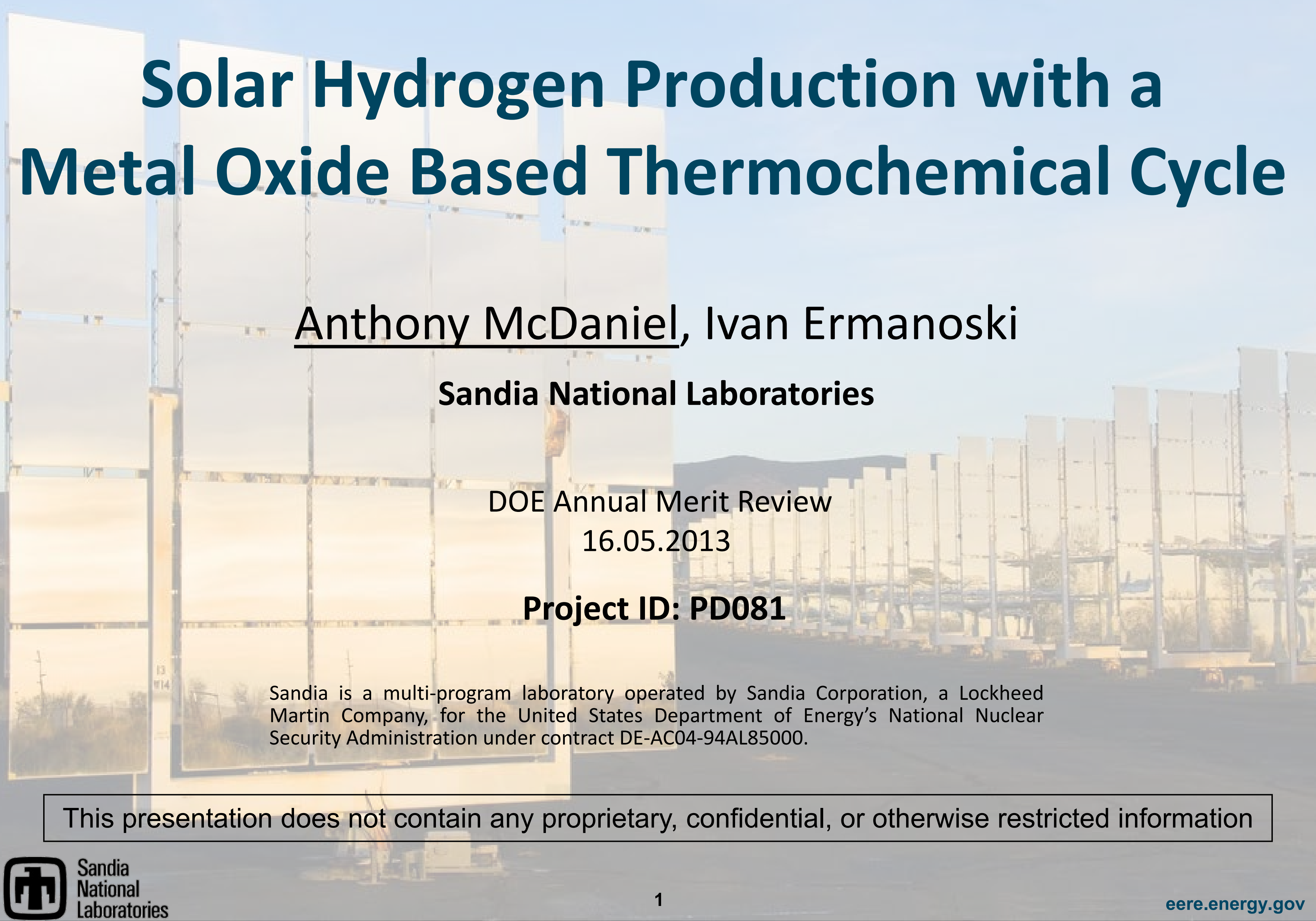

Solar Hydrogen Production with a Metal Oxide Based Thermochemical Cycle

Anthony McDaniel, Ivan Ermanoski

Sandia National Laboratories

DOE Annual Merit Review
16.05.2013

Project ID: PD081

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.

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.
- X. Chemical Reactor Development and Capital Costs.
- 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

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*Project continuation and direction determined annually by DOE.

Relevance

•<u>DOE Objective</u>: 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.

- **<u>Project Objective</u>: 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

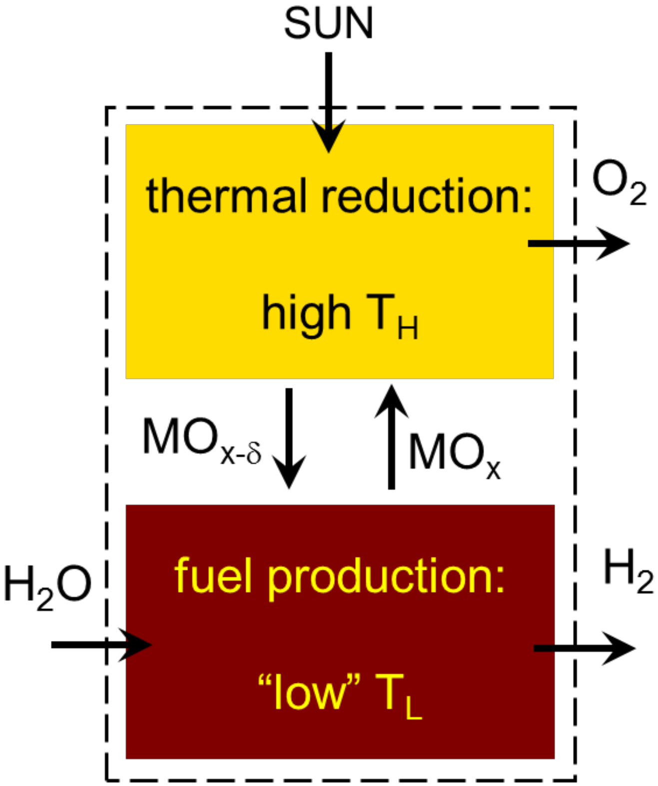
property	ceria (CeO_2)	perovskite (ABO_3)	ideal
redox kinetics	**FAST**	**TBD**	**FAST**
redox capacity	**LOW**	**HIGH**	**HIGH**
reduction T_H	**HIGH**	**LOW**	**LOW**
durability	**HIGH**	**TBD**	**HIGH**
earth abundance	**LOW/MED**	**HIGH**	**HIGH**

  - 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



Two-step metal oxide cycle

• Reactor efficiency is the biggest cost driver.

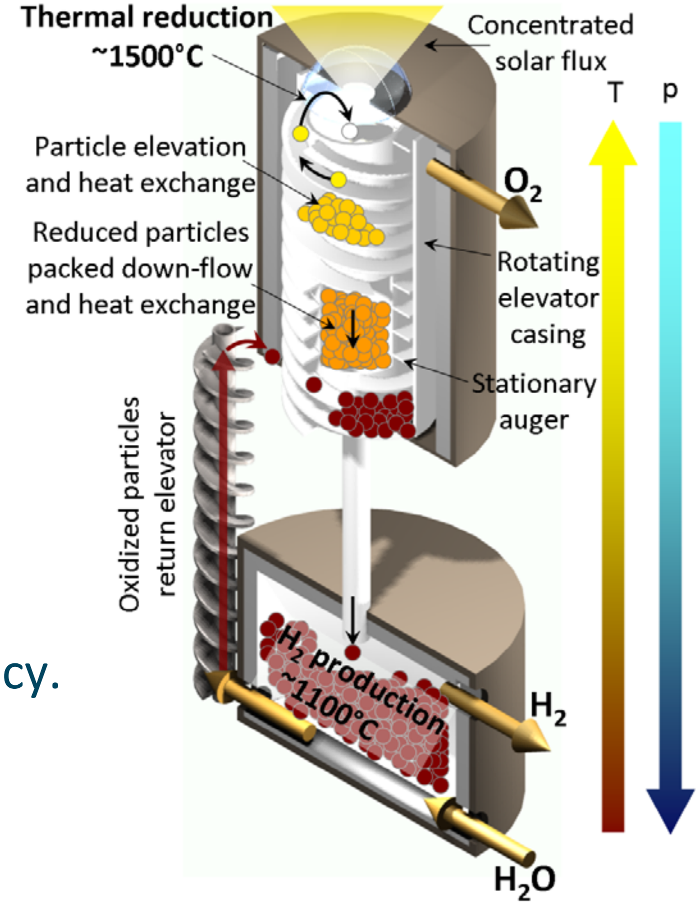
Milestones and Progress

03.2012-03.2013 Accomplishments

ACTIVITY	MILESTONE	COMPLETE
Assess hydrogen production cost from a particle reactor using the H2A3 tool	analyzed 100,000 kg H_2/day parabolic-dish based facility using CeO_2, sensitivity analysis reveals reactor efficiency is the biggest cost driver	**80%**
Develop design principles for perovskite modification.	formulated three methods based on thermodynamics (ΔH, ΔS, $[V_O^{\bullet\bullet}]$) and perovskite structure theory	**30%**
Synthesize a small number of candidate redox materials.	sol-gel and solid state reactive sintering used to synthesize 45 perovskite and 5 ceria compounds	**100%**
Characterize the thermodynamic and kinetic performance of new materials.	new materials screened using TGA protocol, conducted detailed kinetic studies on 6 materials	**50%**
Discover new redox active perovskites.	$Sr_{1-x}La_xMn_{1-y}Al_yO_3$ has ~3× greater redox capacity than CeO_2 at 150 °C lower $T_{reduction}$, patent filed	**20%**
Theoretically analyze Sandia particle reactor performance	demonstrated that reactor operates near peak solar-to-H_2 efficiency on an annual average, also can produce excess electricity AND water from waste heat	**100%**
Design and test particle reactor concepts	constructed testing platform, measured >30 g/s particle conveyance on recuperating auger prototype, found bed permeability is low enough for pressure seal	**60%**
Develop system-level designs and analyses of a central-receiver based platform.	designed novel beam-down optics for 3 MW tower, assessed thermal management of secondary reflector	**50%**

Reactor Efficiency Drives R&D

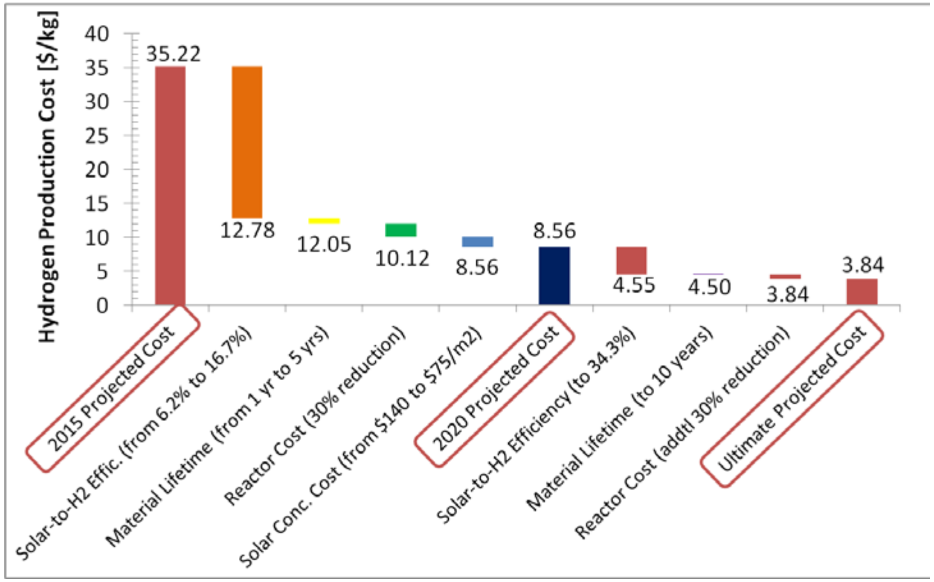
- Moving material to sun increases efficiency.
  - Particle transport necessary for continuous operation
- Temperature cycling increases efficiency.
  - Solid-solid heat exchange necessary for recuperation
- Reducing under vacuum increases efficiency.
  - Particle bed necessary for pressure separation
- 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 H_2 production.**

H2A3 Analysis of 100,000 kg H_2/day Plant

- Sandia dish-based particle reactor.
  - CeO_2 active material: variable solar efficiency
  - 22,155 parabolic dishes over 13 km^2
  - 88 m^2 per dish
  - Meteorological data for Daggett, CA
  - Centralized delivery at 300 psia H_2

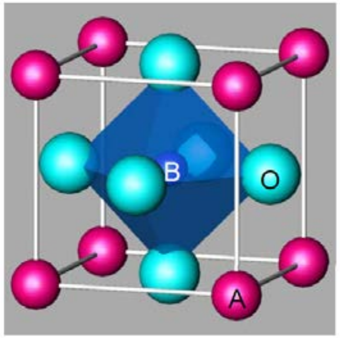


- 380 MW_{TH}.
  - Main electrical loads are dish drives, H_2 pumping, and H_2O pumping provide by solar

- Analysis conducted in collaboration with Strategic Analysis, Inc.

- **Increased reactor efficiency yields significant reduction in H_2 costs.**
- **Reactor design and materials are critically important.**

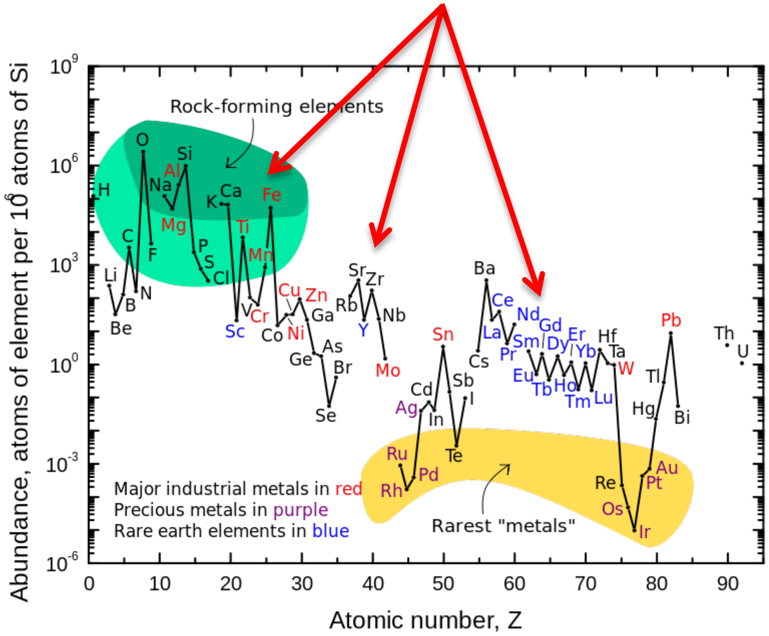
Material Discovery Effort Focused on Perovskites



ABO_3

- 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.

perovskites fall in these regions



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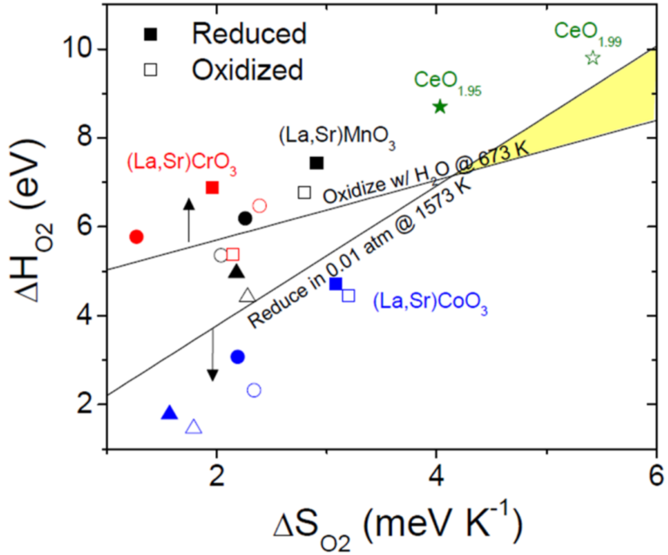
earth abundance	**LOW/MED**	**HIGH**	**HIGH**

- **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 ($n'_{A'} \neq n_A$)



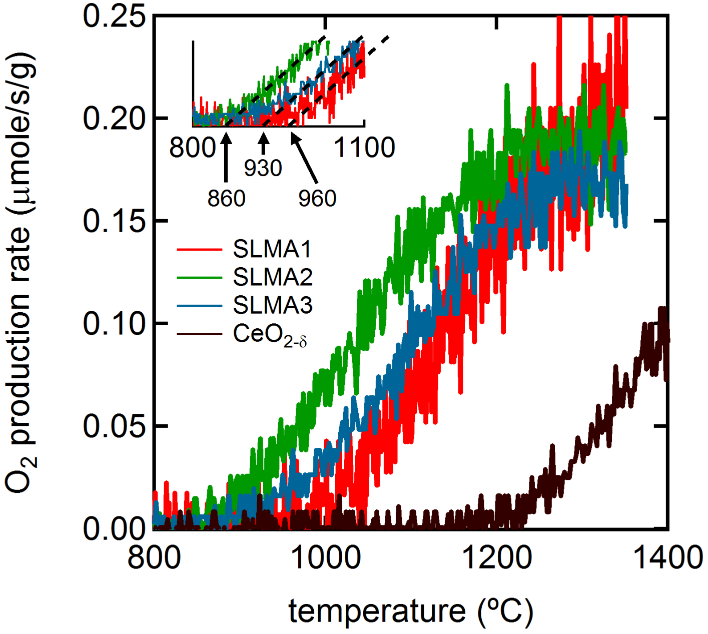
$$(A^{n+}_{1-x}A'^{n'+}_{x})(B^{m+}_{1-y}B'^{m'+}_{y})O_{3-\delta}$$

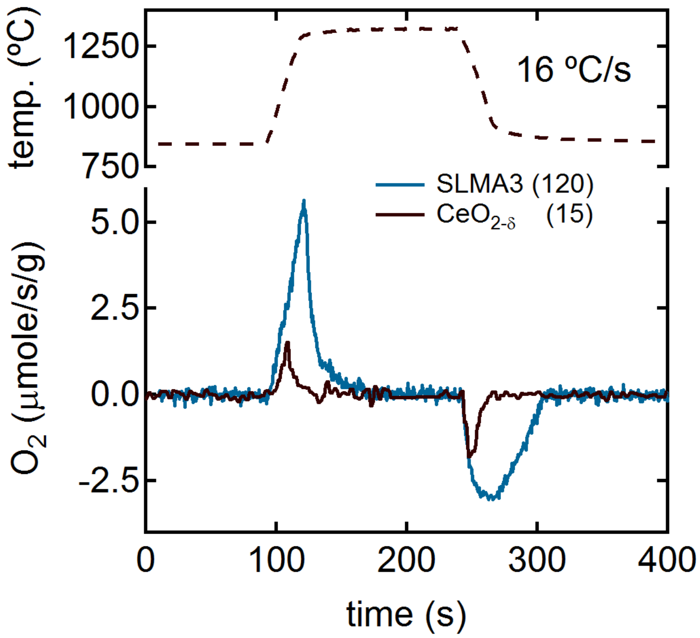
$$(r_A + r_O)/\sqrt{2}(r_B + r_O) \sim 1$$

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

Discovered Perovskite with Lower Reduction Enthalpy than CeO_2

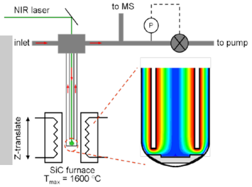
$SLMAn = Sr_xLa_{1-x}Mn_yAl_{1-y}O_{3-\delta}$





- Onset of O_2 evolution 300 °C lower than CeO_2.

- Perovskite oxygen yield 8 × > CeO_2 at T_R = 1350 °C.
- $\delta_{PEROVSKITE} >> \delta_{CERIA}$

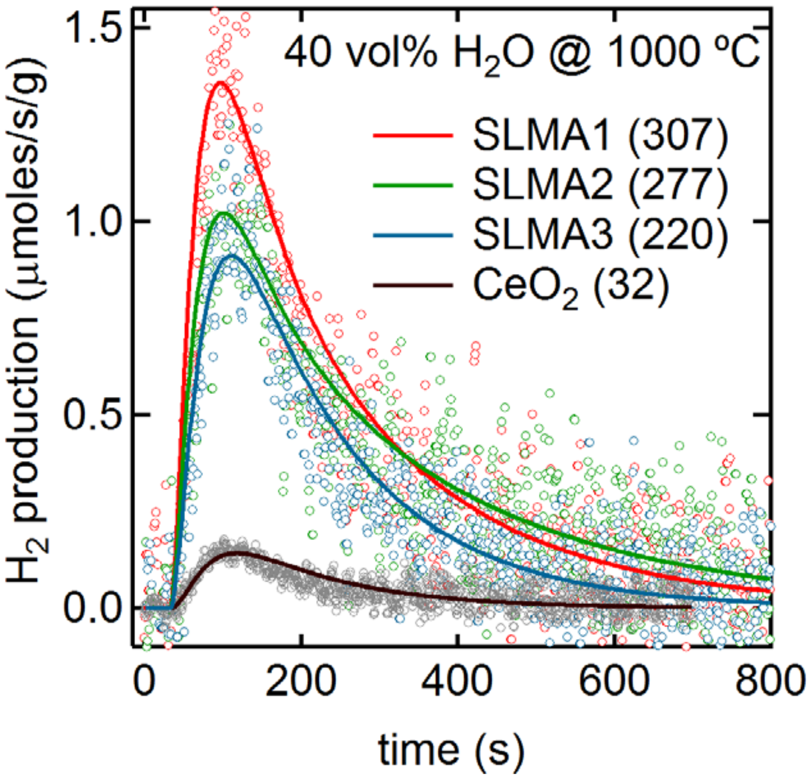


- **Lower reduction temperature and larger non-stoichiometry (δ) increase solar-to-hydrogen efficiency.**

Discovered Perovskite with Higher Capacity at lower T_R than CeO_2

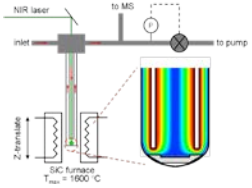
- Perovskite compounds split H_2O in a thermochemical cycle.
  - First of a kind observation
- Kinetics benchmarked against CeO_2.
  - Similarly fast oxidation rates
- Make ~9× more H_2 than CeO_2 at T_R = 1350 °C.

SLMAn = $Sr_xLa_{1-x}Mn_yAl_{1-y}O_{3-\delta}$



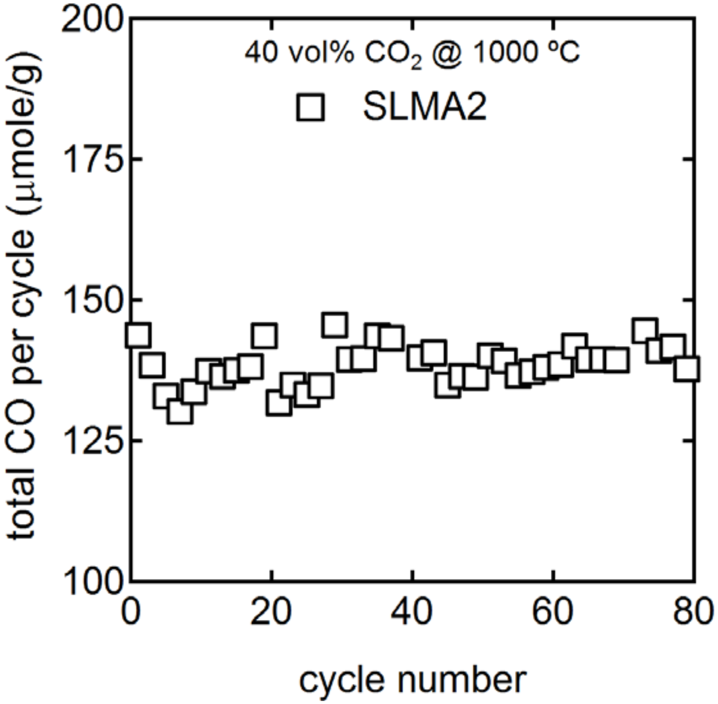
compound	H_2 (μmole/g)
SLMA1	307
SLMA2	277
SLMA3	220
$CeO_{2-\delta}$	32

- **Patent filed on a family of Sr- and Mn- substituted $LaAlO_3$.**
- **Likely many other perovskites that can perform even better!**



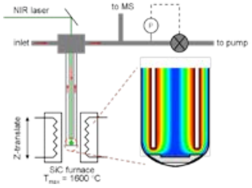
Perovskite Materials are Durable

SLMAn = $Sr_xLa_{1-x}Mn_yAl_{1-y}O_{3-\delta}$



- Conducted 80, 30 minute CO_2 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.**



Theoretical Analysis of Sandia Reactor Concept: Solar-to-H_2 Efficiency

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

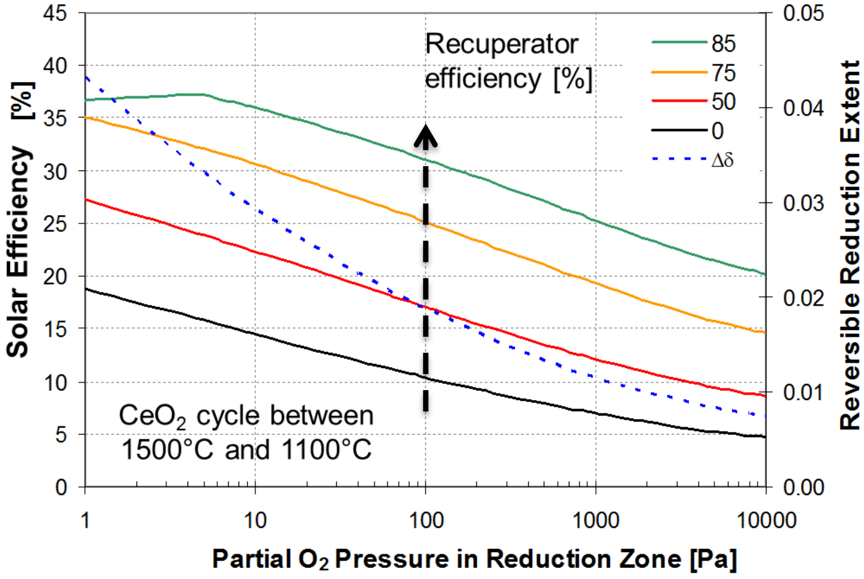
$$P_{TH} = r_{12} * r_d * t_W * A * P_S - P_{rad}$$

$$Q = Q_{TR} + Q_{SH} + Q_{AUX}$$

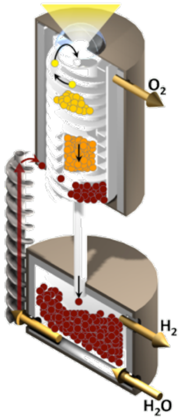
new materials impact Q and P_{TH}

All-inclusive efficiency metric:

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



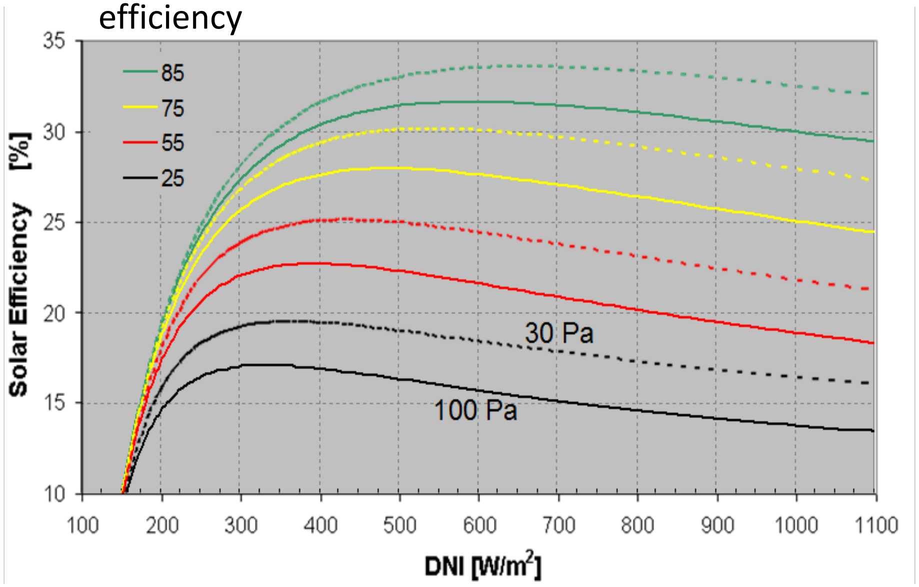
increased efficiency at larger Δδ

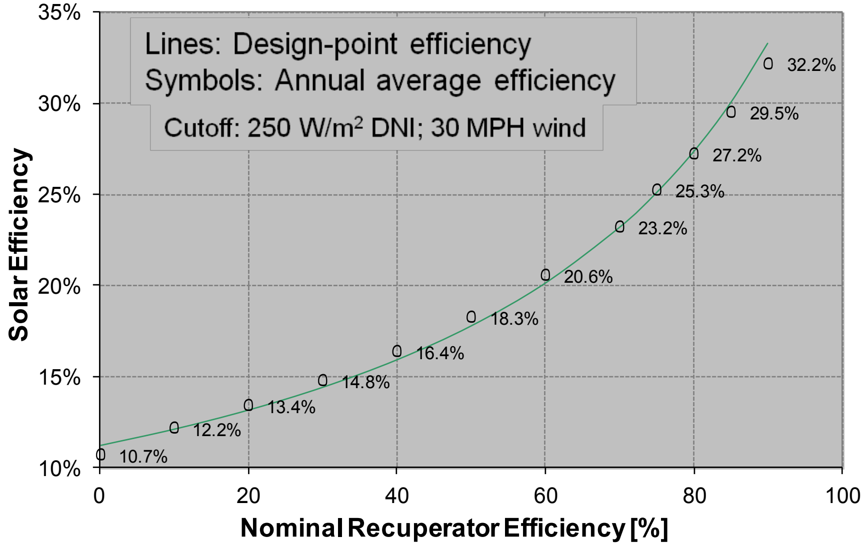


- **Solar Efficiency = Solar-to-H_2 conversion efficiency based on HHV.**
- **Model is used to explore optimal reactor operating conditions.**
- **Model is used to assess performance gains from new materials.**

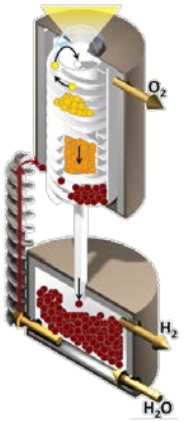
Annual Average Solar Efficiency ≈ Peak Efficiency

Based on solar resource available in Daggett, CA



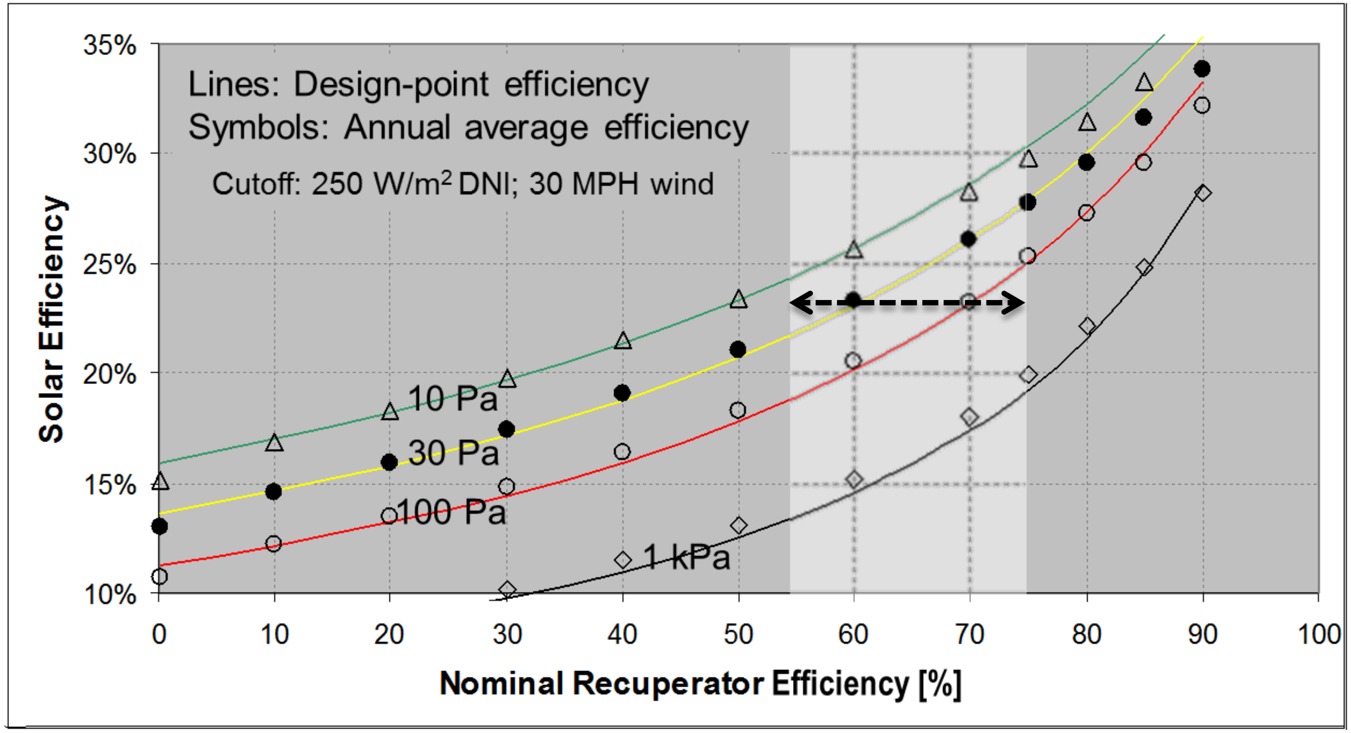


- Solar efficiency weakly dependent on DNI in particle reactor.
  - Change particle flow rate to maintain design point efficiency
- Annual average efficiency nearly equal to design point efficiency.
  - Weak DNI dependence



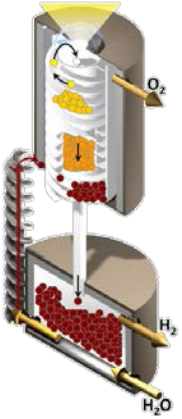
- **Reactor ALWAYS operates near peak efficiency.**
- **Compensate for solar variability (400 < DNI < 1000).**

Annual Average Efficiency Dependent on O_2 Pressure



increased efficiency at lower O_2 pressure

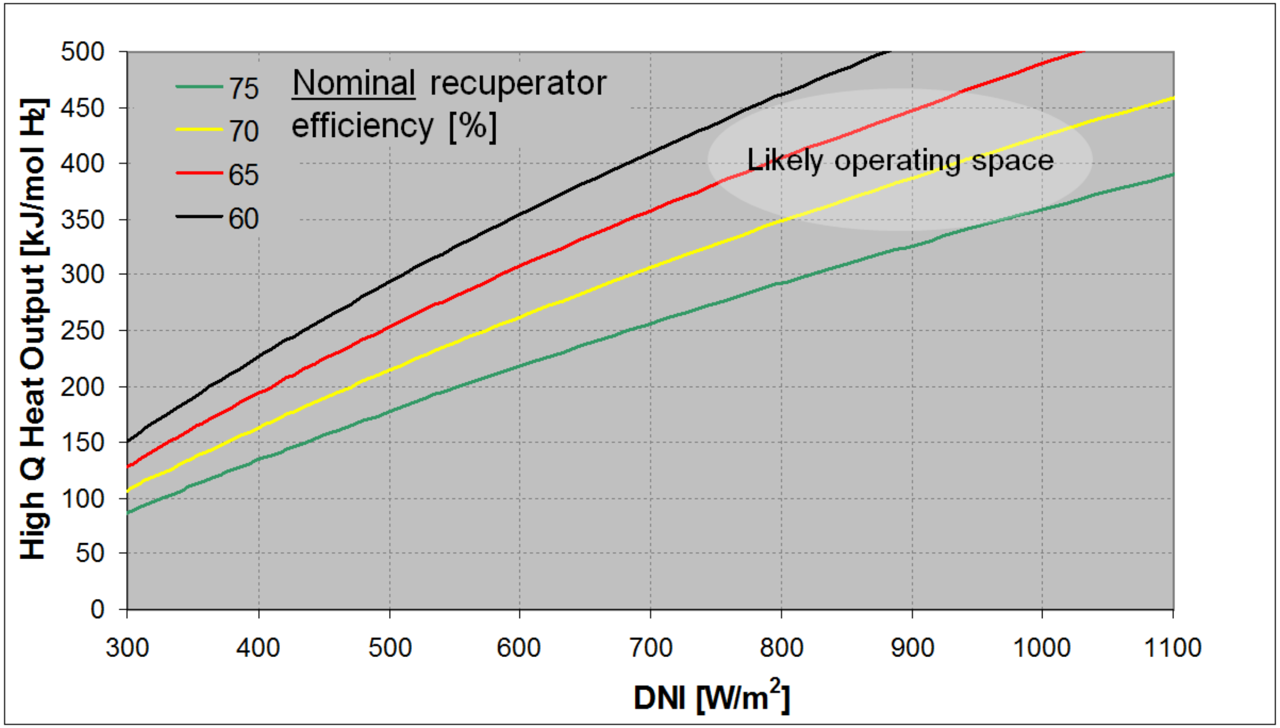
- Pumping speed and recuperator efficiency affect solar efficiency.
- Increase solar efficiency by lowering O_2 pressure and raising recuperator efficiency.



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

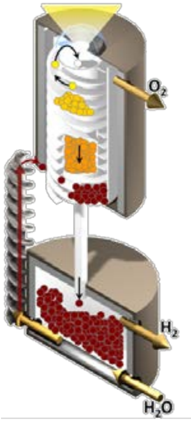
Produce H_2O and Excess Electricity

Water condensation: ~ 3 kJ/mol (0.85 kJ/mol theoretical)

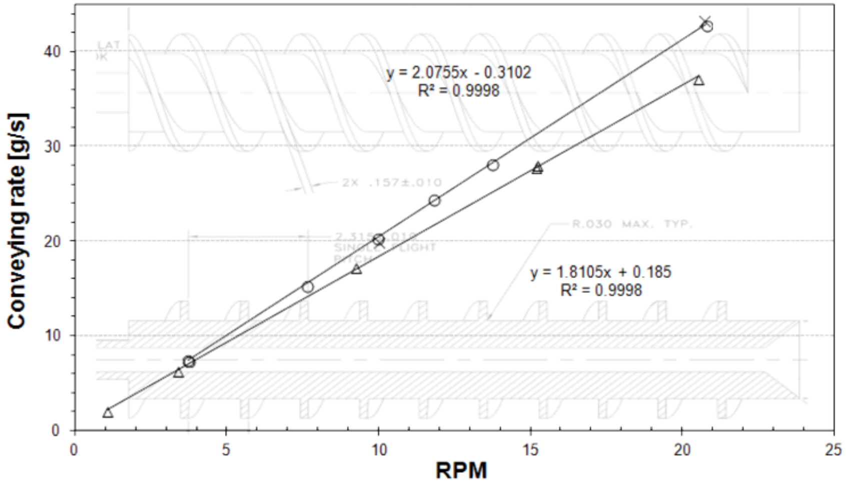


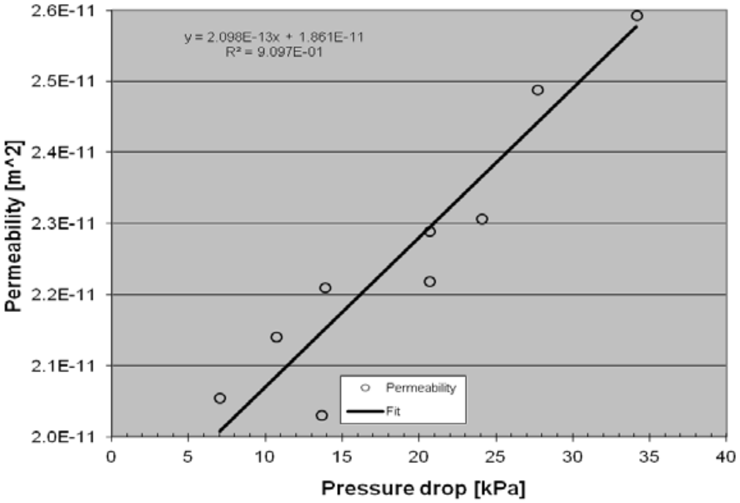
- High quality waste heat can generate electricity and produce water.
  - Use absorption chiller to condense water from the atmosphere
  - Sell excess electricity

- **Year-round operation using only sunshine and air.**
- **No need to find or pipe H_2O into desert.**



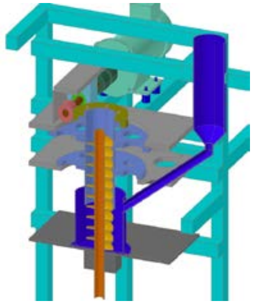
Prototype Validates Conveyance and Pressure Separation





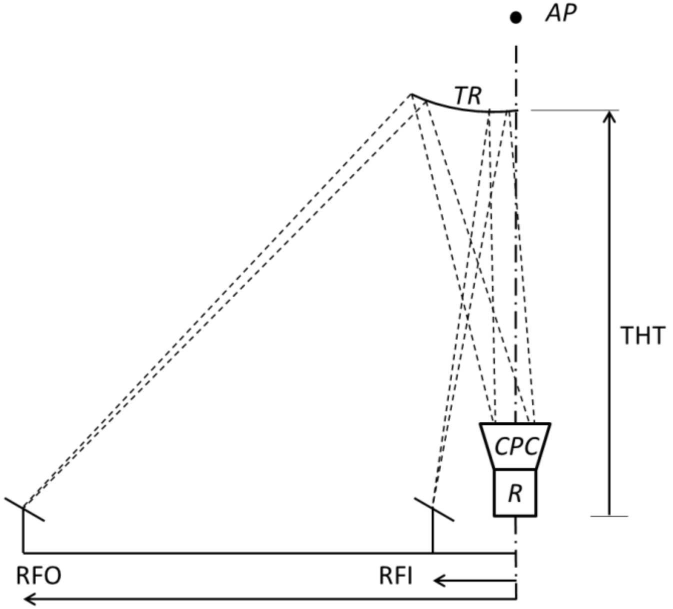
- Conveying rate far exceeds particle flow requirement.
  - Tested prototype auger designed for heat recuperation
  - Narrow fined, double helix

- Bed permeability sufficient for sealing.
  - Pressure separation key to high efficiency

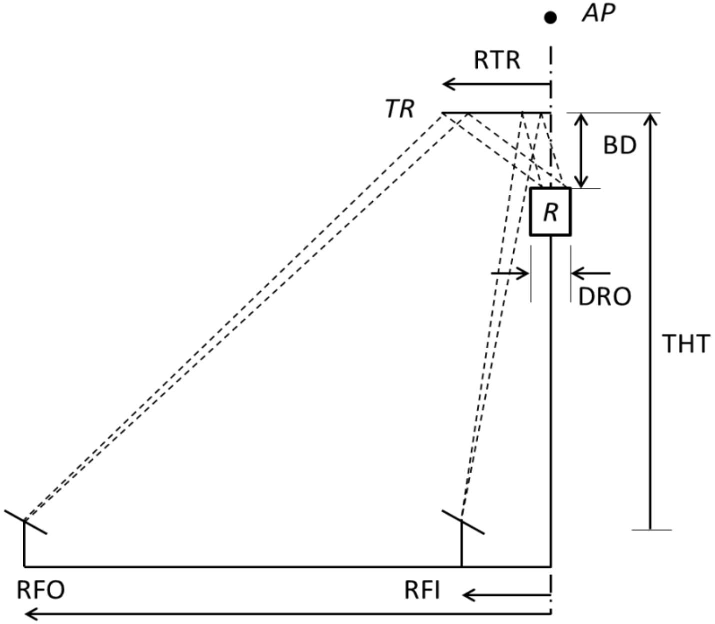


- **No technical show stoppers!**
- **A clear path to high temperature prototype development.**

Particle Reactor Requires Beam Down Optics



Conventional Beam Down Tower



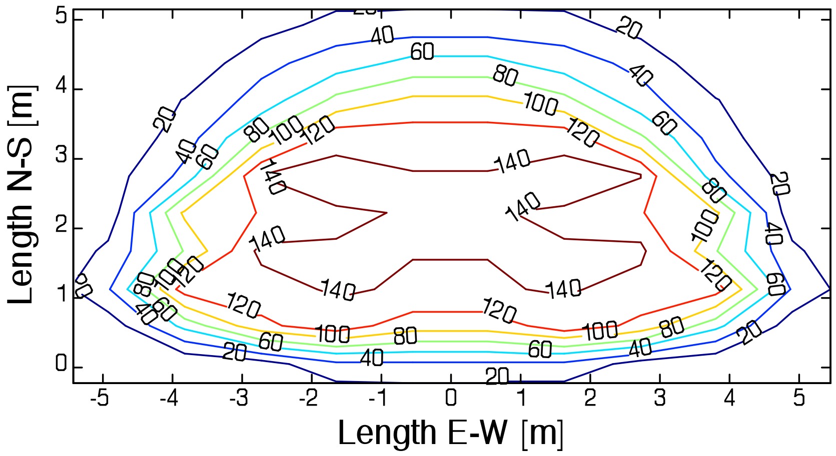
Modified Beam Down Tower

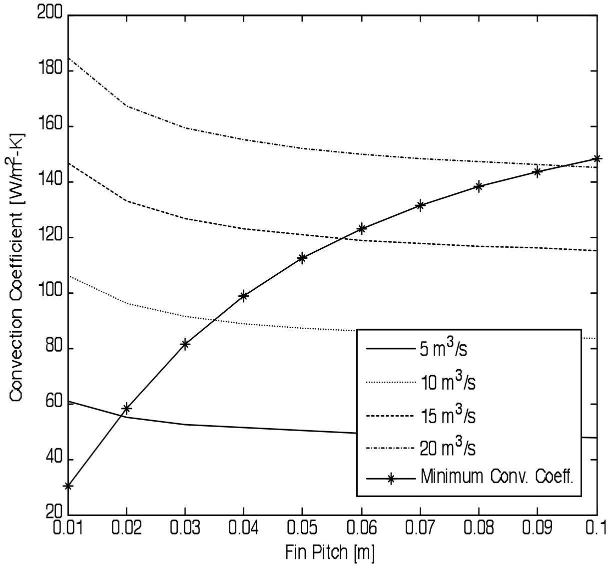
- 3 MW_{TH}, 75 m tower height, 6606 heliostats (1 m^2 mirror).
  - Reactor located near tower reflector
  - 1,600 kW/m^2 on 2 m aperture, peak flux > 6,000 kW/m^2
  - Terminal concentrator not needed
- Flat tower reflector must tolerate high solar flux ~ 140 kW/m^2 (140 suns).

- **Basis for a central receiver H2A3 analysis.**

Assess Thermal Management of Reflector

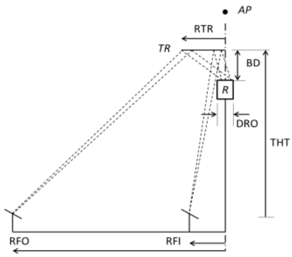
flux map (kW / m²)





$$h_{min} = \frac{\alpha * \text{Flux}}{(T_{surface} - T_{air})\left(\frac{2H_{fin}\eta_{fin}}{\text{Pitch}} + 1\right)}$$

- 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).

Summary

- Analyzed H_2 production costs for a parabolic-dish based particle reactor.
  - 100,000 kg H_2/day, DOE's ultimate cost targets are achievable
  - Sensitivity analysis reveals the importance of reactor efficiency
- Discovered $Sr_{1-x}La_xMn_{1-y}Al_yO_3$ perovskite that outperforms CeO_2.
  - Developed methodology for perovskite modification and material discovery
  - Synthesized and screened 45 compounds
  - Perovskite produces 9× more H_2 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

System Level: Many Losses and High Annual Efficiency

Resource efficiency = 95% for Daggett, CA (DNI > 300W/m^2)

Operational ~ 94%

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

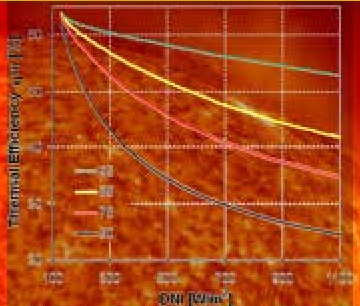
Optical ~ 79%

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 H$_2$ annual average**

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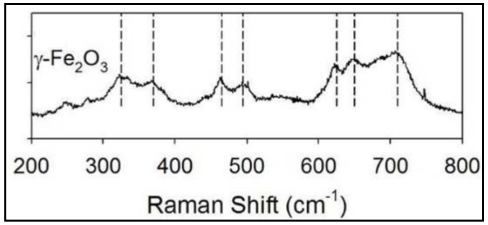
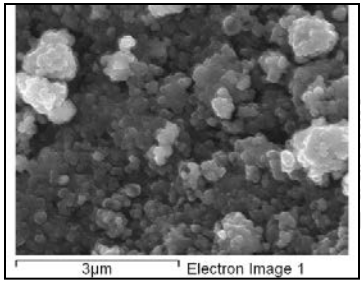
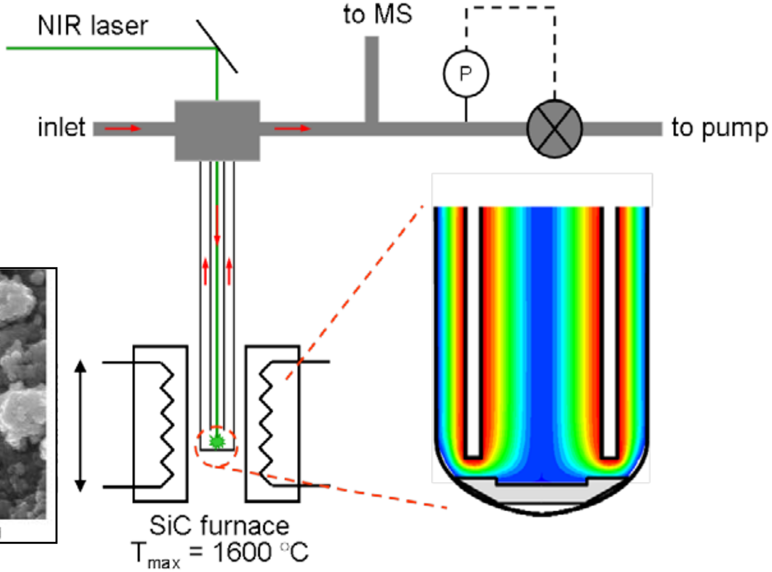
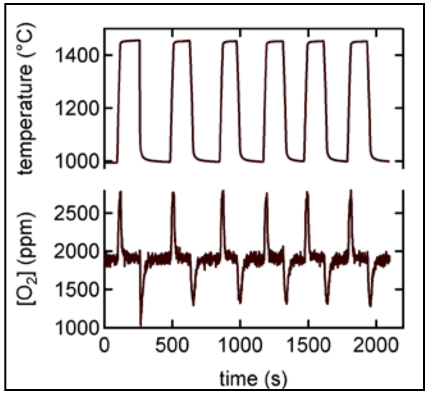
Experimental Methods for Characterizing Redox Materials

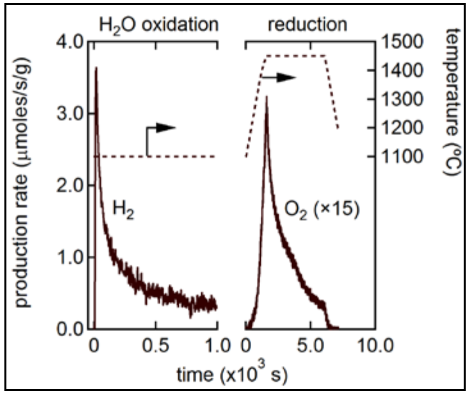
- Surface analysis.
  - Surface Raman, XPS
- Material properties.
  - BET surface area
  - SEM-EDX, TEM-EELS, XRD
- Kinetic measurements.
  - Stagnation flow reactor
    - 500 W CW NIR laser heating
    - Modulated beam mass spectrometer
- Screen for O_2 uptake and release.
  - Assess redox viability
- Resolve thermal reduction behavior.
- Resolve water splitting behavior.
  - Variable T, P, $[H_2O]$
- Analysis.
  - Resolve rate limiting mechanisms
  - Develop kinetic models
  - Evaluate material stability
  - Test cycle performance





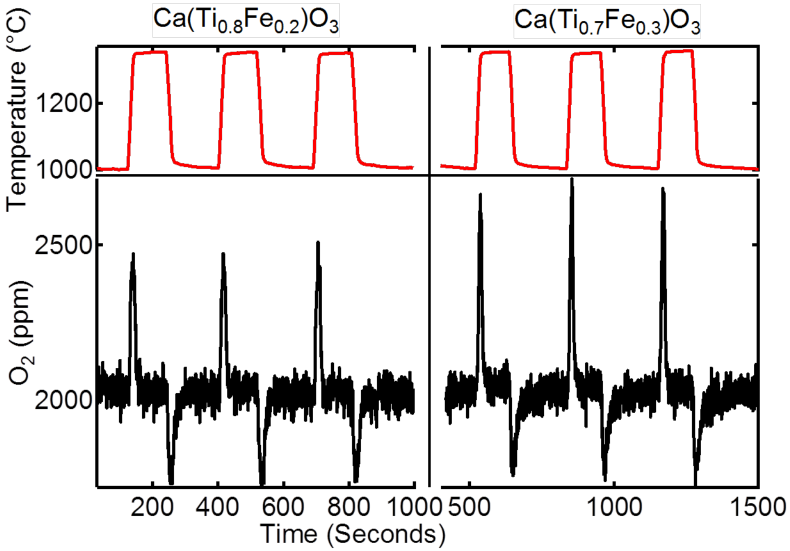




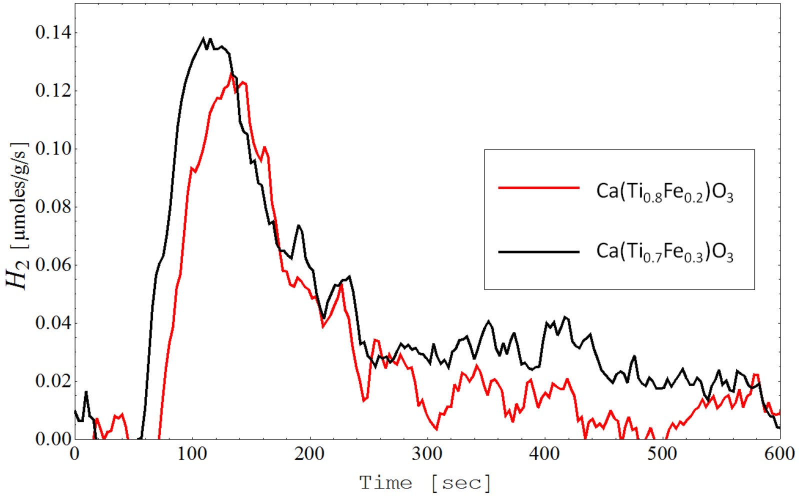


- **Assess material behavior at heating rates > 10°C/s.**
- **Expose material to many rapid heating cycles.**

Discovered Perovskite Formulated without Rare-Earth Elements



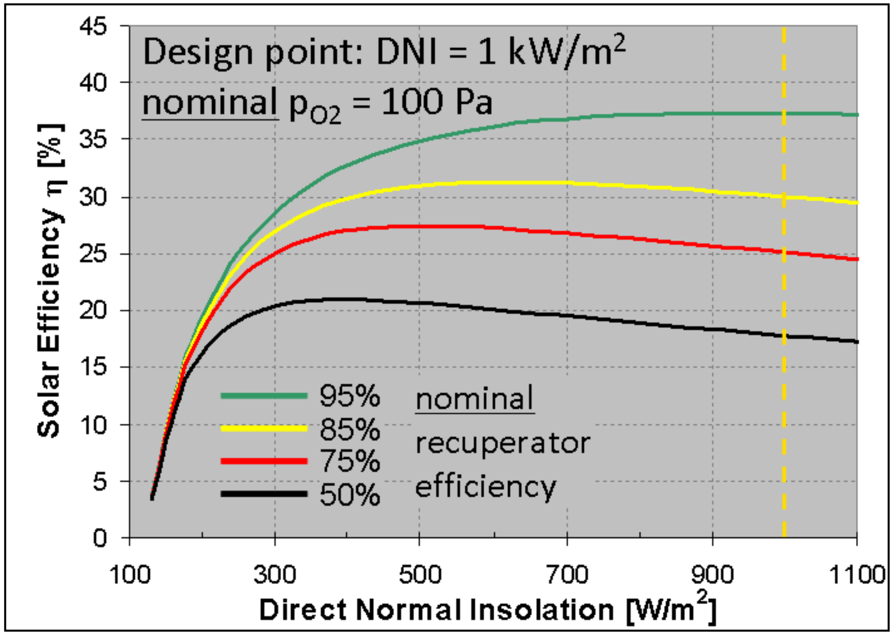
- Perovskite oxygen non-stoichiometry comparable to CeO_2 @ T_R = 1350 °C.

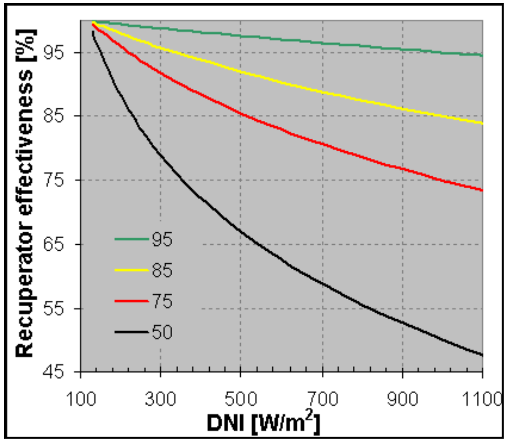


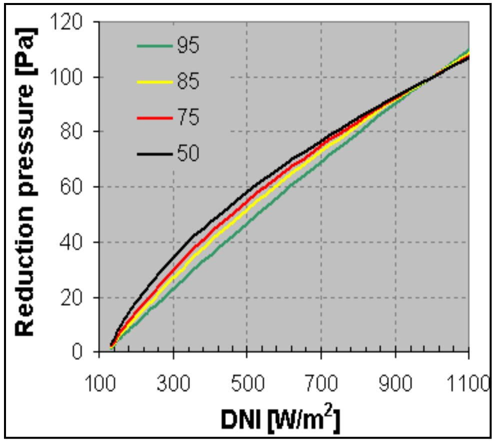
- Perovskite splits H_2O.
- Produce ~5× less H_2 at lower T_R (1350 °C vs. 1500 °C).

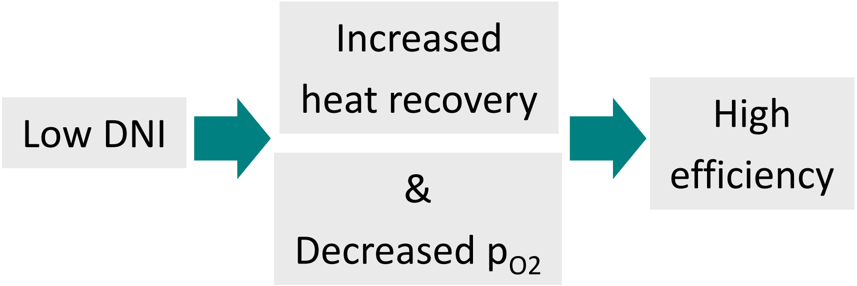
- **$Ca(Ti_xFe_{1-x})O_3$ comprised of earth-abundant rock-forming elements.**
- **Discovery of cheap materials avoids rare-earth market volatility issues.**

Sandia Reactor Also Operates Efficiently at Low DNI









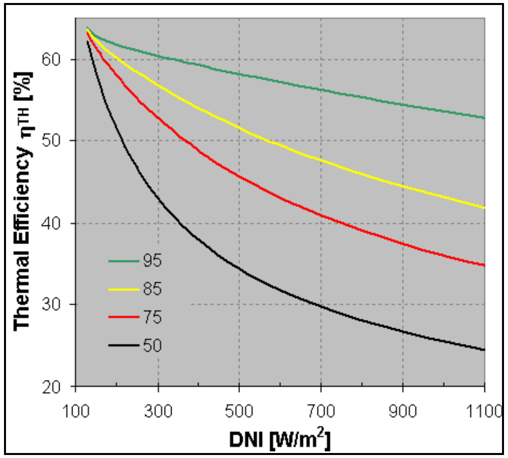
Low DNI

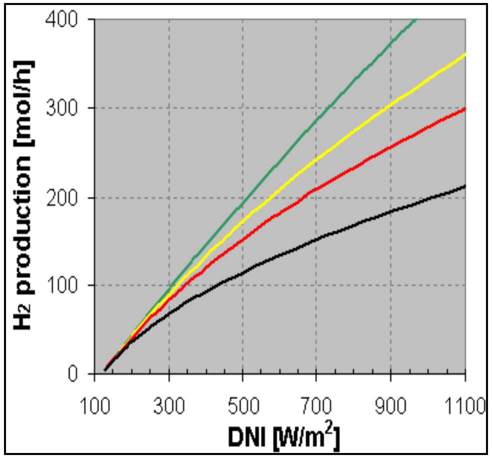
Increased heat recovery

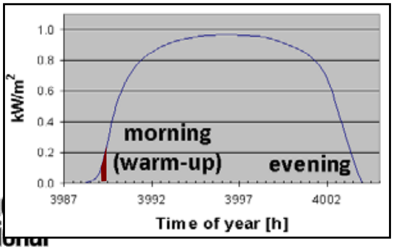
&

Decreased p_{O2}

High efficiency







Sandia National Laboratories

- **High solar utilization under most operating conditions.**
  - 25% solar-to-H_2 annual average efficiency expected
- **Use low DNI in the morning for system warm-up.**

Prototype Platform Construction and Testing