High Temperature Alkaline Water Electrolysis

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Giner Inc.
Newton, MA

June 7, 2017
## Project Overview

### Timeline
- **Project Start Date:** January 1, 2017
- **Project End Date:** December 31, 2020

### Budget
- **Overall:** $1,722,885
  - **DOE share:** $1,375,123
  - **Contractors share:** $347,762
  - **Spent:** $60,363 (as of April 30, 2017)

### Giner Researchers
- Kailash Patil and Winfield Greene

### Collaborator
- Zircar Zirconia, Inc. (Vendor)

### Barriers Addressed for HTWE
- Operating cost: prohibitive electricity consumption for water electrolysis
- Capital cost: associated with PGM or expensive high temperature materials

### Technical Targets
- Composite electrolyte OH⁻ conductivity > 0.3 S/cm in temperature of 350 to 550 °C
- Per-cell area-specific resistance (ASR) of ≤ 0.2 Ohm-cm² at 350 to 550 °C using a membrane thickness of 200 µm.
- Stack electrical efficiency > 90% LHV H₂ with current density at 1.2 A/cm²
# High Temperature Alkaline Water Electrolysis

DOE: Distributed Forecourt Water Electrolysis Hydrogen Production

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Units</th>
<th>2011 Status</th>
<th>2015 Target</th>
<th>2020 Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Levelized Cost (^d) (Production Only)</td>
<td>$/kg</td>
<td>4.20 (^d)</td>
<td>3.90 (^d)</td>
<td>2.30 (^d)</td>
</tr>
<tr>
<td>Electrolyzer System Capital Cost</td>
<td>$/kg</td>
<td>0.70 (^e,f)</td>
<td>0.50 (^f)</td>
<td>0.50 (^f)</td>
</tr>
<tr>
<td></td>
<td>$/kW</td>
<td>430</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>System Energy Efficiency (^g)</td>
<td>% (LHV)</td>
<td>67</td>
<td>72</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>kWh/kg</td>
<td>50</td>
<td>46</td>
<td>44</td>
</tr>
<tr>
<td>Stack Energy Efficiency (^h)</td>
<td>% (LHV)</td>
<td>74</td>
<td>76</td>
<td>77</td>
</tr>
<tr>
<td></td>
<td>kWh/kg</td>
<td>45</td>
<td>44</td>
<td>43</td>
</tr>
<tr>
<td>Electricity Price</td>
<td>$/kWh</td>
<td>From AEO 2009(^i)</td>
<td>From AEO 2009(^i)</td>
<td>0.037(^j)</td>
</tr>
</tbody>
</table>
Feedstock costs (electricity) consists of 50% of total cost: energy costs of $3.09/kg $H_2$, 2x higher vs. DOE 2020 total cost target, $1.60/kg $H_2$

High-temperature electrolysis offer the advantage of lower energy requirements due to both higher kinetics and greatly reduced equilibrium voltages.
Technical Approaches

**Key to Success**
- Porous metal oxide matrices resistant to molten hydroxides
- Microstructures of the porous oxide matrices determine whether they can successfully retain molten hydroxides - thickness, porosity and pore structures

**Major Advantages**
- Flexible temperatures-intermediate T compared to PEM and SO system)
- Less expensive materials
# Tasks and Performance of Schedule

| ID | Task Name                                      | Period 1                                      | Period 2                                      |
---|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| 1 | Task 1: Develop alumina and zirconia matrices | Q1 → Q2 → Q3 → Q4 → Q5 → Q6 → Q7 → Q8 → Q9 → Q10 | Q11 → Q12                                    |
| 2 | 1.1 Develop LiAlO₂ Matrix                     |                                              |                                              |
| 3 | 1.2 Prepare ZrO₂ and YSZ Matrix               |                                              |                                              |
| 4 | Task 2: Impregnate hydroxides into porous matrices |                                             |                                              |
| 5 | 2.1 Electrolyte impregnating                 |                                              |                                              |
| 6 | 2.2 OH⁻ conductivity measurement              |                                              |                                              |
| 7 | 2.3 Electrolyte structure characterization     |                                              |                                              |
| 8 | 2.4 Wettability and Capillary Pressure        |                                              |                                              |
| 9 | Task 3: Select anode and cathode catalysts    |                                              |                                              |
| 10| 3.1 Anode catalyst                            |                                              |                                              |
| 11| 3.2 Cathode catalyst                          |                                              |                                              |
| 12| Task 4: Assemble and test 25 cm² single cells |                                              |                                              |
| 13| 4.1 Single cell fabrication                   |                                              |                                              |
| 14| 4.2 Crossover Measurement                     |                                              |                                              |
| 15| 4.3 Performance test                          |                                              |                                              |
| 16| 4.4 Durability test                           |                                              |                                              |
| 17| Task 5: Construct and test 1.8-KW electrolyzer stack |                             |                                              |
| 18| 5.1 Design parameter                          |                                              |                                              |
| 19| 5.2 Component selection                       |                                              |                                              |
| 20| 5.3 Stack Fabrication                         |                                              |                                              |
| 21| 5.4 Stack Test                                |                                              |                                              |
| 22| Task 6: Perform systematic and economic analysis |                                          |                                              |
| 23| Program Management                            |                                              |                                              |
## Milestones

### Milestone Summary Table

**Project Title:** High Temperature Alkaline Water Electrolysis

<table>
<thead>
<tr>
<th>Task No.</th>
<th>Task Title or Subtask Title</th>
<th>Milestone Type</th>
<th>Milestone Number</th>
<th>Milestone Description</th>
<th>Milestone Verification Process</th>
<th>Anticipated Date</th>
<th>Anticipated Quarter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Develop alumina and zirconia matrices</td>
<td>Milestone</td>
<td>M1-1</td>
<td>Produce five LiAlO₂ matrices with various porosity (50-80%) and thickness (200-300 µm)</td>
<td>Using tape-casting technique, pore size, 20-200 nm pores &gt;50%</td>
<td>M3</td>
<td>Q1</td>
</tr>
<tr>
<td>1</td>
<td>Develop alumina and zirconia matrices</td>
<td>Milestone</td>
<td>M1-2</td>
<td>Produce six ZrO₂ and YSZ matrices with various porosity (50-80%) and thickness (200-300 µm)</td>
<td>Using tape-casting technique 20-200 nm pores &gt; 50%</td>
<td>M6</td>
<td>Q2</td>
</tr>
<tr>
<td>2</td>
<td>Impregnate hydroxides into porous matrices</td>
<td>Milestone</td>
<td>M2-1</td>
<td>Downselect at least six composite electrolytes with OH⁻ σ &gt; 0.1 S/cm</td>
<td>Using AC Impedance at 350 to 550 °C</td>
<td>M8</td>
<td>Q3</td>
</tr>
<tr>
<td>2</td>
<td>Impregnate hydroxides into porous matrices</td>
<td>Milestone</td>
<td>M2-2</td>
<td>Downselect at least four composite electrolyte membranes with ASR &lt;0.2 Ohm·cm²</td>
<td>Using 4-probe resistance measurement, at 350 to 550 °C</td>
<td>M12</td>
<td>Q4</td>
</tr>
<tr>
<td>3</td>
<td>Select anode and cathode catalysts</td>
<td>Milestone</td>
<td>M3-1</td>
<td>Synthesized four OER catalysts with particle size &lt; 20 nm, activity comparable to Ir black</td>
<td>Using hydrothermal approach for synthesis and XRD for particle size</td>
<td>M15</td>
<td>Q5</td>
</tr>
<tr>
<td>3</td>
<td>Assemble and test 25-cm² single cells</td>
<td>Milestone</td>
<td>M4-1</td>
<td>Complete testing at least 5, 25 cm² cells with composite electrolytes</td>
<td>Using Giner corrosion-resistant hardware</td>
<td>M15</td>
<td>Q5</td>
</tr>
<tr>
<td>4</td>
<td>Assemble and test 25-cm² single cells</td>
<td>Go/No-Go decision</td>
<td>M4-2</td>
<td>Achieve single cell performance V &lt; 1.50 V at 1.0 A/cm² or 1.4 V at 0.5 A/cm²</td>
<td>Using polarization curves</td>
<td>M18</td>
<td>Q6</td>
</tr>
<tr>
<td>4</td>
<td>Assemble and test 25-cm² single cells</td>
<td>Milestone</td>
<td>M4-3</td>
<td>Achieve 300-h durability test at 0.5 A/cm² for 300 hours with a degradation rate &lt; 0.1 V/1000 hours</td>
<td>Using constant current at 0.5 A/cm²</td>
<td>M21</td>
<td>Q7</td>
</tr>
<tr>
<td>5</td>
<td>Construct and test electrolyzer stack</td>
<td>Milestone</td>
<td>M5-1</td>
<td>Complete design of the stack</td>
<td>Using CAD and solid works</td>
<td>M24</td>
<td>Q8</td>
</tr>
<tr>
<td>5</td>
<td>Construct and test electrolyzer stack</td>
<td>Milestone</td>
<td>M5-2</td>
<td>Complete construction of the stack</td>
<td>Using selected components</td>
<td>M27</td>
<td>Q9</td>
</tr>
<tr>
<td>5</td>
<td>Construct and test electrolyzer stack</td>
<td>Milestone</td>
<td>M5-3</td>
<td>Achieve stack electrical efficiency &gt; 90% LHV H₂ at 1.0 A/cm²</td>
<td>Using I-V polarization curves</td>
<td>M30</td>
<td>Q10</td>
</tr>
<tr>
<td>5</td>
<td>Construct and test electrolyzer stack</td>
<td>Milestone</td>
<td>M5-4</td>
<td>Demonstrate degradation rate of &lt; 0.1 V/500 hours at ~0.5 A/cm²</td>
<td>Measuring voltage at constant current</td>
<td>M33</td>
<td>Q11</td>
</tr>
<tr>
<td>6</td>
<td>Perform systematic and economic analysis</td>
<td>Milestone</td>
<td>M6-1</td>
<td>Deliver a 5-page cost analysis for developed supports and catalysts</td>
<td>Using small-scale short production</td>
<td>M36</td>
<td>Q12</td>
</tr>
</tbody>
</table>
Project Flow Chart

Develop Ceramic Matrices (Alumina and Zr-based matrices) → Impregnated Selected Hydroxide into Porous Matrices → Select Anode and Cathode Catalysts

High Temperature Alkaline Water Electrolysis

Performance Test

Perform System and Economic Analysis-Materials Cost and System Efficiency

- Matrix Long-term Stability;
- Electrolyte Matrix and Electrode Fabrication Technology
Accomplishment 1: Stability of Metal Oxides in Hydroxide System

<table>
<thead>
<tr>
<th>No.</th>
<th>Metal oxides</th>
<th>Surface Area (m²/g)</th>
<th>Hydroxide system</th>
<th>Single/ Eutectic Composition</th>
<th>Melting Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Baseline α-Al₂O₃</td>
<td>7-9</td>
<td>LiOH</td>
<td>100</td>
<td>462</td>
</tr>
<tr>
<td>2</td>
<td>MO-1</td>
<td>5-20</td>
<td>LiOH-NaOH</td>
<td>52-48</td>
<td>~300</td>
</tr>
<tr>
<td>3</td>
<td>MO-2</td>
<td>10-15</td>
<td>LiOH-KOH</td>
<td>62-38</td>
<td>~325</td>
</tr>
<tr>
<td>4</td>
<td>MO-3</td>
<td>13-19</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Approach: Metal oxide immersed in molten Hydroxides

- Heat treated at 450-550°C for 10 h
- Washed and Dried at overnight

Characterizations

- Baseline MO powder
- α-Al₂O₃ powder after immersed in LiOH
- α-Al₂O₃ powder after immersed in molten LiOH-NaOH

- The baseline metal oxide (α-Al₂O₃) shows significant particle changes after immersion test
- in Rod-shape structure was observed in α-Al₂O₃ powder after immersed in single or binary hydroxide melts
Stability of Metal Oxide in Hydroxide System (II)

- No significant morphological changes was observed in MO-1 and MO-2 powders after immersed in single or binary hydroxide melts.
- MO-1 and MO-2 powders showed stable morphology at 450 or 550 °C during immersed time of 10 h.
The MO-3 powder shows stable morphology after immersion in both LiOH or LiNa hydroxide systems.

- Stability of Metal Oxide in Hydroxide System (III)

- MO-3 powder after immersed in LiOH
  - As received powder
  - At 550°C for 10 h

- MO-3 powder after immersed in molten LiOH-NaOH
  - At 450°C for 10 h
  - At 550°C for 10 h
Accomplishment 2: Measurement of OH⁻ Conductivity

<table>
<thead>
<tr>
<th>Experimental Metrics</th>
<th>Hydroxide system</th>
<th>Single/Eutectic composition (mol %)</th>
<th>Melting Temperature (°C)</th>
<th>Electrolyte (Wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal Oxide</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metal oxides (MO-1, MO-2, MO-3) and Baseline MO (Al₂O₃)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>-</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>LiOH</td>
<td>100</td>
<td>462</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>NaOH</td>
<td>100</td>
<td>318</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>KOH</td>
<td>100</td>
<td>406</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>LiOH-NaOH</td>
<td>52-48</td>
<td>~300</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>LiOH-KOH</td>
<td>62-38</td>
<td>~325</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>NaOH-KOH</td>
<td>52-48</td>
<td>~225</td>
<td>25</td>
<td></td>
</tr>
</tbody>
</table>

Metal oxide and Hydroxides

Mixture and agate mortar

Pressing Pellet @ 5~10 Ton

Ag paste coated on both side

Sintered @ 650 °C for 2 h

Conductivity measurement:
- Electrochemical Impedance spectroscopy
- Area-Specific resistance

Schematic and Test Assembly for OH⁻ conductivity measurement
Accomplishment 3: Fabrication of Electrodes and Electrolyte Support Matrix

- Tape casting process for Fabrication of Electrodes and Matrix green tape

- Assembled Lab-scale tape casting machine with heating system
- Fabrication of electrodes and matrices will optimized using tape casting process
- Solvent based slurry process will be optimized the green tape of matrices
Fabrication of Electrolyte Support Matrix

Parameters of before and after sintered green sheet matrix

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Matrix Thickness (mm)</th>
<th>Solid content (%)</th>
<th>Solid content (%)</th>
<th>Porosity (%)</th>
<th>Pore size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Green sheet tape</td>
<td>After sintered</td>
<td>before sintered</td>
<td>after sintered</td>
<td></td>
</tr>
<tr>
<td>MO-1</td>
<td>0.6</td>
<td>0.5</td>
<td>69.78</td>
<td>66.57</td>
<td>In progress</td>
</tr>
</tbody>
</table>

Fabrication of MO-1 matrix has been developed and optimized through tape casting process

The SEM images show porous MO-1 matrix after sintered at 550 °C for 2 h in air atmosphere

Porosity and pore size of fabricated matrix will be characterize by Hg-porosimetry technique
SEM images of sintered porous matrices

Pore size distribution of commercial matrices:
- Pore size distribution of metal oxide matrices sintered at 550°C for 2 h in air
- Pores size distribution of commercial matrices showed very narrow pore size structure
- Both matrices showed narrow pore size distribution in the range of 0.09 to 0.14µm
- MO-3 based matrix showed higher porosity compared to baseline matrix

<table>
<thead>
<tr>
<th>Matrices</th>
<th>Median Pore Diameter (µm)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline Matrix</td>
<td>0.0957</td>
<td>59.1840</td>
</tr>
<tr>
<td>MO-3</td>
<td>0.1424</td>
<td>76.1506</td>
</tr>
</tbody>
</table>
Stability of Electrolyte Matrix in Molten Hydroxides

- Physical and chemical properties of metal oxide and molten hydroxides

<table>
<thead>
<tr>
<th>Physical properties of Metal oxide</th>
<th>Hydroxide system</th>
<th>Single/Eutectic composition</th>
<th>Melting Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.</td>
<td>MO Matrix</td>
<td>Surface Area (m²/g)</td>
<td>LiOH</td>
</tr>
<tr>
<td>1</td>
<td>Baseline matrix</td>
<td>7-9</td>
<td>LiOH-NaOH</td>
</tr>
<tr>
<td>2</td>
<td>MO-1</td>
<td>15-20</td>
<td>LiOH-KOH</td>
</tr>
<tr>
<td>3</td>
<td>MO-2</td>
<td>10-15</td>
<td>LiOH-KOH</td>
</tr>
<tr>
<td>4</td>
<td>MO-3</td>
<td>13-19</td>
<td>LiOH-KOH</td>
</tr>
</tbody>
</table>

Experimental plan:
- **Approach**
  - Stability of matrix in hydroxide media
- **Conditions**:
  - Temperatures: 350 to 550 °C
  - Atmospheres: Air and 3%H₂-Ar
- **Characterizations**
  - XRD, SEM, and BET

- Experimental approach is to understand the physical and microstructure stability of electrolyte matrix in molten hydroxide melts

Electrolyte Matrix Immersed in Hydroxide melt
- Heat treated at 350 ~ 550°C for 10 h
- Washed with Water
- Overnight Dried at 100°C
- Characterizations
Accomplishment 4: Button Cell/Single Cell Electrolyzer Assembly

- **Design of Button Cell Electrolyzer Testing:**

  - Complete button cell assembly

  - Anode and Cathode cell frame

  - Anode and Cathode current collector

- **Button Cell capacity**
  - Screening the anode, cathode and electrolyte matrix materials
  - 2” diameter cell testing

- **Single Cell capacity**
  - 5x5 cm or 10x10 cm cell testing

- **Single Cell Testing: Box furnace**

  - 4x4” opening in center of doors. Water will be fed to the electrolyzer cell through four 0.25” ø tubes. These tubes will pass through an insulating block.

  - 3” ø loose-fit holes in both the top and bottom of furnace. A pressure bar will apply a clamping force to the electrolyzer cell through these ports.

  - The customized box furnace for 5x5 cm or 10x10 cm cell testing has been requested to Mellen Company
Summary

- The short term stability of different metal oxides has been performed in single and binary hydroxide melts:
  - The MO-1, 2, and 3 powders showed stable microstructure in molten LiOH-NaOH system at different temperatures
  - Changes in morphology has been observed in baseline powder in both LiOH and LiOH-NaOH melts

- Testing facilities for OH⁻ conductivity measurement and matrix stability in molten hydroxide systems have been assembled

- Lab-scale tape casting machine has been in place for fabrication of the electrodes and electrolyte matrix and green tape of matrix (MO-1) using tape casting process developed

- Commercial baseline matrix and MO-3 matrices have been characterized with pore size distribution and porosity.
  - The ideal pore size distribution is instrumental in retaining the electrolyte for long term operation

- Button electrolyzer cell has been obtained and customized box furnace for 5x5 cm² or 10x10 cm² single cell designed
## Collaborations

<table>
<thead>
<tr>
<th>Institutions</th>
<th>Roles</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Giner Inc. (Giner)</strong></td>
<td>Oversees the project; composite electrolyte development; catalyst selection, button cell, single cell and stack evaluation; cost analysis</td>
</tr>
<tr>
<td>Hui Xu (PI), Kailash Patil, Cortney Mittelsteadt</td>
<td></td>
</tr>
<tr>
<td><strong>Zircar Zirconia Inc.</strong></td>
<td>Vendor for customized metal oxide matrices</td>
</tr>
<tr>
<td><strong>Fuel Cell Energy</strong></td>
<td>Will provide advice on stack assembly (w/o financial commitment)</td>
</tr>
<tr>
<td>Dr. Chao-yi Yuh</td>
<td></td>
</tr>
</tbody>
</table>
Future Plans

- Perform OH⁻ conductivity measurement
- Optimize in-house fabrication of electrolyte matrix
- Perform characterizations of prepared green tape matrix
- Assemble and testing button and single electrolyzer cells with selected HER and OER catalysts
Select Catalysts for Anode (OER) and Cathode (HER)

- **Cathode:** Ni-Al or Ni-Cu alloy catalyst
- **Anode:** $\text{Co}_3\text{O}_4$/CNT or NiCo$_2$O$_4$

- Data validated from low-temperature water electrolysis;
- Elevated temperature enhance electrode kinetics
Acknowledgments

- Financial support from DOE EERE Fuel Cell Technology Office under award # DE-EE0007644

- DOE program manager: Dr. David Peterson

- Giner Personnel
  - Corky Mittelsteadt and Winfield Greene

- Fuel Cell Energy: Dr. Chao-yi Yuh

- University of Connecticut: Prof. Prabhatkar Singh