High Efficiency Solar Thermochemical Reactor for Hydrogen Production

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Sandia National Laboratories

DOE Annual Merit Review
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Project ID: PD113

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Overview

**Timeline**
- Project Start Date: 10/01/2014
- Project End Date: 10/01/2016
- Project Complete: 25%

**Budget**
- Total Project Budget: $2.600M
- Total Recipient Share: $0.243M
- Total Federal Share: $2.357M
- Total DOE Funds Spent: $0.391M

**Barriers Addressed**
- S: High-Temperature Robust Materials.
- T: Coupling Concentrated Solar Energy and Thermochemical Cycles.
- AC: Solar Receiver and Reactor Interface Development.

**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 Jianhua Tong
- Northwestern University, Evanston IL.
  - Prof. Christopher Wolverton
- Stanford University, Stanford CA.
  - Prof. William Chueh

*As of 03/31/15*
• **DOE Objective:** By 2015, 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 2015 Objectives:**
  • Discover and characterize suitable materials for two-step, non-volatile metal oxide thermochemical water-splitting cycles. *(Barrier S & T)*
  • Design a particle receiver-reactor capable of continuous operation at 3kW thermal input. *(Barrier T & AC)*
  • Develop a detailed unit operations model of a large scale single tower, multiple receiver solar thermochemical reactor. *(Barrier X)*
Approach

Reactor and Materials Innovation

- Overcoming barriers to high-temperature solar thermochemical H₂ production.
  - Novel cascading pressure design achieves very low O₂ pressures during reduction
  - Novel material formulations (perovskites, others) for lower reduction temperature
  - Maximize STH efficiency by reactor-material synergies
  - Reducing dependence on high-temperature solid-solid heat recovery

\[ \text{Cascading Pressure Reactor/Receiver} = \text{CPR2} \]

- Advancing solar H₂ production technology through materials and engineering innovation.

\[
\begin{align*}
MO_x & \rightarrow MO_{x-\delta} + \frac{\delta}{2}O_2 \quad \text{(1) Reduction} \\
MO_{x-\delta} + \delta \cdot H_2O & \rightarrow MO_x + \delta \cdot H_2 \quad \text{(2) Oxidation} \\
\delta \cdot H_2O & \rightarrow \frac{\delta}{2}O_2 + \delta \cdot H_2 \quad \text{(3) Thermolysis}
\end{align*}
\]
## 10.2014-03.2015 Accomplishments

<table>
<thead>
<tr>
<th>Q1</th>
<th>Q2</th>
<th>Q3</th>
<th>Q4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formulate and synthesize redox active oxides from doped LaAlO₃. (variants of La-Sr-Mn system)</td>
<td>70%</td>
<td>Formulate and synthesize redox active oxides from earth abundant elements. (explore Fe, Mn, Ti, V redox systems)</td>
<td>25%</td>
</tr>
<tr>
<td>Formulate and synthesize redox active oxides from A₂B₂O₉ crystal structure. (explore Mo redox system)</td>
<td>10%</td>
<td>Characterize thermodynamic, kinetic, and other relevant properties of newly synthesized materials.</td>
<td>25%</td>
</tr>
<tr>
<td>Build-out of particle elevator, demonstrate continuous particle flow &gt;10 g/s, pressure separation &gt;25kPa, vacuum pressure of &lt;1kPa, and particle T&gt;300°C.</td>
<td>80%</td>
<td>Design and construct <del>7kW solar simulator at Sandia capable of supplying heat to CPR2 solar receivers operating at T</del>1500°C, and at p&lt;1kPa.</td>
<td>20%</td>
</tr>
<tr>
<td>Develop designs for CPR2 solar-particle interface and reduction chambers.</td>
<td>60%</td>
<td>Finalize CPR2 design.</td>
<td></td>
</tr>
<tr>
<td>Develop mass and energy flow models of large scale H₂ production plant. High-level, one-dimensional, steady state models of discrete unit operations.</td>
<td>50%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Approach

**Materials**

**Reactor**

**Analysis**
## Approach

### Milestones

### 10.2014-03.2015 Accomplishments

<table>
<thead>
<tr>
<th>ACTIVITY</th>
<th>MILESTONE</th>
<th>COMPLETE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Discover new redox material</td>
<td>New perovskite material will have a redox capacity &gt;&gt; 250 micromole H2/g material, that reduces effectively at T &lt; 1623K (threshold established by SLMA), and has kinetics and thermodynamics tuned for optimal STH efficiency (&gt; 10%) in a particle bed reactor.</td>
<td>0%</td>
</tr>
<tr>
<td>Produce CPR2 engineering drawings and show it can meet &gt;5%STH efficiency at&lt;5kW.</td>
<td><strong>Specific</strong> (engineering drawings are tangible items that are sufficiently detailed so that a skilled machinist can cut, weld, bend, etc. metal, glass, and other materials to produce a 3-D rendering from the CPR2 design) <strong>Measureable</strong> (the design will create a reactor capable of operating at an STH efficiency &gt;5% on the 2-5kW scale. Ultimately this will be measured and validated when the CPR2 is fabricated and tested. However, in design space the CPR2 performance will be extrapolated from simple experiments that test for criteria compliance. For example, 5% STH at 3kW = 150 J/s chemical. This translates into 0.83 L/min H2 (based on LHV). The CPR2 will need to process 0.0006*MW_{oxide}/\Delta\delta of oxide [g/s]. MW_{oxide} is the molecular weight of the oxide in g/mol. Simple experiments used to test particle motion, heat transfer, and steam oxidation within and through designed components will measure this (among other things). <strong>Achievable</strong> (it is well within the skillset of our team provided that there are no issues with the DLR contracting process.) <strong>Relevant</strong> (drawings are absolutely critical to component fabrication and reactor assembly.) <strong>Timed</strong> (it is well within our project plan to complete this by end of year 1 provided that there are no issues with the DLR contracting process.)</td>
<td>50%</td>
</tr>
</tbody>
</table>
Technical Accomplishments and Progress

Engineering Material Thermochemistry

**Why is it important?**

- **Determines operating conditions.**
  - Heat flux, $T_{TR}$, $T_{WS}$
  - Mass fluxes: $MO_x$, steam, $H_2$

- **Determines cost of $H_2$.**
  - Plant design and operation
  - $\eta_C$ is one component of STH efficiency

**How is it done?**

- **Identify candidate oxides.**
- **Manipulate crystal structure.**
  - A & B site doping
  - A & B site substitution
  - Introduce new phases

\[\Delta H_{RXN} = \text{y-intercept}, \quad \Delta S_{RXN} = \text{slope}\]

\[\delta H_2O \rightarrow \delta H_2 + \delta/2O_2\]

\[MO_x \rightarrow MO_{x-\delta} + \delta/2O_2\]

- $\eta_C \sim (T_{TR} - T_{WS}) / T_{TR}$

- Reduce $T_{TR}$ and optimize STH efficiency.
Technical Accomplishments and Progress

Synthesis and Screening of Novel Compounds

- Synthesized more than 50 new compounds.
- Explored redox activity of 1st row transition metals (TMs).
  - Ti, V, Mn, Fe
- Perovskite and similar crystal structures.
  - ABO$_3$, ABO$_4$, A$_2$B$_2$O$_9$
- Further developed an O$_2$-TPD screening protocol.
  - Faster than TGA
  - Correlate onset of O$_2$ evolution to reduction enthalpy ($\Delta H_{\text{RED}}$) and water-splitting activity

<table>
<thead>
<tr>
<th>Material</th>
<th>T (C)</th>
<th>Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>SLMA6464</td>
<td>875</td>
<td>-0.2</td>
</tr>
<tr>
<td>COMP X</td>
<td>1150</td>
<td>-0.05</td>
</tr>
<tr>
<td>Ceria</td>
<td>1220</td>
<td>-0.01</td>
</tr>
</tbody>
</table>

- Discovered a doping strategy to improve SLMA performance.
Technical Accomplishments and Progress

Quantum Theory to Aid Understanding of Redox Behavior

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

Technical Accomplishments and Progress

• Validate Density Functional Theory (DFT+U) calculation against experiment.
• Use DFT simulations to find water-splitting compounds.
  – Assess thermodynamic descriptors to RAPIDLY screen libraries of known structures

Calculation energy required to remove one O atom

Ce activates gas splitting
**Engineering Entropy Instead of Enthalpy**

\[
\begin{array}{c}
O^\times \xrightarrow{\Delta H_{\text{red}}, \Delta S_{\text{red}}} V_O^\ast + 2e^' + \frac{1}{2}O_2 \\
\uparrow \quad \uparrow \\
\text{Solid state entropy (material specific)}
\end{array}
\]

- \( \Delta G = \Delta H - T \Delta S \)
  - \( T \Delta S \) term is large at high \( T \)
  - Decrease \( T_{TR} \) more than \( T_{WS} \)
- **Raise configurational entropy of TM d-electrons by site doping.**
  - A site (lattice distortion)
  - B site (ligand field)
- **Raise vibrational entropy through lattice softening.**
  - Increase lattice volume on vacancy formation

**Solid state entropy (material specific)**

- Gas phase entropy (fixed)

**Increase reduction entropy in perovskite:**
- Decrease \( T_{TR} \)
- Increase WS efficiency
Technical Accomplishments and Progress

Cascading Pressure Reactor/Receiver (CPR2)

- **FOA requirement:**
  - 8 hours continuous operation
  - greater than 3 liters of H₂

- **High-efficiency attributes of CPR2.**
  - Pressure and temperature separation
  - Continuous operation
  - Pressure cascade to drive reduction extent

- **Finalized conceptual system design.**
  - Receiver configuration
  - Heat flux and heat transport
  - Oxide flow rate and control
  - Pumping requirements

- **Evaluated multiple receiver options.**
- **Established key design criteria.**
Technical Accomplishments and Progress

Designing the Solar Receiver

- **Solar interface.**
  - Direct or indirect particle irradiation
  - Beam-up or beam-down optics

- **Pressure separation.**
  - Particle diameter and mass
  - Bed permeation and fluidization

- **Particle flow control.**
  - Valves, vibrating plates, actuated drives

\[
\frac{dp}{dz} = \frac{m_g}{A(z) p M_p} \frac{RT}{1 - \phi} \left[ \frac{150(1 - \phi) \mu}{f_c(Kn) D_p} + 1.75 \frac{m_g}{A(z)} \right]
\]

- \( p_{TR2} = 25 \) Pa
- \( H_2 = 0.2 \) m
- \( p_B = 1 \) kPa
- \( H_1 = 1.8 \) m

- \( p_{ox} = 50 \) kPa

- Key design criteria established by detailed modeling when necessary.
Technical Accomplishments and Progress

Understanding Radiative Particle Heating

- Vacuum lowers heat transfer efficiency.
- Static particle bed.
  - Worst case scenario

**Experimental setup**

**Placement of TCs**

**Heat propagation**

- Qualified: Particle heating to 1500°C using simulated sunshine.
Technical Accomplishments and Progress

CPR2: From Concept to Device

• Particle transport via Olds™ lift design.
  – Fixed auger, rotating wall
  – Mass conveying rate well above design requirements

• Particle column establishes pressure separation.
  – Rotating chamber seals maintain high vacuum

• Particle lift will operate at T~800°C.
  – Heating tests underway

• Qualified: Particle conveyance and vacuum.
Technical Accomplishments and Progress

Improving Economic Analysis

- **Add fidelity and accuracy to H2Av3 cost analysis.**
  - Verify the potential for solar thermochemical hydrogen production to be competitive in the long term
  - Conduct trade-off analysis on plant design and operation

- **Target H₂ production is 100,000 kg/day.**
  - Integrate H₂ production with CSP in a single tower, multiple receiver design

- **Leveraging CSP concepts development for integration with H₂ production.**
Technical Accomplishments and Progress

Establish Data Requirements and Inputs to Model

- **Single tower, multiple receiver model.**
  - 14 model elements
  - 43 mass and energy states
- **Calculate mass and energy flows at each solar insolation.**
  - Validation/upscaling data measured on 3kW reactor
- **Single tower is one of many in a large-scale plant design.**
  - ~230-four MWth towers
  - located on 750 acres

Matlab™ implementation underway

- This level of detail is currently lacking in H2Av3 analysis.
Collaborations

Material Discovery and Characterization Team

- Colorado School of Mines, Golden CO.
  - Prof. Ryan O’Hayre, Prof. Jianhua Tong, Dr. 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

- 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

Reactor Design, Testing, and Demonstration 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

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

**Mitigation Strategy**

- Use SLMA or CeO$_2$ in the CPR2 test.
  - Either of these materials 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
- “Learn by doing” will improve STH efficiency and show clear pathway to commercialization.
Proposed Future Work

Remainder of FY2015

• **Continue material discovery and optimization R&D.**
  
  – Make decision on material for CPR2 test

• **Finalize CPR2 design and produce engineering drawings for fabrication.**
  
  – Develop detailed models of sub-component behavior as necessary to validate concepts
  – Conduct experiments of sub-component behavior as necessary to validate concepts
  – Satisfy FY15 project milestone

• **Design solar field and BOP for $10^5$ kg H$_2$/day plant.**

FY2016

• **Continue material discovery and optimization R&D.**
  
  – Develop thermodynamic and kinetic models of material performance

• **Produce ~100 kg of redox material for CPR2 tests.**
  
  – Choice based on outcome of FY15 material decision point.

• **Fabricate components, assemble, and test CPR2 “on-sun”.**
  
  – Run at least 8 continuous hours at ~3kW producing more than 3L H$_2$
  – Satisfy FY16 project milestone

• **Full technoeconomic analysis of a $10^5$ kg H$_2$/day plant.**
  
  – Based on a detailed model of up-scaled CPR2 performance, solar field, and BOP
  – Extend/Validate H2Av3 result, conduct detailed sensitivity and trade-off analysis
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.
- Business interest exists from Olds Elevator LLC.
- Operating the CPR2 is paramount to technology transfer plan.
  - Roadmap based on demonstration, advancing TRL, and economic analysis
Summary

• Extended approach to material discovery and engineering of thermochemical properties.
  – Exploring several TM redox pairs (Fe, Mn, Mo, Ti, V)
  – Focused on entropy engineering to optimize material performance
  – Validating DFT theory against experiments to enable computational screening

• Designing a 3kW cascading pressure reactor/receiver (CPR2).
  – Established key criteria and down-selected receiver design
  – Windowed cavities, particle transport by gravity and vibration
  – Pressure separation achieves high STH efficiency

• Assembled and tested Olds™ particle elevator.
  – Qualified conveyance rates and vacuum separation

• Established data requirements for single tower, multiple receiver reactor model for 10^5 kg H₂/day plant.
  – Building unit-ops models for detailed technoeconomic analysis beyond H2Av3
  – Better model for establishing STCH criteria necessary for meeting DOE goals

FY15 Accomplishments represent significant progress towards overcoming technical barriers to STCH development.
Thank You.

Questions?
Technical Back-Up Slides
Vibrational reduction entropy of CeO$_2$ is negative which elevates the reduction temperature.

We expect substituting CeO$_2$ with $< 2\%$ mol dopant of a large ionic radius will change the sign of the vibrational reduction entropy.

- Decrease the reduction temperature of ceria through low-level cation substitution
Systems Thermodynamic Modeling: Tower + Receivers

- **MS-5.1** – Produce a list of data requirements and input needs for high-level unit operations models. Information pulled form all tasks. Model mass and energy flows at each solar isolation.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
<th>Variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solar Field</td>
<td>46325 m²</td>
<td>Metal-oxide molar mass</td>
<td>216.1 g/mol</td>
</tr>
<tr>
<td>Solar field efficiency</td>
<td>60%</td>
<td>Metal-oxide specific heat</td>
<td>124.7 J / mol×K</td>
</tr>
<tr>
<td>Concentration Factor</td>
<td>3000</td>
<td>δ&lt;sub&gt;RC1&lt;/sub&gt; reduction extent</td>
<td>0.01</td>
</tr>
<tr>
<td>RC1 aperture area</td>
<td>4.5 m²</td>
<td>H&lt;sub&gt;rxn&lt;/sub&gt;(δ&lt;sub&gt;RC1&lt;/sub&gt;) heat of reduction reaction</td>
<td>820 kJ / mol-O&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>RC1 re-radiation temp</td>
<td>1635 K</td>
<td>δ&lt;sub&gt;Ox&lt;/sub&gt; re-oxidation extent</td>
<td>0.01</td>
</tr>
<tr>
<td>RC1 emissivity</td>
<td>0.9</td>
<td>H&lt;sub&gt;rxn&lt;/sub&gt;(δ&lt;sub&gt;Ox&lt;/sub&gt;)</td>
<td>820 kJ / mol-O&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>RC1 additional heat loss % of net radiation</td>
<td>5%</td>
<td>δ&lt;sub&gt;RC2&lt;/sub&gt; final reduction extent</td>
<td>0.25</td>
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<tr>
<td>RC1 particle outlet temp</td>
<td>1635 K</td>
<td>H&lt;sub&gt;rxn&lt;/sub&gt;(δ&lt;sub&gt;RC2&lt;/sub&gt;)</td>
<td>820 kJ / mol-O&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>RC2 aperture area (total)</td>
<td>Pi D&lt;sup&gt;2&lt;/sup&gt; or ~3.8 m&lt;sup&gt;2&lt;/sup&gt;</td>
<td>T&lt;sub&gt;0&lt;/sub&gt; (ambient temperature)</td>
<td>298 K</td>
</tr>
<tr>
<td>Equivalent of 4 receivers D=1.1 m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RC2 re-radiation temp</td>
<td>1635 K</td>
<td>PO&lt;sub&gt;2&lt;/sub&gt; (partial pressure of oxygen)</td>
<td>10 Pa</td>
</tr>
<tr>
<td>RC2 emissivity</td>
<td>0.9</td>
<td>P&lt;sub&gt;RC2&lt;/sub&gt; (pressure of n&lt;sup&gt;th&lt;/sup&gt; receiver)</td>
<td>10 Pa</td>
</tr>
<tr>
<td>RC2 additional heat loss % of net radiation</td>
<td>5%</td>
<td>T&lt;sub&gt;ox&lt;/sub&gt; (temperature of reoxidation)</td>
<td>1073 K</td>
</tr>
<tr>
<td>RC2 particle inlet temp</td>
<td>1635 K</td>
<td>Water (11) inlet temp</td>
<td>298 K</td>
</tr>
<tr>
<td>RC2 particle outlet temp</td>
<td>1635 K</td>
<td>HxA heat transfer coeff.</td>
<td>12 W / m²×K</td>
</tr>
<tr>
<td>HxA heat transfer coeff.</td>
<td>12 W / m²×K</td>
<td>Recuperator efficiency</td>
<td>50%</td>
</tr>
<tr>
<td>HxA contact area</td>
<td>5000 m²</td>
<td>Elevator A height</td>
<td>11 m</td>
</tr>
<tr>
<td>HxB heat transfer coeff.</td>
<td>12 W / m²×K</td>
<td>Elevator B height</td>
<td>8 m</td>
</tr>
<tr>
<td>HxB contact area</td>
<td>5000 m²</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
STCH Technology Similar to Cement Manufacture

- 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: \( \text{CaCO}_3 \rightarrow \text{CaO} \)
- 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