High-Performance, Long-Lifetime Catalysts for Proton Exchange Membrane Electrolysis

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Giner Inc.
Newton, MA

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Project ID#: PD103

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Project Overview

Timeline
• Project Start Date: 4/24/2013
• Project End Date: 4/23/2015
• Percent Complete: 55%

Budget
• Total Funding Spent: $337,130*
• Total Project Value: $999,983
• Cost Share Percentage: 0% (SBIR)

* as of 3/31/14

Partners
• NREL: Dr. Bryan Pivovar (Co-PI)
• 3M: Dr. Krzysztof Lewinski (Co-PI)

Barriers Addressed
• High precious group metal (PGM) loading (Ir loading >2mg/cm²)
  - Low catalytic activity for oxygen evolution reaction (OER)
• Low system efficiency
  - Significant anode over-potential
• Prohibitive PEM electrolysis cost
- DOE $H_2$ Production Target for Electrolysis

**Technical Targets:** Distributed Forecourt Water Electrolysis

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Units</th>
<th>2015</th>
<th>2020</th>
<th>Giner Status (2013)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Levelized Cost²</td>
<td>$/kg-H_2$</td>
<td>3.90</td>
<td>&lt;2.30</td>
<td>3.64³ (5.11)⁴</td>
</tr>
<tr>
<td>Electrolyzer Cap. Cost</td>
<td>$/kg-H_2$</td>
<td>0.50</td>
<td>0.50</td>
<td>1.30 (0.74)⁵</td>
</tr>
<tr>
<td>Efficiency</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>System %LHV (kWh/kg)</td>
<td></td>
<td>72 (46)</td>
<td>75 (44)</td>
<td>65 (51)</td>
</tr>
<tr>
<td>Stack %LHV (kWh/kg)</td>
<td></td>
<td>76 (44)</td>
<td>77 (43)</td>
<td>74 (45)</td>
</tr>
</tbody>
</table>

¹ 2012 MYRDD Plan. ² Production Only. ³ Utilizing H2A Ver.2. ⁴ Utilizing H2A Ver.3 (Electric costs increased to $0.057/kW from 0.039$/kW). ⁵ Stack Only

- **Objectives**
  - Develop advanced, low PGM loading catalysts for high-efficiency and long lifetime PEM water electrolysis
    - Improved both mass and specific activity
  - Evaluate the impact of newly developed catalysts on the PEM electrolyzer efficiency and cost
    - Materials and system cost analysis
Approaches

- Irridium Black
  - On Support:
    - Sputtering
    - Chemical reduction
    - Mechano-chemical
  - Various Supports (Giner)
  - Nanostructured Thin Film (3M)
- No Support
  - Ag nanowire-aided
  - Irridium Nanotubes (NREL)
- Corrosion and Activity Screening (Giner and NREL)
- Characterization (X-Ray, microscopies..) (NREL)
- Electrolyzer MEA Tests (Giner and 3M)
- Short Production and Cost Analysis (Giner, NREL and 3M)
## Milestones

<table>
<thead>
<tr>
<th>Number</th>
<th>Milestones</th>
<th>Delivery Time</th>
<th>Completion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><strong>SAMPLE PREPARATION</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3 samples of supported catalysts (5g for each)- Giner</td>
<td>10/31/2013</td>
<td>95%*</td>
</tr>
<tr>
<td></td>
<td>5 samples of NSTF based MEAs (2g for each) – 3M</td>
<td>10/31/2013</td>
<td>100%</td>
</tr>
<tr>
<td></td>
<td>5 samples of iridium nanotube catalysts (1g for each)- NREL</td>
<td>10/31/2013</td>
<td>95%*</td>
</tr>
<tr>
<td>2</td>
<td><em>Corrosion/oxidation resistance</em> ≥ 1.8 V</td>
<td>1/31/2014</td>
<td>100%</td>
</tr>
<tr>
<td>3</td>
<td><strong>Performance Metrics</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>PGM &lt; 0.5 mg/cm²</td>
<td>7/31/2014</td>
<td>100%</td>
</tr>
<tr>
<td></td>
<td>1.7 V@ 1A/cm² target</td>
<td>7/31/2014</td>
<td>100%</td>
</tr>
<tr>
<td></td>
<td>&gt; 100 h at 1.5 A/cm²</td>
<td>7/31/2014</td>
<td>100%</td>
</tr>
<tr>
<td>4</td>
<td><strong>Durability</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>&lt; 20 mV drop after 1000 hours at 1.5A/cm²</td>
<td>1/31/2015</td>
<td>Ongoing</td>
</tr>
<tr>
<td>5</td>
<td><strong>Commercialization</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Delivering 100' of roll-to-roll produced catalyst</td>
<td>1/31/2015</td>
<td>Not started yet</td>
</tr>
</tbody>
</table>

* Not 100% completion due to large volume catalyst production needed
### Achievement 1: Various Catalyst Supports (Giner)

<table>
<thead>
<tr>
<th>Material</th>
<th>Conductivity</th>
<th>Electrochemical Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium Carbide</td>
<td>High</td>
<td>Poor</td>
</tr>
<tr>
<td>ITO (90% In$_2$O$_3$: 10% SnO$_2$)</td>
<td>High</td>
<td>Poor</td>
</tr>
<tr>
<td>Titanium Nitride</td>
<td>Medium</td>
<td>Poor</td>
</tr>
<tr>
<td>W-doped TiO$<em>2$ (Ti$</em>{0.9}$W$_{0.1}$O$_2$)</td>
<td>Medium</td>
<td>Good</td>
</tr>
<tr>
<td>TiO$_2$ Nanowire</td>
<td>Low</td>
<td>Good</td>
</tr>
<tr>
<td>Graphitic-Carbon Nitride</td>
<td>Low</td>
<td>Poor</td>
</tr>
<tr>
<td>Beta (β)-Carbon Nitride</td>
<td>Low</td>
<td>Poor</td>
</tr>
</tbody>
</table>

- **Sp$^3$ hybrid orbitals**
- **Sp$^2$ hybrid orbitals**

**Conductivity:** high (>0.1 S/cm); medium (0.001-0.1 S/cm); low: <0.001 S/cm

**Stability:** Voltage cycling performed between 1.2 to 1.8V

- Original Target: β-carbon nitride, but low conductivity and instability
- Good supports for oxygen reduction reaction (ORR) catalysts not necessarily applicable for OER catalysts due to high voltage for electrolysis operations
- Doping TiO$_2$ with other metals (W, or Ta) may gain good conductivity and stability

Nano-sized Ir on various supports have been synthesized via chemical deposition.

Iridium (Ir) on Various Supports

Ir/\text{TiO}_2\hspace{1cm}\text{Nanowires (Ir: 48 w.t.%)}

\text{Ir/W-doped TiO}_2\hspace{1cm}\text{nanoparticles (Ir: 38 w.t.%)}

\text{Ir Black from JM (Ir: 99 w.t.%)}

\text{XRD Spectroscopy}
Catalyst OER Activity and Stability from RDE

**Initial OER Activity**

Scan rate: 50 mV/s; RPM: 1960 rpm; Ir loading: 40-80 µg/cm²; Solution: 0.5M H₂SO₄

- Ir/Ti₀.₉W₀.₁O₂ (TiO₂: W) two times higher activity than baseline Ir black (at 1.8V)
- Ir/Ti₀.₃W₀.₇O₂ also demonstrates good stability during voltage cycling
Achievement 2: Ir/Metal Nanowires (NREL)

- Extended Continuous Nano-Structured Catalysts
- Partial Galvanic Displacement
  - “Thrifting” of the iridium layer
  - Various metal templates (Ag, Ni or Co)
- Ir Loading can be further controlled by acid leaching
Ir/Metal Nanowires Based on Various Templates

**Ag Template**
- IrRu (Ag, 30 wt. %)
- Ir (Ag, 35 wt. %)
- Ir (Ag, 49 wt. %)
- Ir (Ag, 83 wt. %)
- Ir black

**Ni Template**
- IrNi (24 wt. %)
- IrNi (43 wt. %)
- IrNi (64 wt. %)
- Ir black

**Co Template**
- IrCo (22 wt. %)
- IrCo (55 wt. %)
- IrCo (87 wt. %)
- Ir black

- Ir/Co nanowires demonstrates highest activity
- Addition of Ru dramatically improves activity at OER onset
Specific activity of Ir/Co and Ir/Ni NTs essentially independent of displacement level
Mass activity changes reflective of changes in ECAs (measured by Hg underpotential deposition)
Specific OER Activity Vs. OER Activities

Contour lines are of constant mass OER activity (500, 1000, 1500 mA mg_{PGM}^{-1}).

- Ir/Co best activity compared to Ir black
  - 3.8 times specificity greater than Ir black
  - 3 times mass activity greater than Ir black
Ir/Metal Stability after Voltage Cycling

- Voltage cycling from 1.4 V to 1.8V 30,000 cycles, 100mV/sec.
- The lower Ir loading, the higher initial activity, the faster activity decay
- Acid leaching stabilizes the catalyst activity
Achievement 3: IrNTs/IrNWs from Template (Giner)

- Template can be alumina or polycarbonate
- Template is removed by sodium hydrogen oxide solution
- Sintering after template removal is performed to modify structure and property
SEM and TEM of IrNTs

- IrNTs diameter can be 200, 100, 50 or 20nm
  - dependent on alumina pore size
- IrNTs length from 5 to 20 µm
IrNTs OER Activity from RDE

- Ir NTs exhibits 50% higher OER activity than Ir black
- Activity may further improve by altering process conditions (temp., template, precursor)
- Need to compare with NREL Ir/metal nanowires

Scan rate: 50 mV/s
RPM: 1960 rpm
Ir loading: 40-80 µg/cm²
Solution: 0.5M H₂SO₄
Achievement 4: Ir Coated Whiskers on Nano-Structured Substrate (3M)

3M IrNSTF anode demonstrates comparable performance to standard anode but at 1/8 Ir loading and 1/16 PGM loading.

Roll-to-roll web processing
MEA-to-MEA and Cell-to-Cell Performance Reproducibility of Baseline IrNSTF

- Excellent performance is also confirmed by tests at 3M facility;
- Super high current densities (5.7A/cm²) with minimal mass transport limitations

**Experimental Details**

Giner’s proprietary anode flow field and GDLs used for the test

Each graph is a composite of 5 individual tests (10 MEAs total)

Two different cells tested on two test stands (cells were swapped around between test stations)
Impact of Ir Loading on Performance of Ir-NSTF MEAs

• Increasing Ir loading from 0.25 to 0.5mg/cm² barely changes the performance, indicating high activity of Ir/NSTF catalyst

Experimental Details
Same baseline membrane used throughout these experiments

The same catalysts used throughout these experiments (exc. loading)

Electrode catalyst loadings were increased on both anode and cathode at the same levels
Performance Milestone: 100 hours
1.5 A/cm² @ 1.7 V/cell or less

Milestone (by July 2014)
- PGM < 0.5 mg/cm²
- 1.7 V @ 1A/cm² target
- Reaching 100 hour at 1.5 A/cm²

Milestone has been surpassed 3 months earlier than delivery date
### Collaborations

<table>
<thead>
<tr>
<th>Institutions</th>
<th>Roles</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Giner Inc. (Giner)</strong>&lt;br&gt;Hui Xu (PI), Brian Rasimick, Allison Stocks, Tom McCallum</td>
<td>Prime, oversees the project; broad screening of catalyst supports; electrolyzer hardware design and validation; electrolyzer cell tests, cost analysis</td>
</tr>
<tr>
<td><strong>National Renewable Energy Laboratory (NREL)</strong>&lt;br&gt;Bryan Pivovar, Shaun Alia, K. C. Neyerlin</td>
<td>Sub; iridium/metal nanowires development and screening, iridium surface area characterization</td>
</tr>
<tr>
<td><strong>3M Company (3M)</strong>&lt;br&gt;Krzysztof Lewinski, Sean Luopa</td>
<td>Sub; NSTF based catalyst development, electrolyzer cell tests, short production, cost analysis</td>
</tr>
</tbody>
</table>

- Participating institutes maintain active interactions via frequent teleconferences and regular visits for exchanging ideas, providing inputs and updating research progress.
- NREL provides fundamental insights on iridium mass and specific activity via RDE for initial catalyst screening.
- 3M and Giner provide an industry perspective performing benchmarking, durability testing, and large scale MEA fabrication and testing.
Future Research

Focus will be given on MEA tests and catalyst cost analysis for the 2nd year:

- **3M:** Extend MEA durability to 1000 hours

- **NREL and Giner:**
  - Design electrode for developed catalysts: Ir nanotubes, Ir nanowires, and Ir supported on W-doped TiO₂
  - Perform In-situ electrolyzer MEA tests to select one best catalyst
  - Compare the selected catalyst with 3M NSTF catalyst

- Develop economical analysis of materials and system
  - Catalyst and MEA cost from short production
  - Electrolyzer system cost and efficiency
Project Summary

- Ir-based OER catalysts for PEM electrolysis have been successfully synthesized and characterized at NREL, 3M and Giner:
  - Giner: various supports and Ir nanotubes
  - NREL: Ir/metal nanowires
  - 3M: Ir NTSF

- 3M NSTF catalyst demonstrates superior performance:
  - Comparable performance to standard Ir black catalyst but at 1/8 Ir loading
  - 1.675 V at 1.5 A/cm² for 100 hours, with Ir loading < 0.5mg/cm²
  - Significantly exceeding the milestone set for July 2014.

- Giner and NREL: RDE data show promising activity of developed catalysts compared to commercial Ir black:
  - Ir supported on W-doped TiO₂ mass activity increased by 2 times
  - Ir/Co nanowires mass and specific activity increased by 3 times
  - MEA tests ongoing to select one best catalyst to be compare with 3M catalyst
Acknowledgments

- Financial support from DOE under the contract # DE-SC0007471

- DOE Fuel Cell Technologies Office
  - David Peterson
  - Erika Sutherland

- Giner Personnel
  - Monjid Hamden
  - Tim Norman
  - Corky Mittelsteadt

- UMass Lowell for conducting TEM
  - Prof. Zhiyoung Gu
  - Dr. Gao Fan