Solar Hydrogen Production with a Metal Oxide Based Thermochemical Cycle

Nathan Siegel, Tony McDaniel, Ivan Ermanoski

Sandia National Laboratories
Solar Technologies Department

DOE Annual Merit Review
5/12/2011

Project ID: PD081

Overview

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Timeline

- Project Start Date: 06/2004
- Project End Date: 10/01/2011*
- Project Complete: 80%

Budget

- Total project funding to date
  - DOE share: $ 3,452K (2004-2011)
  - Contractor share: 20% cost share on contracts
- Funding received in FY10: $ 60K
- Funding for FY11: $ 250K + $620K (c/o)

Barriers

- Barriers addressed
  - U: High temperature thermochemical tech.
  - V: High temperature robust materials
  - X: Coupling solar and thermochemical cycles

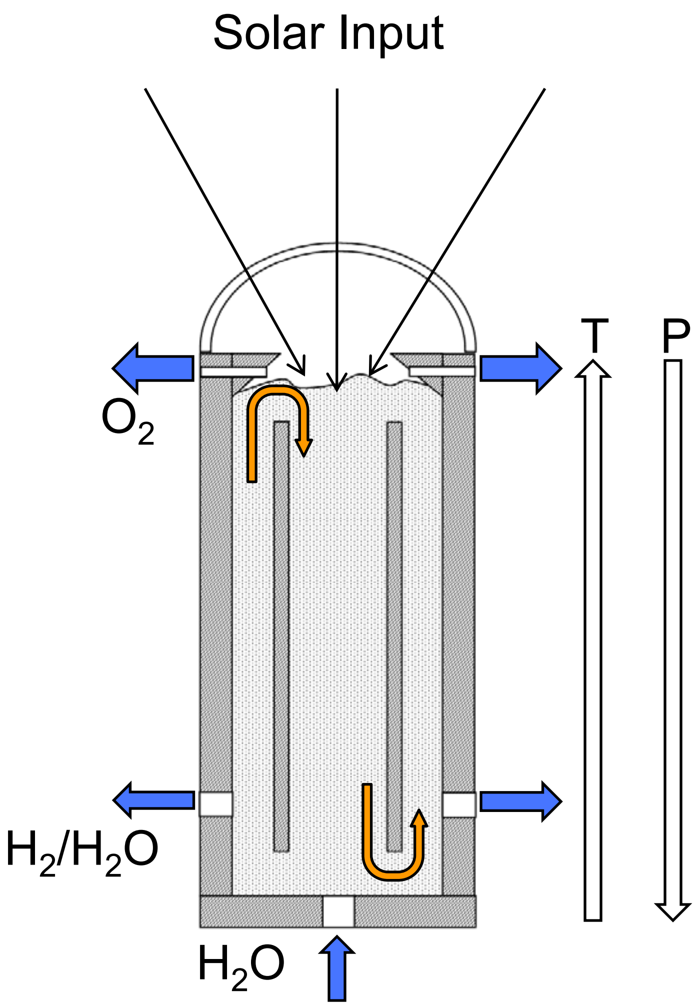
Partners

- Collaboration with the University of Colorado at Boulder (Al Weimer)

*Project continuation and direction determined annually by DOE

Sandia National Laboratories

Conceptual Design and Operation of the Particle Reactor



$$CeO_2 \rightarrow CeO_{2-\delta} + \frac{\delta}{2} O_2 \qquad ca.\ 1500\,^{o}C$$

$$CeO_{2-\delta} + \delta \cdot H_2O \rightarrow CeO_2 + \delta \cdot H_2 \quad 600-1200\,^{o}C$$

- Direct solar irradiation of the reactive particles (thermal reduction)
- Spatial separation of reaction products (O_2 and H_2)
- Internal pressure separation
- Continuous flow
- Internal heat recovery (recuperation)
- Requires beam down optics

Sandia National Laboratories

Relevance

- **Objective:** To develop a particle based thermochemical reactor for efficient solar hydrogen production. The successful development of this reactor will provide a solar interface for most two-step, non-volatile metal oxide cycles that are considered to be among the most efficient solar thermochemical processes.
- **Targets:**
  - $3/gge at the solar plant gate by 2020 (DOE)
  - System level solar to hydrogen production efficiency ~ 20 % (annual average)
    - Maximizing efficiency is key to reducing costs
- **FY 11 Accomplishments and impact:**
  - Identified a reactor system concept capable of annual average solar to hydrogen production efficiency in excess of 20%
    - Reactor utilizes a particulate reactant to maximize kinetics and avoid issues with mechanical stress/failure
  - Built a test platform suited to the characterization of rapid thermochemical processes (materials development)

Sandia National Laboratories

Approach

Technical efforts target three areas

- Materials Discovery and characterization
  - Evaluate the kinetic and thermodynamic performance space of several reactant systems starting with cerium oxide
- Reactor Development
  - High temperature material compatibility
  - Packed bed solids conveyance
  - Advanced solar optics
  - Prototype
- System Analysis
  - High level performance models used to predict annual average performance
  - Detailed ASPEN flow sheets for reactor optimization

Sandia National Laboratories

Technical Accomplishments and Progress

- Materials Discovery and Characterization
  - Laser heated reactor is operational: Heating rates of 100°C/s
  - Initial characterization of cerium oxide reduction and oxidation
- Reactor Development
  - Performance model has been developed
  - Particle transport properties have been measured (CeO_2 powder)
  - Particle packed-bed conveyor has been designed
  - 10 kW_{th} prototype design underway
- System Model
  - Annual average efficiency of a dish-based system has been calculated for a range of conditions

Sandia National Laboratories

System Level Performance (1 of 2)

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

- Reactor model combined with TMY2 meteorological data to estimate hourly performance for an entire year
  - Results are geographically dependent
  - Model enables prediction of annual average efficiency
  - Dish-based reactor system model is complete, towers are next.
- System level model is being ported to Aspen Plus® for detailed design and analysis

Sandia National Laboratories

System Level Performance (2 of 2)

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

T_{TR}= 1500°C, T_{OX} = 1000°C
P_{TR} = 100 Pa

Sunlight

Resource eff.=(Resource>300 DNI)/Resource= **95%** for Daggett

Operational ~ 94%
Equip. Availability = 97%, B&S = 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 Available Heat = 58%

Reactor/Thermochemical ~ 37%
Pumping ~ 96% (100 Pa)

H_2

Annual Average Solar to Hydrogen
Design Point: 21%
Range: 20%-24%

National Laboratories

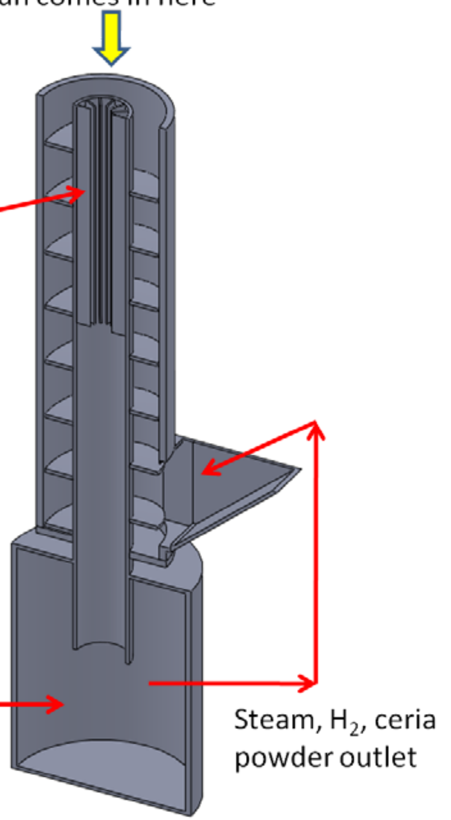
Reactor Development (1 of 3)

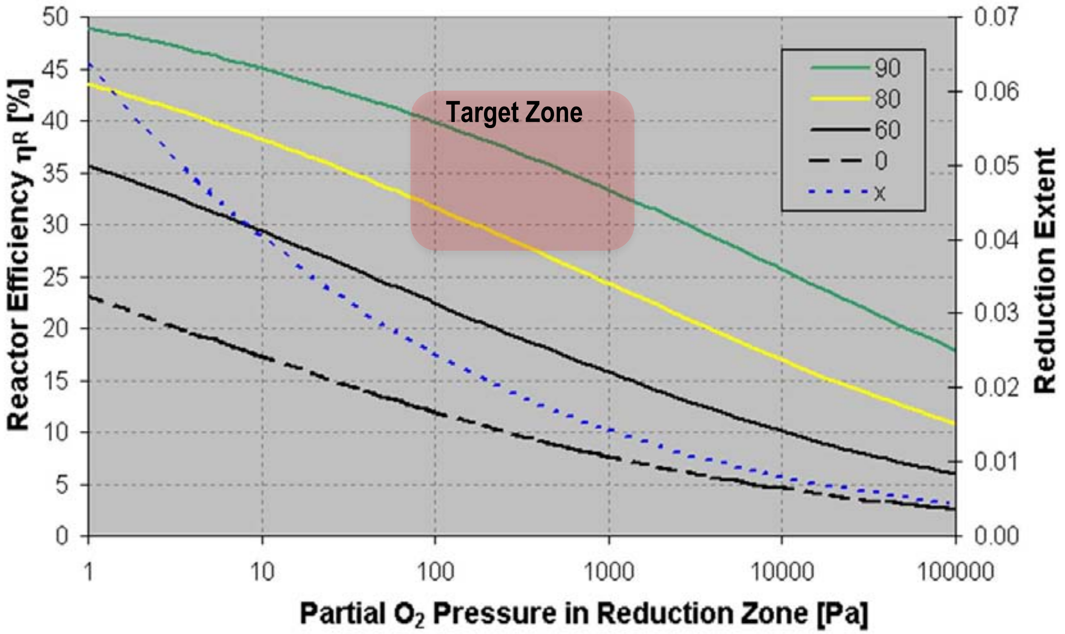
- Cerium oxide powders (~5 µm) are the near term reactant
- Much effort has focused on conveying ceria powder within a reactor under the appropriate conditions
  - Solid phase transport of ceria powder has been measured including bulk density, permeability, and wall friction
  - Conveyor conceptual designs have been developed
- Compatibility of ceria powder with alumina and Haynes 214 was experimentally demonstrated to 1400^{o}C
- Models of reactor operation have been developed
  - Recuperation is critical to efficient operation
  - There is room for improvement with respect to the reactive material performance

Sandia National Laboratories

Reactor Development (2 of 3)

- Particles can be vertically conveyed using an "Olds" elevator
  - Works for dish and tower platforms
- Steam is used to react, cool, and convey particles
- Models predict potentially high conversion efficiency with recuperation

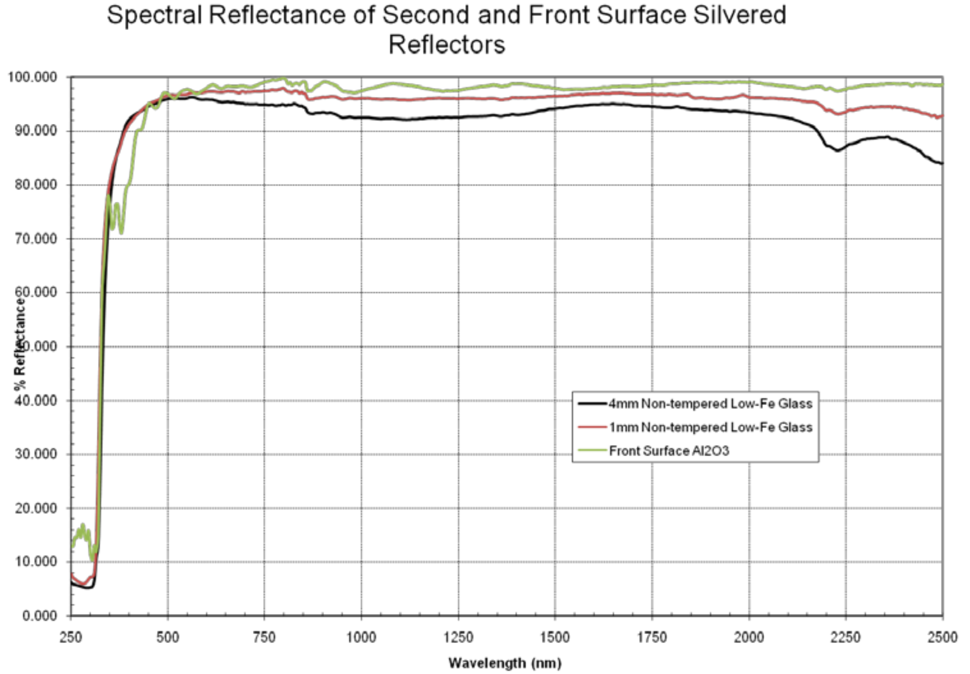




Thermochemical performance for pure cerium oxide reactant powder

Sandia National Laboratories

- An on-sun prototype of the particle reactor is being designed
  - T_{TR} = >1400°C, T_{OX} <1000°C, P_{tot} = 1000-10000 Pa
  - Reactor power input 10 kW_{th} on the solar furnace facility at SNL
  - Target hydrogen production between: 4-20 Liter/min
    - Ceria flow between 20-100 g/s
  - Conveyor and optics design underway

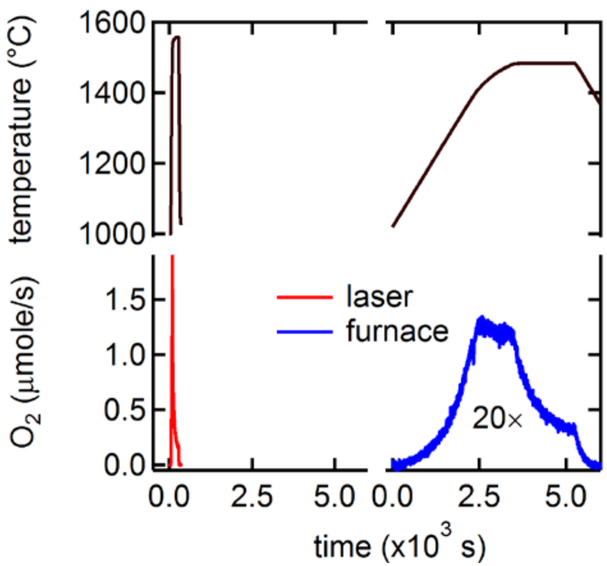


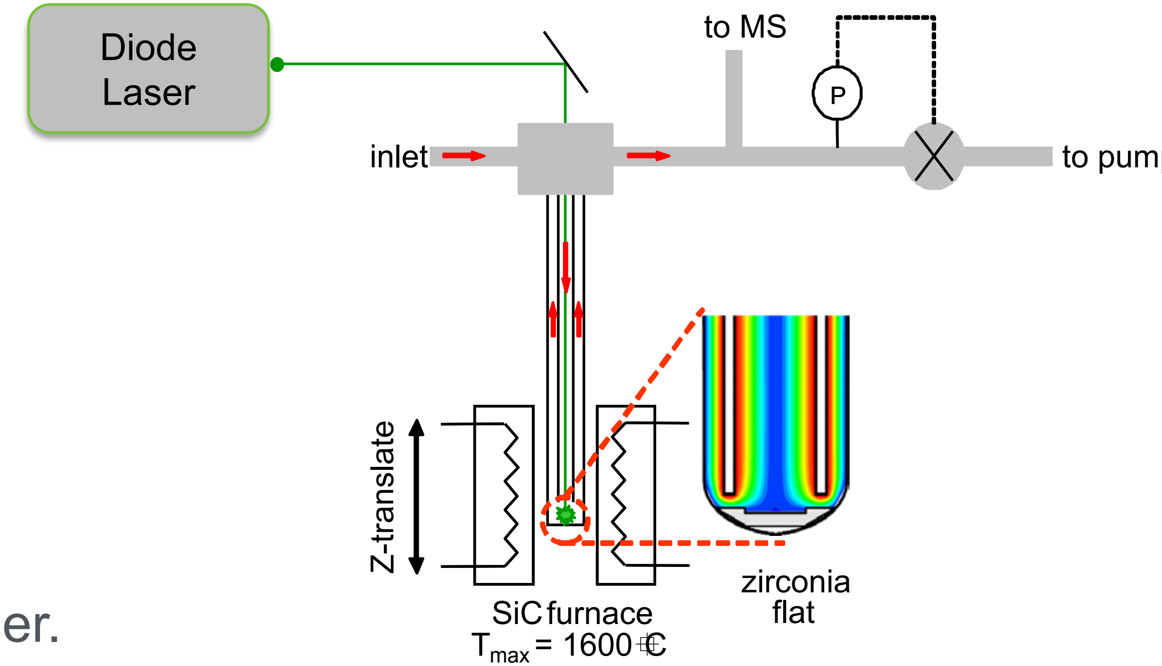
Spectral reflectivity of solar optics. Compound solar reflectivity for the prototype (two reflections) is 93%. Heat load on the second reflector is 0.7 kW, but its non-uniform. Data provided by NREL

Sandia National Laboratories

Materials Discovery and Characterization (1 of 4)

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

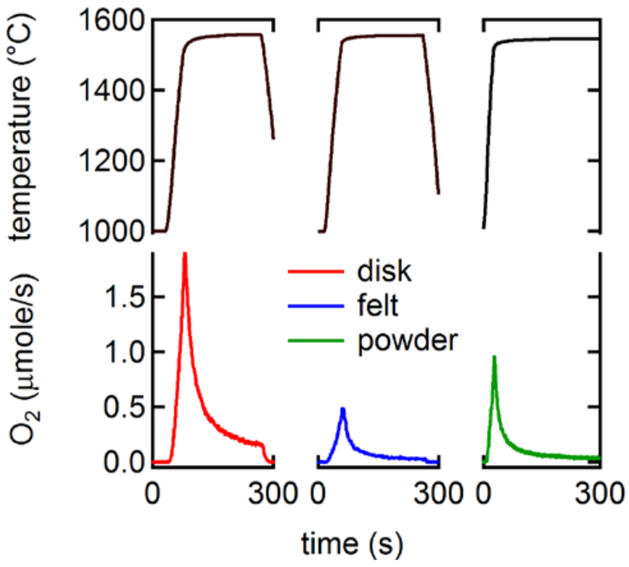




- 500 W CW near IR laser.
  - Achieve heating rates in excess of 100 °C/s.
  - Adjust radiative flux with optics and power control.
  - 0 to >> 5000 suns
- Thermodynamic and kinetic characterizations over a range of conditions
- Investigate thermal reduction.
  - More closely mimic CSP conditions in a “model” environment.

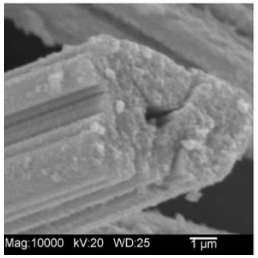
Sandia National Laboratories

Materials Discovery and Characterization (2 of 4)



form	mass (mg)	mole O ($\times 10^{-6}$)	δ
disk	960	220	0.0394
felt	207	48	0.0398
powder	454	91	0.0350

felt



powder

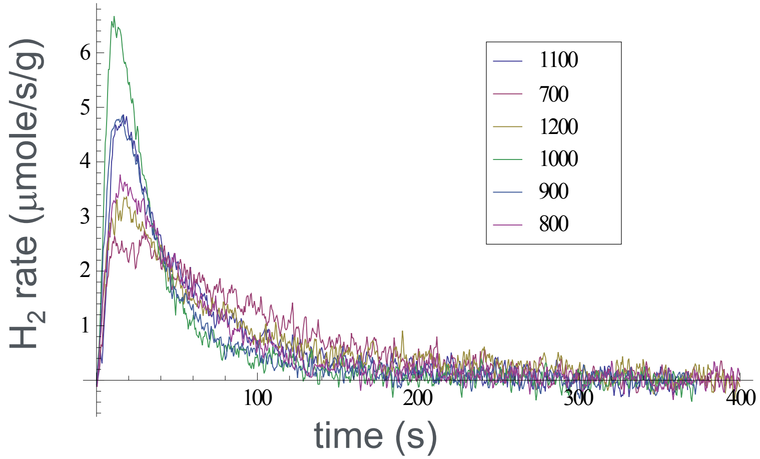
- Disk 1000 μm thick.
- Felt primary fiber diameter ~ 10 μm.
- Powder primary particle diameter ~ 5 μm.
- Solid-state dynamics at *these length scales and heating rates* do not limit reduction kinetics.
  - Rates scale with mass
  - Thermal conduction, vacancy diffusion, surface chemistry

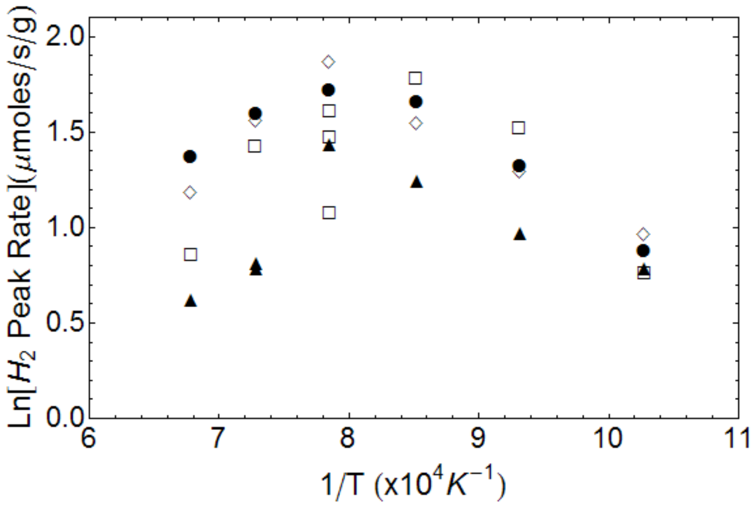
Materials Discovery and Characterization (3 of 4)

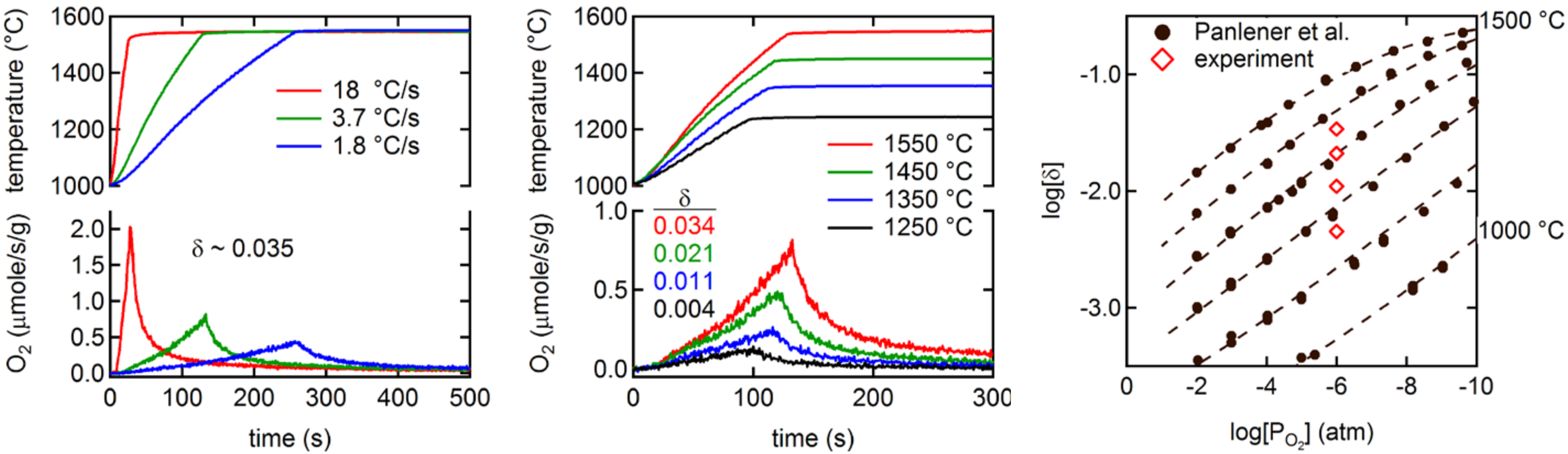
temperature (°C)	total H_2 (μmole/g)	peak H_2 (μmole/s/g)
1200	274	3.27
1100	273	4.76
1000	249	6.51
900	229	4.75
800	235	3.60
700	285	2.64

- Total H_2 produced is nearly constant but peak rates are variable.
  - Material is stable upon cycling
    - no degradation up to 30 cycles
- Detailed kinetic analysis is ongoing.
  - Transition between rate controlling mechanisms evident
    - T < 1000 °C and T > 1100 °C

Data presented for ceria felt







- Varying heating rate and plateau temperature required for kinetic analysis.
  - **Solid-state kinetic theory**
    - Screen for rate limiting mechanisms
    - Evaluate kinetic parameters (activation energy)
- Develop kinetic model for predicting reduction behavior.
- Assess the extent of reduction likely achievable in CSP reactor concepts.

Sandia National Laboratories

Collaborations

- Currently working with Al Weimer's group at the University of Colorado
  - Several students are working at SNL/CA in the area of materials discovery and characterization
- Jenike and Johanson Inc. are supporting the development of particle conveyor concepts.

Sandia National Laboratories

Proposed Future Work

- Continue materials characterization and identify more favorable systems
- Build and test a prototype reactor at the solar furnace
  - Additional technical challenges may become apparent during testing
- Perform a detailed design of a central receiver-based reactor.
  - Possibly results in a larger scale prototype
  - Provides a basis for detailed cost assessment

Summary

- A new solar thermochemical hydrogen production reactor was designed
  - The reactor has the potential to achieve heat to hydrogen conversion efficiency ~ 40 %,
    - > 20% solar to hydrogen efficiency at 100 Pa (2011 Milestone)
  - Includes all of the key performance attributes of a solar TC reactor
  - Scalable to central receivers
  - 10kW_{th} prototype design is underway
- Materials characterization using a laser heated reactor for evaluation of "realistic" material performance
  - Preliminary reaction kinetics for pure ceria have been measured
  - Full characterization of pure ceria powders in progress
- System models have been developed that predict annual average solar to hydrogen efficiency up to 23%

Sandia National Laboratories

Thank you for your attention

Questions?

Sandia National Laboratories