High Efficiency Solar Thermochemical Reactor for Hydrogen Production

DOE Annual Merit Review
Project ID: PD113

Anthony McDaniel, Ivan Ermanoski
Sandia National Laboratories

June 6, 2017
**Timeline**
- Project Start Date: 10/01/2014
- Project End Date: 09/30/2017*
- Project Complete: 99%

**Budget**
- Total Project Budget: $3.343M
- Total Recipient Share: $0.244M
- Total Federal Share: $3.250M
- Total DOE Funds Spent: $3.250M

**Barriers Addressed**
- S: High-Temperature Robust Materials
- T: Coupling Concentrated Solar Energy and Thermochemical Cycles
- X. Chemical Reactor Development and Capital Costs

**Collaborators**
- German Aerospace Center-DLR, Cologne DE.
- Arizona State University, Tempe AZ.
- Bucknell University, Lewisburg PA.
- Colorado School of Mines, Golden CO.
- Northwestern University, Evanston IL.
- Stanford University, Stanford CA.

*Contingent upon completion of FOA GNG.*
DOE Objective (2015 MYRDDP): Verify the potential for solar thermochemical (STCH) cycles for hydrogen production to be competitive in the long term and by 2020, develop this technology to produce hydrogen with a projected cost of $3.00/gge at the plant gate.

<table>
<thead>
<tr>
<th>Task</th>
<th>Description</th>
<th>SNL Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>High-Temperature, Solar-Driven, Thermochemical Processes</td>
<td>• Quantified conversion efficiency and kinetics of novel STCH materials and derived insight into improving performance.</td>
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<td>• Optimize sub-cycle reactions and verify effective hydrogen production at laboratory scale.</td>
<td>• Developed a fully operational hydrogen producing reactor to verify system performance at ~5 kW.</td>
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<td>• Quantify and verify conversion efficiency and kinetics for reaction cycles.</td>
<td>• Designed a central receiver based hydrogen production plant to investigate how a fully-integrated system can achieve 2020 targeted costs and yields.</td>
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<td>• Develop a viable integrated, solar-driven high-temperature thermochemical water-splitting process.</td>
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<tr>
<td></td>
<td>• Verify an integrated, solar-driven high-temperature thermochemical water-splitting cycle with targeted costs.</td>
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<td></td>
<td>• Develop a solar field configuration and design to match chemical plant requirements.</td>
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<td>• Identify strategies for full integration of solar thermal energy collection and storage with the chemical reaction cycle for thermochemical water-splitting.</td>
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<td></td>
<td>• Verify performance of a semi-integrated system at small scale (5-100 kW).</td>
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<td></td>
<td>• Verify that a fully-integrated system can achieve 2020 targeted costs and yields.</td>
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</table>
**Approach: Project Phases and Milestones**

- **F15Q1** Formulate and synthesize redox active oxides from LaAlO$_3$ (variants of La-Sr-Mn system).
- **F15Q2** Design CPR2 and produce engineering drawings for fabrication.
- **F15Q3** Formulate and synthesize redox active oxides from earth abundant elements (AE, 3dTM) and explore methods for entropy engineering.
- **F15Q4** Acquire 150 kg of CeO$_2$ particles for CPR2 tests.
- **F16Q1** Characterize thermodynamic, kinetic, and other relevant properties of newly synthesized materials.
- **F16Q2** Design CPR2 and produce engineering drawings for fabrication.
- **F16Q3** Design and construct ~20kW$_{\text{ele}}$ solar simulator for CPR2 test.
- **F16Q4** Fabricate CPR2 components, procure non-custom components, execute staged buildout and testing plan.
- **F17Q1** Develop mass and energy flow models of large scale H$_2$ production plant. One-dimensional, steady state models of discrete unit operations.
- **F17Q2** Conduct technoeconomic and trade-off analysis for STCH plant.

*Contingent upon completion of FOA GNG.*
Approach: FY16-17 Objectives

- Discover and characterize select oxide materials for water-splitting cycles. (Barrier S & T)
- Construct and demonstrate a particle receiver-reactor capable of continuous operation at >3kW$_{th}$ thermal input. (Barrier T)
- Conduct technoeconomic and trade-off analysis of large-scale H$_2$ production facility using a plant-specific predictor model. (Barrier X)

Advancing solar H$_2$ production through materials and engineering innovation.
Technical Accomplishments and Progress: Generated a Great Deal of STCH Materials Knowledge

- Emerging perovskite design rules based on A-site and B-site compositions.
  - Exploited $\Delta H_R$ reduction trends reported in literature
  - Entropy engineering proving more difficult (no obvious trends)
- (AE, RE)Mn-based perovskites other than SLMA show promise.
  - Find balance between $\Delta \delta$ ($H_2$ capacity) and $\Delta H_R$ (lowering $T_R$)
- Exploiting complex crystallography and solid-solid phase transitions possible.
  - Double perovskites ($A_2BB'O_6$)
Technical Accomplishments and Progress: **Completed CPR2 assembly**

**Engineering & Safety reviews complete, authorized for full operation.**

STCH hydrogen production reactor facility specifications:

- Vacuum system with ~10 Pa (0.0001 atm) base pressure at 1700 K cavity temperature
- 10.6 kW\textsubscript{el} four-lamp solar simulator (~3.4 kW\textsubscript{th} at cavity aperture)
- Instrumented with ~100 TC’s, optical pyrometer, motorized particle flow control, gas flow and pressure sensing/control, Sandia’s MIS H\textsubscript{2} sensor, CCTV system, etc.
- DAQ is LabVIEW-based and provides measurement & control through custom GUI
Technical Accomplishments and Progress: **Scale of CPR2 assembly**

Bootstrapped a unique STCH research facility in less than 3 years.

- Simulator
- Particle source
- Heat rejection
- Flex, B3-B2 p/Sep
- WS-B3 pressure separation
- WS chamber
- Particle drain

15 ft. = 4.56m

4m

2m
Technical Accomplishments and Progress: Achieved H₂ production

T_R\sim 1700 \text{ K.}

0.25 SLPM peak H₂ rate.

Can achieve FOA GNG in <<8 hrs.
Technical Accomplishments and Progress: Completed Plant Predictor Model

Sensitivity and cost-performance tradeoff analysis now possible.

**Features**

- Beam-up solar field design with CPC secondary concentrators
- Multiple receivers and multiple windows for particle reduction and pre-heating
- Heat exchange and recuperation
- Full mass/energy balance at each DNI
- Rankine cycle to produce electricity from the steam

- Detailed sub-models for 17 major components coupled using mass and energy balances between 42 streams.
- Quasi-steady state solution method that dynamically follows DNI.
- Operational and design parameters directly inform cost analysis.
Technical Accomplishments and Progress: Co-gen Electricity & H₂

- Electricity production from waste heat can offset H₂ cost.
  - Ratio of H₂:Electricity dependent on DNI
  - System efficiency is more complex
  - Impact of high-temperature waste heat amplified by integration with CSP

Cogeneration can achieve DOE H₂ cost targets even if solar-to-H₂ conversion efficiency for H₂ plant does not meet DOE targets.
## Response to Previous Year Reviewer’s Comments

**Comments are paraphrased and thematic.**

<table>
<thead>
<tr>
<th>FY16 Comments</th>
<th>FY17 Response</th>
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<tr>
<td>Technology is in its infancy, and while it has potential to make an impact, many technical challenges need to be solved before future impact can be assessed.</td>
<td>STCH is a low TRL, advanced approach to water splitting that promises to meet DOE cost targets. This project has made great strides to address both materials and reactor design challenges, and is currently poised to verify performance of Sandia’s patented moving particle bed technology at small scale (3-5 kW\textsubscript{th}). This will further inform our understanding of future impact.</td>
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<td>The techno-economic analysis is important because it helps to identify the critical technical challenges, which might influence project strategy. It should have been an earlier objective in order to make a convincing case for achieving $2/kg hydrogen.</td>
<td>H2A was used for TEA early in the project to assess and address key technical challenges. Since then, our approach has produced a much higher fidelity full-system model, which has informed and advanced our thinking about plant design. For example, we have investigated the value of cogenerating H\textsubscript{2} and electricity and found synergies with CSP-electricity generation that have the potential to achieve $2/kg H\textsubscript{2} even at lower STH efficiency.</td>
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<tr>
<td>Has progress has been made in coordinating across research communities to establish conventions for analysis, best practices, and key measurements, and in coordinating and communicating materials discovery approaches, testing protocols, and reporting standards.</td>
<td>Yes, as a result of new DOE investments, the Hydrogen Advanced Water Splitting Materials Consortium has been established. This effort spans AE, PEC, and STCH technology pathways, and mandates the aforementioned activities.</td>
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</tbody>
</table>
Collaborations

Material Discovery and Characterization Team
- Colorado School of Mines, Golden CO.
  - Prof. Ryan O’Hayre, Prof. Michael Sanders, Ms. Debora Barcellos
  - Novel material formulations, synthesis, and screening
- Northwestern University, Evanston IL.
  - Prof. Christopher Wolverton, Mr. Antonie Emery
  - Application of quantum theory to engineering materials
- Stanford University, Stanford CA.
  - Prof. William Chueh, Dr. BG Gopal, Ms. Nadia Ahlborg
  - Entropy engineering of materials

Reactor Design, Testing, and Demonstration Team
- Bucknell University, Lewisburg PA.
  - Prof. Nathan Siegel
  - Particle heat transfer, solar simulator design, CPR2 assembly and testing
- German Aerospace Center-DLR, Cologne DE
  - Dr. Christian Sattler, Dr. Justin Lapp, Dr. Abisheck Singh, Dr. Stefan Brendelberger, Mr. Johannes Grobbel
  - Solar particle receiver design, fabrication, and testing

Systems Analysis Team
- Arizona State University, Tempe AZ.
  - Prof. Ellen Stechel, Prof. Nathan Johnson, Dr. Briana Lucero
  - Development of unit operations models, detailed large-scale plant design, technoeconomic analysis
- German Aerospace Center-DLR, Cologne DE
  - Dr. Martin Roeb
  - Detailed large-scale plant design, technoeconomic analysis
Remaining Challenges, Barriers, & Future Work

Challenges

- Discovering a redox material that will meet or exceed DOE cost and performance targets.
  - DOE’s Hydrogen Advanced Water Splitting Materials Consortium (H2awsm.org) investments will focus on material discovery
- Establishing the CPR2 as a “routine-use” R&D tool to support H2awsm and attract commercial interest/investment.
  - Identified issues with particle flow control and thermal management that stymied efforts to achieve FOA GNG
  - Other technical issues will present themselves as we “learn by doing”

Future work*

- Upgrade CPR2 to increase reliability and provide service to H2aswm’s customers.
  - Resolve known issues, rescale certain components for use with small material batches, and integrate second receiver-reactor and simulator to fully explore pressure cascade
- Publish project results in peer-reviewed journals.
  - 13 manuscripts in preparation on materials, reactor design, and TEA

*Project continuation and direction determined by DOE.
Technology Transfer Activities

- Sandia holds several patents on CSP, materials, and reactor technology.
  - Operating the CPR2 is paramount to technology transfer plan in order to attract and develop industry relations.
    - Roadmap based on demonstration, advancing TRL, and economic analysis
    - Need to present value-added propositions to industrial gas suppliers & CSP electricity providers
- Leverage relationship with DLR to promote international interest in technology development.
Summary

- Developed new knowledge about (AE, RE)Mn-based redox active perovskites that is gradually leading towards material design rules.
- Completed construction and shakedown tests of CPR2.
  - Reactor fully operational
  - Poised to meet FOA requirement making 3L H₂ in <<8 hours
- Demonstrated a clear path towards commercialization that leverages the value of H₂ and electricity cogeneration.
  - STC-H₂ is the only renewable hydrogen production technology that generates and can export high-quality waste heat

Accomplishments represent significant progress towards overcoming technical barriers to STCH development.
Thank You.

Questions?
Technical Back-Up Slides
System Components in TEA and Performance Modeling

- Solar Field – Focuses solar radiation to multiple windows and multiple cavity receivers.
- Tower – Contains receiver, reactor, and supporting components.
- Receiver 1 – Used to pre-heat particles (three windows and three CPCs).
- Elevator – Moves particles up to the tower.
- Receiver 2 – Used to reduce particles (multiple windows, multiple receivers, CPCs that cascade to the final reduction pressure while removing oxygen from particles).
- Solid-Solid Recuperator – Exchanges heat between particles going moving upward to (re-oxidized) and downward from (reduced).
- G-S Recuperator – Cools reduced particles to the re-oxidation temperature and generates steam for water splitting and electricity.
- Fuel Production Chamber – Mixes reduced particles with steam to generate H₂.
- Heat Exchanger A – Cools oxygen exiting solar receivers.
- Steam Mixture – Mixes steam from G-S Recuperator and water to cool receiver components.
- Heat Rejecter – Cools oxygen to room temperature (to improve pump performance).
- Vacuum Pump – Pumps oxygen out of the receivers.
- Steam Pump – Pumps steam through the system.
- Condenser – Separates H₂ from steam and rejects heat for use in a power cycle.
- Rankine Cycle – Power cycle used to convert heat energy into mechanical power.
- Water Tank with Pump – Water storage and supply.
- Generator – Produces electrical power from mechanical power in Rankine Cycle.
Detailed Cost Estimation

- Increased fidelity of CAPEX estimation.
- Includes scaling relations that are not strictly linear with size.
- Initial cost estimate $9.86/kg H₂.
  - Assumes $60/MWH revenue for electricity
  - $170/m² Heliostats
  - 11%/year CAPEX charge
  - $3.2 B (exports electricity) vs original estimate of $1.5B (+ purchased electricity)

- Realistic cost reductions for Ultimate Case.
  - Increased H₂ per tower, decreased electricity production, and reduced revenue per electrical unit
  - $75/m² Heliostats
  - Decreased cost of particles, increased lifetime
  - Modest cost reduction of receivers and vacuum pumps
  - More favorable cost of money 8%/yr
  - Ultimate estimate $2.11/kg H₂

<table>
<thead>
<tr>
<th>Component</th>
<th>$M</th>
<th>Reduction</th>
<th>% change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solar Field</td>
<td>15.429</td>
<td>6.807</td>
<td>44.1%</td>
</tr>
<tr>
<td>Land</td>
<td>0.349</td>
<td>0.349</td>
<td></td>
</tr>
<tr>
<td>Land preparation</td>
<td>1.414</td>
<td>1.414</td>
<td></td>
</tr>
<tr>
<td>Tower</td>
<td>3.606</td>
<td>3.606</td>
<td></td>
</tr>
<tr>
<td>Receivers</td>
<td>2.981</td>
<td>2.385</td>
<td>80.0%</td>
</tr>
<tr>
<td>CPC + Windows</td>
<td>0.132</td>
<td>0.132</td>
<td></td>
</tr>
<tr>
<td>Elevator</td>
<td>0.227</td>
<td>0.227</td>
<td></td>
</tr>
<tr>
<td>Particles</td>
<td>3.356</td>
<td>1.678</td>
<td>50.0%</td>
</tr>
<tr>
<td>Fuel Production Reactor</td>
<td>4.777</td>
<td>3.822</td>
<td>80.0%</td>
</tr>
<tr>
<td>Water Pumps and water system</td>
<td>0.025</td>
<td>0.025</td>
<td></td>
</tr>
<tr>
<td>Steam pumps and steam system</td>
<td>0.074</td>
<td>0.074</td>
<td></td>
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<tr>
<td>Heat Exchanger -A</td>
<td>0.041</td>
<td>0.041</td>
<td></td>
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<tr>
<td>Gas-Solid Recuperator</td>
<td>0.367</td>
<td>0.367</td>
<td></td>
</tr>
<tr>
<td>Condenser</td>
<td>0.134</td>
<td>0.134</td>
<td></td>
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<tr>
<td>Heat Rejcctor</td>
<td>0.027</td>
<td>0.027</td>
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<tr>
<td>Vacuum pump</td>
<td>0.896</td>
<td>0.672</td>
<td>75.0%</td>
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<tr>
<td>Hydrogen Compressor</td>
<td>0.538</td>
<td>0.538</td>
<td></td>
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<tr>
<td>Rankine Cycle</td>
<td>1.714</td>
<td>1.714</td>
<td></td>
</tr>
<tr>
<td>Total per tower</td>
<td>36.087</td>
<td>24.011</td>
<td>66.5%</td>
</tr>
<tr>
<td>All Towers</td>
<td>2959.147</td>
<td>1310.079</td>
<td>75.0%</td>
</tr>
<tr>
<td>Controls</td>
<td>147.957</td>
<td>65.504</td>
<td>44.3%</td>
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<tr>
<td>Balance of Plant</td>
<td>88.774</td>
<td>39.302</td>
<td>44.3%</td>
</tr>
<tr>
<td>Total CAPEX including Installation</td>
<td>3195.879</td>
<td>1414.885</td>
<td>44.3%</td>
</tr>
<tr>
<td>Contingency+Indirect</td>
<td>1105.774</td>
<td>489.500</td>
<td>44.3%</td>
</tr>
<tr>
<td>Total Fixed Cost</td>
<td>4301.653</td>
<td>1904.335</td>
<td>44.3%</td>
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<tr>
<td>Annual capital charge</td>
<td>473.182</td>
<td>152.355</td>
<td>72.7%</td>
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<tr>
<td>Particle Replacement</td>
<td>0.671</td>
<td>0.168</td>
<td>50.0%</td>
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<tr>
<td>Total Variable Cost</td>
<td>1.910</td>
<td>1.528</td>
<td>80.0%</td>
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<tr>
<td>Total Annual Cost</td>
<td>475.763</td>
<td>154.051</td>
<td>32.4%</td>
</tr>
<tr>
<td>Average Production per Tower</td>
<td>447.56</td>
<td>671.33</td>
<td>150.0%</td>
</tr>
<tr>
<td>Total Production</td>
<td>100.55</td>
<td>150.82</td>
<td>150.0%</td>
</tr>
<tr>
<td>Revenue Hydrogen</td>
<td>361.683</td>
<td>116.024</td>
<td>21.4%</td>
</tr>
<tr>
<td>Average Net Electrical per Tower</td>
<td>23.19</td>
<td>11.59</td>
<td>50.0%</td>
</tr>
<tr>
<td>Total Production</td>
<td>5.21</td>
<td>2.60</td>
<td>50.0%</td>
</tr>
<tr>
<td>Revenue Electricity</td>
<td>114.080</td>
<td>38.027</td>
<td>66.7%</td>
</tr>
<tr>
<td>Unit hydrogen</td>
<td>9.860</td>
<td>2.110</td>
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</tbody>
</table>
• Biggest cost reduction opportunity per tower is the solar field.
• Next biggest opportunity comes from productivity, i.e., fewer towers.