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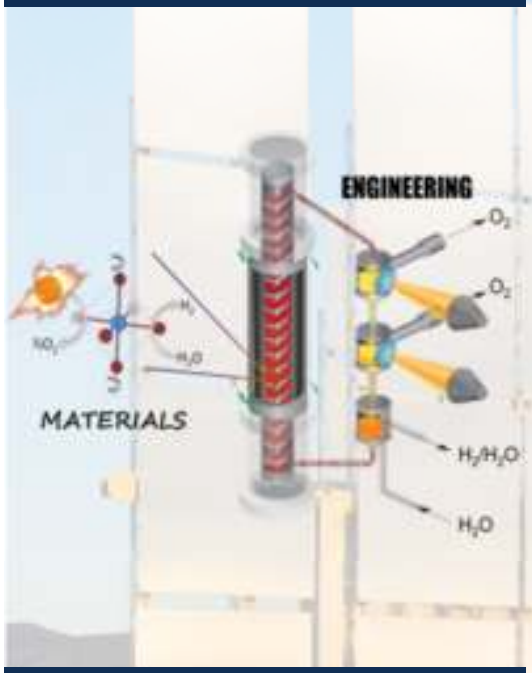

Benchmarking a Metal Oxide-Based Thermochemical Cycle for Solar Hydrogen Production

Anthony McDaniel, Ivan Ermanoski

Sandia National Labs

May 29, 2015
227th ECS Conference, Chicago, IL

Sandia National Laboratories

Exceptional service in the national interest

U.S. DEPARTMENT OF ENERGY

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Outline

- Introduce concentrated solar water splitting concept.
  - How does STC H_2 compare to other solar-based technologies
- Sandia's approach to establishing technology benchmarks.
  - Reactor design and operation
  - Material requirements
  - Opportunities for standard approaches
- Key benchmarks that impact solar-to-fuel efficiency.
  - Temperature separation (ΔT)
  - O_2 reduction pressure (p_{TR})
  - Heat recovery effectiveness (ε_S and ε_G)
- Summary and concluding remarks.

Solar powered two-step thermochemical water-splitting cycle

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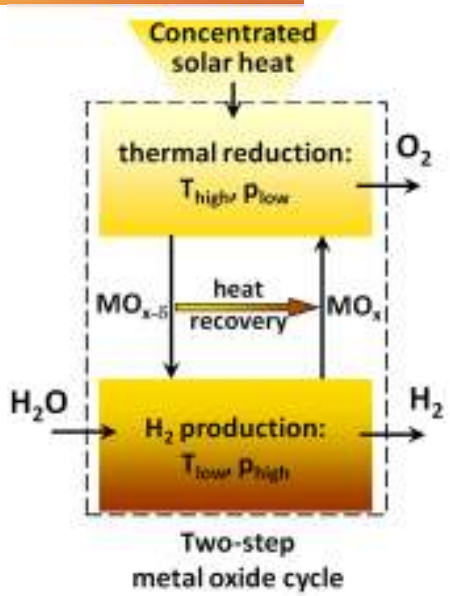
MW scale concentrating solar power facilities provide heat



Two-step metal oxide cycle

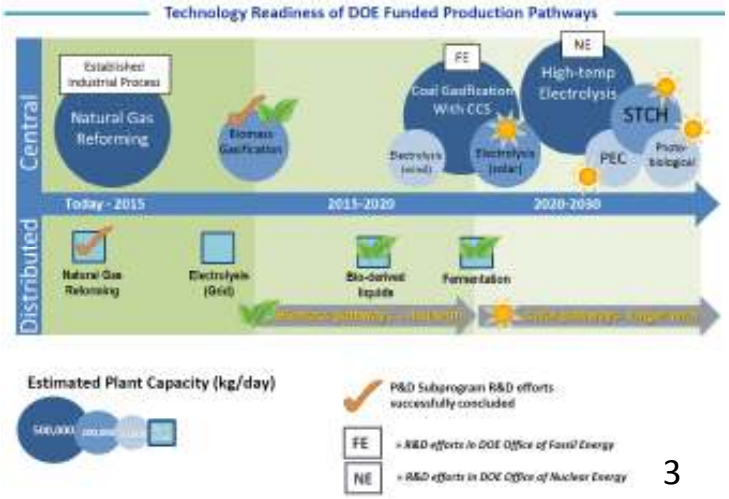
Non-volatile metal oxide cycle:

$$MO_x \rightarrow MO_{x-\delta} + \frac{\delta}{2} O_2 \qquad \text{(1) Reduction}$$

$$MO_{x-\delta} + \delta \cdot H_2O \rightarrow MO_x + \delta \cdot H_2 \qquad \text{(2) Oxidation}$$

$$\delta \cdot H_2O \rightarrow \frac{\delta}{2} O_2 + \delta \cdot H_2 \qquad \text{(3) Thermolysis}$$

- The challenge is to develop efficient and scalable solar-powered reactors.



STC H_2 vs. Alternative Technologies

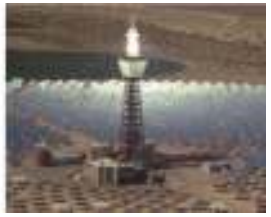
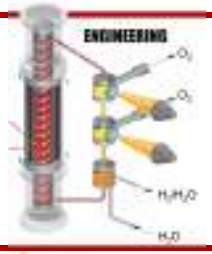
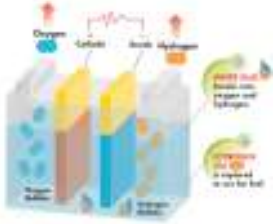
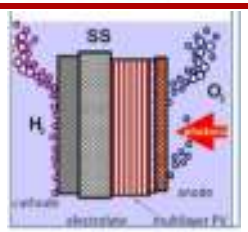
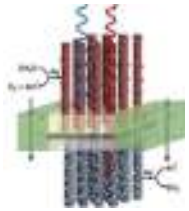
Theoretical
vs. DOE Target
Efficiency

STC offers a simpler technology than alternatives and higher theoretical efficiency.

$$\eta_{STH} = LHV(H_2) / Q_{solar}$$

Theoretical Efficiency

Technical Simplicity

>40% vs. 26%	STC H_2	 + 	high temperature reactor no bugs/wires/membranes >1000 suns
~28% vs. 20%	Solar Thermal or PV+ Electrolysis	 + 	Stirling heat engine conventional electrolyzer >1000 suns
~28% vs. 25%	PEC	 	inorganic PV cells complex, multi-layered intrinsic electrolysis 1-15 suns
??% vs. 1%	Emerging Technologies JCAP & Artificial Leaf		complex nano-engineered synthetic membranes 1 sun

Efficiency Drives Reactor Development

Table 3.1.7 Technical Targets: Solar-Driven High-Temperature Thermochemical Hydrogen Production [a]

Characteristics	Units	2011 Status	2015 Target	2020 Target	Ultimate Target
Solar-Driven High-Temperature Thermochemical Cycle Hydrogen Cost [b]	$/kg	NA	14.60	3.70	2.00
Chemical Tower Capital Cost (installed cost) [c]	$/TPD H_2	NA	4.1MM	2.3MM	1.1MM
Annual Reaction Material Cost per TPD H_2 [d]	$/yr-TPD H_2	NA	1.47M	89K	11K
Solar to Hydrogen (STH) Energy Conversion Ratio [e,f]	%	NA	10	20	26%
1-Sun Hydrogen Production Rate [g]	kg/s per m^2	NA	6.1E-7	1.2E-6	2.1E-6

Efficiency is a key metric for US R&D

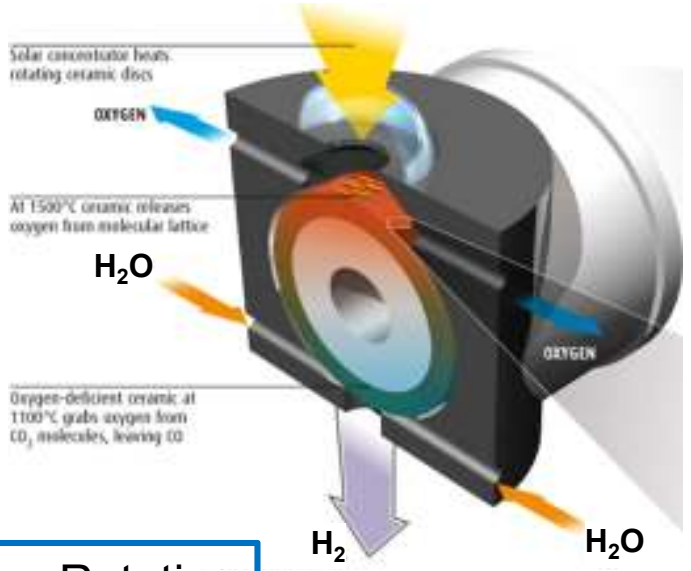
High cost of solar collection

- Many different reactor designs have been proposed.
- Material models required to evaluate reactor performance.
  - Thermodynamics, kinetics, transport, durability, etc.

J. E. Miller, A. H. McDaniel, M. D. Allendorf, *Advanced Energy Materials*. **4**, 1300469 (2014).

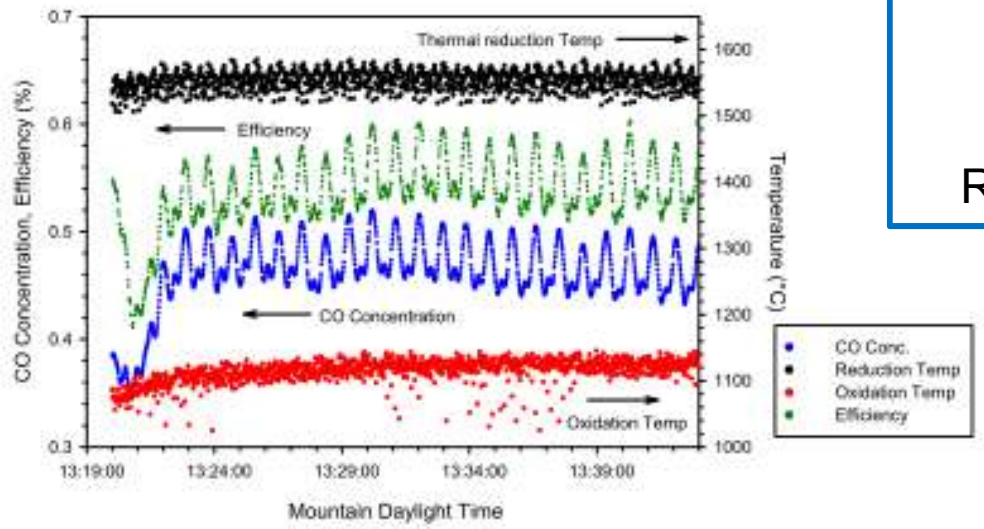
Key Design Concepts for High Efficiency

- Continuous on-sun operation
- Direct solar absorption
- Temperature and product separation
- Heat recovery between T_{TR} and T_{WS}

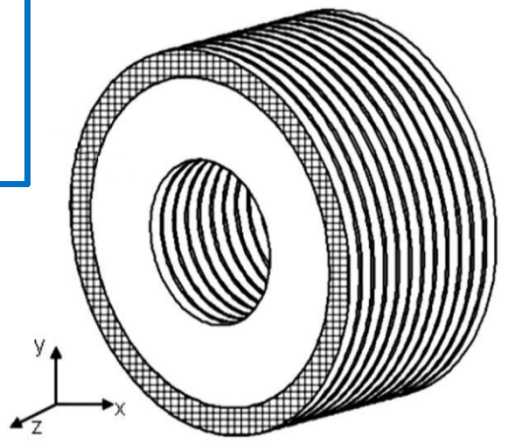


J. E. Miller *et al.*, SAND2012-5658 (2012)

CO_2 splitting Demonstrated at ~10kW$_{th}$



Counter-Rotating
Ring
Receiver
Reactor
Recuperator



Particle Bed Reactor that Maximizes Efficiency

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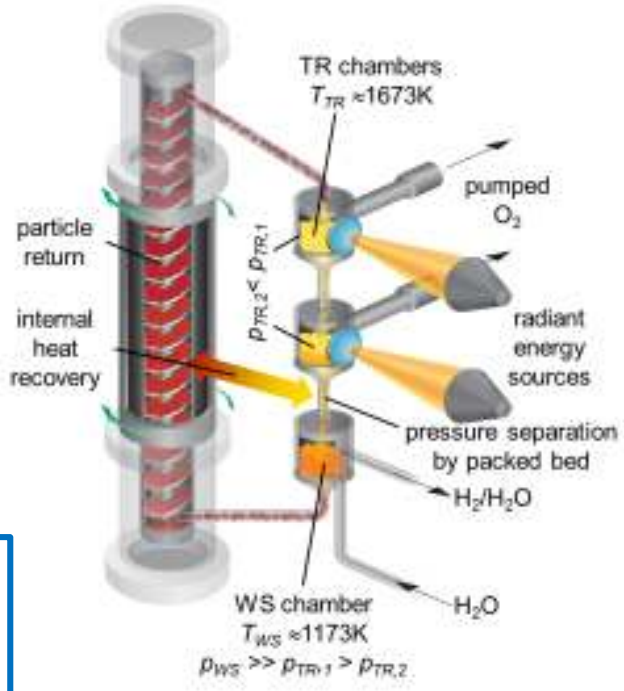
Key improvements:

- Ultra-low reduction pressure (0.1-10Pa)
- Decreased solids heat recovery requirement
- Decreased pump work requirement
- Non-monolithic reactive oxide
- Reaction kinetics decoupled from reactor mechanics



Specific design advantages:

- Small reactive particles (~100μm).
- Only particles are thermally cycled.
- Only one high T moving part, a metal tube.
- Independent component optimization.

Cascading Pressure Receiver Reactor

H_2O splitting ~3kW_{th}

Design compatible with a MW-scale plant

I. Ermanoski, *International Journal of Hydrogen Energy*. **39**, 13114–13117 (2014).

Sandia's Theoretical Approach

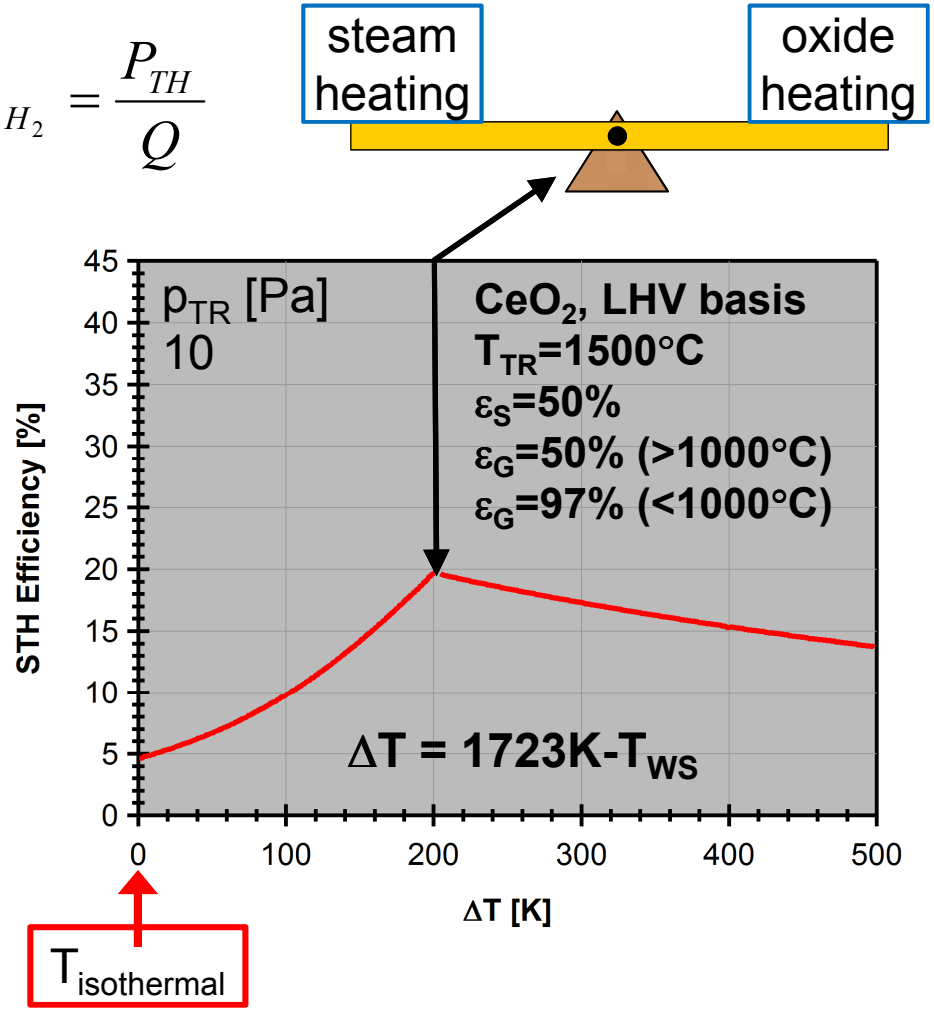
$$\eta = \left(\frac{P_{TH}}{P_S}\right)\left(\frac{LHV_{H_2}}{Q}\right) = \frac{\dot{n}_{H_2} LHV_{H_2}}{P_S} \rightarrow \dot{n}_{H_2} = \frac{P_{TH}}{Q}$$

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

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

All inclusive efficiency metric

- Collection losses (P_{TH}).
- Concentrator and re-radiation.
- Oxide thermal reduction (Q_{TR}).
- Oxide heating (Q_{SH}).
- Steam heating (Q_{AUX}).
- Pump work (Q_{AUX}).
- Electrical/mechanical work (Q_{AUX}).



p_{TR}= O_2 reduction pressure
ε_S= solid heat recovery effectiveness
ε_G= gas heat recovery effectiveness

I. Ermanoski, N. P. Siegel, E. B. Stechel, *J. Solar Energy Engineering*. **135**, 031002 (2013).

Benchmarks for Redox Active Materials

- Moderate T_{TR}, (ΔH_{TR} & ΔS_{TR})
- Large, reversible oxygen deficiency (δ)
- Fast redox rates matched to solar flux
- High WS potential (ΔH_{TR} & ΔS_{TR})
- Stable and durable oxide
- Earth abundant and easy to produce

Ideal material IS NOT unobtainium

SLMA=$Sr_{1-x}La_xMn_{1-y}Al_yO_3$ perovskite

A. H. McDaniel *et al.*, *Energy Environ. Sci.* **6**, 2424–2428 (2013)

property	SLMA	IDEAL	CeO_2
T_{WS}	900°C	600-800°C	500°C
T_{TR}	1350°C	SLMA	1550°C
δ	0.25	SLMA	0.05
H_2O/H_2	200/1	CeO_2	1/1
*$Rate_{WS}$	~0.04 s^{-1}	CeO_2	~0.01 s^{-1}
*$\Delta H(\delta)_{TR}$	250-320	350-400	400-500
*$\Delta S(\delta)_{TR}$	100-130	~CeO_2	150-300

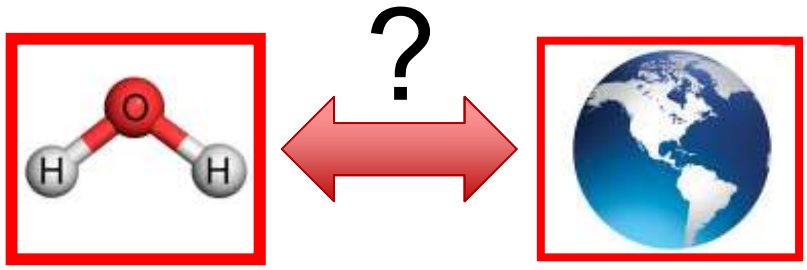
* Rate=pseudo first order, $\Delta H(\delta)$=kJ/mol O, $\Delta S(\delta)$=J/K mol O

- Ideal material properties bounded by known compounds.
  - Still a vast material space
- Desire a deeper understanding of material behavior.
  - Fundamental research through Basic Energy Sciences

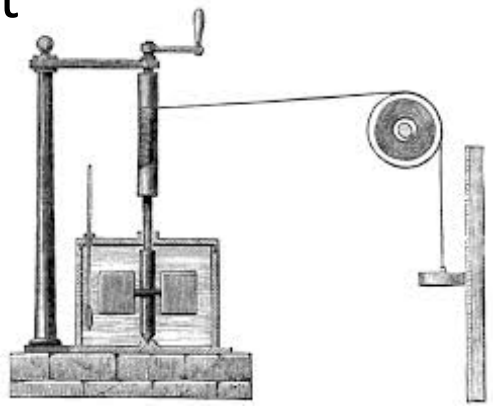
J. E. Miller, A. H. McDaniel, M. D. Allendorf, *Advanced Energy Materials*. **4**, 1300469 (2014).

Opportunities for Establishing Standard Approaches

- Standard system boundary for analysis.
  - Solar collection and receiver
  - Thermochemical reactor
  - Balance of plant (i.e., separations)

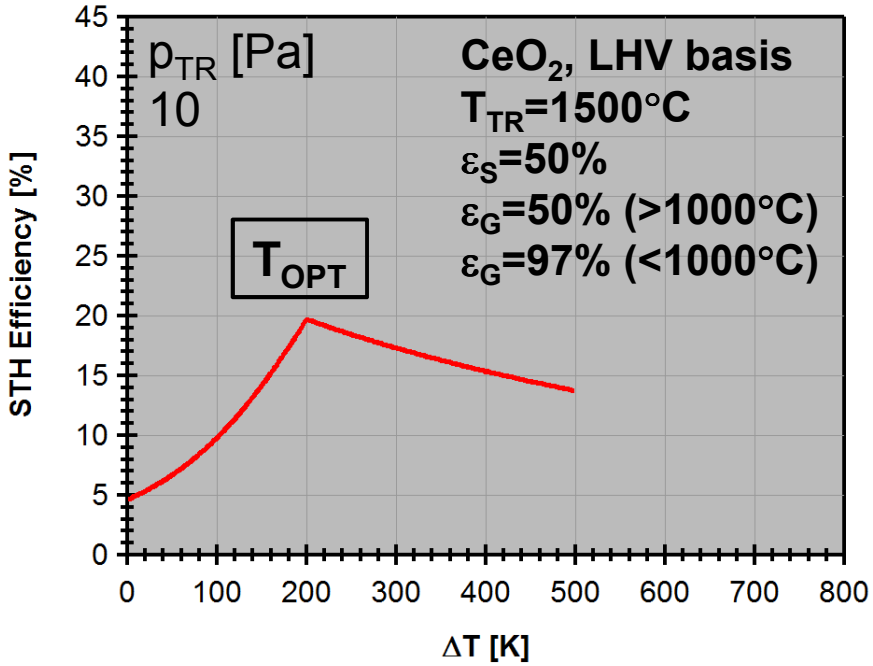


- Standard conversion metrics for work to heat equivalent.
  - Determining the (Q_{AUX}) term
  - Currency = energy/mole H_2



- Standard use of material properties.
  - Sufficiently detailed map of P_{O2}-δ-T phase space (Q_{TR})
  - Knowledge of heat capacity (Q_{SH})

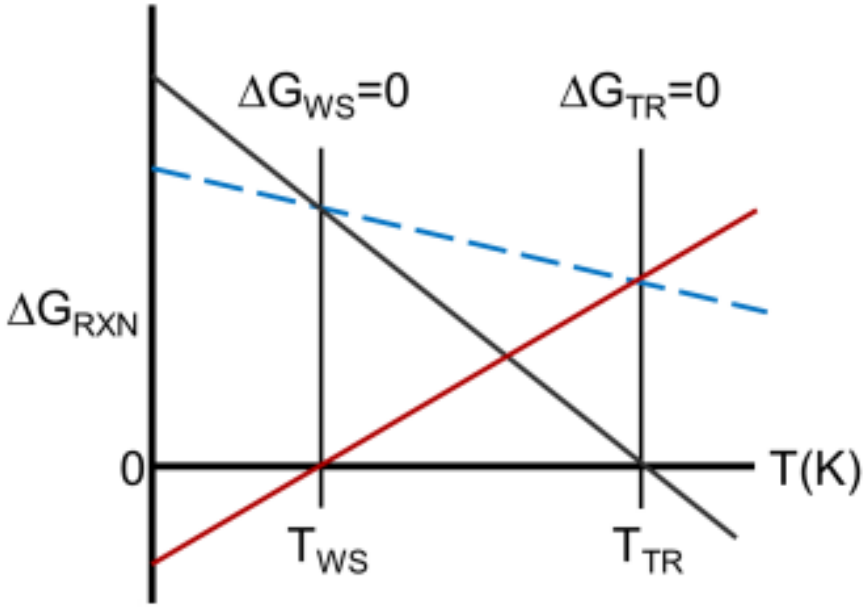
The "ΔTemperature > 0" Benchmark



$$MO_x \rightarrow MO_{x-\delta} + \frac{\delta}{2} O_2 \quad (1)\ \text{TR}$$

$$MO_{x-\delta} + \delta \cdot H_2O \rightarrow MO_x + \delta \cdot H_2 \quad (2)\ \text{WS}$$

$$\delta \cdot H_2O \rightarrow \frac{\delta}{2} O_2 + \delta \cdot H_2 \quad (3)\ \text{NET}$$



- Temperature swing process.
  - Convert heat to chemical energy
- Largest possible ΔT may not the most efficient operating point.

Temperature separation key to efficient Carnot process

The "ΔTemperature = 0" Benchmark

- Pressure swing process.
  - Convert mechanical work to chemical energy
- Zero efficiency from expensive, ultra-high temperature heat

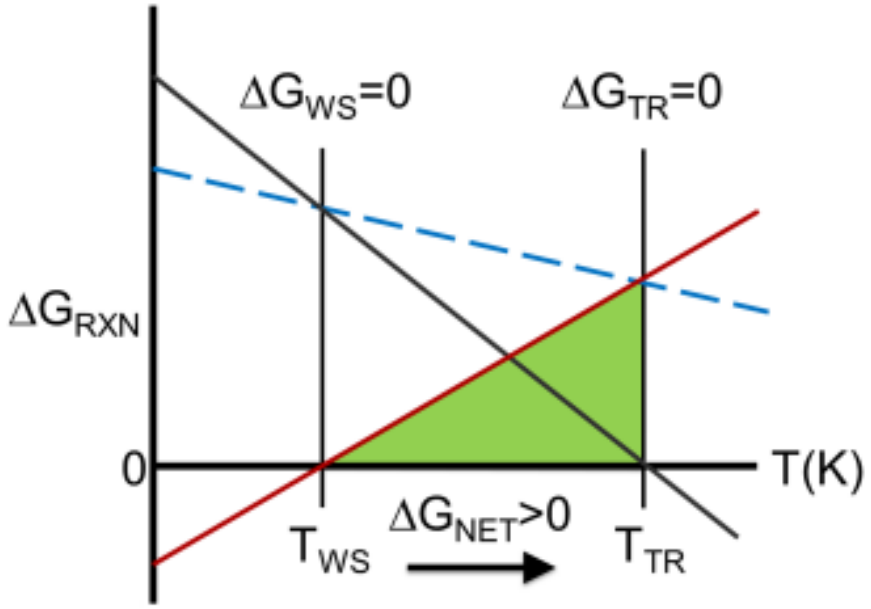
$$\eta_{Carnot} = 1 - \frac{T_{WS}}{T_{TR}} = 0$$

- Less efficient under all practical conditions.

$$MO_x \rightarrow MO_{x-\delta} + \frac{\delta}{2} O_2 \quad (1)\ \text{TR}$$

$$MO_{x-\delta} + \delta \cdot H_2O \rightarrow MO_x + \delta \cdot H_2 \quad (2)\ \text{WS}$$

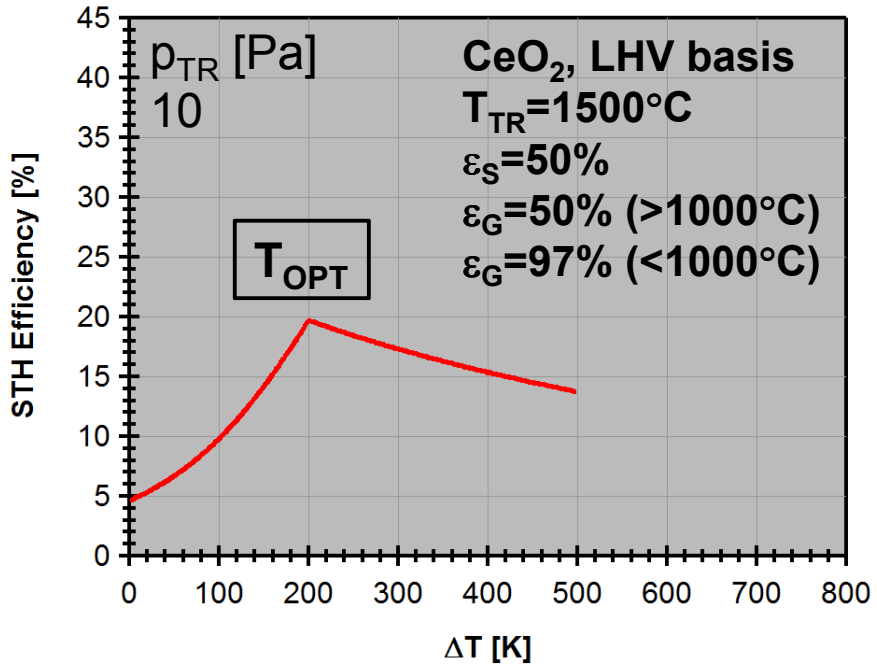
$$\delta \cdot H_2O \rightarrow \frac{\delta}{2} O_2 + \delta \cdot H_2 \quad (3)\ \text{NET}$$

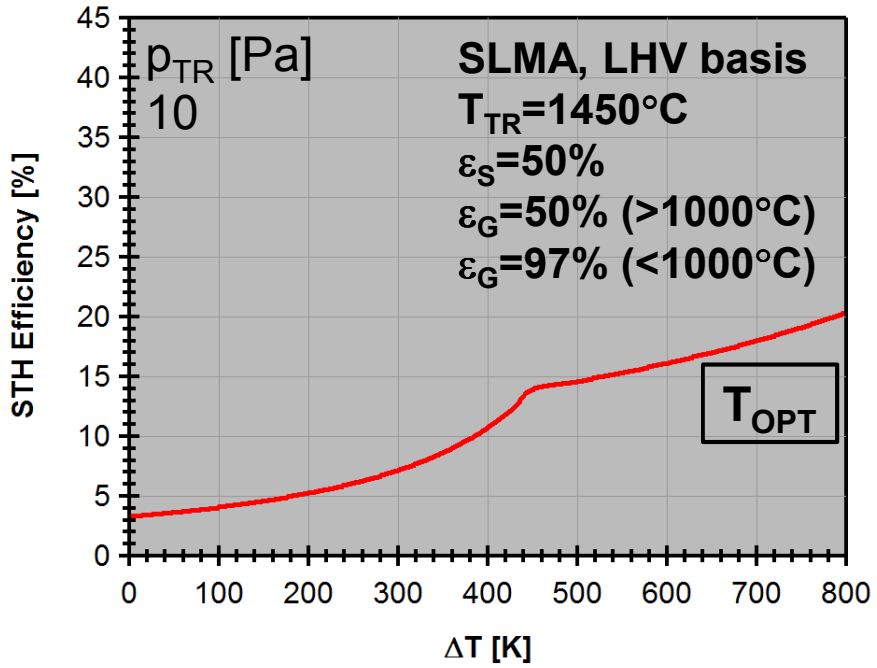


$$\eta_{STH} = \eta_{thermal} * \eta_{electrical} * \eta_{mechanical} * \eta_{chemical} << \eta_{thermal} * \eta_{chemcial}$$

I. Ermanoski, J. E. Miller, M. D. Allendorf, *Physical Chemistry Chemical Physics*. **16**, 8418 (2014).

Material Affects "$\Delta T_{OPT} > 0$" Benchmark



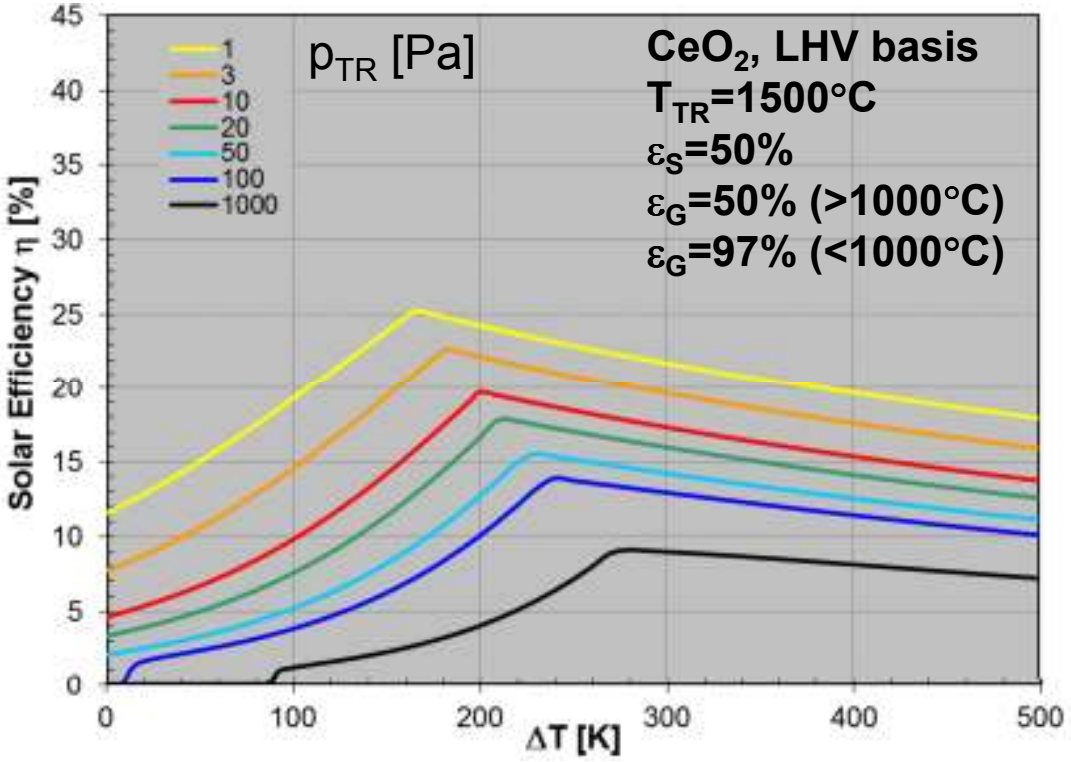


- ΔT_{OPT} (CeO_2) << ΔT_{OPT} (SLMA).
- CeO_2 limited by oxide heating due to large ΔH_{TR} and small δ.
- SLMA limited by steam heating due to small ΔH_{TR}.

Search for advanced materials underway

The "O_2 Reduction Pressure (p_{TR})" Benchmark

p_{TR}=1 Pa

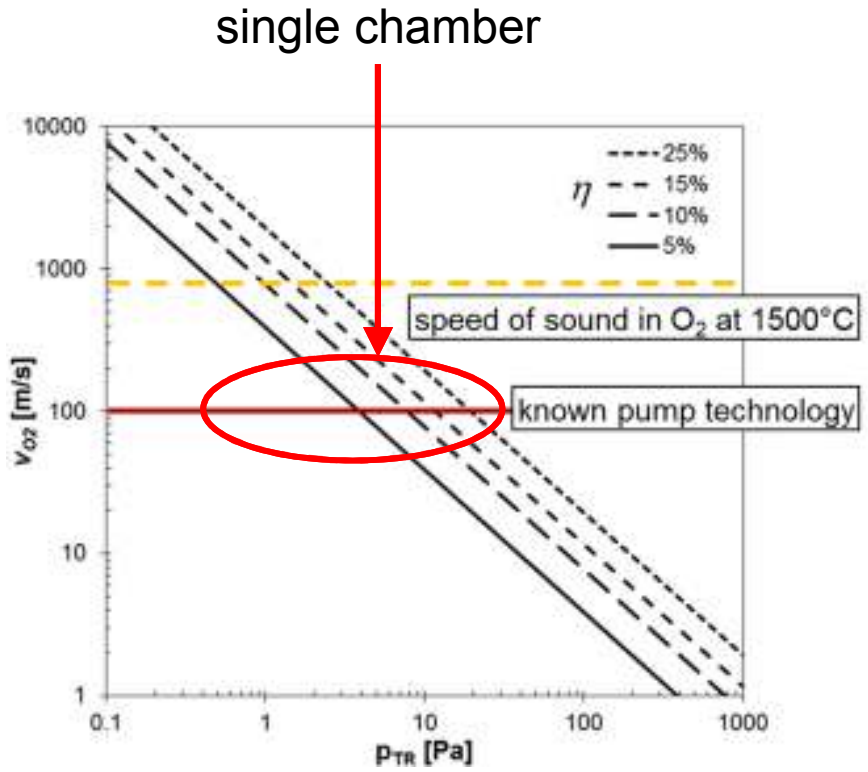


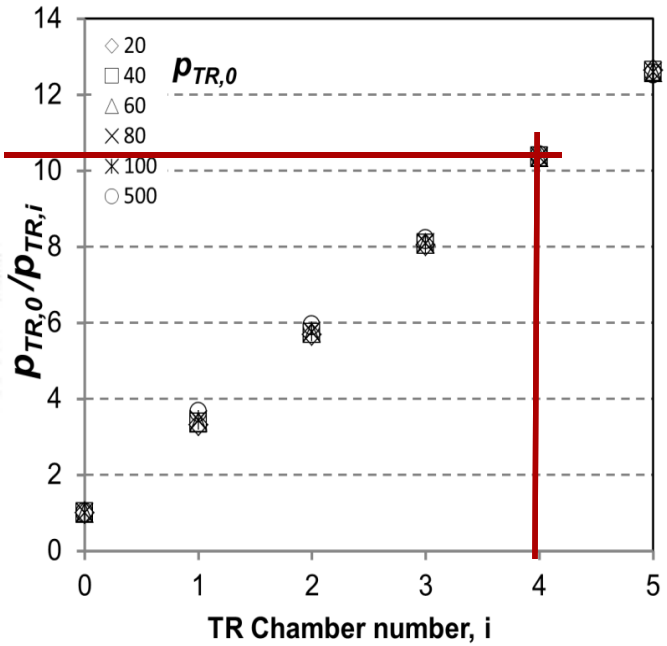
p_{TR}=1000 Pa

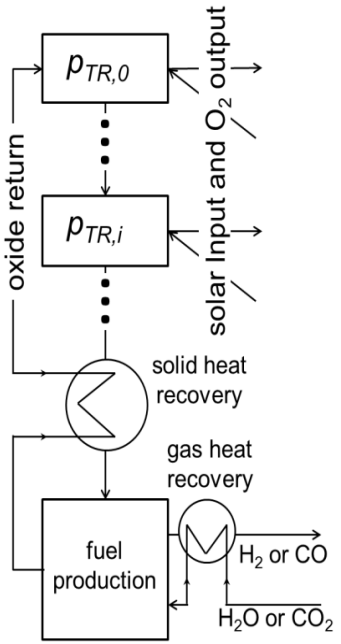
- Efficiency strongly dependent on O_2 partial pressure.
  - Lower p_{TR} yields greater δ at all reduction temperatures

Achieve high STH efficiency at low p_{TR}

Low p_{TR} is Challenging at Large Scale



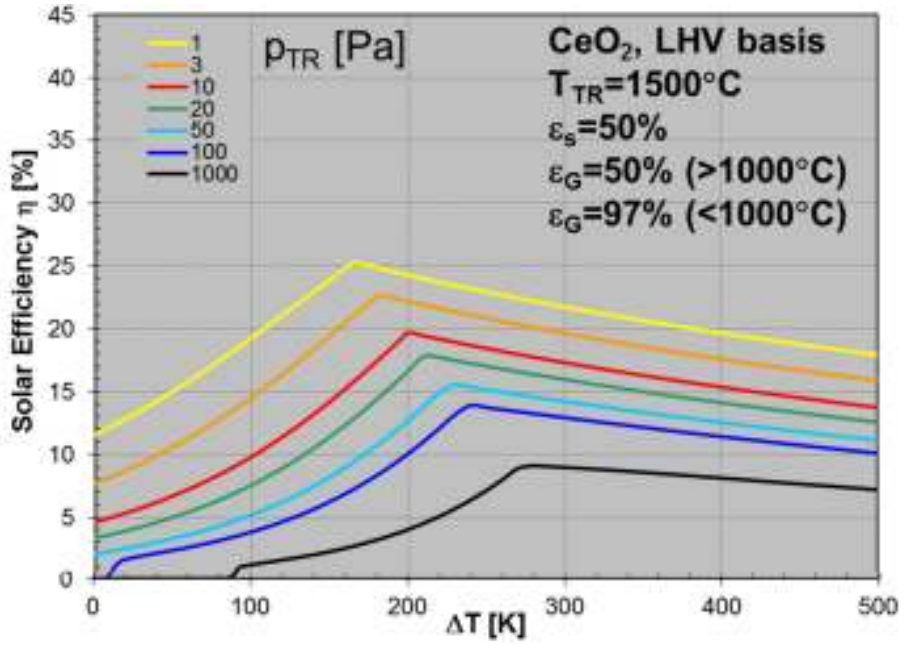


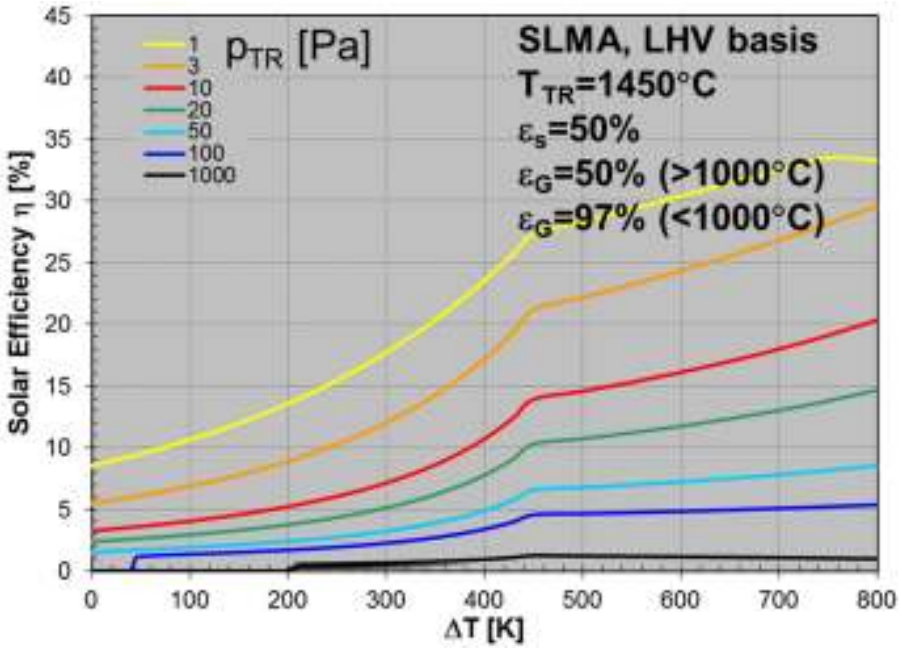


- Not possible to achieve low O_2 partial pressure in a single chamber with high efficiency.

Multiple cascading pressure chambers achieves ultra-low p_{TR}

Material Affects "p_{TR}" Benchmark

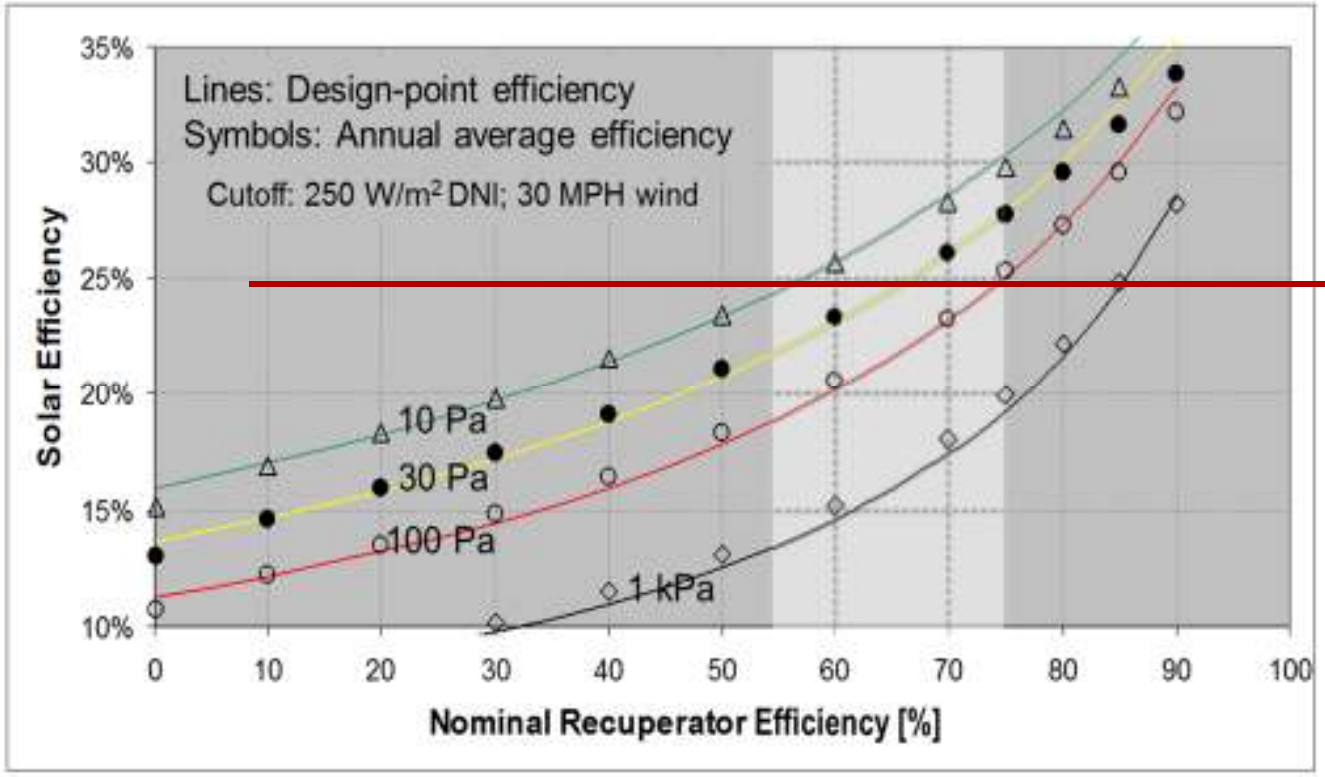




- Difficult to achieve ultimate DOE STH target using CeO_2.

Search for advanced materials underway

The "Heat Recovery Effectiveness" Benchmark



- Efficiency strongly depends on recuperator effectiveness.
  - Heat recovery compensates for poor pumping and vice versa

Achieve high STH efficiency at high recuperator effectiveness

Summary and Concluding Remarks

- STH efficiency guides R&D.
  - η_{STH}>20% to be commercially viable
- Established “high efficiency” reactor design benchmarks
  - Temperature separation (ΔT_{OPT}>0)
  - Pressure separation (ultra-low p_{TR}, 1-10Pa)
  - Efficient heat recuperation (ε_S and ε_G>75%)
- Opportunities exists to standardize metrics and protocols
  - Systems analysis
  - Material characterization

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- Martin Roeb (DLR)
- Nathan Siegel (Bucknell)
- Ryan O'Hayre (CSM)
- Jianhua Tong (CSM)
- William Chueh (Stanford)
- Ellen Stechel (ASU)
- Chris Wolverton (NU)

Team has over 35 STC H_2 related publications since 2008

Sandia has patented technology

Demonstrated STCH at 10-100 kW scales on sun

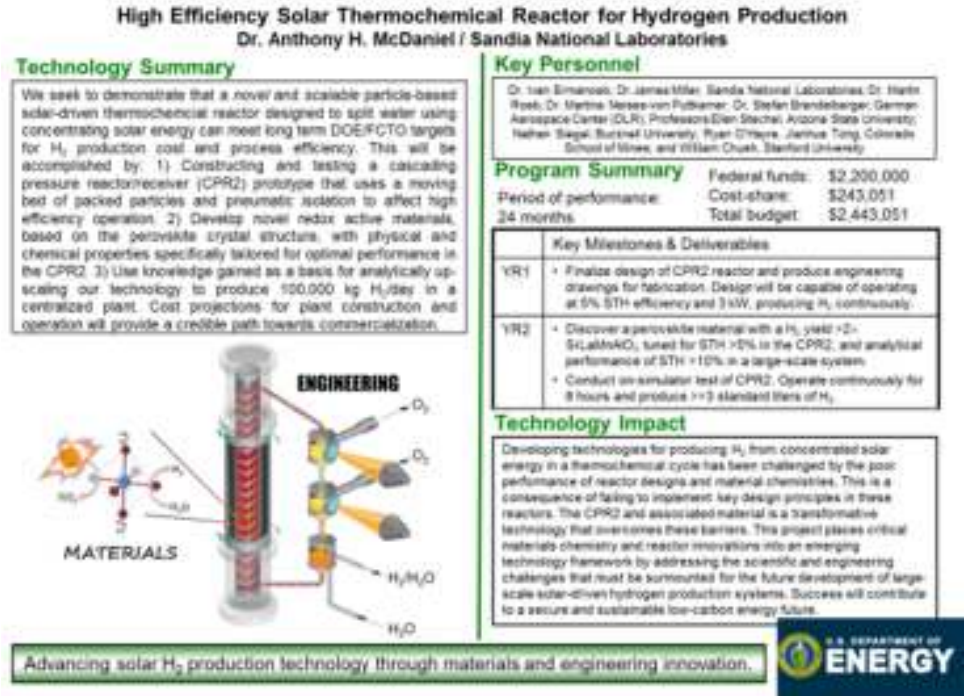
Work supported by the U.S. Department of Energy Fuel Cell Technologies Office.

Deutsches Zentrum für Luft- und Raumfahrt
German Aerospace Center

Novel and Scalable Particle-Based Solar-Driven Thermochemical Reactor

Benchmarks for DOE Targets:

- p_{TR}<10 Pa
- T_{TR}<1450°C
- T_{WS}~800°C-1000°C
- NO high-T heat recovery



THANK YOU FOR YOUR ATTENTION

Selected Sandia Publications

1) I. Ermanoski, Cascading Pressure Thermal Reduction for Efficient Solar Fuel Production. *Int. J. Hydrog. Energy* (2014), doi:10.1016/j.ijhydene.2014.06.143.
2) A. H. McDaniel *et al.*, Nonstoichiometric Perovskite Oxides for Solar Thermochemical H_2 and CO Production. *Energy Procedia*. **49**, 2009–2018 (2014).
3) J. E. Miller, A. Ambrosini, E. N. Coker, M. D. Allendorf, A. H. McDaniel, Advancing Oxide Materials for Thermochemical Production of Solar Fuels. *Energy Procedia*. **49**, 2019–2026 (2014).
4) J. E. Miller, A. H. McDaniel, M. D. Allendorf, Considerations in the Design of Materials for Solar-Driven Fuel Production Using Metal-Oxide Thermochemical Cycles. *Adv. Energy Mater.* **4**, 1300469 (2014).
5) I. Ermanoski, J. E. Miller, M. D. Allendorf, Efficiency maximization in solar-thermochemical fuel production: challenging the concept of isothermal water splitting. *Phys. Chem. Chem. Phys.* **16**, 8418 (2014).
6) A. H. McDaniel *et al.*, Sr- and Mn-doped $LaAlO_{3-\delta}$ for Solar Thermochemical H_2 and CO Production. *Energy Environ. Sci.* **6**, 2424–2428 (2013).
7) M. D. Allendorf, J. E. Miller, A. H. McDaniel, Design of Materials for Solar-Driven Fuel Production by Metal-Oxide Thermochemical Cycles. *Electrochem. Soc. Interface*. **22**, 63–68 (2013).
8) J. R. Scheffe, A. H. McDaniel, M. D. Allendorf, A. W. Weimer, Kinetics and Mechanism of Solar-Thermochemical H_2 Production by Oxidation of a Cobalt Ferrite–Zirconia Composite. *Energy Environ. Sci.* **6**, 963 (2013).
9) I. Ermanoski, N. P. Siegel, E. B. Stechel, A New Reactor Concept for Efficient Solar-Thermochemical Fuel Production. *J. Sol. Energy Eng.* **135**, 031002 (2013).
10) K. M. Allen, N. Auyeung, N. Rahmatian, J. F. Klausner, E. N. Coker, Cobalt Ferrite in YSZ for Use as Reactive Material in Solar Thermochemical Water and Carbon Dioxide Splitting, Part II: Kinetic Modeling. *JOM* (2013), doi:10.1007/s11837-013-0774-1.
11) E. B. Stechel, J. E. Miller, Re-energizing CO_2 to fuels with the sun: Issues of efficiency, scale, and economics. *J. CO_2 Util.* **1**, 28–36 (2013).
12) N. P. Siegel, J. E. Miller, I. Ermanoski, R. B. Diver, E. B. Stechel, Factors Affecting the Efficiency of Solar Driven Metal Oxide Thermochemical Cycles. *Ind. Eng. Chem. Res.* **52**, 3276–3286 (2013).
13) D. Arifin, V. J. Aston, X. Liang, A. H. McDaniel, A. W. Weimer, $CoFe_2O_4$ on a Porous Al_2O_3 Nanostructure for Solar Thermochemical CO_2 Splitting. *Energy Environ. Sci.* **5**, 9438–9444 (2012).
14) J. Kim, T. A. Johnson, J. E. Miller, E. B. Stechel, C. T. Maravelias, Fuel Production from CO_2 Using Solar-thermal Energy: System Level Analysis. *Energy Environ. Sci.* **5**, 8417 (2012).
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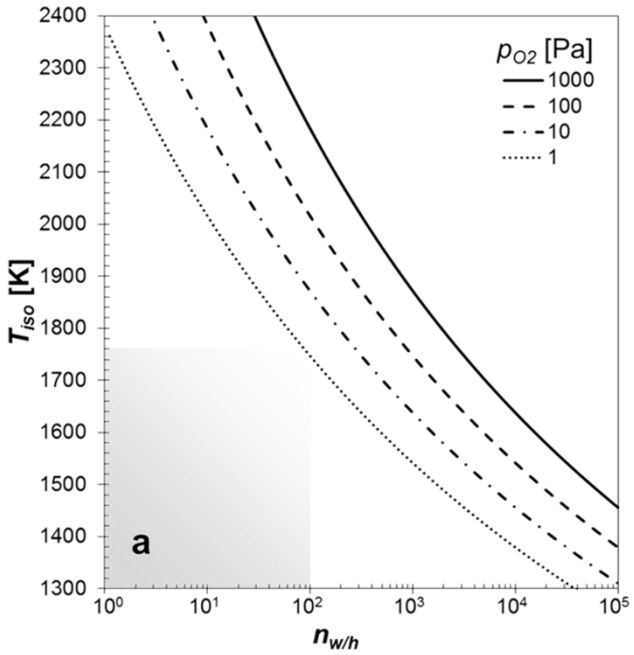
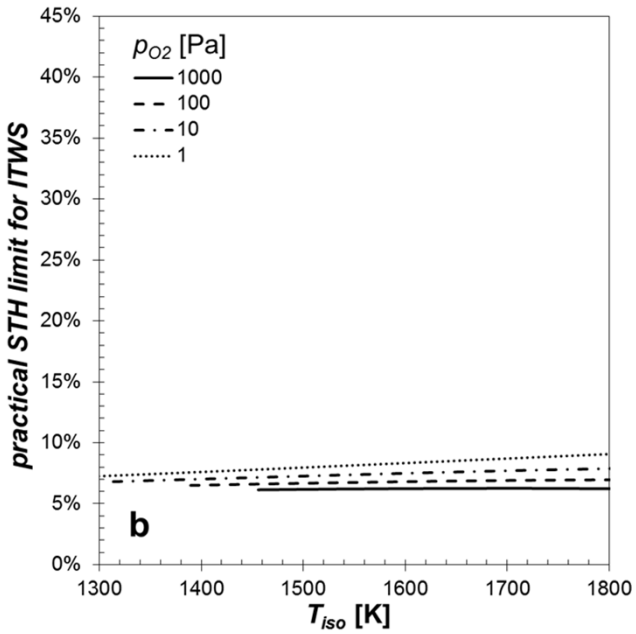
The "ΔTemperature = 0" Benchmark.



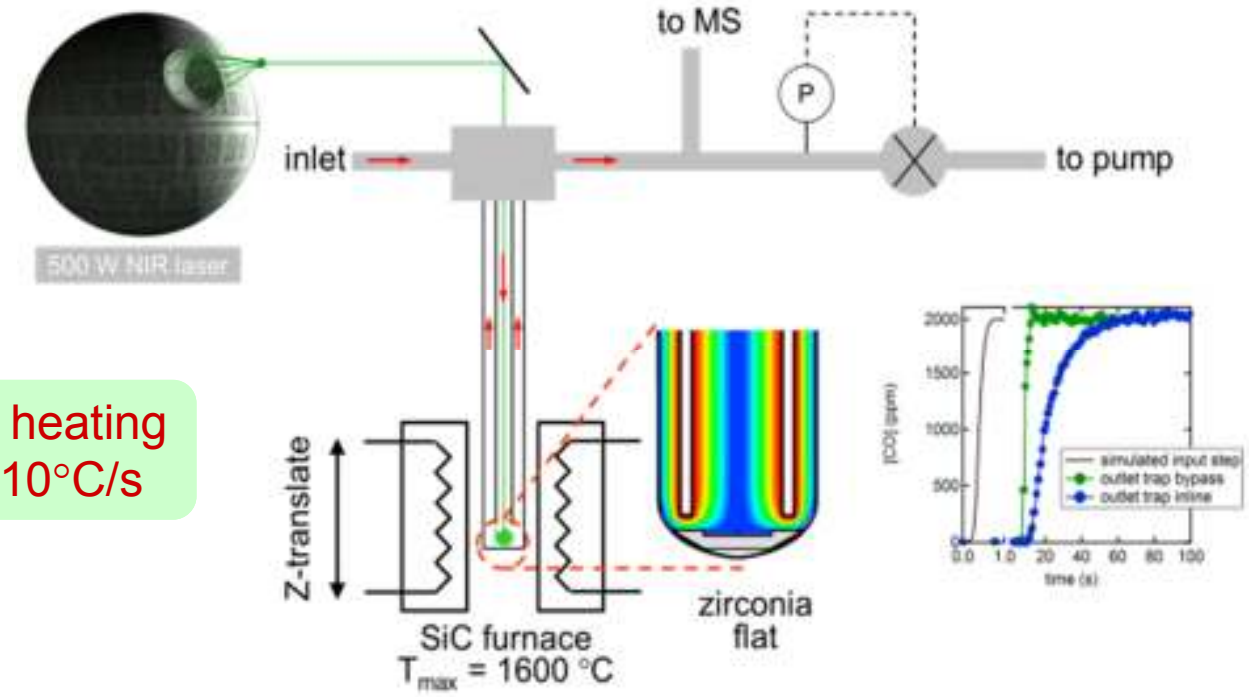


- Pressure swing process, not temperature swing.
  - Convert mechanical work to chemical work
  - Zero efficiency from expensive, ultra-high temperature heat
- Less efficient under all practical conditions.

$$\eta = 1 - \frac{T_{WS}}{T_{TR}} = 0$$

$$\eta_{STH} = \eta_{thermal} * \eta_{electrical} * \eta_{mechanical} * \eta_{chemical} << \eta_{thermal} * \eta_{chemcial}$$

Methods for Measuring Redox Activity



Material heating rates >10°C/s

- Kinetic measurements.
  - Stagnation flow reactor (SFR) with 500 W CW NIR laser for heating
  - Modulated beam mass spectrometer
- Analysis using idealized flow model (CSTR).
  - Resolve rate limiting mechanisms and develop kinetic models

Evaluation of popular material systems

Sandia National Laboratories

Fe^{2+}/Fe^{3+} redox system:

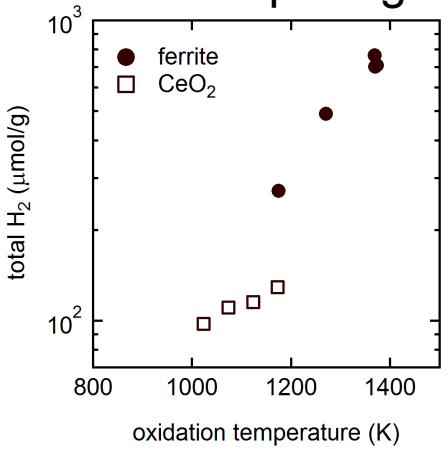
- Deep reduction at 1400 °C.
- High redox capacity ($\Delta\delta$>0.1).
- Slow H_2O oxidation kinetics.
- YSZ, ZrO_2, Al_2O_3 matrix needed to prevent sintering.

Ce^{3+}/Ce^{4+} redox system:

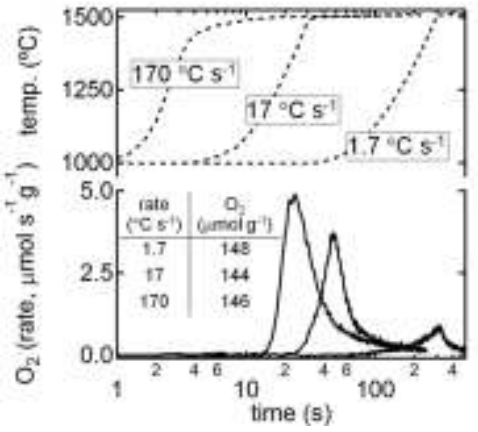
- Shallow reduction at 1500 °C.
- Low redox capacity ($\Delta\delta$<0.05).
- Fast H_2O oxidation kinetics.
- Durable under high heating rates.

PROPERTY	CERIA (CeO_2)	FERRITE ($MFeO_x/ZrO_2$)	IDEAL
Redox Kinetics	FAST	SLOW	FAST
Capacity ($\Delta\delta$)	LOW	HIGH	HIGH
T_{TR} @ Reduction	HIGH	MED/HIGH	LOW
H_2O/H_2 @ Oxidation	LOW	MED	LOW
Durability	HIGH	MED/HIGH	HIGH
Earth Abundance	LOW/MED	HIGH	HIGH

water-splitting



CeO_2 reduction



J. E. Miller, A. H. McDaniel, M. D. Allendorf, *Advanced Energy Materials*. **4**, 1300469 (2014).

SFR Used to Characterize and Screen Several Redox Materials

- Ceria and doped ceria.
  - Co, Fe, La, Mo, Mn, Ni, Pr, Zr
- Supported mixed-metal ferrites.
  - $CoFe_2O_4$ / Al_2O_3
  - $CoFe_2O_4$ / ZrO_2
  - Fe_3O_4 / Y-ZrO_2
- Perovskites.
  - $Sr_xLa_{1-x}Mn_yAl_{1-y}O_3$ (SLMA)
  - $(Ca, La, Sr)^A(Al, Ce, Fe, Mn, Ti, Zr)^BO_3$