Solar Hydrogen Production with a Metal Oxide Based Thermochemical Cycle

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Sandia National Laboratories

DOE Annual Merit Review
16.05.2013

Project ID: PD081

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Overview

Timeline
- Project Start Date: 10/2008
- Project End Date: 10/01/2013*
- Project Complete: TBD

Budget
- Total project funding to date.
  DOE share: $4737K (2008-2013)
  Contractor share: $608K
- Funding for FY13.
  $435K (SNL)
- Planned Funding for FY14.
  $500K (SNL)

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

Partners
- Bucknell University, Lewisburg PA.
  Prof. Nathan Siegel
- Colorado School of Mines, Golden CO.
  Prof. Jianhua Tong
- University of Colorado, Boulder CO.
  Prof. Alan Weimer

*Project continuation and direction determined annually by DOE.
**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 a high-temperature solar-thermochemical reactor and redox materials for *efficient* hydrogen production based on a two-step, non-volatile metal oxide cycle.

**2012-2013 Objectives:**
- Design particle receiver-reactor concepts and assess feasibility.
- Discover and characterize suitable materials for two-step, non-volatile metal oxide thermochemical cycles.
- Construct and test reactor prototypes.
Technical Efforts Target Three Key Areas

- **Systems analysis.**
  - Refine estimates for $H_2$ production cost

- **Materials discovery and characterization.**
  - Target perovskite oxides exclusively

<table>
<thead>
<tr>
<th>property</th>
<th>ceria (CeO$_2$)</th>
<th>perovskite (ABO$_3$)</th>
<th>ideal</th>
</tr>
</thead>
<tbody>
<tr>
<td>redox kinetics</td>
<td>FAST</td>
<td>TBD</td>
<td>FAST</td>
</tr>
<tr>
<td>redox capacity</td>
<td>LOW</td>
<td>HIGH</td>
<td>HIGH</td>
</tr>
<tr>
<td>reduction $T_H$</td>
<td>HIGH</td>
<td>LOW</td>
<td>LOW</td>
</tr>
<tr>
<td>durability</td>
<td>HIGH</td>
<td>TBD</td>
<td>HIGH</td>
</tr>
<tr>
<td>earth abundance</td>
<td>LOW/MED</td>
<td>HIGH</td>
<td>HIGH</td>
</tr>
</tbody>
</table>

  - Assess 3 critical material functions:
    - $O_2$ uptake-and-release
    - Onset temperature for thermal reduction
    - Oxidation kinetics

- **Reactor design and development.**
  - Particle reactor with novel beam-down optics
  - Reactor design and material are critically linked

- **Reactor efficiency is the biggest cost driver.**
## Approach

### Milestones and Progress

### 03.2012-03.2013 Accomplishments

<table>
<thead>
<tr>
<th>ACTIVITY</th>
<th>MILESTONE</th>
<th>COMPLETE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Assess hydrogen production cost from a particle reactor using the H2A3 tool</td>
<td>analyzed 100,000 kg H₂/day parabolic-dish based facility using CeO₂, sensitivity analysis reveals reactor efficiency is the biggest cost driver</td>
<td>80%</td>
</tr>
<tr>
<td>Develop design principles for perovskite modification.</td>
<td>formulated three methods based on thermodynamics (ΔH, ΔS, [V°₂⁺]) and perovskite structure theory</td>
<td>30%</td>
</tr>
<tr>
<td>Synthesize a small number of candidate redox materials.</td>
<td>sol-gel and solid state reactive sintering used to synthesize 45 perovskite and 5 ceria compounds</td>
<td>100%</td>
</tr>
<tr>
<td>Characterize the thermodynamic and kinetic performance of new materials.</td>
<td>new materials screened using TGA protocol, conducted detailed kinetic studies on 6 materials</td>
<td>50%</td>
</tr>
<tr>
<td>Discover new redox active perovskites.</td>
<td>Sr₁₋ₓLaₓMn₁₋₀.₅Al₀.₅O₃ has ∼3× greater redox capacity than CeO₂ at 150 °C lower T_reduction, patent filed</td>
<td>20%</td>
</tr>
<tr>
<td>Theoretically analyze Sandia particle reactor performance</td>
<td>demonstrated that reactor operates near peak solar-to-H₂ efficiency on an annual average, also can produce excess electricity AND water from waste heat</td>
<td>100%</td>
</tr>
<tr>
<td>Design and test particle reactor concepts</td>
<td>constructed testing platform, measured &gt;30 g/s particle conveyance on recuperating auger prototype, found bed permeability is low enough for pressure seal</td>
<td>60%</td>
</tr>
<tr>
<td>Develop system-level designs and analyses of a central-receiver based platform.</td>
<td>designed novel beam-down optics for 3 MW tower, assessed thermal management of secondary reflector</td>
<td>50%</td>
</tr>
</tbody>
</table>
Reactor Efficiency Drives R&D

- Moving material to sun increases efficiency.
  - Particle transport necessary for continuous operation
- Temperature cycling increases efficiency.
  - Solid-solid heat exchange necessary for recuperation
- Reducing under vacuum increases efficiency.
  - Particle bed necessary for pressure separation
- High redox capacity material increases efficiency.
  - Bulk materials with low reduction enthalpy necessary for deep cycling

- Incorporating ALL design attributes make it possible to achieve DOE ultimate cost target for H₂ production.
Technical Accomplishments and Progress

H2A3 Analysis of 100,000 kg H₂/day Plant

- **Sandia dish-based particle reactor.**
  - CeO₂ active material:
    - variable solar efficiency
  - 22,155 parabolic dishes over 13 km²
  - 88 m² per dish
  - Meteorological data for Daggett, CA
  - Centralized delivery at 300 psia H₂

- **380 MW_TH.**
  - Main electrical loads are dish drives, H₂ pumping, and H₂O pumping provide by solar

- Analysis conducted in collaboration with Strategic Analysis, Inc.

- Increased reactor efficiency yields significant reduction in H₂ costs.
- Reactor design and materials are critically important.
Material Discovery Effort Focused on Perovskites

- Synthesized 45 compounds from 9 elements:
  - Al, Cr, Ce, Fe, La, O, Sr, Ti, Zr
  - Sol-gel or Solid State Reactive Sintering
- Identified promising candidates using TGA screening.
- Detailed kinetic measurements on 6 materials in Sandia’s laser-heated stagnation flow reactor.

More ideal materials increase solar-to-hydrogen efficiency.
Design Principles for Perovskite Modification

- **Method 1**: reduction enthalpy and entropy.
  - Taken from published data

- **Method 2**: oxygen non-stoichiometry.
  - Taken from published data

- **Method 3**: perovskite structure theory.
  - Goldschmidt tolerance factor
    - Ionic radii \( r_A, r_B, r_O \)
  - Redox active B-site transition metal
  - Heterosize A-site substitution \( r_{A'} \neq r_A \)
  - Heterovalent A-site substitution \( n_{A'} \neq n_A \)

\[
(A_{1-x}A'_x)^{n' +} \left(B_{1-y}B'_y \right)^{m' +} O_{3-\delta}
\]

\[
\frac{(r_A + r_O)}{\sqrt{2}(r_B + r_O)} \sim 1
\]

- **Large oxygen non-stoichiometry** \( (ABO_{3-\delta}, 0.5 \geq \delta \geq 0.1) = \text{high capacity.} \)
- **High oxygen mobility** = fast kinetics.
Technical Accomplishments and Progress

Discovered Perovskite with Lower Reduction Enthalpy than CeO$_2$

SLMAn = Sr$_x$La$_{1-x}$Mn$_y$Al$_{1-y}$O$_{3-\delta}$

- Onset of O$_2$ evolution 300 °C lower than CeO$_2$.
- Perovskite oxygen yield 8 × > CeO$_2$ at $T_R = 1350$ °C.
- $\delta_{\text{PEROVSKITE}} \gg \delta_{\text{CERIA}}$
- Lower reduction temperature and larger non-stoichiometry ($\delta$) increase solar-to-hydrogen efficiency.
Technical Accomplishments and Progress

Discovered Perovskite with Higher Capacity at lower $T_R$ than CeO$_2$

- Perovskite compounds split $H_2O$ in a thermochemical cycle.
  - First of a kind observation
- Kinetics benchmarked against CeO$_2$.
  - Similarly fast oxidation rates
- Make $\sim 9 \times$ more $H_2$ than CeO$_2$ at $T_R = 1350 \, ^\circ C$.

<table>
<thead>
<tr>
<th>compound</th>
<th>$H_2$ (µmole/g)</th>
</tr>
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<tbody>
<tr>
<td>SLMA1</td>
<td>307</td>
</tr>
<tr>
<td>SLMA2</td>
<td>277</td>
</tr>
<tr>
<td>SLMA3</td>
<td>220</td>
</tr>
<tr>
<td>CeO$_{2-\delta}$</td>
<td>32</td>
</tr>
</tbody>
</table>

- Patent filed on a family of Sr- and Mn- substituted LaAlO$_3$.
- Likely many other perovskites that can perform even better!

SLMAn = $Sr_xLa_{1-x}Mn_yAl_{1-y}O_3-\delta$
Technical Accomplishments and Progress

Perovskite Materials are Durable

- Conducted 80, 30 minute CO₂ splitting cycles.
- 15 min reduction at 1350 °C, 15 min oxidation at 1000 °C.
  - Heating rate = 6 °C/s

- **No short-term degradation mechanisms visible in perovskite.**
Technical Accomplishments and Progress

Theoretical Analysis of Sandia Reactor Concept: Solar-to-H₂ Efficiency

\[ \eta = \left( \frac{P_{TH}}{P_S} \right) \left( \frac{HHV_{H_2}}{Q} \right) = \frac{\dot{n}_{H_2} HHV_{H_2}}{P_S} \]

\[ \Rightarrow \dot{n}_{H_2} = \frac{P_{TH}}{Q} \]

\[ P_{TH} = r_{12} * r_d * t_W * A * P_S - P_{rad} \]

\[ Q = Q_{TR} + Q_{SH} + Q_{AUX} \]

All-inclusive efficiency metric:

- Collection losses.
  - Concentrator and re-radiation
- Oxide heating.
- Oxide thermal reduction.
- Feedstock heating (steam).
- Pumping.
- Electrical/mechanical work.

- Solar Efficiency = Solar-to-H₂ conversion efficiency based on HHV.
- Model is used to explore optimal reactor operating conditions.
- Model is used to assess performance gains from new materials.
Technical Accomplishments and Progress

Annual Average Solar Efficiency ≈ Peak Efficiency

Based on solar resource available in Daggett, CA

- Solar efficiency weakly dependent on DNI in particle reactor.
  - Change particle flow rate to maintain design point efficiency

- Annual average efficiency nearly equal to design point efficiency.
  - Weak DNI dependence

- Reactor ALWAYS operates near peak efficiency.
- Compensate for solar variability (400 < DNI < 1000).
Technical Accomplishments and Progress

Annual Average Efficiency Dependent on O₂ Pressure

- Pumping speed and recuperator efficiency affect solar efficiency.
- Increase solar efficiency by lowering O₂ pressure and raising recuperator efficiency.

- Pumping speed can compensate for poor heat recuperation.
- Vice Versa.

Lines: Design-point efficiency
Symbols: Annual average efficiency
Cutoff: 250 W/m² DNI; 30 MPH wind

increased efficiency at lower O₂ pressure
Technical Accomplishments and Progress

Produce $\text{H}_2\text{O}$ and Excess Electricity

Water condensation: $\sim 3$ kJ/mol (0.85 kJ/mol theoretical)

- High quality waste heat can generate electricity and produce water.
  - Use absorption chiller to condense water from the atmosphere
  - Sell excess electricity

- Year-round operation using only sunshine and air.
- No need to find or pipe $\text{H}_2\text{O}$ into desert.
Technical Accomplishments and Progress

Prototype Validates Conveyance and Pressure Separation

- Conveying rate far exceeds particle flow requirement.
  - Tested prototype auger designed for heat recuperation
  - Narrow fined, double helix
- Bed permeability sufficient for sealing.
  - Pressure separation key to high efficiency

- No technical show stoppers!
- A clear path to high temperature prototype development.
Particle Reactor Requires Beam Down Optics

- $3 \text{ MW}_{\text{TH}}$, 75 m tower height, 6606 heliostats (1 m$^2$ mirror).
  - Reactor located near tower reflector
  - 1,600 kW/m$^2$ on 2 m aperture, peak flux > 6,000 kW/m$^2$
  - Terminal concentrator not needed
- Flat tower reflector must tolerate high solar flux ~ 140 kW/m$^2$ (140 suns).

• Basis for a central receiver H2A3 analysis.
Technical Accomplishments and Progress

Assess Thermal Management of Reflector

- Evaluating forced air convection for thermal management.
- Back surface mirror provides durability needed for outdoor operation.
  - 5-10% of incident solar energy absorbed by the mirror
- Max allowable mirror temperature between 100-160 °C.

- Cooling secondary mirror not an issue.
FY13 Collaborations

• Prof. Nathan Siegel at Bucknell University.
  – Solar interface, systems and economic analysis

• Prof. Jianhua Tong at the Colorado School of Mines.
  – Perovskite synthesis and TGA screening

• Prof. Alan Weimer at the University of Colorado.
  – Students in residence at SNL/CA characterizing Sandia materials
Proposed Future Work

- Estimated FY14 funding target.
  - Continue perovskite research and development. Use lessons learned from early success to propose and validate composition—activity relationships. Investigate ABO$_3$ formulations from earth-abundant elements (rock-forming elements).
  - Modify engineering test stand for high-temperature operation ($< 5$ kW$_{TH}$ operating off-sun). Evaluate designs for solid-solid heat exchange, oxidation chamber, particle conveyance, gas flow, durability, etc. Investigate tradeoffs between recuperation, pumping, and material activity. Validate and refine reactor model.
  - Complete H2A3 analysis for our centralized receiver design. Include sensitivity studies to resolve critical paths for reducing H$_2$ production costs.
  - Evaluate optical components for the beam-down design using Bucknell University’s Solar Simulator.

- Funds in modest excess of FY14 estimate.
  - Upgrade stagnation flow reactor to operate at higher pressure (1-2 atm) and higher throughput. Minimize material characterization bottleneck.
  - Initiate computational material screening effort using DFT methods.
  - Build balance of plant infrastructure for engineering test stand to interface with Sandia’s solar furnace (on-sun testing).
• Analyzed H₂ production costs for a parabolic-dish based particle reactor.
  – 100,000 kg H₂/day, DOE’s ultimate cost targets are achievable
  – Sensitivity analysis reveals the importance of reactor efficiency
• Discovered Sr$_{1-x}$La$_x$Mn$_{1-y}$Al$_y$O$_3$ perovskite that outperforms CeO$_2$.
  – Developed methodology for perovskite modification and material discovery
  – Synthesized and screened 45 compounds
  – Perovskite produces 9× more H₂ than CeO$_2$ at 150 °C lower reduction temperature
• Analyzed efficiency of Sandia particle reactor under various operating conditions.
  – Reactor ALWAYS operates at near peak solar-to-hydrogen efficiency
  – Reactor produces high quality waste heat to make excess electricity and provide water
• Validated particle conveyance and pressure separation in cold prototype.
  – Exceeded required particle flow rates (> 30 g/s)
  – Particle bed gas permeability sufficiently small to ensure vacuum-tight seal
• Designed beam-down optical system for particle reactor operating at 3 MW$_{TH}$.
  – Novel design for flat tower reflector
  – Heat management of tower reflector can be accomplished through air cooling

- **FY13 Accomplishments represent significant progress towards overcoming technical barriers to STCH development.**
Technical Back-Up Slides
Resource efficiency = 95% for Daggett, CA (DNI > 300W/m²)

Operational ~ 94%
Equip. Availability = 97%, Blocking & Shading = 98%, Wind Outage = 99%

Optical ~ 79%
Reflectivity = 93% (two reflections)
Dirt = 95%
Window = 95%
Tracking = 99%
Intercept = 95%

Receiver ~ 82%
Radiation = 82%
Conduction/Convection = 0%

Solar-to-heat: ~58%
Thermal ~44%

~25% solar to H₂ annual average
Approach

Experimental Methods for Characterizing Redox Materials

• Surface analysis.
  – Surface Raman, XPS
• Material properties.
  – BET surface area
  – SEM-EDX, TEM-EELS, XRD
• Kinetic measurements.
  – Stagnation flow reactor
    • 500 W CW NIR laser heating
    • Modulated beam mass spectrometer
• Screen for O₂ uptake and release.
  – Assess redox viability
• Resolve thermal reduction behavior.
• Resolve water splitting behavior.
  – Variable T, P, [H₂O]
• Analysis.
  – Resolve rate limiting mechanisms
  – Develop kinetic models
  – Evaluate material stability
  – Test cycle performance

• Assess material behavior at heating rates > 10°C/s.
• Expose material to many rapid heating cycles.
Technical Accomplishments and Progress

Discovered Perovskite Formulated without Rare-Earth Elements

- Perovskite oxygen non-stoichiometry comparable to CeO₂ @ Tᵣ = 1350 °C.

- Perovskite splits H₂O.
- Produce ~5x less H₂ at lower Tᵣ (1350 °C vs. 1500 °C).

- Ca(TiₓFe₁₋ₓ)O₃ comprised of earth-abundant rock-forming elements.
- Discovery of cheap materials avoids rare-earth market volatility issues.
Technical Accomplishments and Progress

Sandia Reactor Also Operates Efficiently at Low DNI

- High solar utilization under most operating conditions.
  - 25% solar-to-H₂ annual average efficiency expected
- Use low DNI in the morning for system warm-up.

**Design point: DNI = 1 kW/m²**

nominal $p_{O_2} = 100$ Pa

- Increased heat recovery
- Decreased $p_{O_2}$

**Recuperator effectiveness [%]**

- 95% nominal
- 85% recuperator
- 75% efficiency
- 50%

**Reduction pressure [Pa]**

- 95
- 85
- 75
- 50

**Thermal Efficiency [%]**

- 95
- 85
- 75
- 50

**H₂ production [mol/h]**

- 95
- 85
- 75
- 50

**Time of year [h]**

- Morning (warm-up) evening
Prototype Platform Construction and Testing