by operating use case and TEA analysis
Task 4 (BP2) – Cost Analysis

Approach:

• Opex and Capex of URFC will be defined and tracked
• To help define the competitive market and storage time/current density required
• Cell materials costs to be tracked based on catalyst loading GDLs and membrane

ALD Systems at Argonne

Beneq TFS500 – up to 20” 3D chamber, larger substrates, scale-up
Technical Accomplishments – URFC test stand

• A Fuel Cell Technologies fuel cell stand was retrofitted for use with this project and integrated with a DC power supply, water bath and pump

• A work planning and control document was written and a successful safety review held for the test stand
Technical Accomplishments – TEA Cost Analysis Protocol Definitions

• Framework for technoeconomic analysis established
• Comparison of discrete system component costs with URFC to be tracked over length of project

<table>
<thead>
<tr>
<th>Component</th>
<th>FC‡</th>
<th>ELEC</th>
<th>URFC§</th>
</tr>
</thead>
<tbody>
<tr>
<td>System ($/kW)</td>
<td>50</td>
<td>900‡</td>
<td></td>
</tr>
<tr>
<td>Stack Cost ($/kW)</td>
<td>22</td>
<td>423‡</td>
<td></td>
</tr>
<tr>
<td>Catalyst+Application (%)*</td>
<td>41</td>
<td>43¶</td>
<td></td>
</tr>
<tr>
<td>Membrane (%)*</td>
<td>12</td>
<td>11¶</td>
<td></td>
</tr>
<tr>
<td>MEA Frame/Gasket (%)*</td>
<td>6</td>
<td>4¶</td>
<td></td>
</tr>
<tr>
<td>Porous transport layer/Gas diffusion layer (%)*</td>
<td>9</td>
<td>19¶</td>
<td></td>
</tr>
<tr>
<td>Bipolar Plates (%)*</td>
<td>25</td>
<td>23¶</td>
<td></td>
</tr>
<tr>
<td>Balance of stack (%)*</td>
<td>11</td>
<td>21¶</td>
<td></td>
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</tbody>
</table>

* Percent of stack cost  
‡ Based on DOE projections from 2017 Hydrogen and Fuel Cells Program Record.  
‡ Based on TEA from Strategic Analysis presented at Electrolyte Hydrogen Production Workshop 2014.  
¶ Based on TEA from Strategic Analysis of H2 Production Pathways, 2013.
## Collaboration & Coordination

<table>
<thead>
<tr>
<th>Entities</th>
<th>Role</th>
<th>Type</th>
<th>Relationship with FCTO</th>
<th>Extent of collaboration</th>
</tr>
</thead>
<tbody>
<tr>
<td>LBNL</td>
<td>Prime</td>
<td>Federal Lab</td>
<td>Within</td>
<td></td>
</tr>
<tr>
<td>ANL</td>
<td>Sub</td>
<td>Federal Lab</td>
<td>Within</td>
<td>Catalyst development and design</td>
</tr>
<tr>
<td>Proton OnSite</td>
<td>In kind</td>
<td>Industry</td>
<td>Within</td>
<td>Materials supplier</td>
</tr>
<tr>
<td>3M</td>
<td>In kind</td>
<td>Industry</td>
<td>Within</td>
<td>Materials supplier</td>
</tr>
</tbody>
</table>
Remaining Challenges and Barriers

• Cost of Pt and Ir catalysts
  • With optimization of the electrode structure we expect a net decrease in PM use (cost) over discrete systems
  • Key is a supported catalyst, using inexpensive support
  • Use of core-shell structures on cathode side will also reduce PM loading

• Stability of Pt and Ir under cycling between operating modes
  • Preliminary testing has shown stability equivalent to current fuel cell/electrolyzer components

• Water management
  • Challenges of water management may remain even with more optimal GDL/PTL layout in proposed design
  • May necessitate other strategies to manage water in cell

• Safety of H₂ storage and operation with O₂ presence
  • Pressurized storage of hydrogen has a strong industrial track record
  • URFC can be designed to output pressurized H₂ (compressor is unnecessary, saving compression energy)
  • Industrial collaborator has assured us that there are no technical or safety obstacles to proposed URFC
Proposed Future Work

• Screen HOR/OER activity and stability in RDE
• Deposit ALD $\text{Pt}_x\text{Ir}_{1-x}$ alloys on TiN and screen in RDE
• Baseline MEA and cell operation
  • Vary anode catalysts and test in discrete operation
  • Vary flowfields with discrete MEAs
  • Evaluate cycling of URFC MEA in down-selected cell hardware
  • Evaluate performance/durability of traditional vs proposed URFC concept
• Evaluate different HOR/OER activity catalysts in URFC MEA and cell
• Track performance and cell costs for TEA

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

• Relevance
  • URFCs energy storage devices that decouple storage from conversion, are enablers for intermittent renewable energy
  • Proposed URFC design could enable active and durable energy storage at low cost

• Approach
  • Address barriers to URFC deployment: Durability and Cost
  • The main focus of this project is to demonstrate a highly efficient and stable URFC achieved through novel cell operation and engineered supported catalysts
    • LBNL: Focus on showing feasibility of the MEA and proposed constant polarity URFC cell vs discrete and traditional cells
    • ANL: Focus on showing feasibility of Pt-Ir coated TiN supports with ALD

• Technical Accomplishments
  • Test stand: Modified and safety review completed, testing protocols established
  • TEA: Defined materials and performance metrics

• Collaborations
  • ANL: sub on project will screen materials and produce novel supported catalysts for MEA integration
  • Established collaborations with two industrial partners
    • Proton OnSite (NEL): Provided catalysts for preliminary testing and for MEA screening
    • 3M: Discussions around utilizing NSTF based MEAs

• Proposed Future Work
  • ANL: Catalysts screening w/ RDE and supported catalyst development
  • LBNL: MEA testing, cell optimization and URFC cycling
Acknowledgments

• Department of Energy for support
• Adam Weber
• Yagya Regmi
• Debbie Myers
• Jeff Elam