Advanced Catalysts and MEAs for Reversible Alkaline Membrane Fuel Cells

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Newton, MA

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DOE Catalyst Work Group Meeting

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Project Overview

Timeline
• Project Start Date: June 1, 2015
• Project End Date: May 31, 2017

Budget
• Total $1,200,496
  - DOE share $959,334
  - Contractors share $241,162

Collaborators
• SUNY-Buffalo:
  Prof. Gang Wu
• NREL
  Dr. Bryan Pivovar

Barriers Addressed
• Activity (catalyst; MEA)
• Durability (catalyst; MEA)
• Cost (catalyst; MEA)

Technical Targets
• Design and develop ORR/OER bi-functional oxide catalysts
• Integrate ORR/OER bifunctional oxide catalysts and alkaline membranes to develop highly efficient reversible alkaline membrane fuel cells (AMFCs) for stationary energy storage
Comparison of Energy Storage Devices

Reversible fuel cells may have higher energy density than most batteries

Source: US Defence Logistics Agency

http://www.mpoweruk.com/performance.htm
Reversible Fuel Cells

- Water electrolyzer is an ideal device to store energy from windmills and solar farms, where surplus (off peak) energy is nearly free.
- Stored H₂ can be used for fuel cells to generate electricity in peak time.
**Research Objective**

### Opportunities
- Non PGM based catalysts drives down capital cost;
- New concepts for oxide catalyst design;
- Surplus electricity from renewable energy;
- Gradual maturity of AEM technology

### Challenges
- Non-PGM bi-functional oxide catalyst activity and stability;
- Fabrication of non-PGM MEAs for AEM fuel cells NOT extensively studied;
- Unitized regenerative fuel cell design and construction

Integrate AEM water electrolyzer and fuel cell together to develop reversible AEM fuel cell for energy storage and conversion
Technical Approaches

- Catalyst Long-term Stability;
- MEA Fabrication Technology
Performance Schedule

Task-1. Design and Develop Perovskite and Spinel Based ORR/OER Catalysts
   Task-1.1. Develop Oxygen-Deficiency Perovskite Oxide Catalysts
   Task-1.2. Develop Spinel Oxide Catalysts

Task-2. Screen Catalysts Towards High ORR/OER Activity and Characterize Their Structure and Composition
   Task-2.1 Screen Catalysts Via RDE
   Task-2.2. Characterize Structure and Compositions of Selected Catalysts

Task-3. Provide Advanced Anion-Exchange Ionomer and Membranes Structure and Composition

Task-4. Design Perovskite and Spinel Based Electrode and MEAs

Task-5. Evaluate the Performance and Durability of MEAs
   Task-5.1. Test the Performance of MEAs Made of Advanced Catalyst and Membranes
   Task-5.2. Test Durability of Selected MEAs (500 hrs for Both Fuel Cell and Electrolyzer)

Task-6. Evaluate Catalyst and System Economics
**Task 1-1: Design Perovskite ORR/OER Catalysts (SUNY)**

Oxygen-Deficient $h$-BaTiO$_{3-x}$

- Perovskite oxide catalysts have emerged as the most promising bifunctional ORR/OER catalysts.
- Controlled oxygen vacancies in the perovskite crystal structure by varying vacuum degrees and temperatures will maximize catalytic activity along with stability.
Task 1-2: Develop Spinel ORR/OER Catalysts (Giner)

Two categories of nanostructured spinel oxides: CoFe$_2$O$_4$ and M$_x$Co$_{1-x}$Fe$_2$O$_4$ (M could be Cu, Ni, Mn or other metals)

- Composition and ball milling process conditions will be varied to achieve optimized activity and stability

Task 2: Screen Catalysts and Characterize their Structure and Composition (Giner and SUNY)

Electrochemical Tests

Auto-Lab_Impedance

<table>
<thead>
<tr>
<th>Techniques to be used</th>
<th>Information to be gained</th>
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<tbody>
<tr>
<td>XRD</td>
<td>Particle size and crystal structure</td>
</tr>
<tr>
<td>SEM</td>
<td>Catalyst morphology</td>
</tr>
<tr>
<td>TEM</td>
<td>Catalyst structure and particle size</td>
</tr>
<tr>
<td>XPS</td>
<td>Catalyst surface species</td>
</tr>
</tbody>
</table>

- The synthesized catalysts will be first screened by rotating disk electrode (RDE) for the ORR and OER activity in alkaline solution
- Oxide based catalysts will be extensively characterize to establish the correlation of synthesis-structure-properties
Task 3: Provide Advanced Anion Exchange Ionomer and Membranes (NREL)

Reaction scheme developed to synthesize novel PF AEMs (left). PF-FP is the sulfonyl fluoride precursor (right).

<table>
<thead>
<tr>
<th>R</th>
<th>Linkage</th>
<th>DFT Hydroxide Stability (kcal/mol)</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Benzyl CH$_2$</td>
</tr>
<tr>
<td>PF-SFP</td>
<td>Amide</td>
<td>NA</td>
</tr>
<tr>
<td>PF-OCH$_3$</td>
<td>Amide</td>
<td>23.4</td>
</tr>
<tr>
<td>PF-OCH$_3$</td>
<td>Aryl</td>
<td>22.1</td>
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- NREL has substantial experience in developing components of AMFCs.
- Integrate advanced catalysts with novel ionomers at developed NREL.
Task 4: Design Perovskite and Spinel-Based Electrode and MEAs (Giner and NREL)

Use Giner’s proprietary water management membrane (WaMM) to build reversible fuel cells

- MEA design using perovskite or spinel catalysts
- Compatibility between catalyst and anion exchange ionomers (catalyst wettability and dispersion)

Advantages of WaMM-based static feed electrolyzer:
- Since no liquid water is involved, water-flooding will be mostly minimized;
- No gas/water separators required to improve simplicity/reliability of fuel cells;
- Only using water vapor mitigates the effect of impurity of water
Task 5: Evaluate the Performance and Durability of MEAs (Giner)

Performance Test
- Polarization curves
- HFR resistance
- Membrane crossover

Durability Test
- Voltage cycling
- Constant current density of 600 mA/cm² for 1000 hours
Task 6: Evaluate Catalyst and System Economics (Giner +NREL)

• Cost of all catalysts will be analyzed in the context of a small-scale, short production as well as a commercial mass production.

• Cost of fuel/electrolyzer system will be analyzed. The analysis will take into consideration factors including materials cost, labor, and facilities.

• The effect of OER/ORR catalysts on the system efficiency (round-trip efficiency) will also be evaluated.
## Milestones

<table>
<thead>
<tr>
<th>Time</th>
<th>Milestone Description</th>
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<tbody>
<tr>
<td>Q1</td>
<td>Synthesize BaTiO$_{3-x}$ perovskites with 3 different oxygen vacancy concentrations</td>
</tr>
<tr>
<td>Q2</td>
<td>Prepare 3 other oxygen-deficient AA’BB’O$<em>{3-x}$ multiple perovskite catalysts (e.g., BaSrCoFeO$</em>{3-x}$ or BaSrMnCrO$_{3-x}$) with optimized defect structures</td>
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<tr>
<td>Q3</td>
<td>Reduce perovskite particle size to nanoscale (&lt;10 nm) with much increased surface areas (&gt;20 m$^2$/g)</td>
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<tr>
<td>Q3</td>
<td>Prepare 3 A$<em>x$B$</em>{1-x}$C$_2$O$_4$ spinel catalysts (A, B and C represent Co, Mn, Fe or other Metals) with particle size &lt;10nm</td>
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<tr>
<td>Q4</td>
<td>In RDE, demonstrate ORR activity &gt; 1 mA/mg oxide at IR-free 0.9 V; and OER activity &gt; 15 mA/mg oxide at IR free 1.6 V.</td>
</tr>
<tr>
<td>Q4</td>
<td>Provide 20g of PF AEM material in membrane/ ionomer form Membrane conductivity &gt;0.05 S/cm at 60°C and 100% RH; H$_2$ permeability: 10$^{-12}$ mol/(kPa.s.cm)</td>
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<tr>
<td>Q5</td>
<td>3 AEI ionomer categories and 5 ionomer loadings will be evaluated to identify the best electrode composition</td>
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<td>Q6</td>
<td>Achieve RFC performance 0.55V for fuel cell and 1.6V for electrolyzer, both at 600mA/cm$^2$</td>
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<tr>
<td>Q7</td>
<td>Achieve fuel cell and electrolyzer life of 500 hours with less than 10% performance decay</td>
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<td>Q8</td>
<td>Generate a full report of catalyst and reversible fuel cell economics</td>
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Acknowledgments

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- NREL: Dr. Bryan Pivovar