High Efficiency Solar Thermochemical Reactor for Hydrogen Production

Anthony McDaniel, Ivan Ermanoski
Sandia National Laboratories

DOE Annual Merit Review
6-8-2016

Project ID: PD113

Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy’s National Nuclear Security Administration under contract DE-AC04-94AL85000.

This presentation does not contain any proprietary, confidential, or otherwise restricted information.
Overview

Timeline
- Project Start Date: 10/01/2014
- Project End Date: 12/31/2016
- Project Complete: 65%

Budget
- Total Project Budget.  
  - $3.293M
- Total Recipient Share.  
  - $0.243M
- Total Federal Share.  
  - $3.050M
- Total DOE Funds Spent:*  
  - $1.849M

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

Partners
- German Aerospace Center-DLR, Cologne DE.  
  - Dr. Christian Sattler
- Arizona State University, Tempe AZ.  
  - Profs. Ellen Stechel and Nathan Johnson
- Bucknell University, Lewisburg PA.  
  - Prof. Nathan Siegel
- Colorado School of Mines, Golden CO.  
  - Profs. Ryan O’Hayre and Michael Sanders
- Northwestern University, Evanston IL.  
  - Prof. Christopher Wolverton
- Stanford University, Stanford CA.  
  - Prof. William Chueh

*As of 03/31/16
Relevance

• **DOE Objective**: 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.

• **Project Objective**: Develop and validate a particle bed reactor for producing hydrogen via a thermochemical water-splitting cycle using a non-volatile metal oxide as the working fluid. Demonstrate 8 continuous hours of “on-sun” operation producing greater than 3 liters of H₂.

• **FY 2016 Objectives**:
  - Discover and characterize suitable materials for two-step, non-volatile metal oxide thermochemical water-splitting cycles. *(Barrier S & T)*
  - Construct and demonstrate a particle receiver-reactor capable of continuous operation at 3kW thermal input. *(Barrier T)*
  - Conduct full technoeconomic, sensitivity, and trade-off analysis of large-scale H₂ production facility using a plant-specific predictor model coupled to H₂A . *(Barrier X)*
Overcoming barriers to high-temperature solar thermochemical $H_2$ production.

- Novel cascading pressure design achieves very low $O_2$ pressures during reduction
- Novel material formulations (perovskites, others) for lower reduction temperature
- Maximize STH efficiency by exploiting reactor-material synergies
- Reduce dependence on high-temperature solid-solid heat recovery by 50%

Advancing solar $H_2$ production technology through materials and engineering innovation.
### 03.2015-03.2016 Accomplishments

<table>
<thead>
<tr>
<th>Q1</th>
<th>Q2</th>
<th>Q3</th>
<th>Q4</th>
<th>Q1</th>
<th>Q2</th>
<th>Q3</th>
<th>Q4</th>
</tr>
</thead>
<tbody>
<tr>
<td>F15Q1</td>
<td>F15Q2</td>
<td>F15Q3</td>
<td>F15Q4</td>
<td>F16Q1</td>
<td>F16Q2</td>
<td>F16Q3</td>
<td>F16Q4</td>
</tr>
</tbody>
</table>

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

**Progress Metrics**

- **F15Q1**: 100%
- **F15Q2**: 70%
- **F15Q3**: 40%
- **F15Q4**: 75%
- **F16Q1**: 100%
- **F16Q2**: 60%
- **F16Q3**: 30%
- **F16Q4**: 75%
- **AMR**: 0%
Technical Accomplishments and Progress

Cascading Pressure Receiver-Reactor (CPR2)

CPR2 design specifications:
• Fully instrumented.
• $20\text{kW}_{\text{ele}}$ solar simulator.
• $T_{\text{TR}} = 1500$ °C, $T_{\text{WS}} = 800$ °C.
• $1700\times$ pressure separation.
• 100 kg redox-active material.
• 2.5 g/s particle flow rate.
• 0.3 slpm H$_2$ continuous.

• From concept to fabrication in 1 year!
Technical Accomplishments and Progress

20kW_{ele} Solar Simulator to Power CPR2

- Designed in collaboration with Bucknell University.
- Each module houses a 2.5kW short-arc Xe bulb.
- Each module independently focused into the CPR2 receiver aperture.
- Design validated by flux mapping combined with ray tracing calculations.

- Provide $7kW_{th}$ of simulated concentrated solar power into the CPR2.
Technical Accomplishments and Progress

Ultra-high Temperature Solar Receiver-Reactor

- Designed in collaboration with DLR and Bucknell University.
  - High vacuum, $P_{TR} = .0005$ atm
  - Radiant cavity, $T_{wall} = 1500 \, ^\circ C$
  - Direct illumination of particles
  - Control particle flow rate and particle irradiation time

- Design validated by numerical models, ray tracing, particle flow tests, etc...

- Precise control of oxide reduction conditions.
- Generate engineering data for scale-up.
Technical Accomplishments and Progress

Pressure Separation and Water Splitting Chamber

- Designed by Sandia.
  - Quench particle temperature, $\Delta T=650$ °C
  - Stand off 0.84 atm pressure
  - Separate $O_2$ from $H_2$
  - Long contact time between $H_2O$ and oxide

- Demonstrate increased $H_2$ production efficiency with pressure separation and countercurrent flow between $H_2O$ and oxide.

1700× pressure reduction without fluidization of moving particle bed
Technical Accomplishments and Progress

Selected Design Validation Activities

• Qualify design choices to mitigate risk of CPR2 failure.

- Qualify design choices to mitigate risk of CPR2 failure.
- Calculate flux on particles.
- Evaluate particle flow at high T.
- Calibrate SLIP-STICK flow rate.
- Test chemical & thermal stress on materials.
Technical Accomplishments and Progress

Aggressive Assembly and Demonstration Schedule

- Staged buildout and component testing through end FY16.
- Validation test of solar receivers at DLR’s high-flux simulator.
Technical Accomplishments and Progress

Combined DFT + Experiments to Accelerate Material Discovery

- Screened ~50 new compounds.
- Discovered 5 new WS perovskites.
- Improved SLMA by Nb-doping.
- CeFeO$_3$ predicted by DFT.
  - Mixed phase and cycle-unstable

- Engineered thermodynamics by adding small amounts of dopant.
  - Raise configurational entropy through lattice softening
- Sr-CeO$_2$ a successful case study.

- Refine approach to material discovery using DFT.

10% increase in H$_2$ production with 1.6mol% Sr added to CeO$_2$
Technical Accomplishments and Progress

Advanced Materials Manufacturing (AMM) / Materials Genome initiative (MGI)

Innovative materials discovery and development for faster product development. Key elements include:
- Integrating experiment, computation, and theory
- Making digital data accessible
- Creating a world-class materials workforce
- Leading a culture shift in materials research

ABO$_3$ network map

<table>
<thead>
<tr>
<th>Formula</th>
<th>B-site</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaCoO$_3$</td>
<td>Co</td>
</tr>
<tr>
<td>CeCoO$_3$</td>
<td>Co</td>
</tr>
<tr>
<td>YCrO$_3$</td>
<td>Cr</td>
</tr>
<tr>
<td>CeCrO$_3$</td>
<td>Cr</td>
</tr>
<tr>
<td>LaCrO$_3$</td>
<td>Cr</td>
</tr>
<tr>
<td>YFeO$_3$</td>
<td>Fe</td>
</tr>
<tr>
<td>LaFeO$_3$</td>
<td>Fe</td>
</tr>
<tr>
<td>CeFeO$_3$</td>
<td>Fe</td>
</tr>
<tr>
<td>YMnO$_3$</td>
<td>Mn</td>
</tr>
<tr>
<td>LaMnO$_3$</td>
<td>Mn</td>
</tr>
<tr>
<td>CeMnO$_3$</td>
<td>Mn</td>
</tr>
<tr>
<td>NaMoO$_3$</td>
<td>Mo</td>
</tr>
<tr>
<td>SrSnO$_3$</td>
<td>Sn</td>
</tr>
<tr>
<td>BaSnO$_3$</td>
<td>Sn</td>
</tr>
<tr>
<td>CaVO$_3$</td>
<td>V</td>
</tr>
<tr>
<td>SrVO$_3$</td>
<td>V</td>
</tr>
<tr>
<td>YVO$_3$</td>
<td>V</td>
</tr>
<tr>
<td>CeVO$_3$</td>
<td>V</td>
</tr>
<tr>
<td>LaVO$_3$</td>
<td>V</td>
</tr>
</tbody>
</table>

CeFeO$_3$: Mixed phase
Ce$^{+4}$ unstable A-site
Incomplete H$_2$O rxn
Cycle unstable

- High throughput DFT of 11,000 calculated simple ABO$_3$ structures.
  - 5400 stable oxides filtered to 19 possible WS-active compounds

Evaluate the WS potential for all possible binary perovskites.
Technical Accomplishments and Progress

Enabling Component-level Technoeconomic Analysis

- Quasi-steady state model that dynamically follows DNI.
- Detailed receiver-reactor system with 8 major components.
  - Account for mass and energy flows
  - Separate solar receivers for particle heating and reduction
  - Counter-flow H₂ production reactor
  - Heat exchange and recuperation
- Exercising model with various water-loop configurations.
  - System needs are material dependent

- Goal to add fidelity and accuracy to H2A cost analysis.
- Conduct sensitivity and cost-performance tradeoff analysis.
## Response to Previous Year Reviewer’s Comments

<table>
<thead>
<tr>
<th>FY15 Comments</th>
<th>FY16 Response</th>
</tr>
</thead>
<tbody>
<tr>
<td>Materials discovery work may be an ever-expanding universe of investigations, rather than one converging on a viable solution for CPR2 testing during the scope of the project. Primary focus for this project should be on performing the reactor tests and demonstrating achievement of the project objective to produce 3 Liters of Hydrogen in 8 hours.</td>
<td>To mitigate this risk, we have confidence that the FOA milestone can be achieved with known materials. Nonetheless, the reviewer comments and the community continue to suggest needing both reactor and materials development. In this project we do our level best to move forward on both fronts.</td>
</tr>
<tr>
<td>Development of any efficient cost-effective direct solar processes for water splitting has the potential to provide a significant expansion of the role of solar energy. This solar thermochemical technology represents one possible pathway for direct solar hydrogen. But it is fraught with several extremely challenging technical issues, from the performance of the redox material, circulation of very high temperature solid particulates, selection of very high-temperature reactor materials, radiative heating of solid particles, etc.. Furthermore, the potential for high-efficiency performance is limited.</td>
<td>Disagree. The reason we are taking such a serious look at, and making investments in, this technology is because of the potential for high-efficiency performance. STCH potential for high-efficiency theoretically exceeds that of PV + electrolysis and PEC. Furthermore, great strides are being made by research groups around the world to advance the TRL of CSP for generating both electricity and industrial process heat.</td>
</tr>
<tr>
<td>Barriers have been identified and addressed and the technical approach to materials design and laboratory reactor testing is feasible, if challenging. The project partners have well defined roles in contributing to success of the project. However the scope of the project does not seem appropriately scaled to the project duration and available funding.</td>
<td>Agree. This two year effort is extremely ambitious. We have already accomplished a great deal of work, and are moving rapidly towards meeting our main demonstration milestone. Sandia looks on this project as a means to elevate and propel our core capability, and remain optimistic that we will have the opportunity to continue advancing this technology’s TRL.</td>
</tr>
</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 and Barriers

**Challenge**

- Discovering a redox material that will meet or exceed a STH efficiency of 5% in the CPR2, or will meet or exceed the 2020 target of 20%.
- Cannot verify the CPR2 design will meet or exceed 5% STH efficiency operating at ~3kW before construction.
  - It is not possible to know with certainty that design choices will meet performance criteria until actually tested

**Mitigation Strategy**

- **Use CeO$_2$ in the CPR2 test.**
  - CeO$_2$ will satisfy the project milestone of 3L H$_2$ in 8 hours
- **Sub-component modeling and experiments will be used to verify design decisions.**
  - Project milestone of 3L H$_2$ in 8 hours will be met even if the STH efficiency is less than 5% in the CPR2
- **Detailed systems analysis and “Learn By Doing” will improve STH efficiency and show clear pathway to commercialization.**
Proposed Future Work

Remainder of FY16:
- Produce ~150 kg of CeO$_2$ particulates (~300µm diam.) for CPR2 tests.
  - Choice based on outcome of FY15 material decision point

- Publish results on material discovery R&D in peer-reviewed journals.

- Fabricate components, assemble, and test CPR2 “on-sun”.
  - Run at least 8 continuous hours at ~3kW producing more than 3L H$_2$
  - Satisfy project milestone by end of calendar year (FY17Q1)

- Conduct full technoeconomic analysis of a 10$^5$ kg H$_2$/day plant.
  - Extend/validate H2A result
  - Conduct detailed sensitivity and trade-off analysis

- Publish results on technoeconomic analysis in peer-reviewed journals.
Technology Transfer Activities

• Collaborating with CoorsTek to produce large batches of redox active materials to support CPR2 test.
  – Large supplier of ceramic and advanced materials to many industries
  – 50 production facilities in 14 countries on four continents
  – Using pilot proppant plant to make pelletized materials for CPR2
• Sandia holds several patents on CSP, materials, and reactor technology.

• Operating the CPR2 is paramount to technology transfer plan.
  – Roadmap based on demonstration, advancing TRL, and economic analysis
Summary

• **Completed CPR2 design and components are in fabrication.**
  – Validated design choices using modeling, simulation, and lab tests in order to reduce risk of reactor failure
  – Solar receivers will be tested in DLR’s high-flux simulator
  – Reactor will demonstrate efficient H$_2$ production using a pressure cascade and countercurrent mass flow in WS chamber

• **Extended approach to material discovery and engineering of thermochemical properties.**
  – Demonstrated entropy engineering concept using Sr-CeO$_2$ showing a 10% increase in H$_2$ productivity with 1.6mol% addition of Sr
  – Applied DFT to guide synthesis and characterization of binary ABO$_3$ perovskites likely excluding simple oxides as viable candidates for efficient WS materials

• **Developed a component-level model of Sandia’s STCH reactor concept to enable more advanced technoeconomic analysis.**
  – Add fidelity and accuracy to H2A cost analysis
  – Conduct sensitivity and cost-performance tradeoff analysis

**FY16 Accomplishments represent significant progress towards overcoming technical barriers to STCH development.**
Thank You.

Questions?
Technical Back-Up Slides
• Operating at 1450°C for years
• Lifts ~15 000 000 kg raw material per day (or about 10 000 kg/min)
• Conducts a thermochemical reaction: CaCO₃ → CaO
• Fuel (natural gas) must be purchased and is part of the operating cost

• Bottom line: 15¢/kg cement – retail!
Heat engines are inexpensive, even gas turbines:
- High temperature operation – up to 1650°C
- High speed – 10,000 to 500,000 RPM
- High pressure – exceeds 30 MPa

Cost: 18-30 ¢/W

Compare to PV, DOE 2020 target of 100 ¢/W and 300 ¢/W current price

Bottom line: heat engines are 10x cheaper than PV
Fuel Production Reactor Modeling

- Material’s model parameterized so new materials can be incorporated readily
  - New fuel-production model
  - Departs from an assumption of equilibrium
  - Option to include none, all, or part of the exothermic heat from the re-oxidation reaction

\[ \dot{n}_g = ((\delta_{\text{red}} - \delta_{\text{ox}}) \cdot (\zeta + 1)) \cdot \dot{n}_p \]
\[ \dot{n}_g = \text{Gas stream molar flowrate} \]
\[ \delta_{\text{red}} = \text{Reduction extent from solar receiver} \]
\[ \delta_{\text{ox}} = \text{Re-oxidation extent} \]
\[ \zeta = \text{Zeta > minimum flow necessary} \]
\[ \dot{n}_p = \text{Particle molar flowrate} \]
\[ y_{17} = \text{Percentage H2 in exiting stream} \]

- Quasi-steady state modelling while dynamically following DNI input.