SAND2015-5535C

Exceptional service in the national interest

Sandia National Laboratories

solar.sandia.gov



Thermochemical Redox Processes and Materials for Producing Solar Fuels and Storing Thermal Energy

Presented by James E. Miller

Sandia National Laboratories

Advanced Materials Laboratory

U.S. DEPARTMENT OF ENERGY

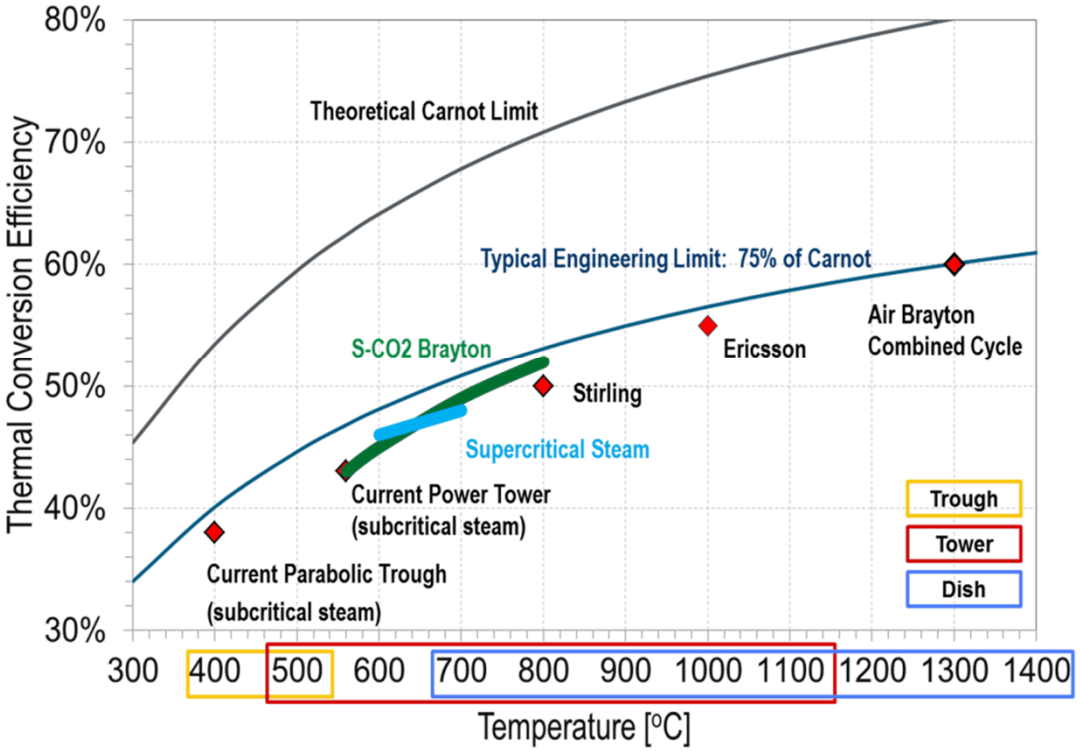
National Nuclear Security Administration

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000

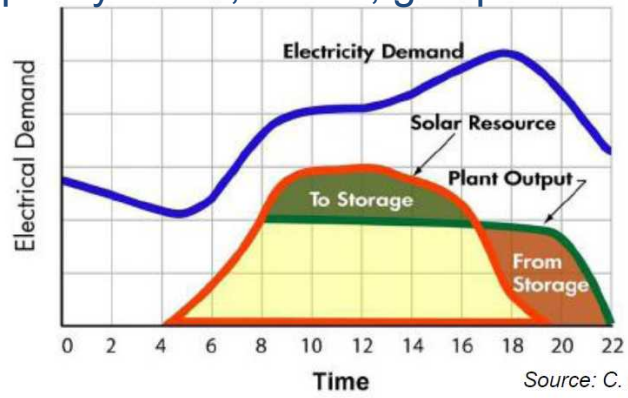
Application Space - Part I

Sandia National Laboratories

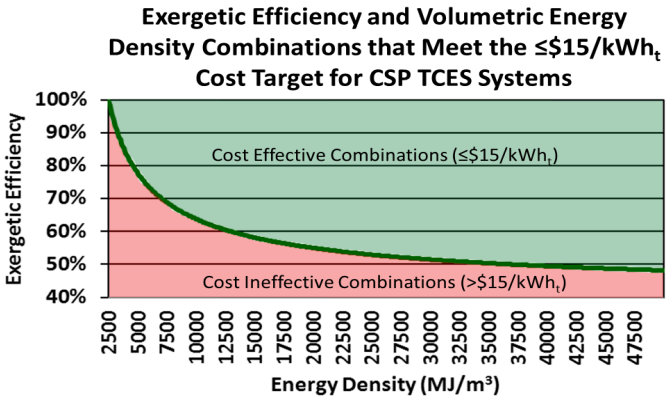
Increase Efficiency



Shift or extend operating hours to improve capacity factor, LCOE, grid penetration



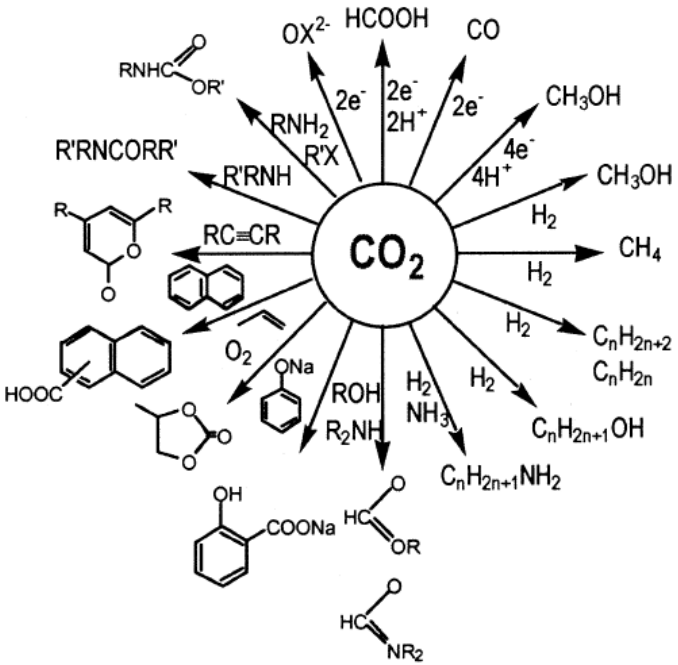
Source: C. Libby, EPRI



Higher Temperature, Higher Energy Density Storage for CSP (Solar Salt: 405 kJ/kg, T < 600-650 °C)

Application Space – Part II

Fuels (H_2 or HC) are a Big Opportunity Space Commensurate with CO_2 production



CO_2 utilization chemistry (From Aresta, Studies in Surface Science and Catalysis 114,1998).

	2004 U.S. production (1,000 metric tons)	CO_2 equivalents* (1,000 metric tons)
Ethylene	25,682	80,641
Propylene	15,345	48,183
Ethylene dichloride	12,163	10,811
Top 3 U.S. Chemicals		139,635
U.S. Petroleum		2,458,000 (5.7%)
Petrol, Coal, NG		5,705,000 (2.4%)

Sources: C&E News July 2, 2007; Report DOE/EIA-0573 (2004).
* Assuming 100% conversion of CO2 into the hydrocarbon, e.g. 2 moles of CO_2 would supply the carbon for 1 mole of C_2H_4.

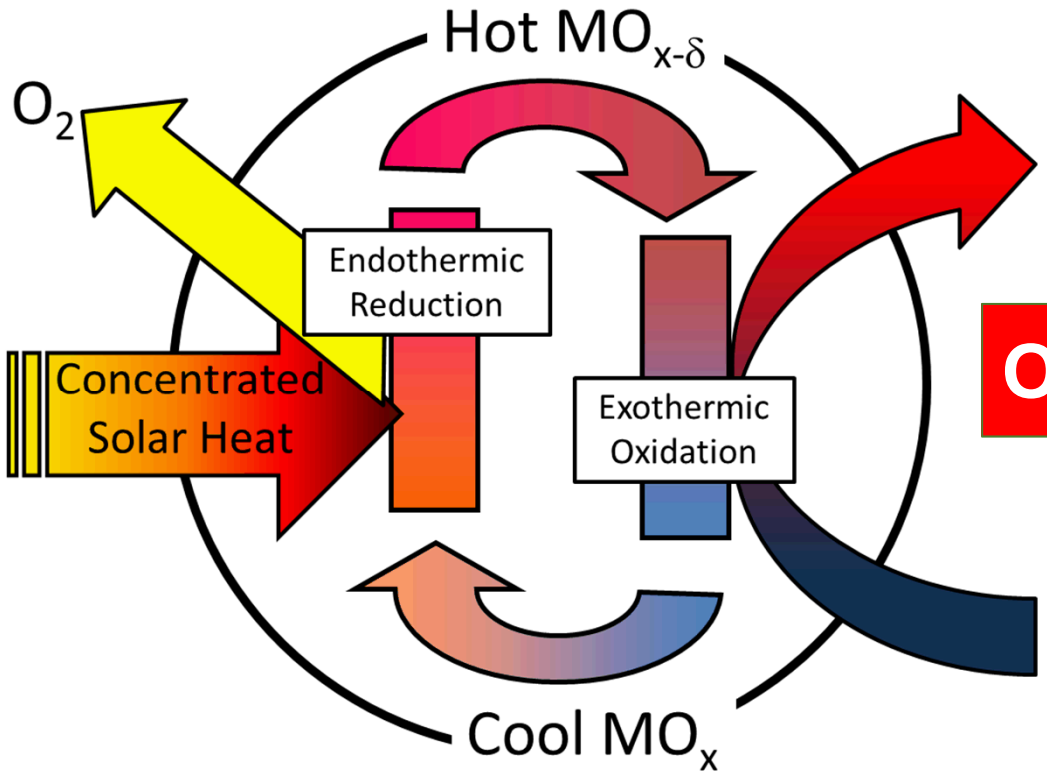
Capitalize on decades of Synfuel technology, e.g.

$$nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O$$

One Straightforward Solution?

Sandia National Laboratories

Energy In, O_2 Out.



Hot Air (CO, H_2)

O_2 In, Energy Out

Air (H_2O, CO_2)

Metal Oxide Thermal Redox Chemistry

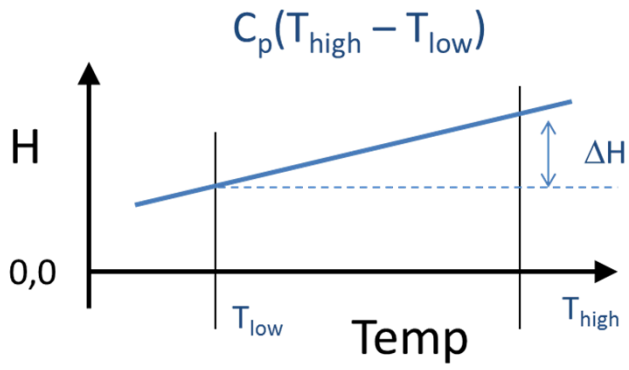
Common Demands of the Oxide

Sandia National Laboratories

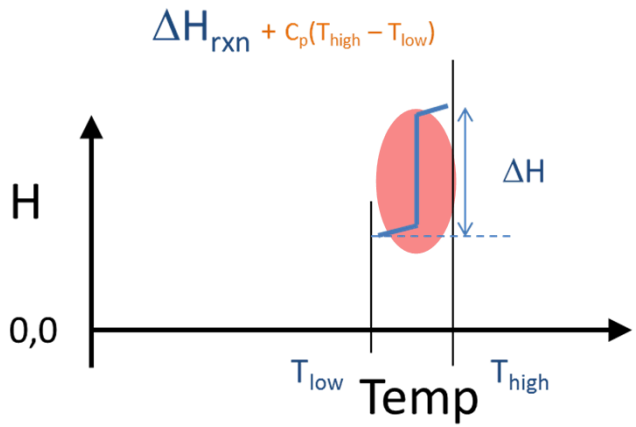
TCES	Attribute	Solar Fuels
✓	Simple, Repeatable Chemistry (No side reactions, No intermediate processing)	✓
✓	Thermodynamics Matched to Application	✓
✓	Long Term Stability – Chemical and Physical (years – 1000s if not millions of cycles)	✓
✓	Efficient volumetric/mass usage (utilization/energy density per cycle)	✓
✓	Rapid Kinetics	✓
✓	High Melting /Low Volatility/Sinter Resistant	✓
✓	Amenable to integration with receivers	✓
✓	Low Cost	✓

Basic Metal Oxide TCES

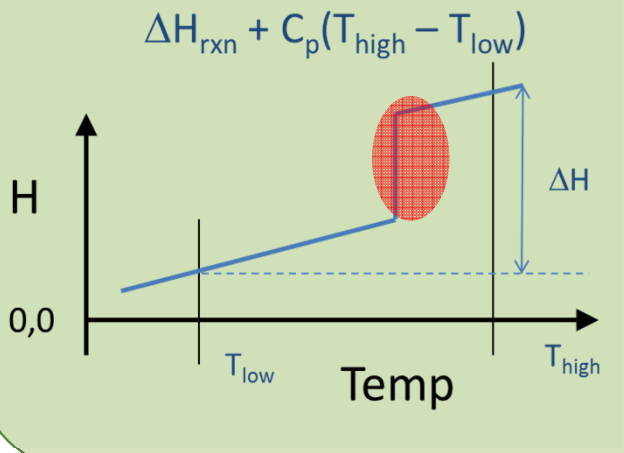
Sensible Energy Storage



Latent or Simple Chemical Energy Storage



Chemical + Sensible Energy Storage



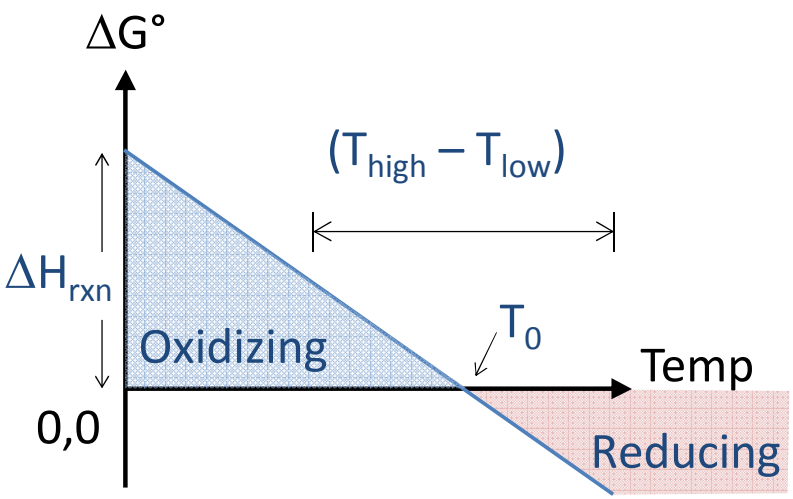
Compatible with Particle Receiver or Reactor Concepts

Metal Oxide TCES State of the Art

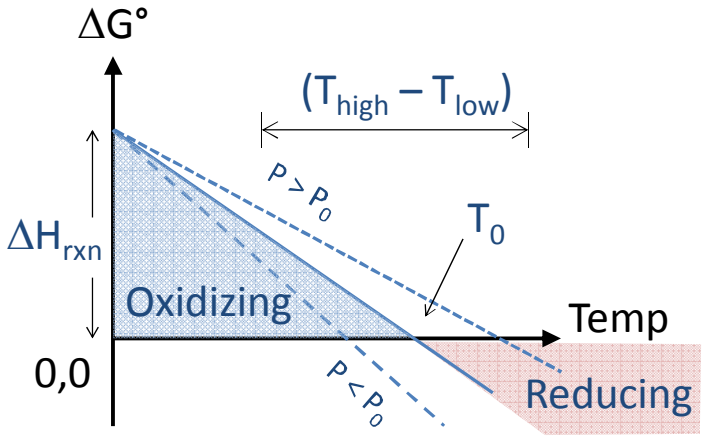
Cyclic Thermal Reduction (storage) and Oxidation (release)

- Binary Oxides (Mn, Co, Fe) with distinct phase transitions.
- Issues include low temperature reaction kinetics (oxidation), poor utilization, sintering, cost, volatility, poor tunability, etc.

Characteristic reaction enthalpy (ΔH_{rxn}) and reaction temperature (T_0).



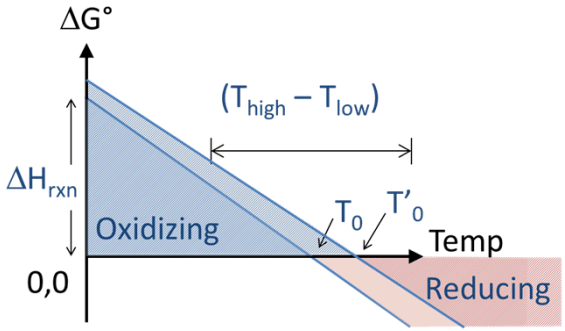
pO_2 influences T_0

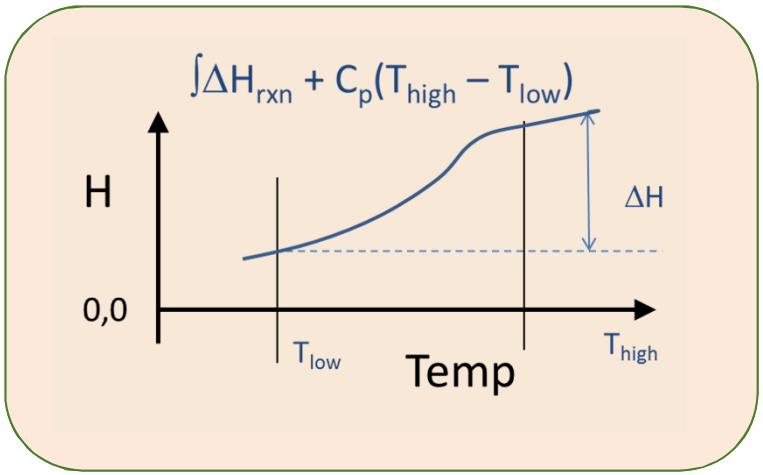


$Co_3O_4 \leftrightarrow 3CoO + ½O_2$

(T_{rxn} ~ 890 °C, ΔH_{rxn} = 844 kJ/kg)

Mixed Ionic-Electronic Conductors





Continuum of oxidation states over variety of T and pO_2

MIECs

- Exhibit both electronic and ionic conductivity
- Ionic conductivity facilitates oxygen transport—improved kinetics and reaction extent
- Electronic conductivity facilitates redox activity

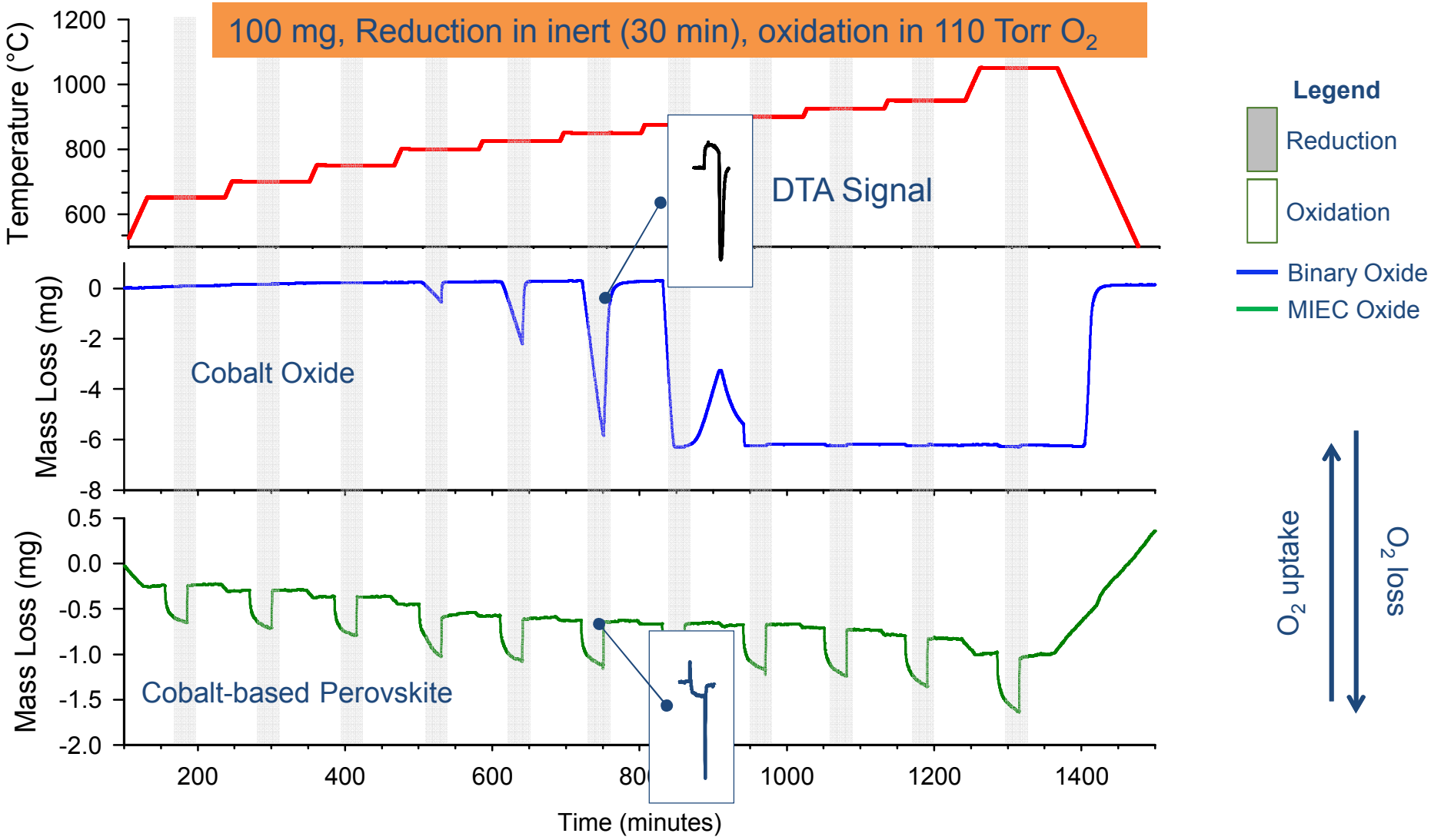
Perovskites

- General formula $ABO_{3-\partial}$
- Amenable to doping --tunability of redox extent and temperature
- Oxygen nonstoichiometry enables redox activity without structure decomposition
- Reaction extent and enthalpy (δ, and ΔH) are a challenge, as they tend to move in opposition to one another.

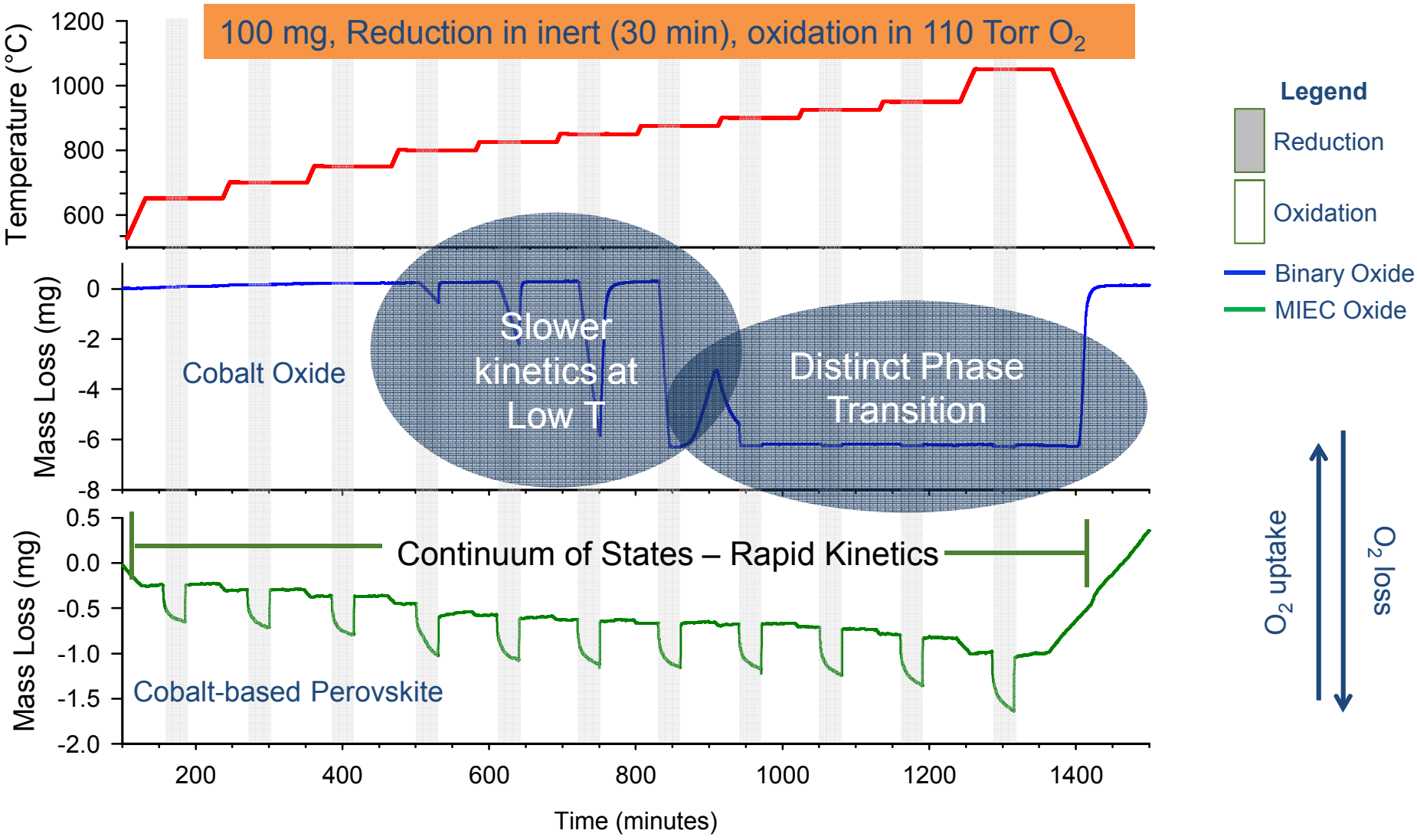
$$2/\delta\ MO_x \leftrightarrow 2/\delta\ MO_{x-\delta} + O_2(g)$$

$$\Delta H_{total} = \frac{\partial}{2}\Delta H_{rxn} + \bar{C}_P(T_{high} - T_{low})$$

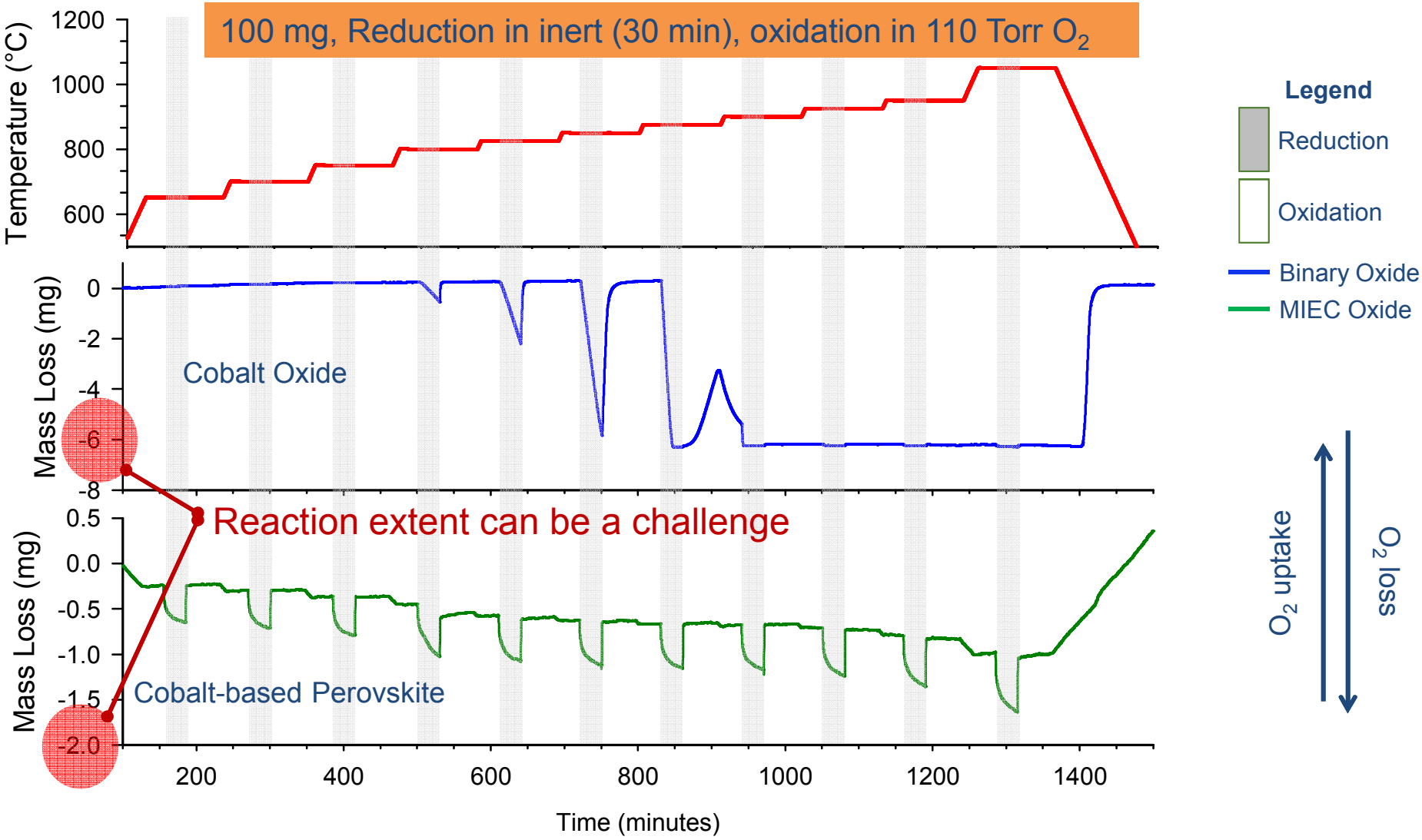
Binary Oxide vs. Perovskite



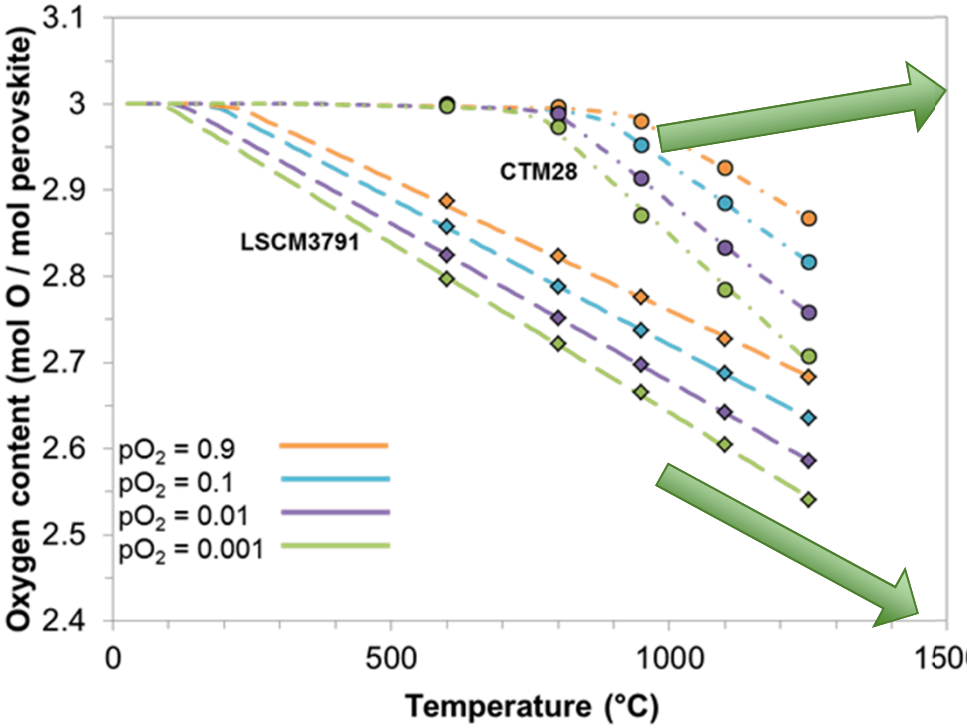
Binary Oxide vs. Perovskite

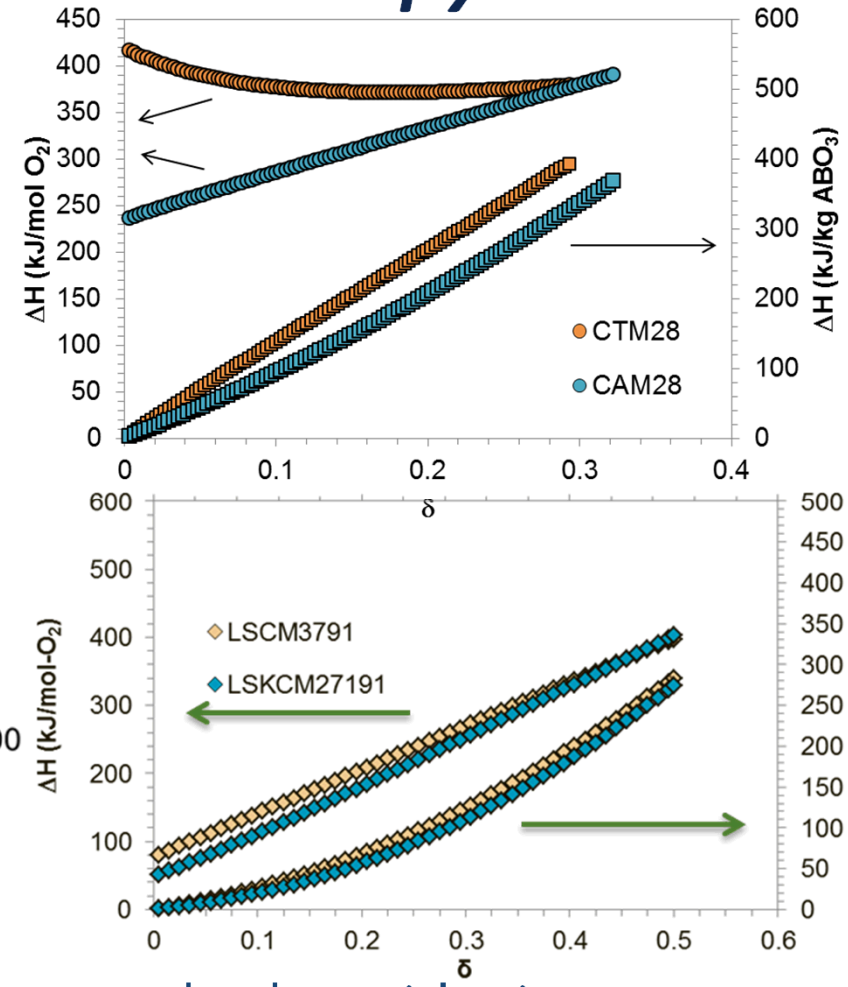


Binary Oxide vs. Perovskite



Advancing the State of the Art: Balancing Reduction extent and Enthalpy





- High reduction onset temperature and lower molecular weights increase partial molar and mass specific enthalpies.
- Earth Abundant Elements manage costs.

Babiniec, Coker, Miller, Ambrosini, Solar Energy 118, 451-459 (2015).

Metal Oxide Thermochemical Conversions: Heat to Re-energize CO_2 and H_2O.

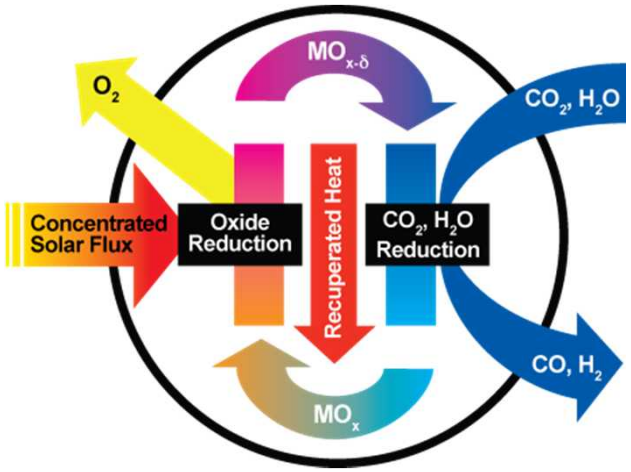
Sandia National Laboratories

Unfavorable reaction
(e.g. $H_2O \rightarrow H_2 + ½\ O_2$
or $CO_2 \rightarrow CO + ½\ O_2$)
divided into two or more favorable reactions.

A thermochemical cycle is essentially an engine that converts heat into work in the form of stored chemical energy.

$1/\delta\ MO_x \rightarrow 1/\delta\ MO_{(x-\delta)} + ½\ O_2$

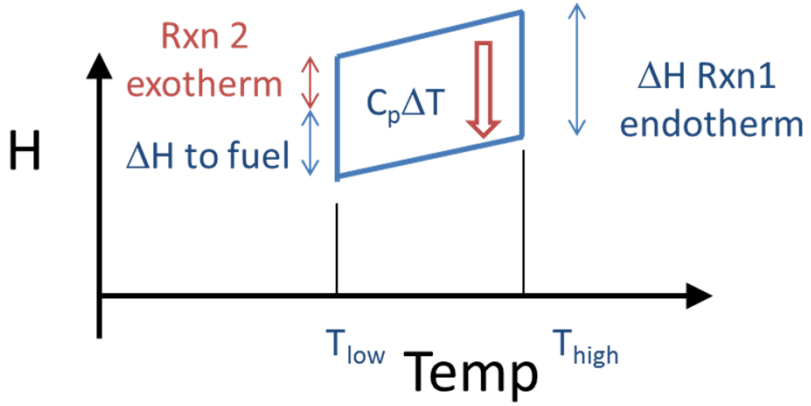
$Fe_3O_4 \rightarrow 3\ FeO + ½\ O_2$



$1/\delta\ MO_{(x-\delta)} + CO_2 \rightarrow 1/\delta\ MO_x + CO$

$3\ FeO + CO_2 \rightarrow Fe_3O_4 + CO$

$\Delta H_{endotherm} - \Delta H_{rxn\ exo} = \Delta H_{fuel}$



Impact:

Sandia National Laboratories

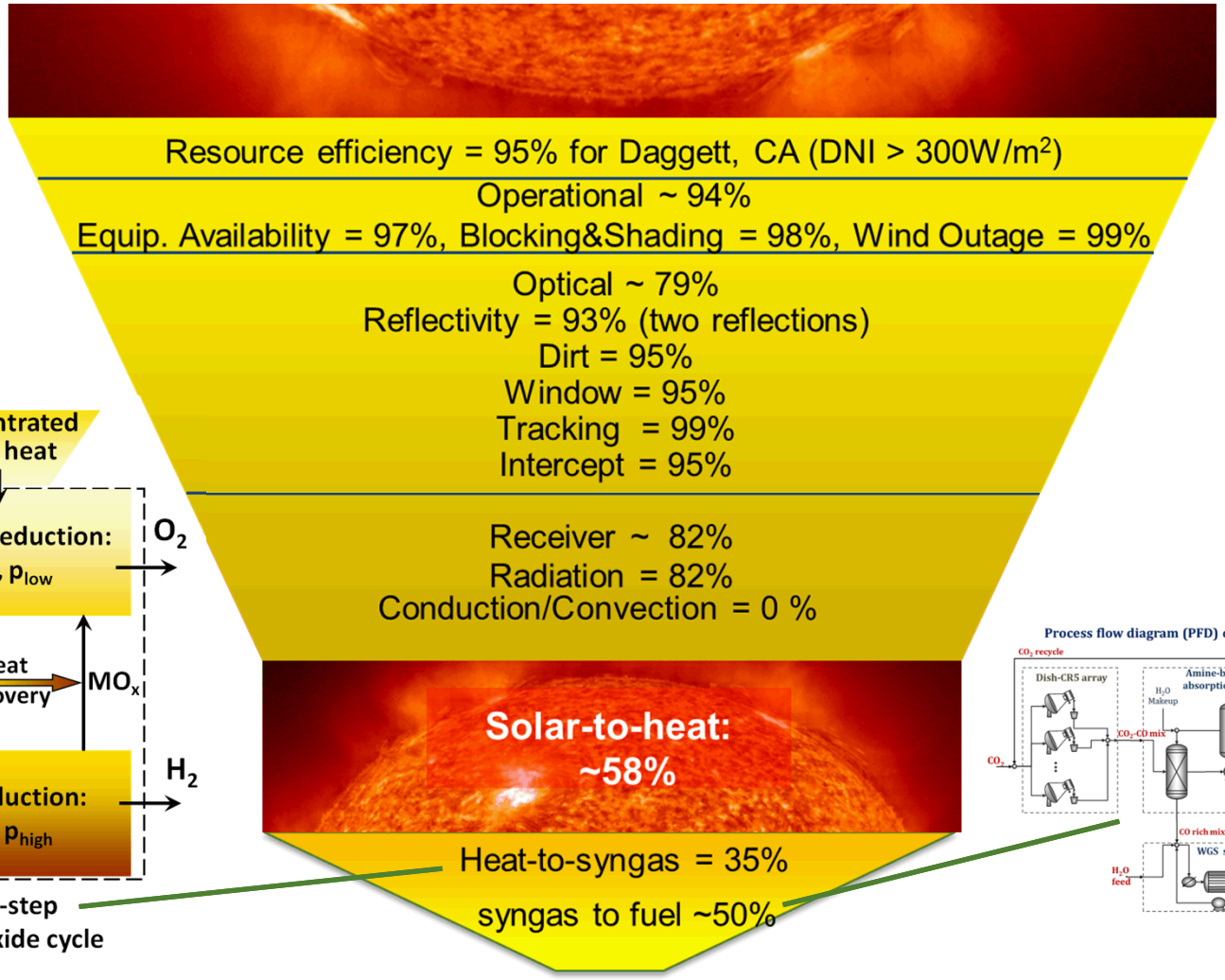
Meeting a significant fraction of transportation fuel demand with solar fuels is certainly plausible!

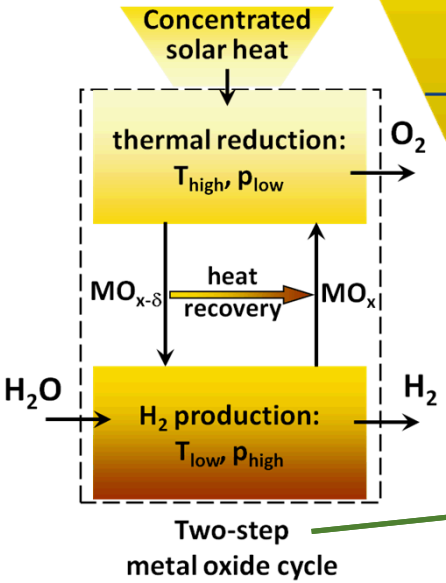
- ***High solar to fuel efficiency (>10%) is absolutely required.***
  - Cost
  - Scale (land, materials of construction)
- *Water, CO_2 are not limiting –*
  - Water consumption/cost relatively low
  - High impact opportunity for CO_2.
- *Consistent with other human activities occurring over multiple decades.*

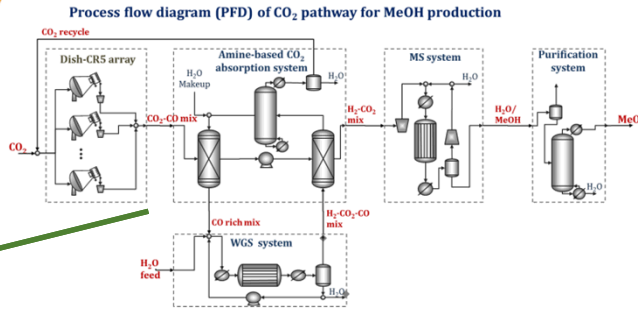
E.B. Stechel and J.E. Miller "Re-energizing CO_2 to fuels with the sun: Issues of efficiency, scale, and economics" Journal of CO_2 Utilization, 1 (2013) 28–36.

Required Heat to Syngas Efficiencies ≥ 60 %

Sandia National Laboratories







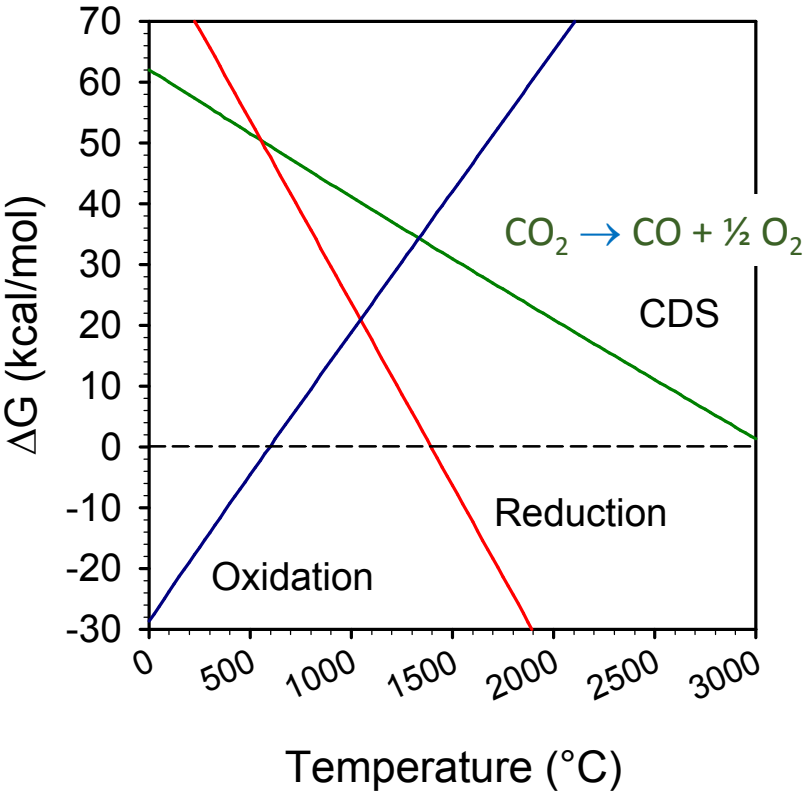
Solar to Fuel = 10%

Thermo More Constrained than TCES

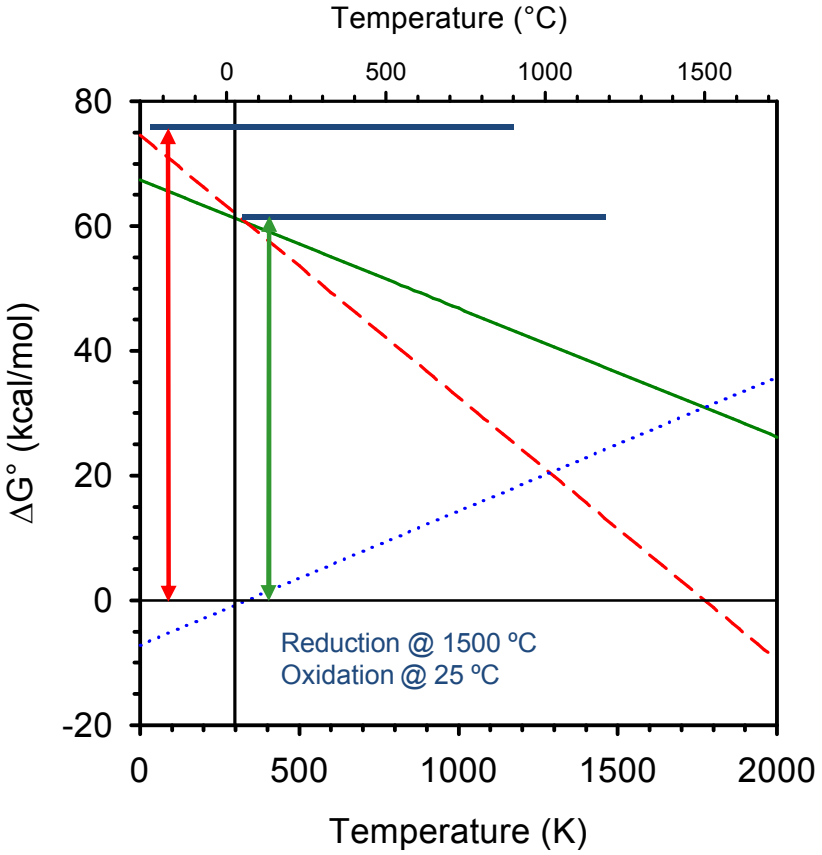
$1/\delta\ MO_x \rightarrow 1/\delta\ MO_{(x-\delta)} + ½\ O_2$

$1/\delta\ MO_{(x-\delta)} + CO_2 \rightarrow 1/\delta\ MO_x + CO$

$CO_2 \rightarrow CO + ½\ O_2$



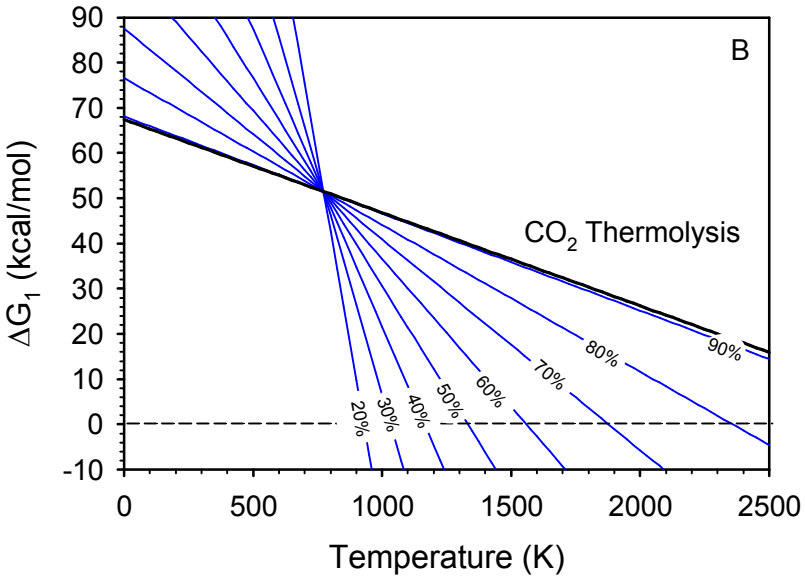
Assumptions: ΔH, $\Delta S \neq f(T)$, P=1 atm



$$\eta = \frac{\Delta G^{298}_{CDS}}{\Delta H_{MOx\ Reduction}} = 0.83$$

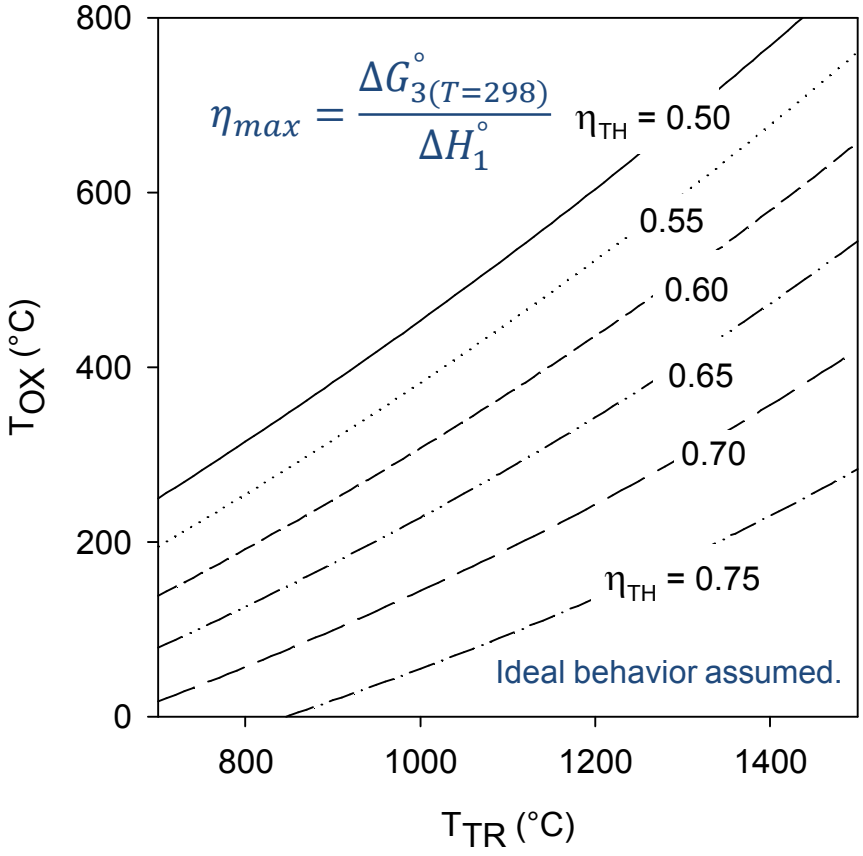
Fuel Cell- Like Theoretical Efficiency

"Thermodynamic Temp" and Efficiency



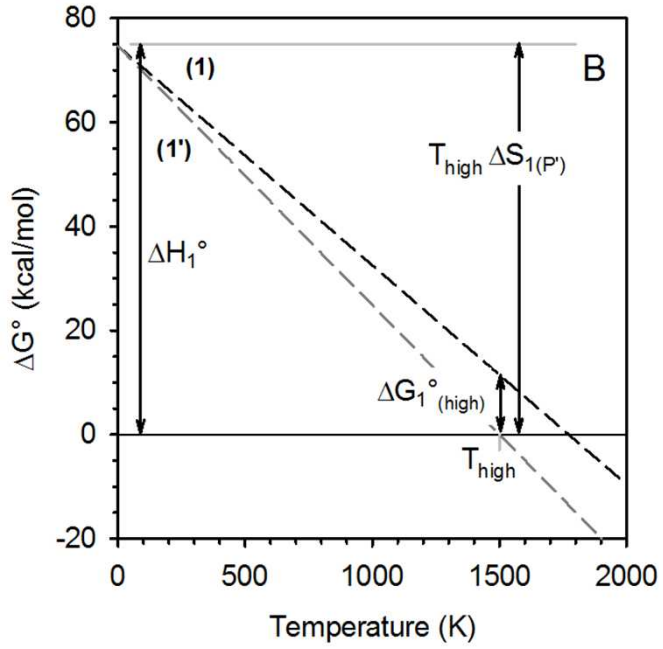
Thermodynamics recommends materials with high reduction temperature, low oxidation temperature (wide spread).

Thermodynamic T_{TR} and T_{OX} imply ΔH and ΔS and vice versa. Not all combinations are realistic.



"Non-thermodynamic "Temperatures?

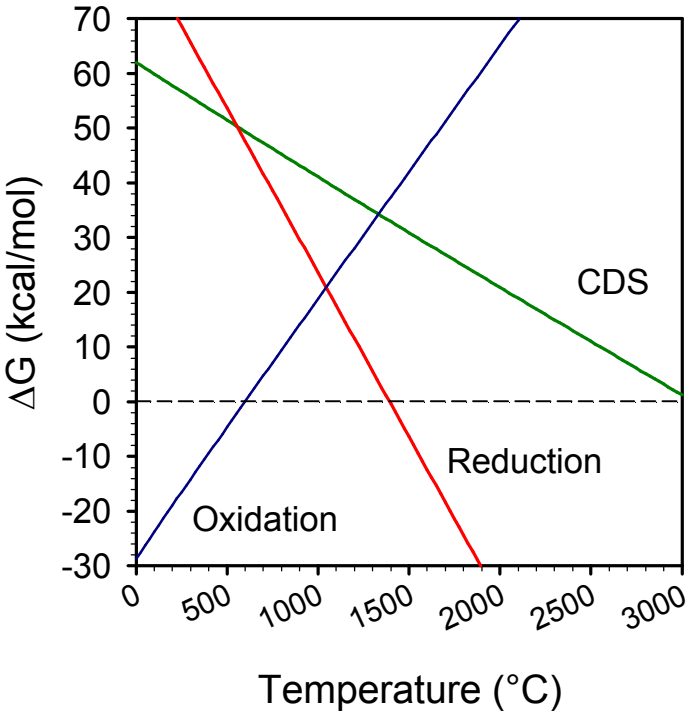
Reduction: Work in the form of Pumping or sweep gas shifts reduction temperature.



Heat to Work Conversion Penalty

Oxidation:

$\Delta G \approx -RT*\ln\{[CO]/[CO_2]\}$

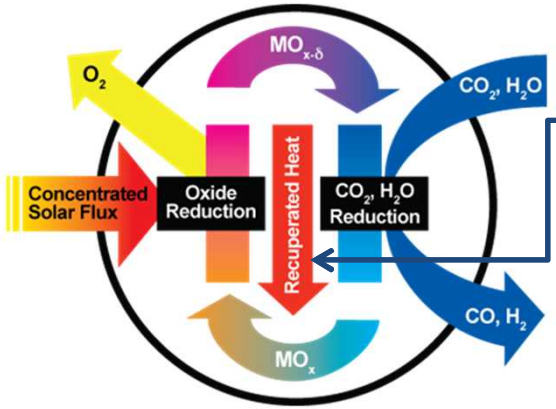


Separation Work Requirement

Yes, but at a price!

Advantage of Smaller Temp. Swing? Recuperation and Kinetics

$MO_x \rightarrow MO_{x-\delta} + \delta/2\ O_2$ (ΔH_1, T_{high}, e.g. 1500 °C)



$MO_{x-\delta} + \delta\ CO_2 \rightarrow MO_x + \delta\ CO$

T_{low}, e.g. 800 °C

Efficiency is a function of:

Thermodynamics: ΔH_1 (T_{high} & T_{low}), δ

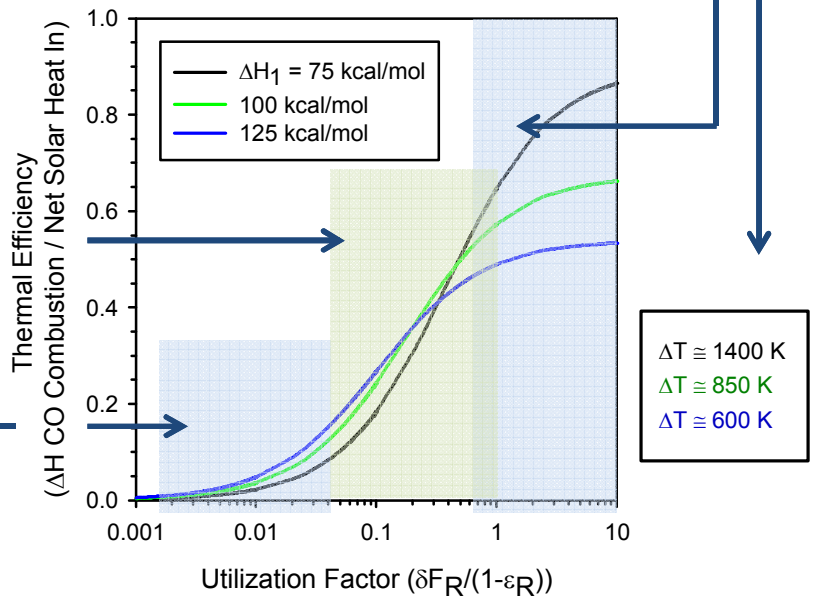
Kinetics: δ

The reactor: recuperation effectiveness & Pressures, sweep etc. (work input

The maximum possible efficiency is limited by ΔH_1.
High efficiency (small ΔH_1) corresponds to a large T_{high}-T_{low}.

The possible efficiency increases with degree of reaction (δ) and/or effectiveness of recuperation.

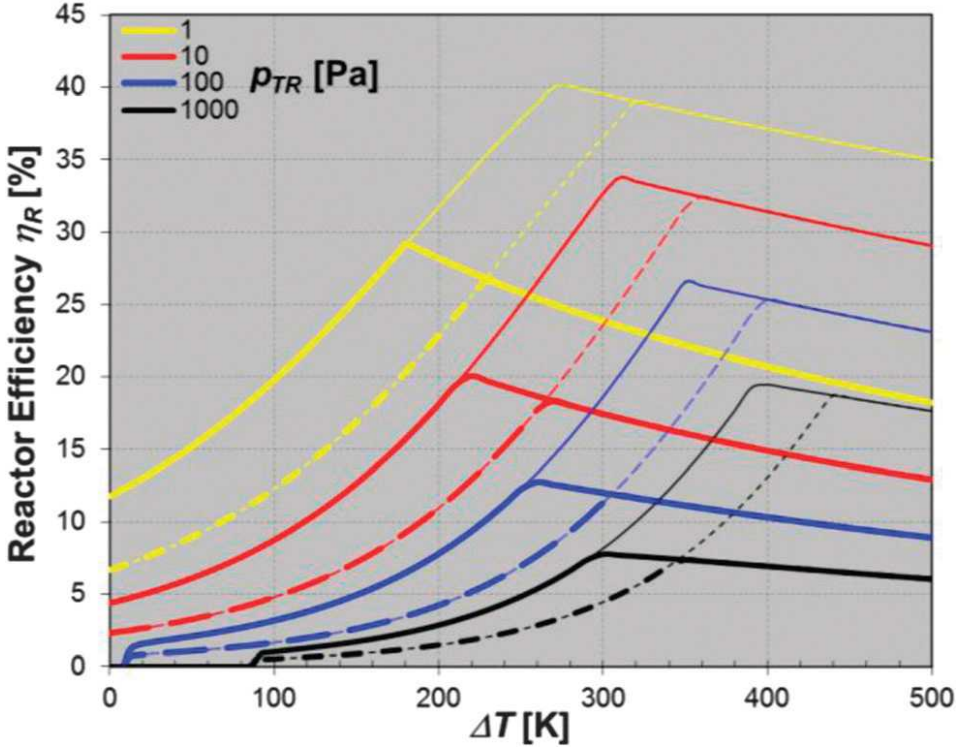
When utilization is low, sensible heat demand becomes a more dominant factor than ΔH_1.

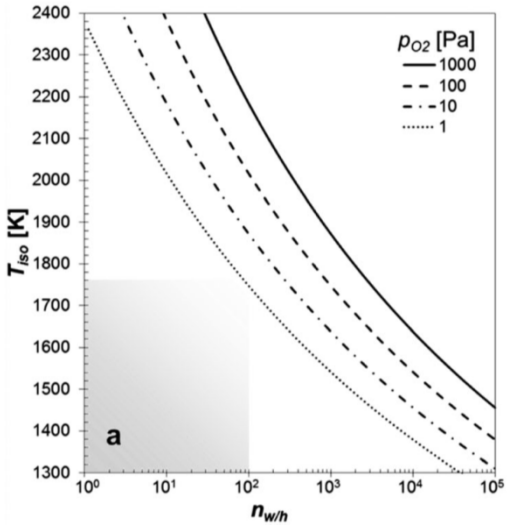


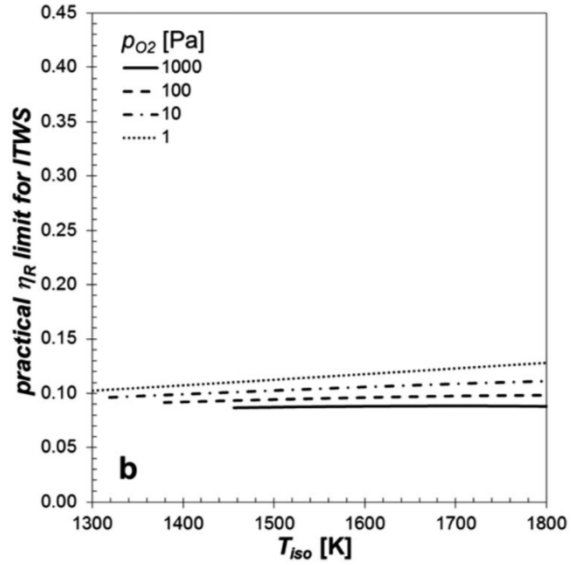
Optimum Temperature Swing

Sandia National Laboratories

Different lines of similar color represent different recuperation extents for gas and solid







Isothermal is possible, but in my opinion inadvisable – can we use that electricity to better advantage?

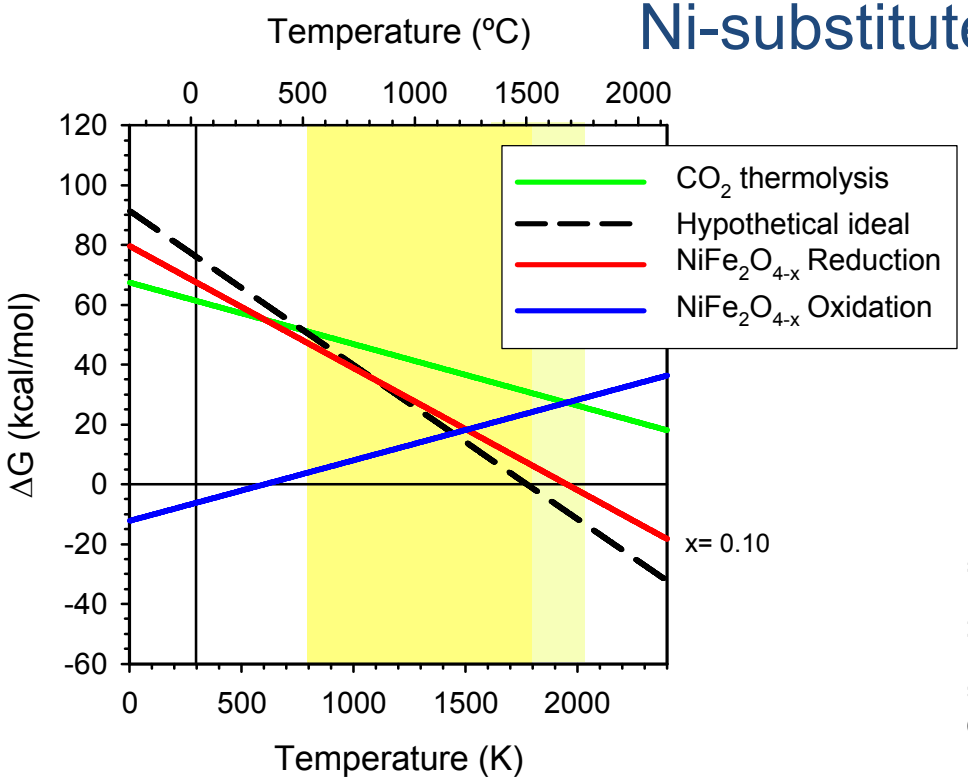
Ermanoski, Miller, Allendorf, Phys. Chem. Chem. Phys., 2014, 16, 8418-8427.

S2P SUNSHINE PETROL

Further Complexities of Real Materials

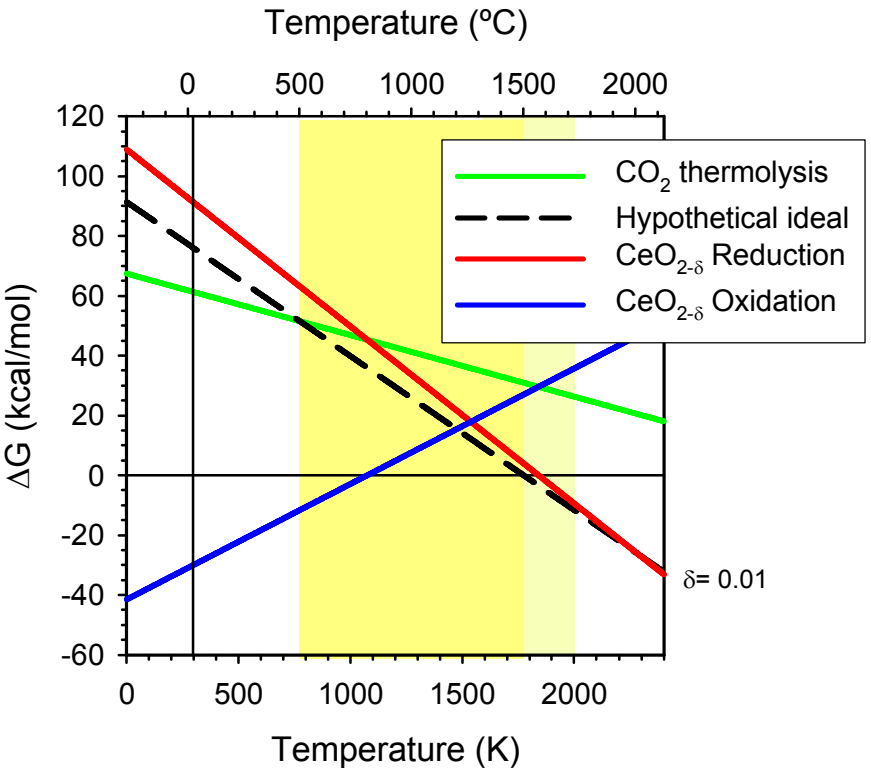
Sandia National Laboratories

Ni-substituted Ferrite



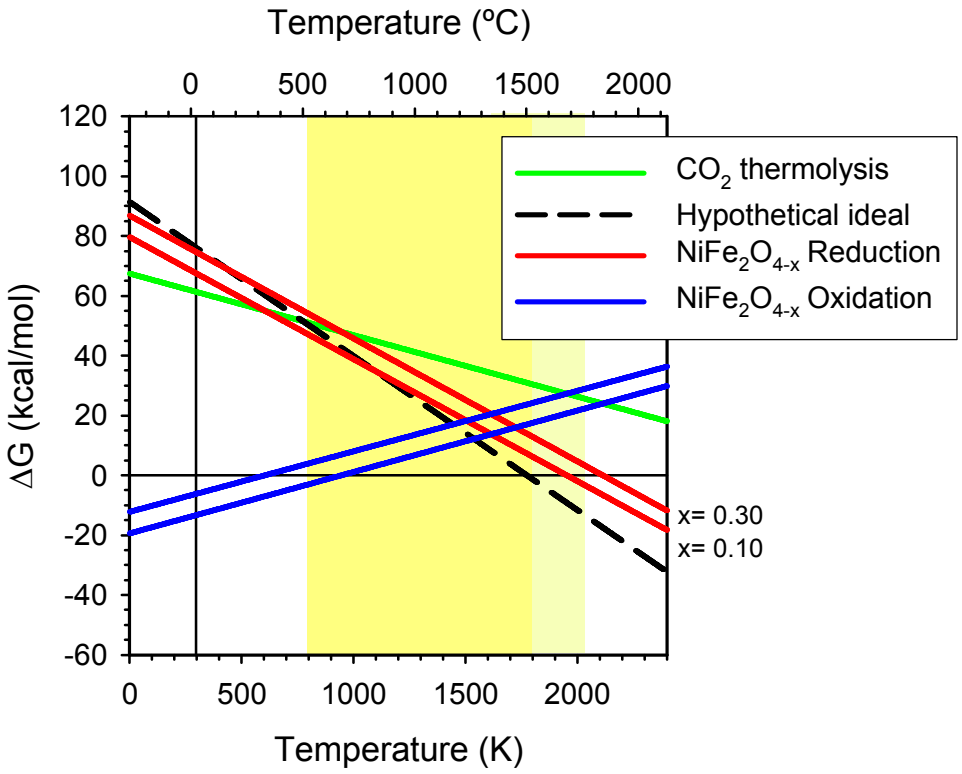
ΔH and ΔS (ΔG) are functions of redox state (δ or x).

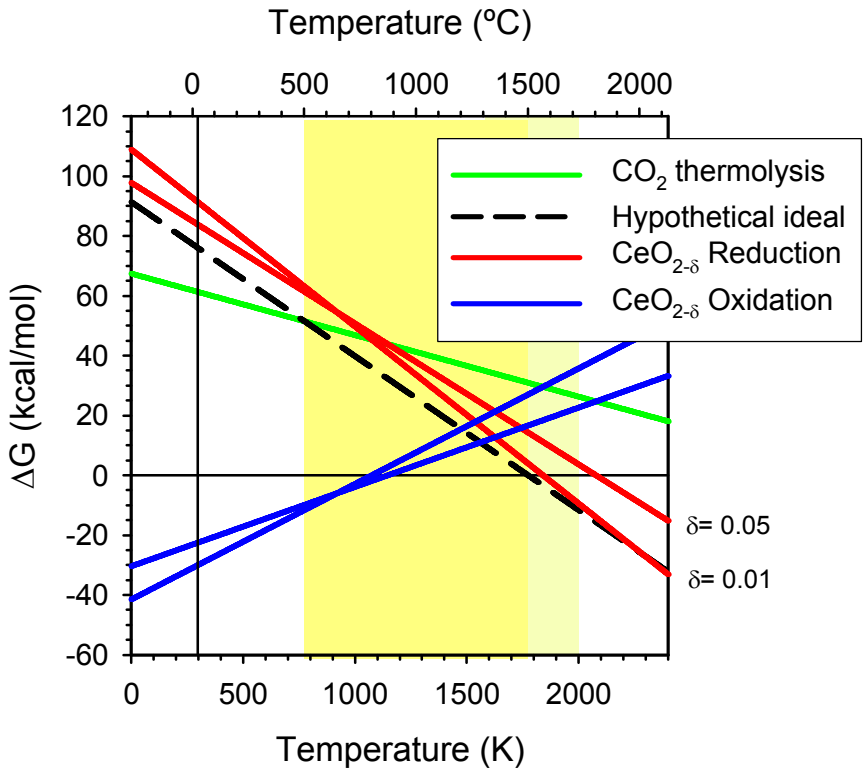
Ceria



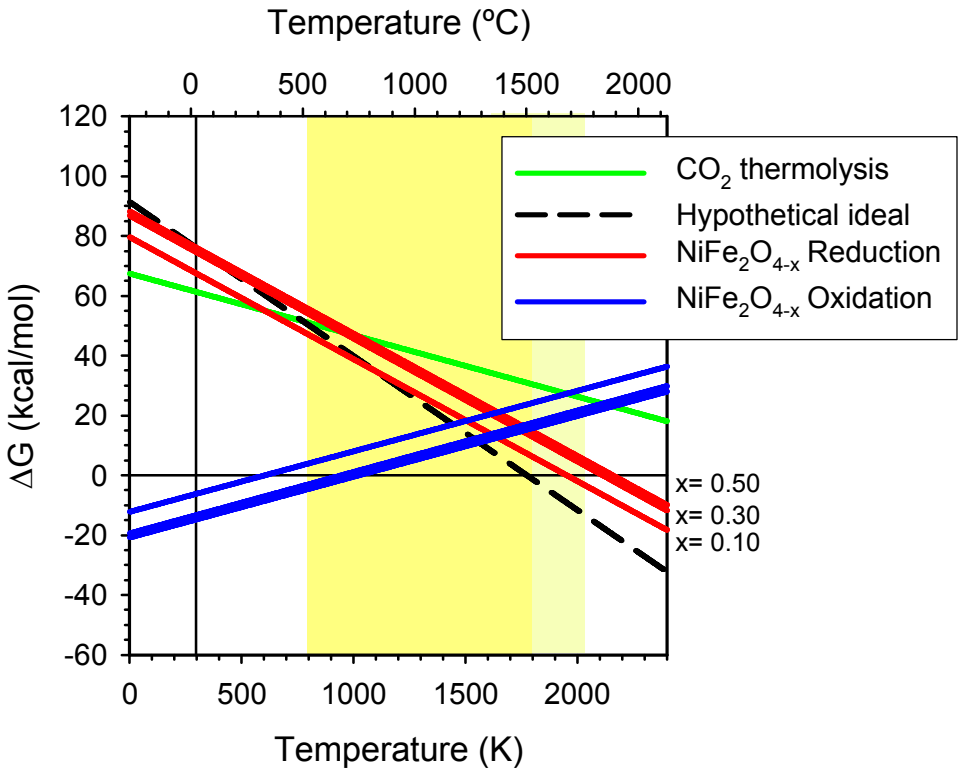
Miller, McDaniel, Allendorf *Adv. Energy Mater 2013.*

Further Complexities of Real Materials



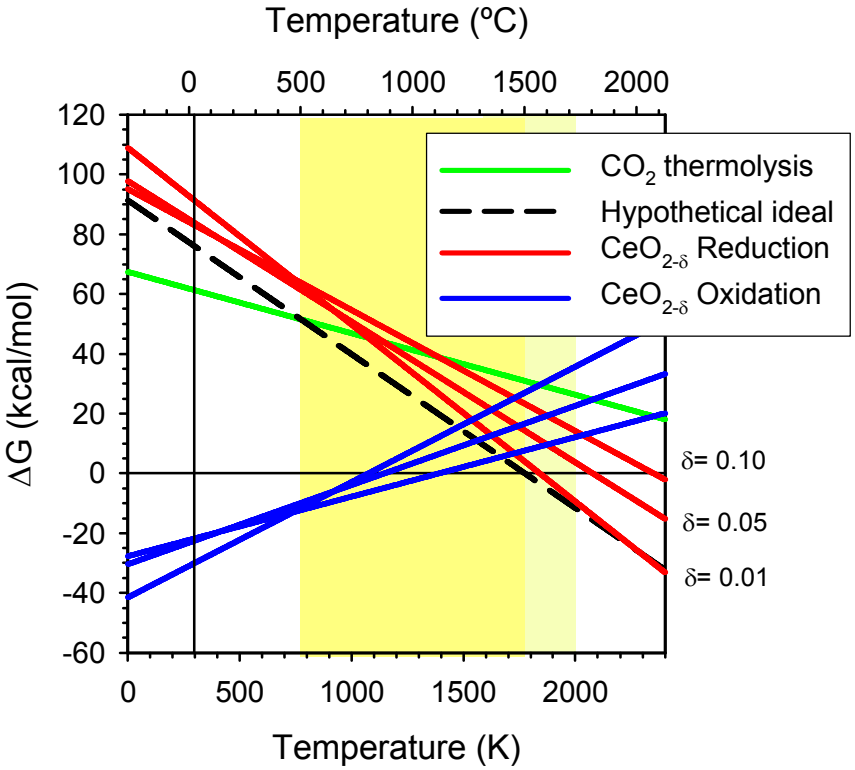


Further Complexities of Real Materials



From a thermodynamic viewpoint, ferrites appear superior to ceria.

With each increment of reduction, materials become harder to reduce, easier to oxidize.

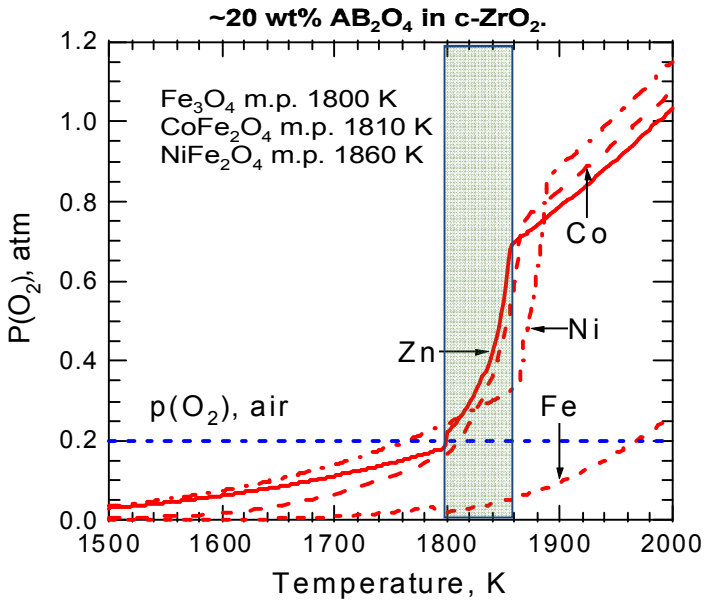


What's the matter with Ferrites?

Idealized Chemistry

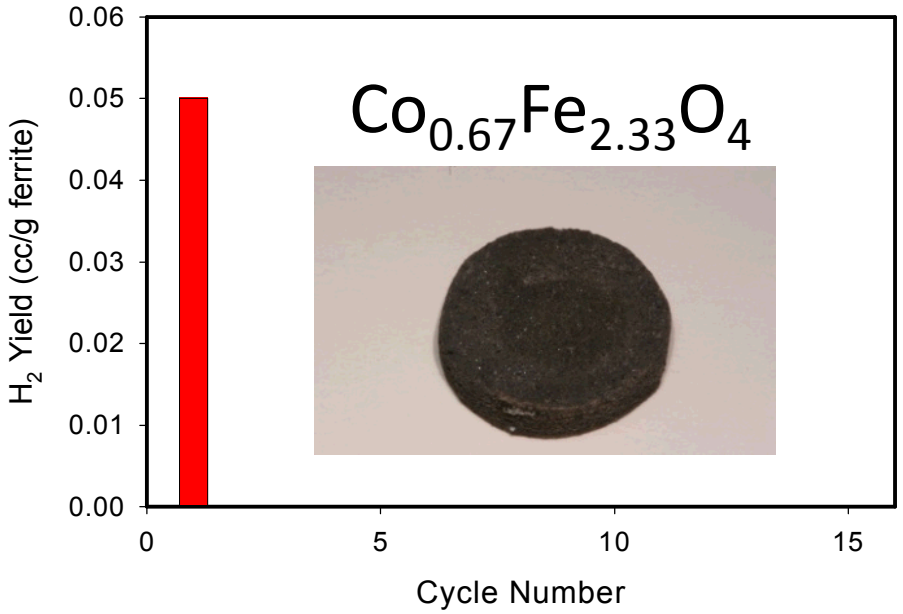
$Fe_3O_4 \rightarrow 3FeO + ½\ O_2$

$3FeO + H_2O \rightarrow Fe_3O_4 + H_2$



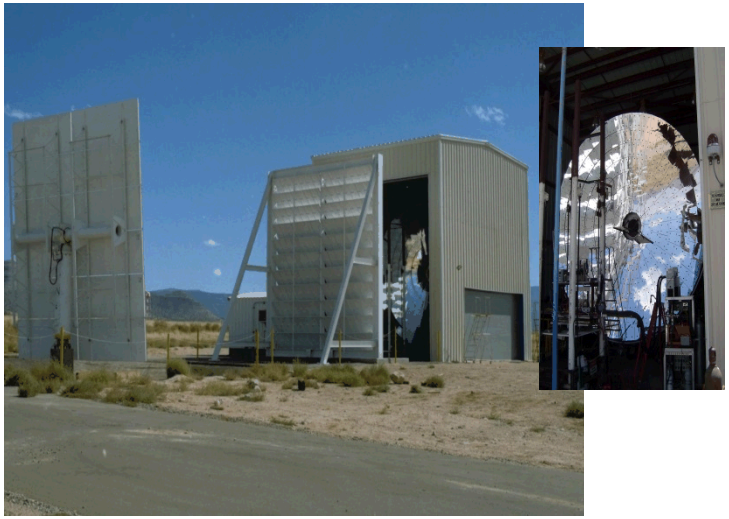
Favorable temperature range (thermodynamics) can be manipulated via metal substitutions in Fe_3O_4.

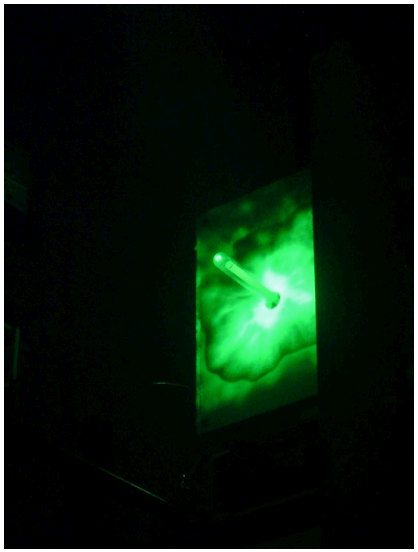
Alter them to keep them from melting.



Even then, "Bulk" materials do not live up to their potential.

What's the matter with Ferrites?

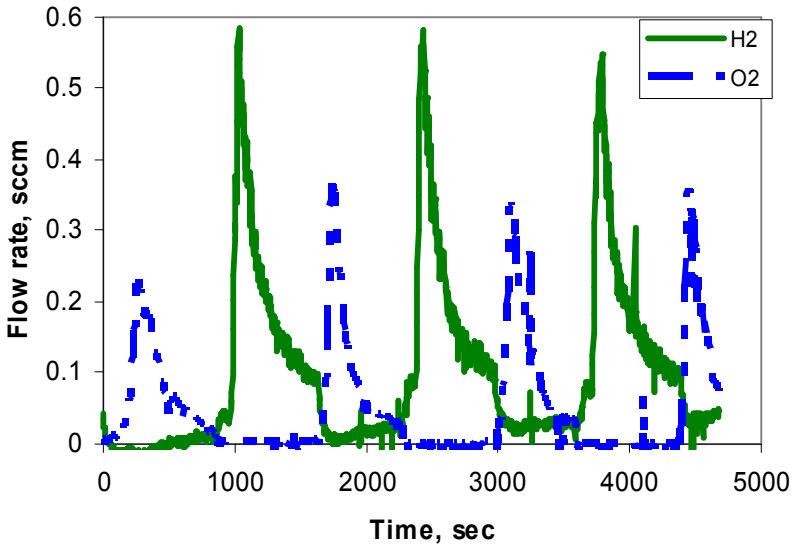




Unless you add zirconia!

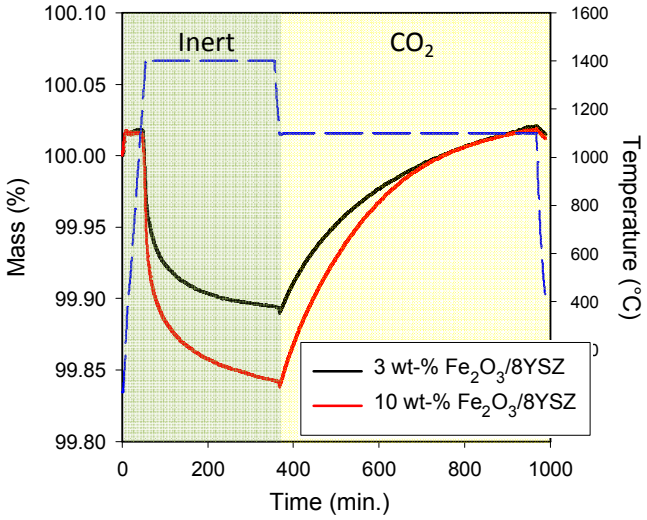
On-Sun Test:
$Co_{0.67}Fe_{2.33}O_4$/YSZ (1:4)

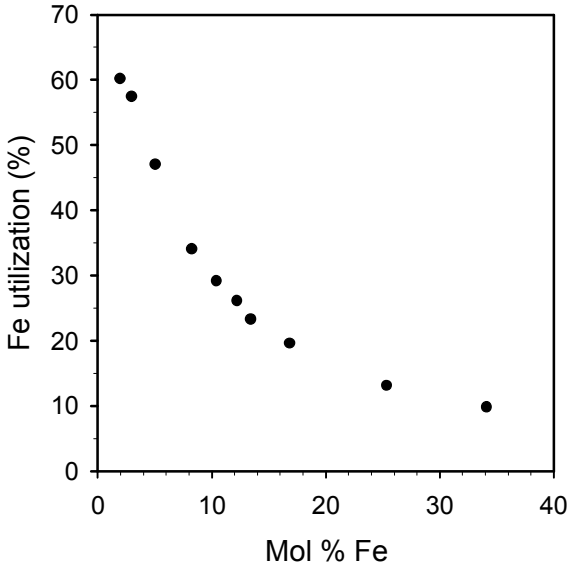
T_{TR} 1580 °C, T_{OX} 1050 °C
H_2 = 3.5-4 scc/g ferrite each cycle



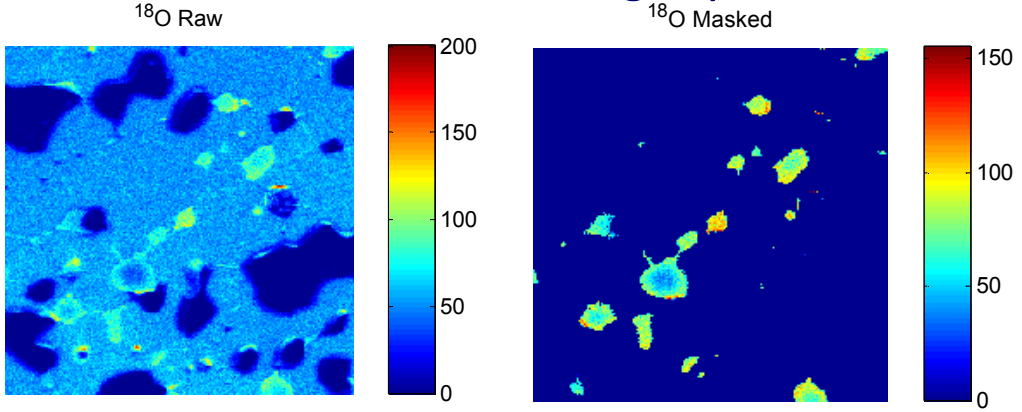
Pioneered by Kodama et. al. (ISEC) 2004, ISEC2004-65063, Portland, OR.

Fe dissolution and oxygen transport are the keys

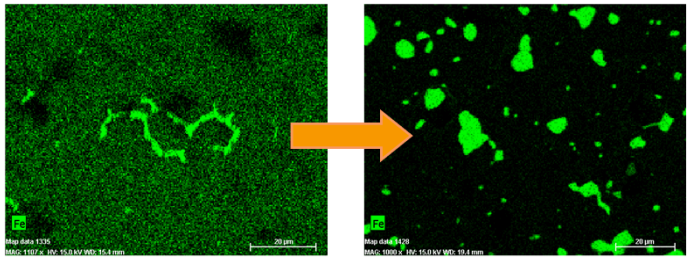




Beyond the solubility limit additional Fe contributes little to the overall gas yield.



Reaction with ^{18}O-labelled CO_2 confirms limited utilization of bulk particles relative to Fe/YSZ.

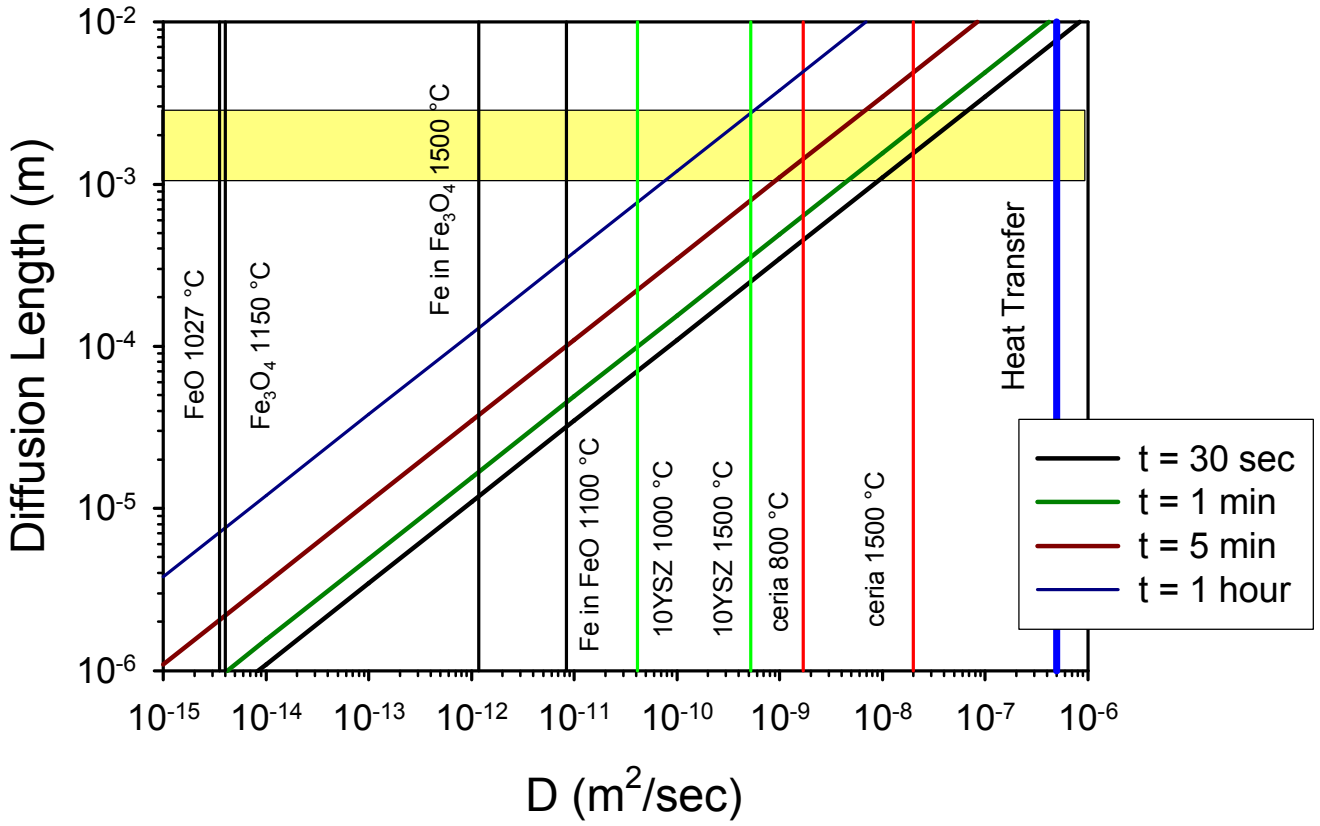


Fe EDS

E.N. Coker, J.A. Ohlhausen, A. Ambrosini, and J.E. Miller J. Mater. Chem., 2012, 22, 6726. DOI:10.1039/C2JM15324F.

Perspective on Ion Transport

$$diffusion\ length = 2\sqrt{Dt}$$



Heat> Ceria > YSZ >> Fe_3O_4

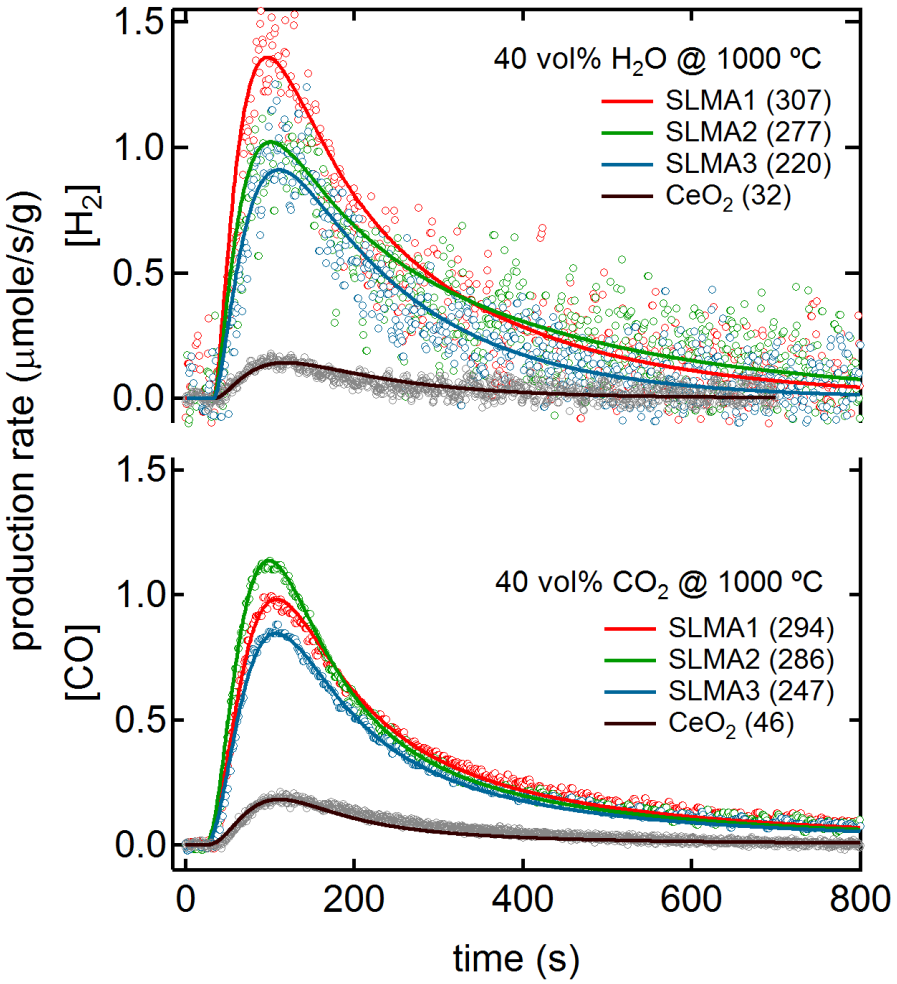
Ion (oxide) diffusion lengths are materials- and temperature-dependent.

MIEC Path Forward: $Sr_xLa_{1-x}Mn_yAl_{1-y}O_{3-\delta}$

- Perovskite compounds oxidize to split H_2 and CO_2 with lower T_{TR}
- Comparable kinetics to ceria, but higher utilization.

9× more H_2, 6× more CO

compound	CO (μmole/g)	H_2 (μmole/g)
LSAM1	294	307
LSAM2	286	277
LSAM3	247	220
$CeO_{2-\delta}$	46	32



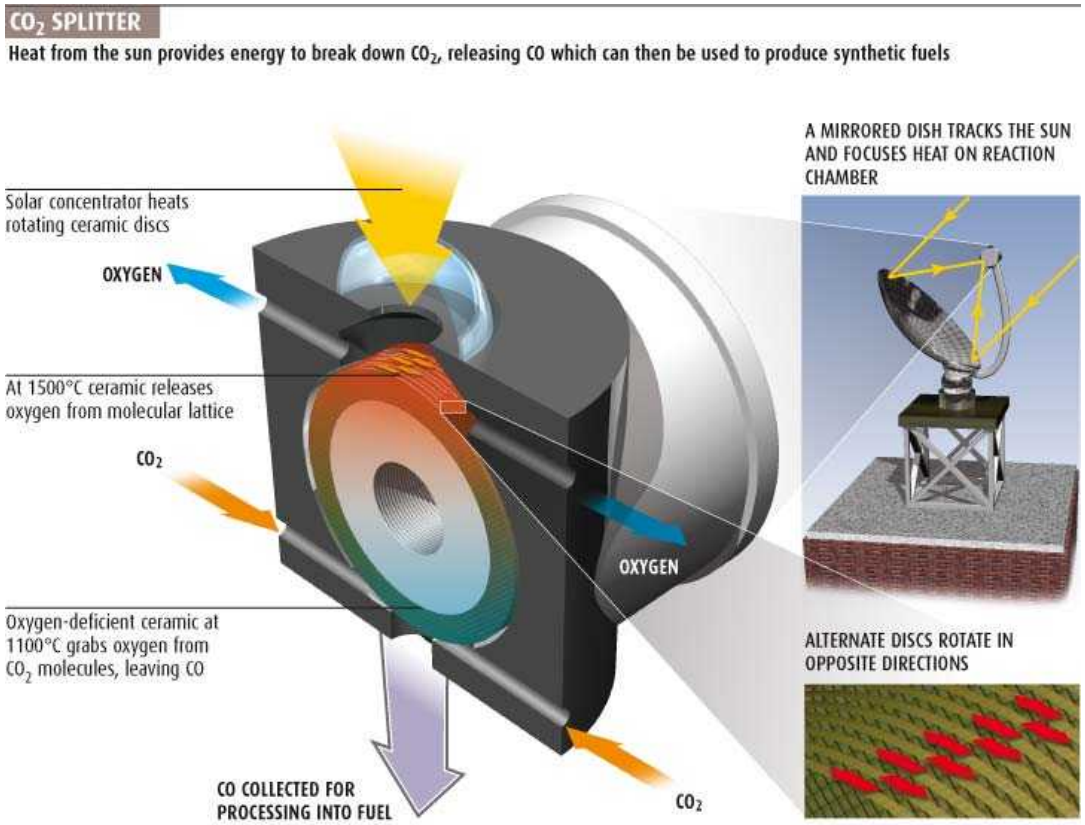
80 cycle durability demonstrated

A.H. McDaniel, Elizabeth C. Miller, Arifin, A. Ambrosini, E.N. Coker, R. O'Hayre, W.C. Chueh and J. Tong, Energy Environ. Sci., 2013,6, 2424-2428

CR5 : First-of-a-kind approach and our attempt to apply the lessons.

Sandia National Laboratories

Counter-Rotating-Ring Receiver/Reactor/Recuperator (CR5)

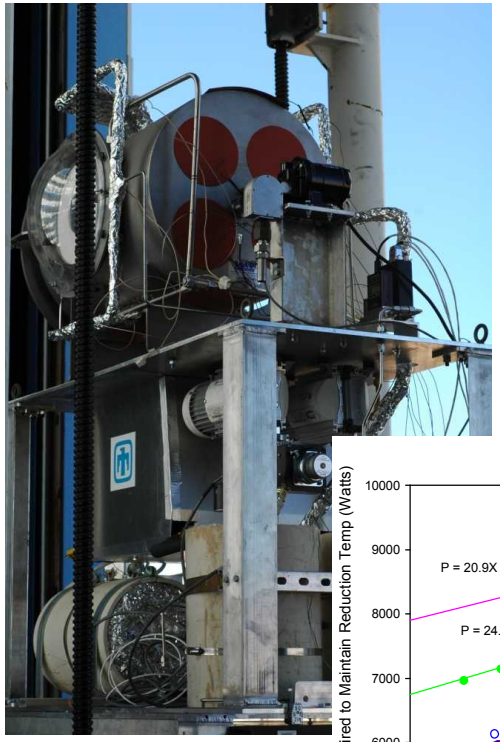


"Reactorizing a Countercurrent Recuperator"

Continuous flow, Spatial separation of products, Thermal recuperation

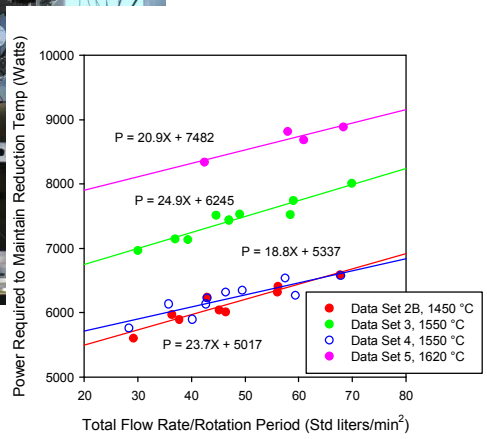
Performance Map of Gen-1 Prototype

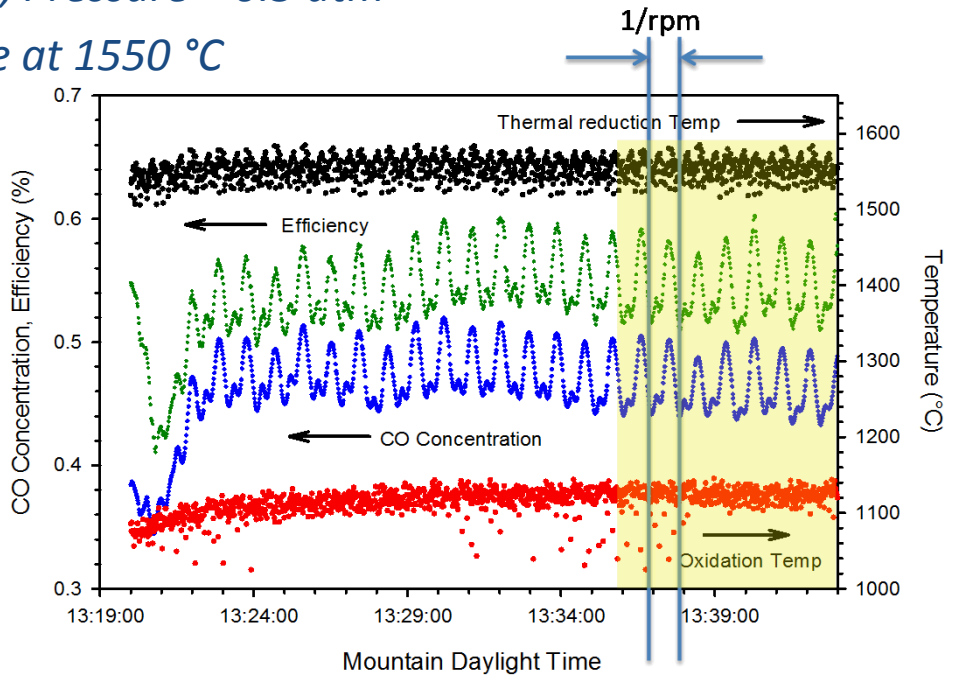
Sandia National Laboratories



Collect data to validate models, guide improvements

- *Ceria-based fins on rings*
- *6 Data Sets: Cold, 2@ 1450 °C, 2@ 1550 °C, 1620 °C*
- *3 ring rotation speeds, 3 CO_2 flow rates for each*
- *Constant Ar flow, Pressure = 0.5 atm*
- *Floating Pressure at 1550 °C*





J.E. Miller, M.A. Allendorf, A. Ambrosini, E.N. Coker, R.B. Diver, I. Ermanoski, L.R. Evans, R.E. Hogan, and A.H. McDaniel "Development and Assessment of Solar-Thermal-Activated Fuel Production: Phase 1 Summary" SAND2012-5658, July 2012

For Your Viewing Pleasure …

Sandia National Laboratories

Operating with 22 Rings

S2P SUNSHINE PETROL

Take-home points

- Thermochemical approaches have potential for large impact, high efficiency
- For TCES energy density and cost are paramount
- For any approach to Solar Fuels- Efficiency is key for cost and scalability – 10% solar to fuel minimum
- Materials, Reactors, and Systems are all areas of opportunity and need.
  - All impact efficiency, all relatively immature for this technology.
  - Small global community has made significant advances in recent years
- Materials are challenging, but we have barely begin to explore the possibilities

Producing solar fuels and storing heat via thermochemical processes has the potential for transitional impact in our future energy mix.

Cast Of Characters (a snapshot)

S2P: Principal Investigator – James E. Miller
Project Managers - Ellen B. Stechel and Tony Martino

Systems

- Terry Johnson, Chad Staiger, Christos Maravelias (U-WI), Carlos Henao (student,) Jiyong Kim (PD), Daniel Dedrick

Reactor

- Solar Reactor - Rich Diver, Tim Moss, Scott Korey, Nathan Siegel
- Reactive Structures - Nathan Siegel, Terry Garino, Nelson Bell, Rich Diver, Brian Ehrhart
- Detailed Reactor Models - Roy Hogan, Ken Chen, Spencer Grange, Siri Khalsa, Darryl James (TTU), Luke Mayer (student)

Materials

- Reactive Materials Characterization & Development - Andrea Ambrosini, Eric Coker, Mark Rodriguez, Lindsey Evans, Stephanie Carroll, Tony Ohlhausen, William Chueh
- Bulk Transport & Surface Reactions - Gary Kellogg, Ivan Ermanoski, Taisuke Ohta, Randy Creighton
- Thermodynamics & Reaction Kinetics - Mark Allendorf, Tony McDaniel, Chris Wolverton (Northwestern University), Bryce Meredig (student), Heine Hansen (PD), Asegun Henry, Al Weimer (CU), Jonathan Scheffe (student)

PROMOTES: Andrea Ambrosini, Sean Babiniec, Eric Coker, Cliff Ho (SNL); Peter Loutzenhiser, Sheldon Jeter (GIT); Hany Al Ansari (KSU), Ellen Stechel, Nathan Johnson (ASU), Many Students. This work is supported by the U.S. Department of Energy SunShot Initiative under Award Number DE-FOA-0000805.


Thank You.