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Materials and Systems for Thermochemical Carbon Dioxide Splitting as a Route to Solar Fuels

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Solar Fuels Impact:

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 (embedded energy))
- *Water, CO_2 are not limiting –*
  - Water consumption/cost relatively low (water rights?)
  - High impact opportunity for CO_2 utilization – long term requires air capture.
- *Consistent with other human activities occurring over multiple decades.*

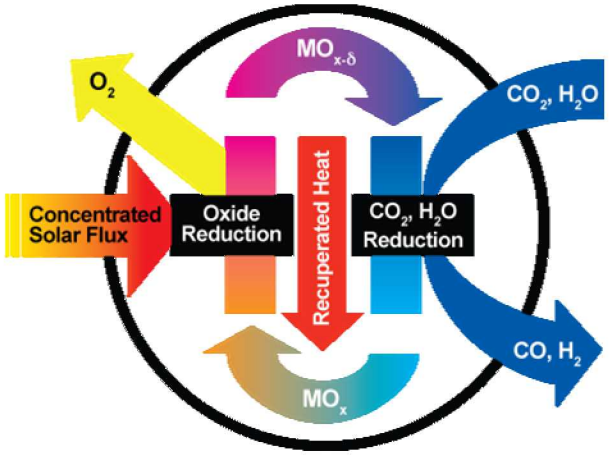
E.B. Stechel and J.E. Miller "Re-energizing CO_2 to fuels with the sun: Issues of efficiency, scale, and economics" Journal of CO_2 Utilization, 1 (2013) 28–36.

Thermochemical Cycles: A Simple Concept …

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

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

2) $1/\delta\ MO_{(x-\delta)} + CO_2 \rightarrow 1/\delta\ MO_x + CO$



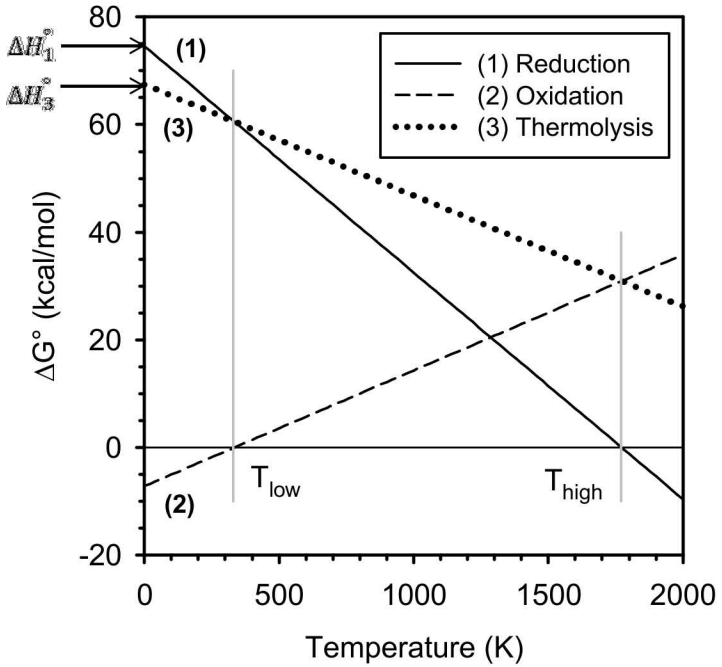
$Fe_3O_4 \rightarrow 3\ FeO + ½\ O_2$

$3FeO + H_2O \rightarrow Fe_3O_4 + H_2$

$H_2O \rightarrow H_2 + ½\ O_2$

Ferrite metal oxide cycle (Nakamura 1977)

3) $CO_2 \rightarrow CO + ½\ O_2$

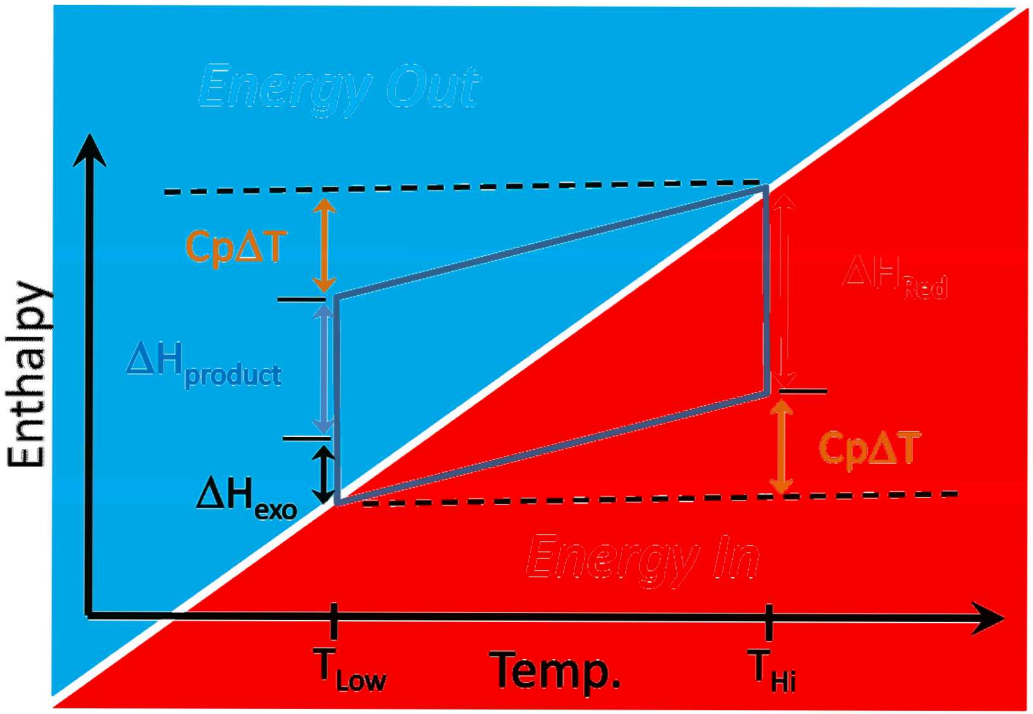


For liquid fuels, capitalize on decades of Synfuel technology, e.g.

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

… Heat In, Fuel out …

$$\Delta H_{red\ endotherm} - \Delta H_{oxid\ exotherm} = \Delta H_{fuel}$$



A thermochemical cycle is essentially an engine that converts heat into work in the form of stored chemical energy. ***Efficiency gains are possible as initial conversion to mechanical work and electricity are avoided.***

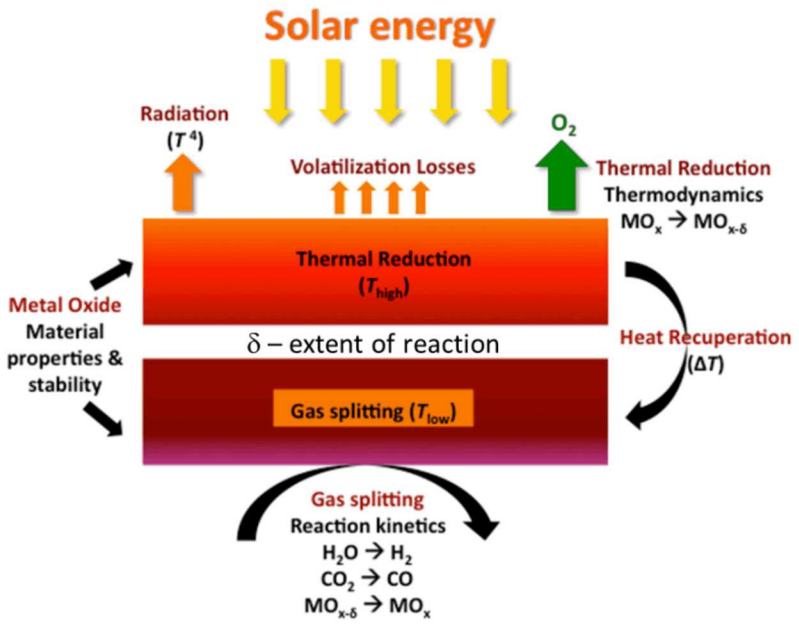
$$\frac{\Delta H_{fuel}}{\Delta H_{red}} = \text{Max. thermal eff.}$$

Recuperation of CpΔT a consideration for high efficiency!

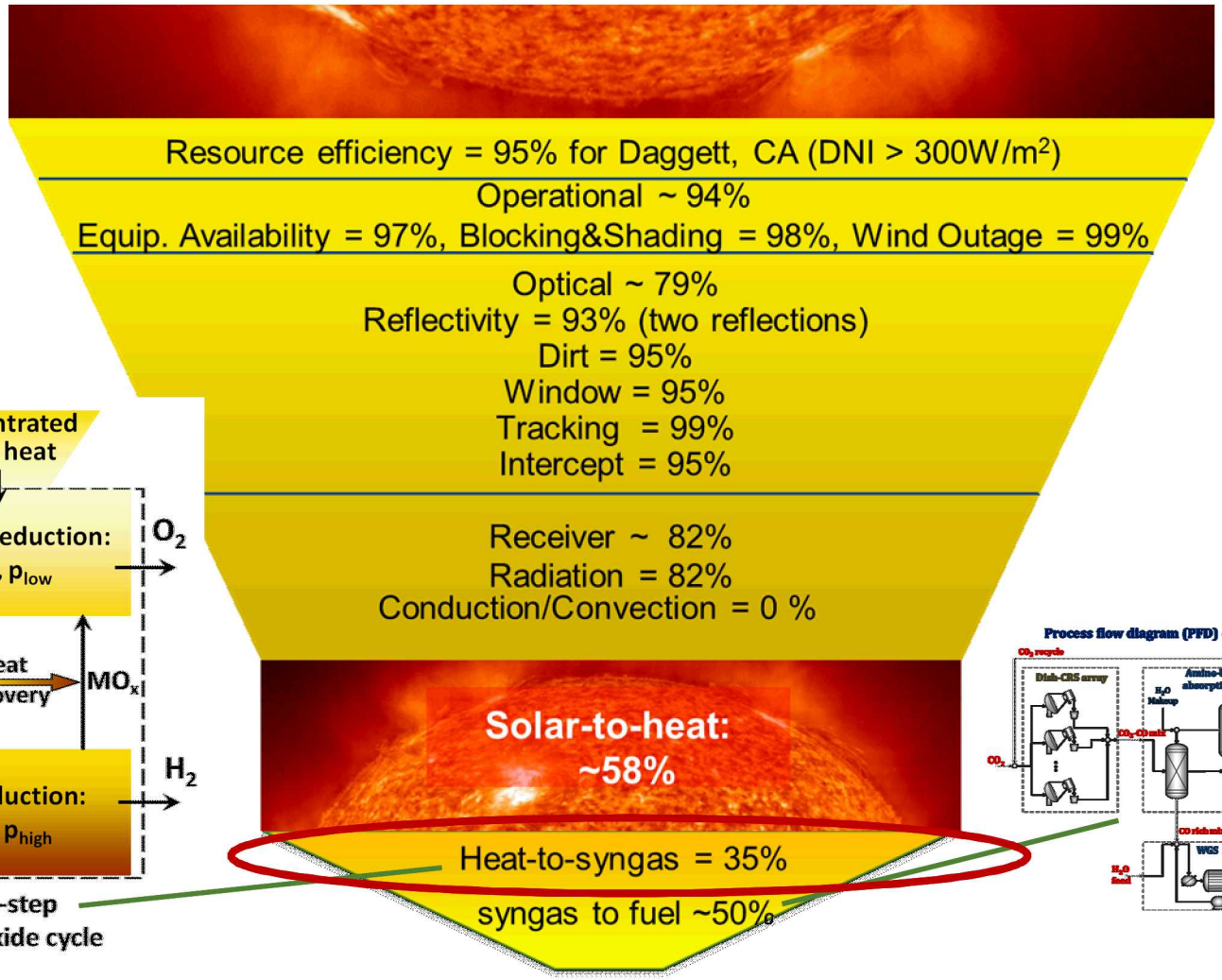
Multiple Technical Challenges

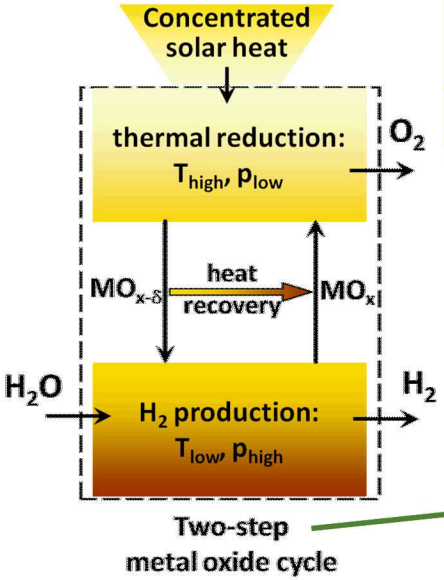
Exploiting complex materials and systems to carry out highly coupled, multi-scale (time, dimensions) dynamic processes under extreme conditions.

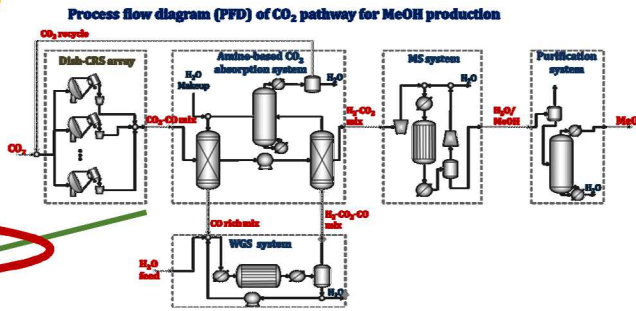
- **Reactors**
  - Maximizing energy usage, Minimizing parasitic work input
  - Interfacing solar with chemistry
  - Decoupling steps
- **Materials**
  - Simple repeatable chemistry
  - Efficient mass and volumetric usage
    - Favorable thermodynamics
    - Rapid kinetics
  - Chemical and Physical Durability
    - 1000s if not 10^6 cycles
    - High melting, Low volatility, Sinter resistant
- **Systems**
  - Setting targets, process optimization , economics, life cycle impacts etc.



Target: Heat to Syngas – 35% actual, ≥ 60 % theoretical

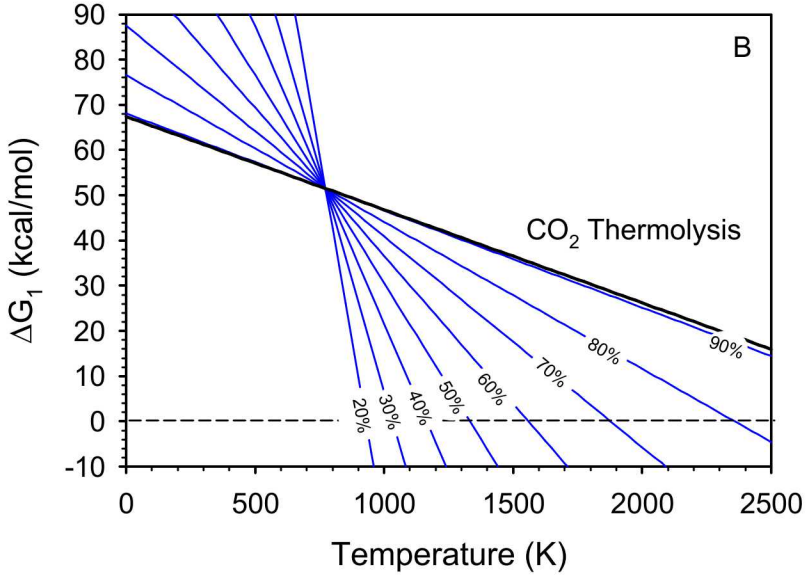






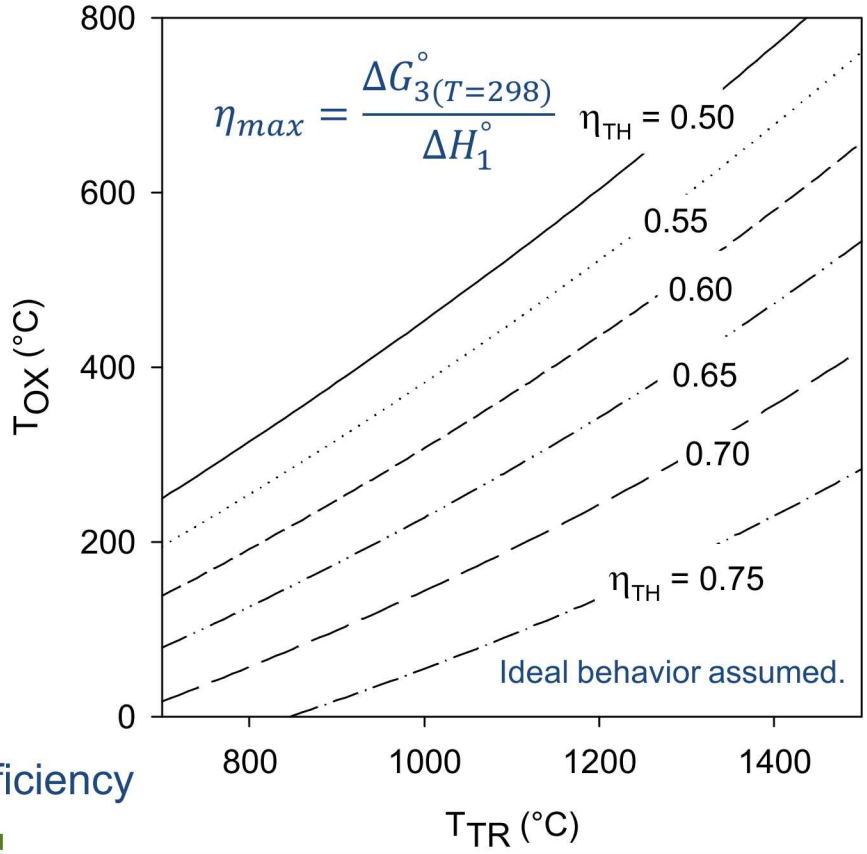
Solar to Fuel = 10%

"Thermodynamic Temp" and Efficiency



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

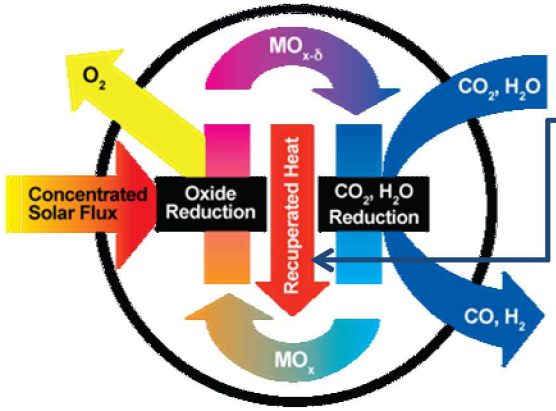
Thermodynamic T_{TR} and T_{OX} imply ΔH and ΔS and vice versa. Not all combinations are realistic.



Note: these use a slightly lower "fuel cell-like" efficiency

Efficiency: Chemical and Thermal Utilization

$MO_x \rightarrow MO_{x-\delta} + \delta/2\ O_2$ (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

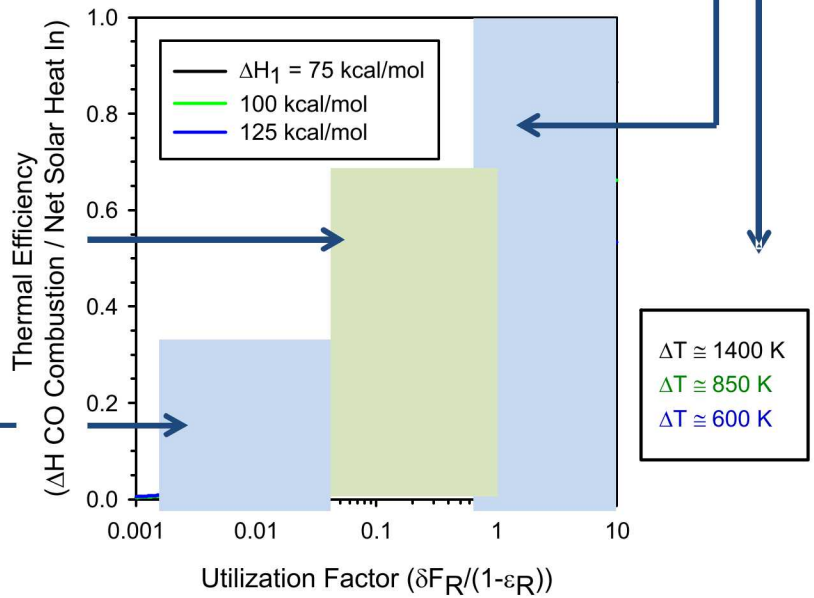
Kinetics: δ

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}.

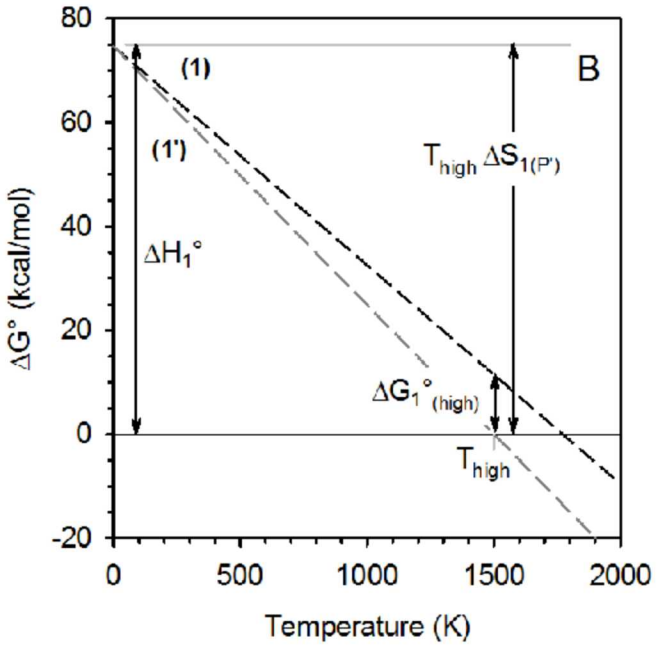


The possible efficiency increases with degree of reaction (δ) and/or effectiveness of recuperation.

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

"Non-thermodynamic "Temperatures?

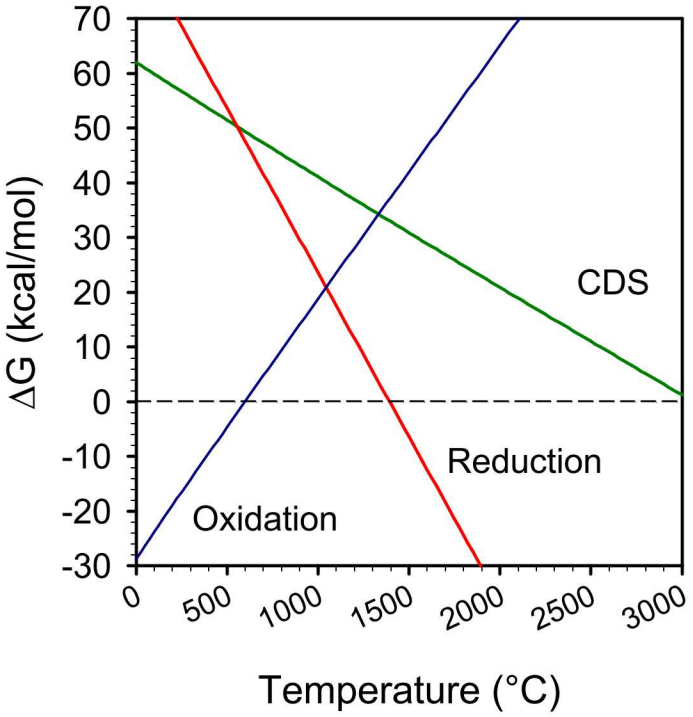
Reduction: Work in the form of Pumping or sweep gas shifts reduction temperature.



Heat to Work Conversion Penalty

Oxidation:

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

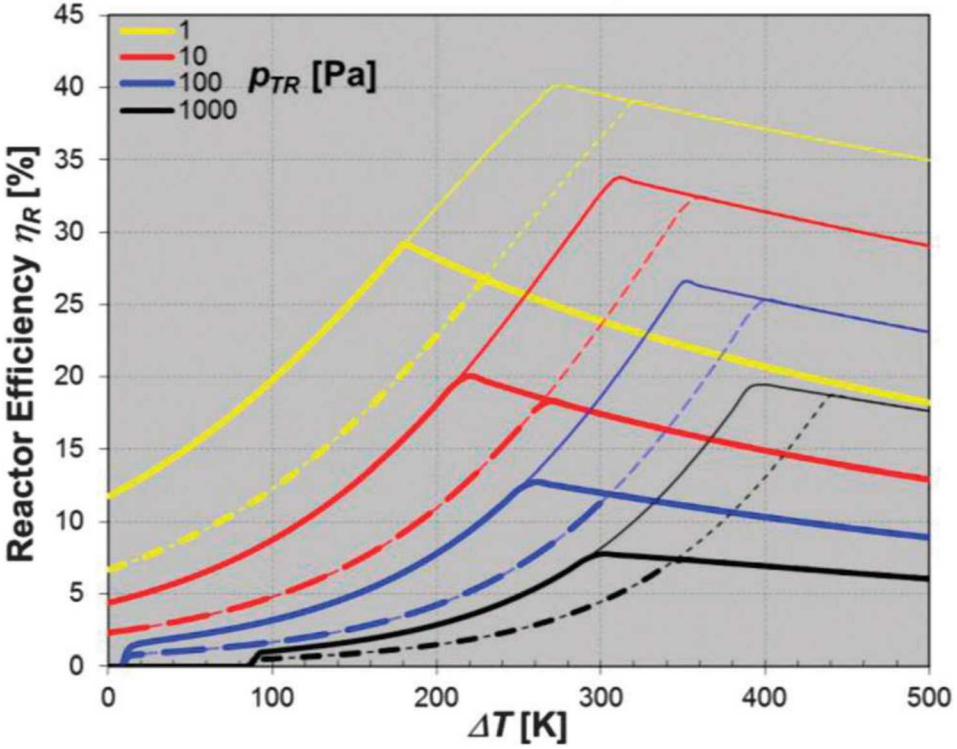


Separation Work Requirement

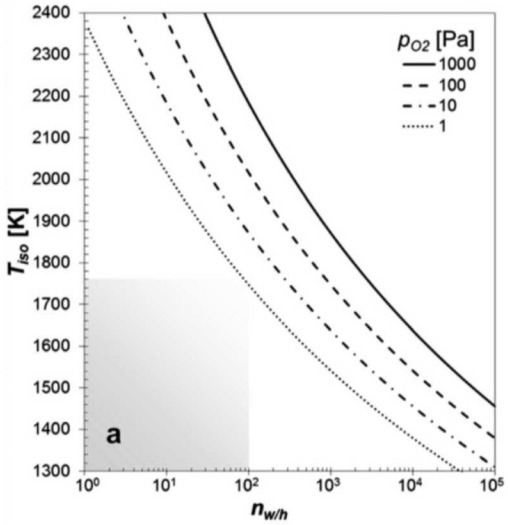
Yes, but at a price!

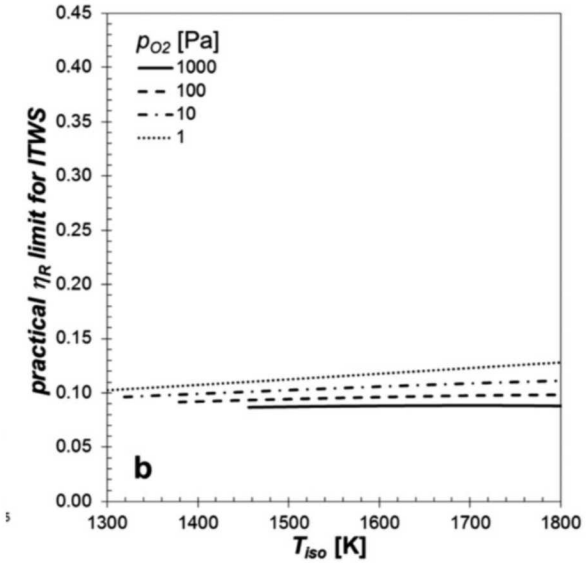
Optimum Temperature Swing

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?

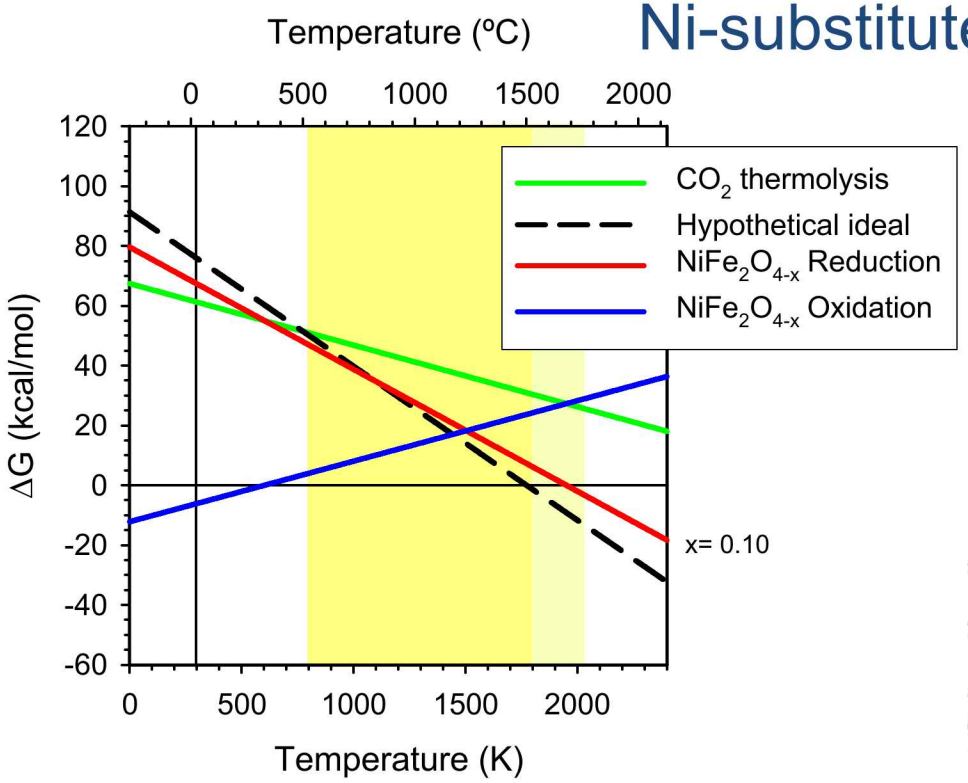




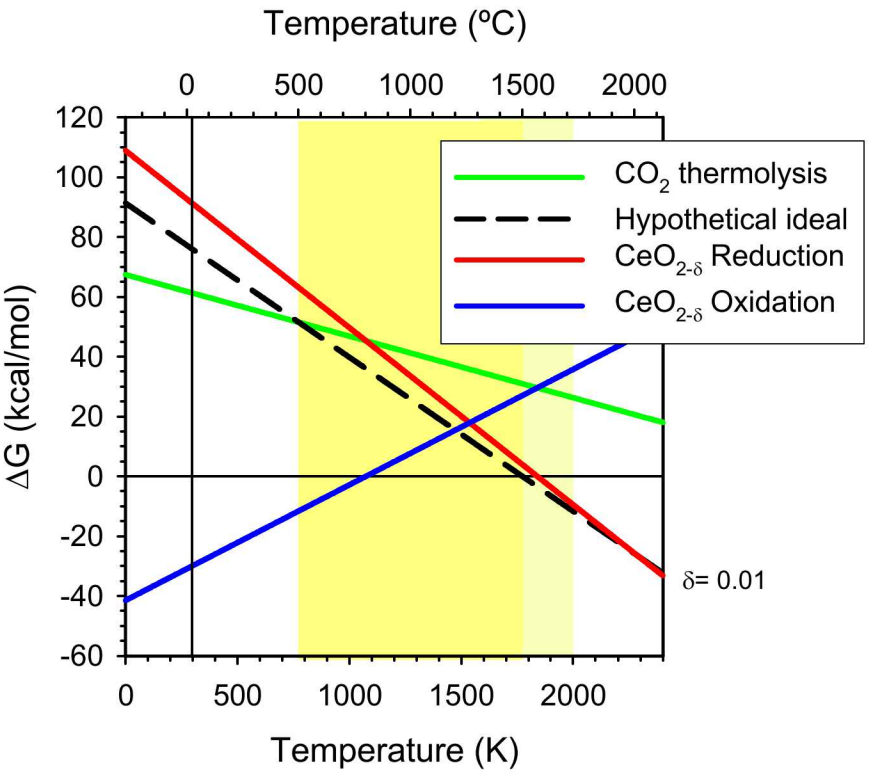
Ermanoski, Miller, Allendorf, Phys. Chem. Chem. Phys., 2014, 16, 8418-8427.

Further Complexities of Real Materials

Ni-substituted Ferrite



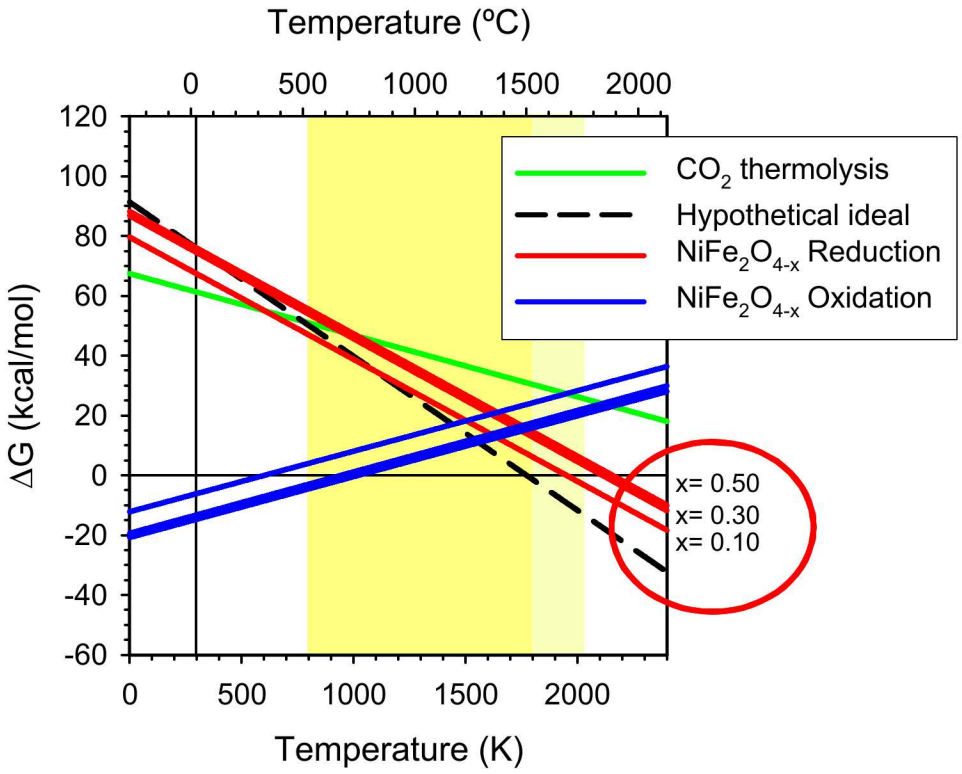
Ceria



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

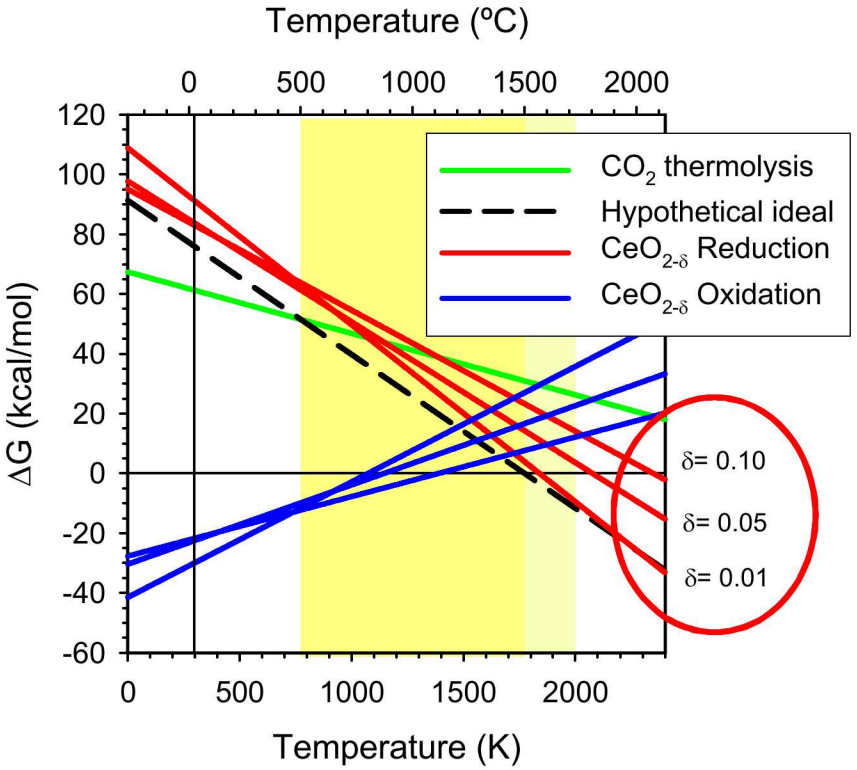
Miller, McDaniel, Allendorf *Adv. Energy Mater 2013.*

Further Complexities of Real Materials



From a thermodynamic viewpoint, ferrites appear superior to ceria (larger δ in target temperature range)

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

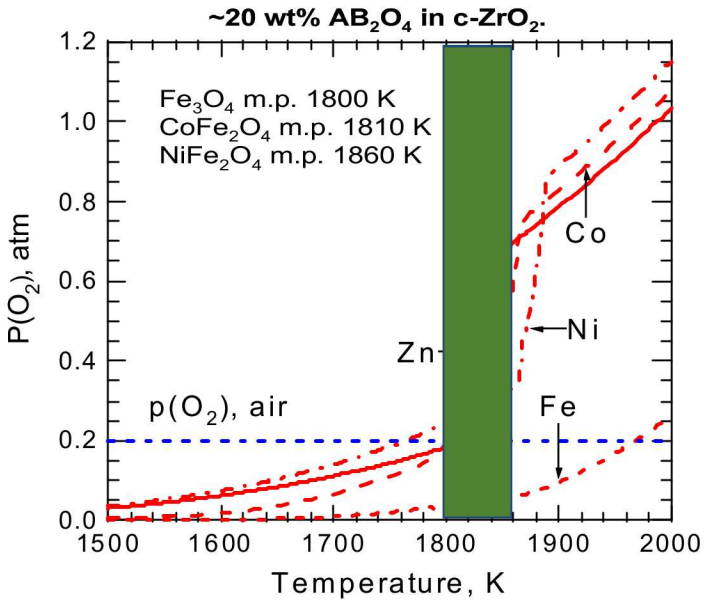


What's the matter with Ferrites?

Idealized Chemistry

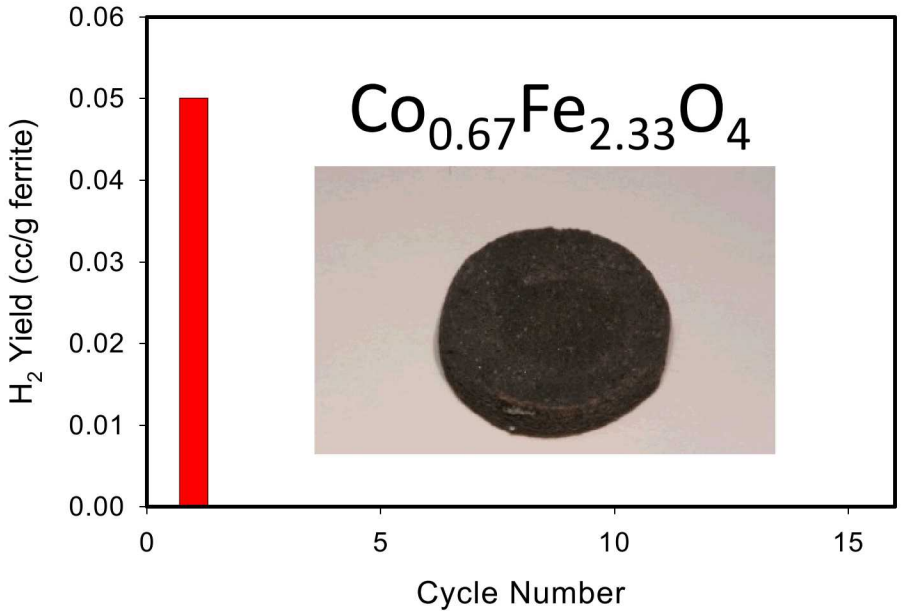
$Fe_3O_4 \rightarrow 3FeO + ½\ O_2$

$3FeO + H_2O \rightarrow Fe_3O_4 + H_2$



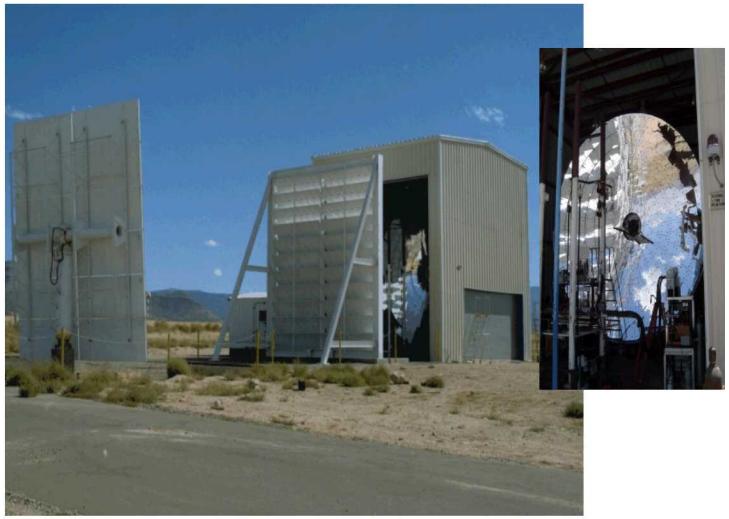
Favorable temperature range (thermodynamics) can be manipulated via metal substitutions in Fe_3O_4.

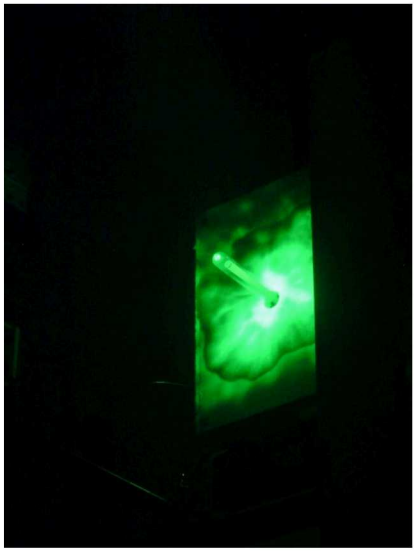
Alter them to keep them from melting.



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

What's the matter with Ferrites?

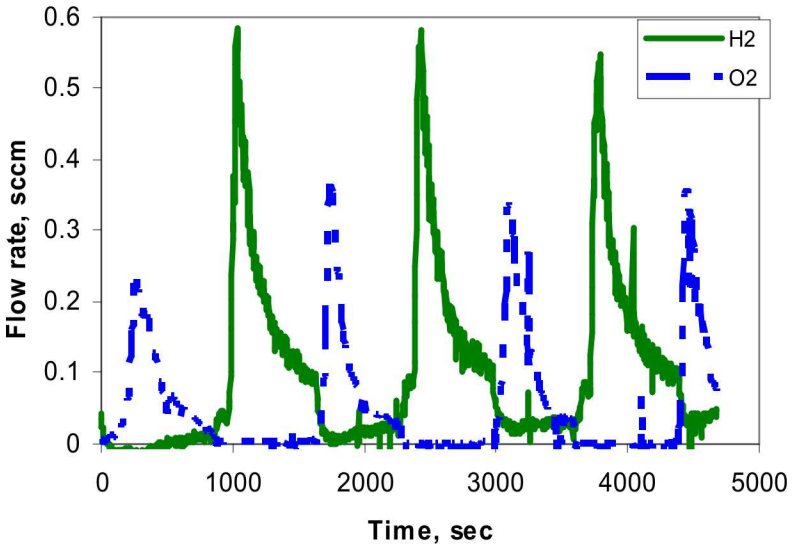




Unless you add zirconia!

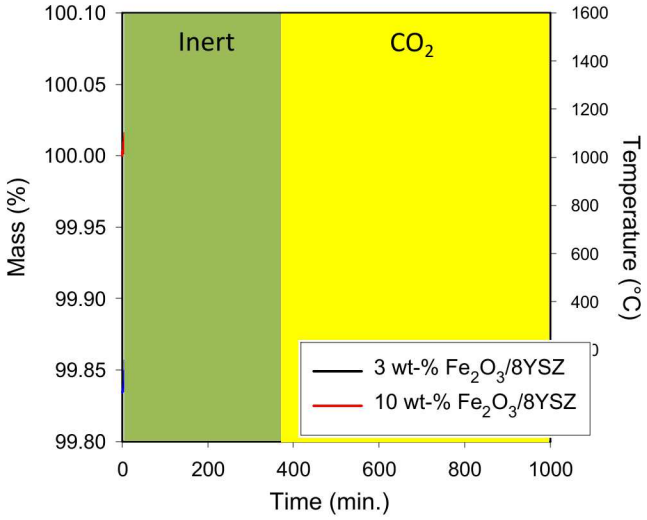
On-Sun Test:
$Co_{0.67}Fe_{2.33}O_4$/YSZ (1:4)

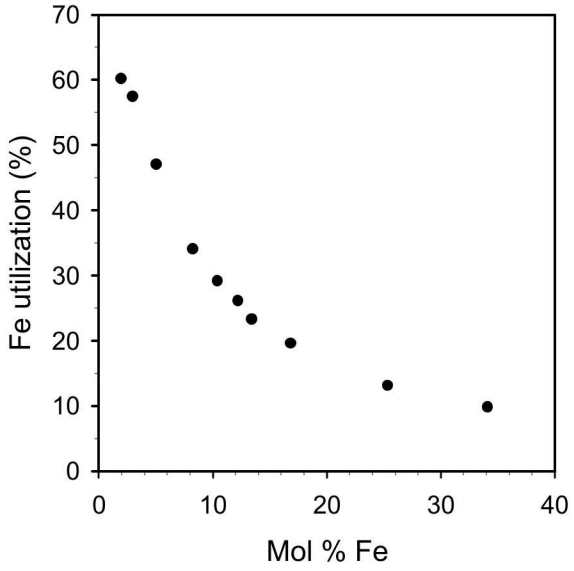
T_{TR} 1580 °C, T_{OX} 1050 °C
H_2 = 3.5-4 scc/g ferrite each cycle



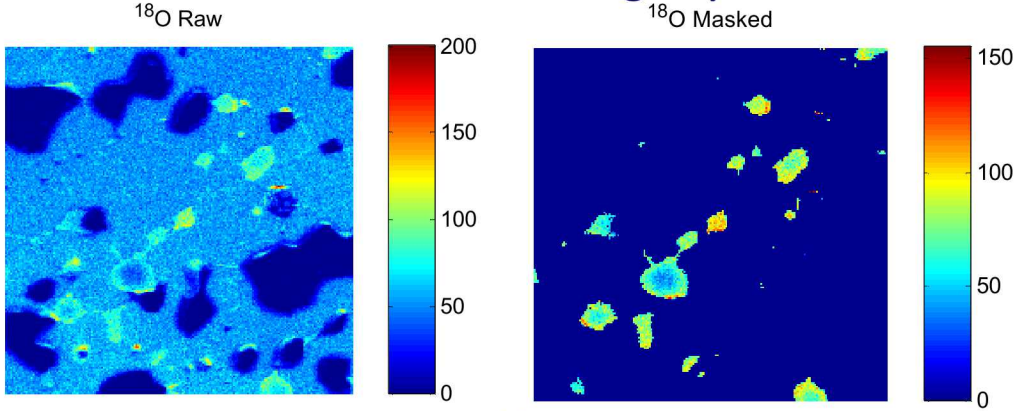
Pioneered by Kodama et. al. (ISEC) 2004, ISEC2004-65063, Portland, OR.

Fe dissolution and oxygen transport are the keys

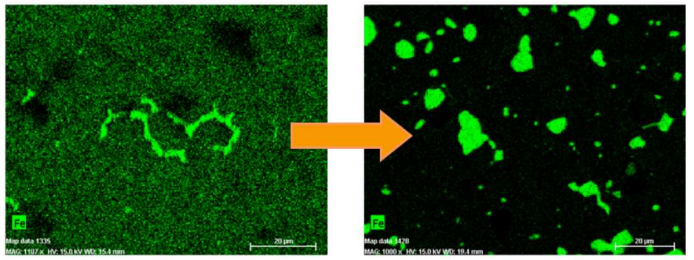




Beyond the solubility limit additional Fe contributes little to the overall gas yield.



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

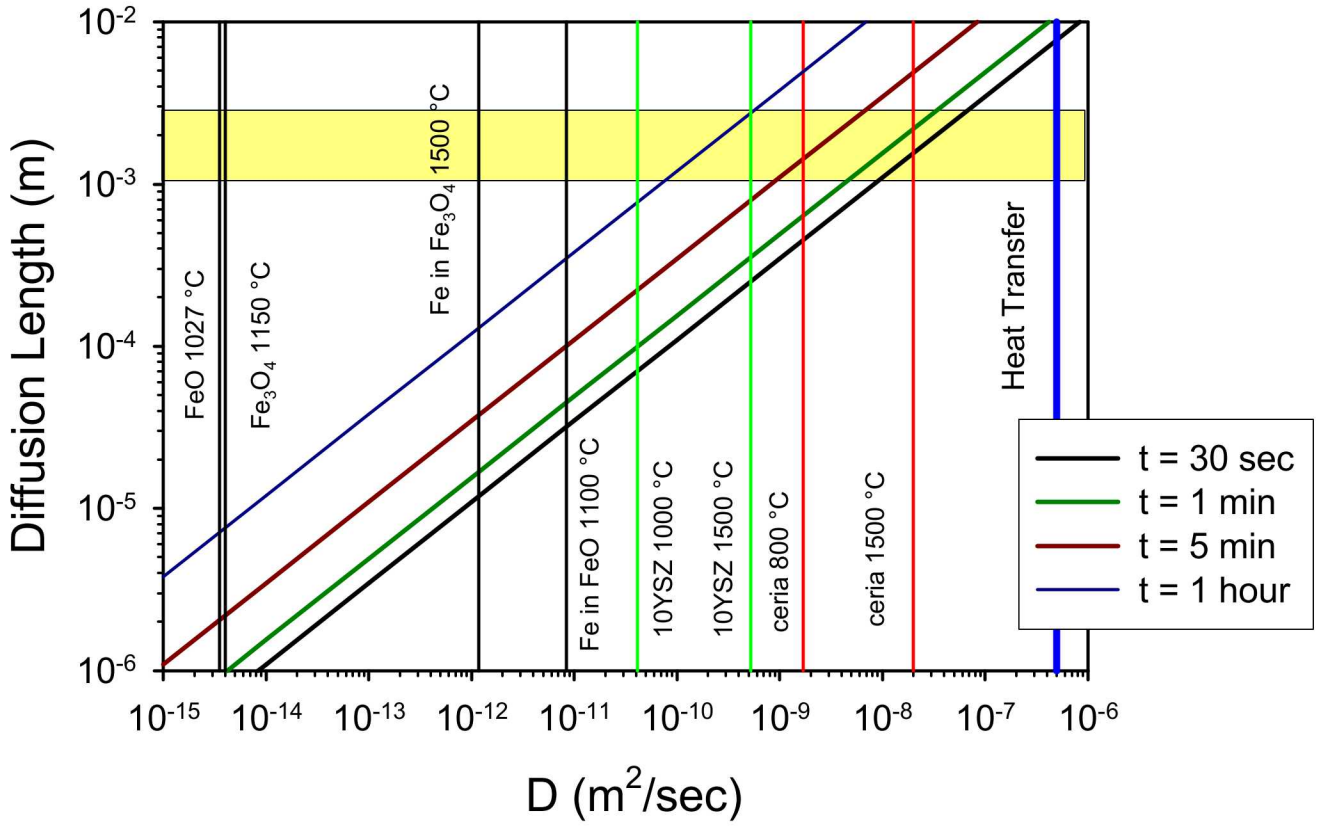


Fe EDS

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

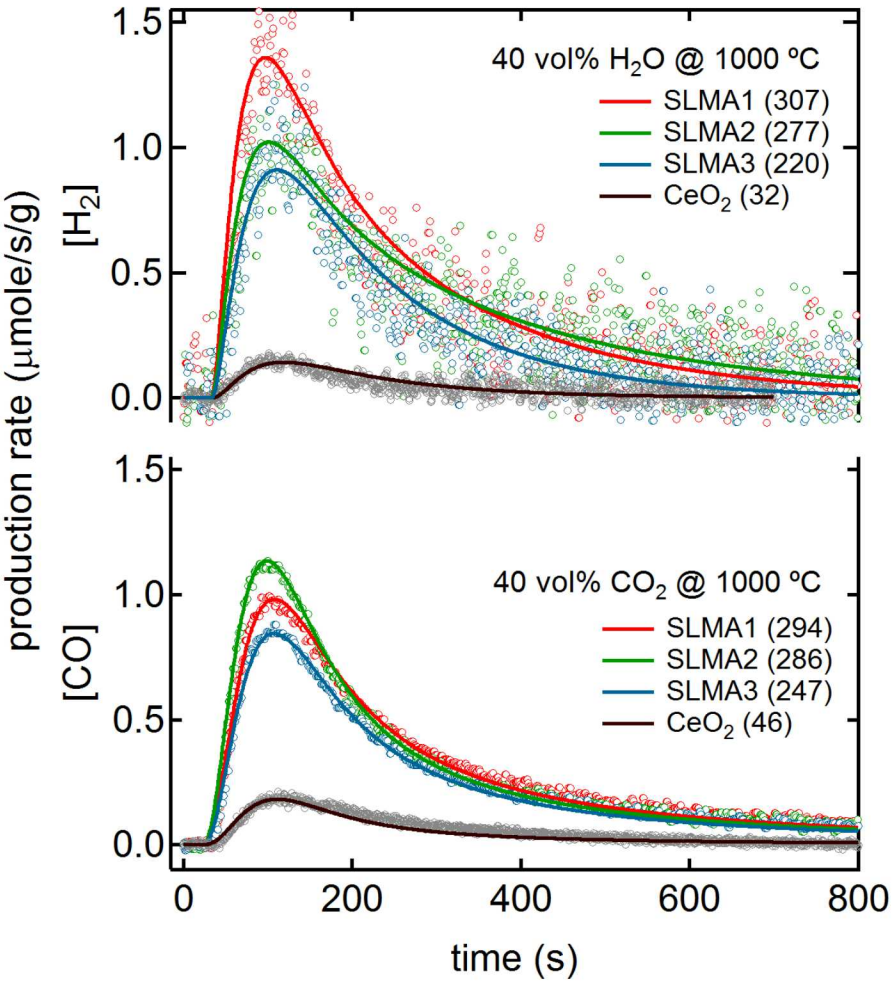
Ion (oxide) diffusion lengths are materials- and temperature-dependent.

One Path Forward: Tailored MIECs for Thermo and Transport

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

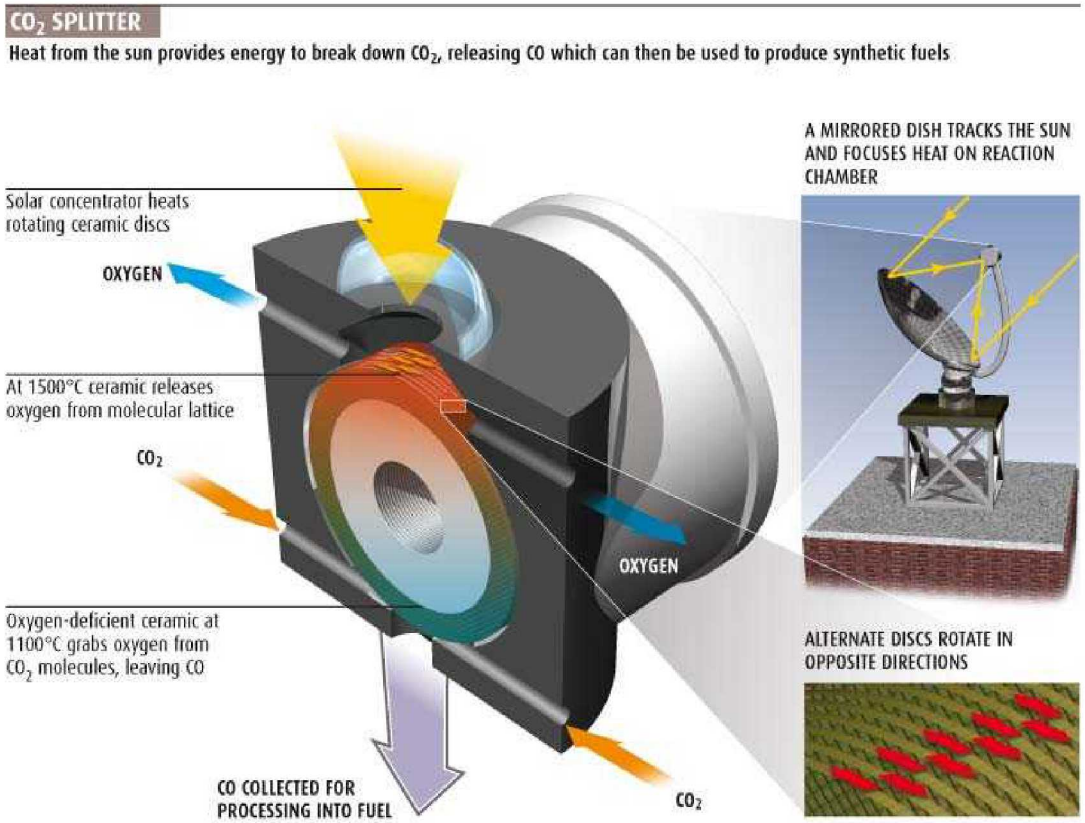


80 cycle durability demonstrated

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.

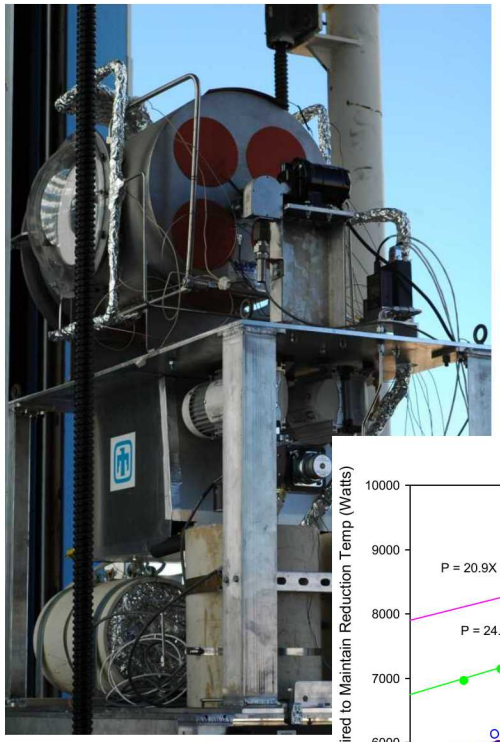
Counter-Rotating-Ring Receiver/Reactor/Recuperator (CR5)



"Reactorizing a Countercurrent Recuperator"

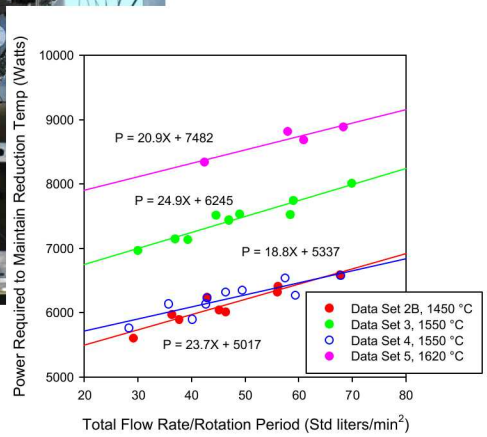
Continuous flow, Spatial separation of products, Thermal recuperation

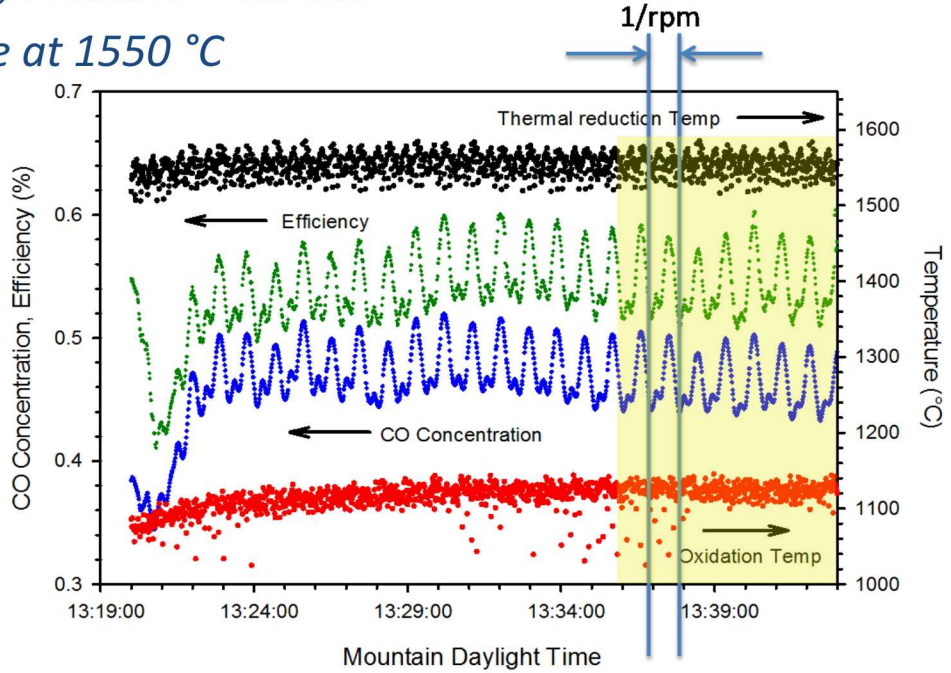
Performance Map of Gen-1 Prototype



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*



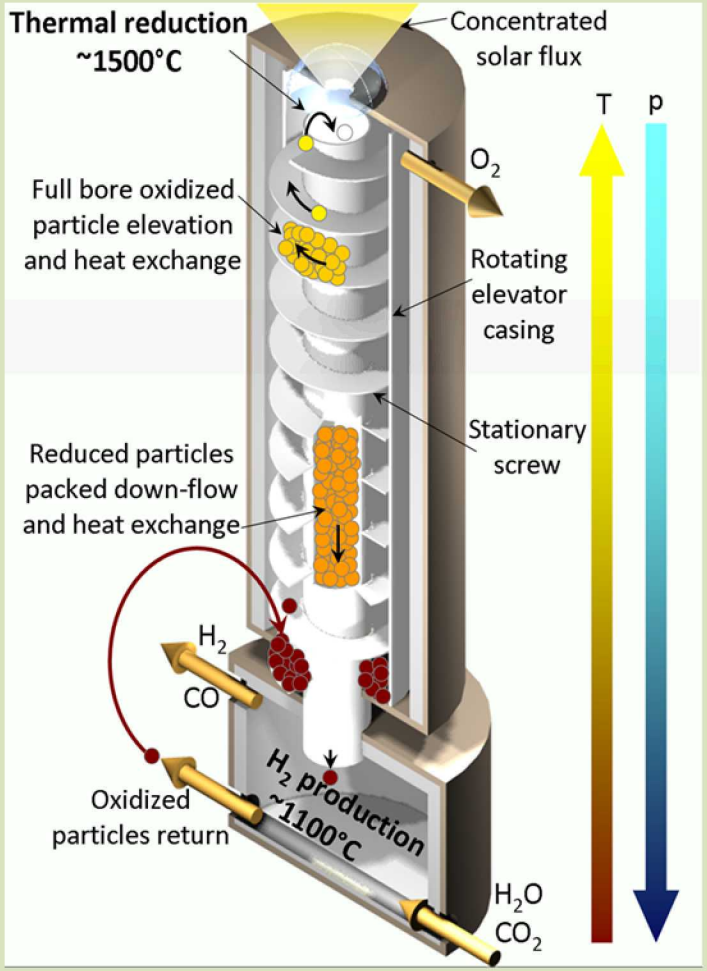


J.E. Miller, M.A. Allendorf, A. Ambrosini, E.N. Coker, R.B. Diver, I. Ermanoski, L.R. Evans, R.E. Hogan, and A.H. McDaniel "Development and Assessment of Solar-Thermal-Activated Fuel Production: Phase 1 Summary" SAND2012-5658, July 2012

For Your Viewing Pleasure …

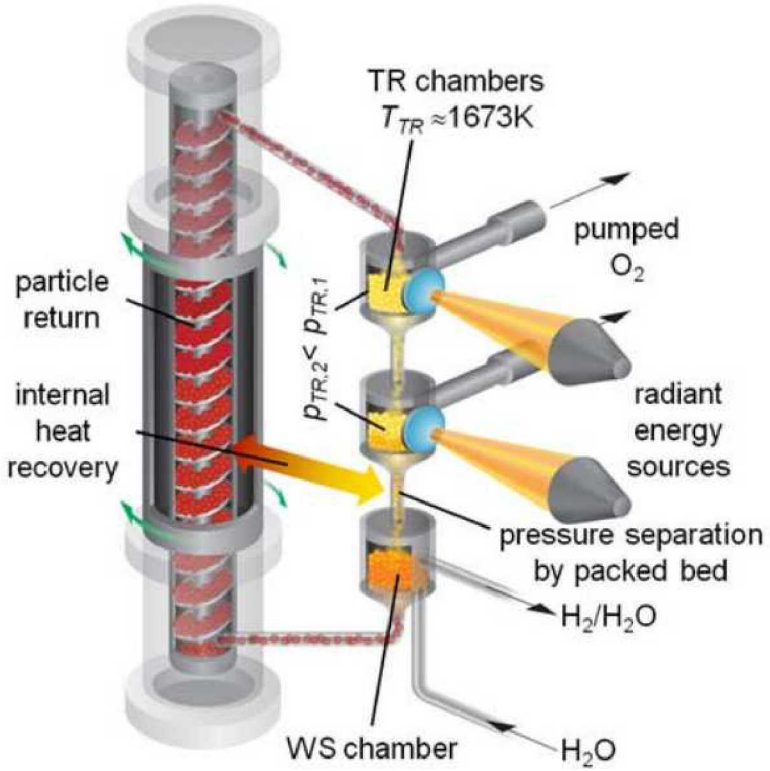
Operating with 22 Rings

Gen 2: Packed Bed Particle Reactor



- **Counter-current heat exchange incorporated into particle lift apparatus**
- **Particle bed provides gas and pressure separation (redox pressures decoupled)**
- **Independent optimization of unit ops**

Gen 2.1: Cascading Pressure PBR



- **Similar features and heat exchange concepts to PBR**
- **Pressure-Staged thermal reduction to facilitate high conversion , maximize efficiency**

I. Ivan Ermanoski, Nathan P. Siegel and Ellen B. Stechel "A New Reactor Concept for Efficient Solar-Thermochemical Fuel Production" J. *Sol. Energy Eng.* 135(3), 2013.
Ermanoski, International Journal of Hydrogen Energy, in press
DOI: 10.1016/j.ijhydene.2014.06.143

Take-home points

- For any approach to Solar Fuels- Efficiency is key for cost and scalability – 10% solar to fuel minimum (lifecycle)
  - Often it is unappreciated that sunlight is a "high cost" feedstock (capital cost)
  - Low efficiencies increase scale, further challenge efficiency and stretch resources.
  - CO_2 and water (and associated energy costs) are not limiting
- Thermochemical approaches have potential for high efficiency and thus high impact
  - TE studies support eventual economic viability – difficult, but not implausible
  - Small global community has made significant advances in recent years
- Materials, Reactors, Systems all areas of opportunity and need
  - All impact efficiency, all relatively immature for this technology.
  - Adjacency to other technologies (e.g. solar electric, solar reforming) can help move technology forward, but focused cross-discipline efforts are also needed.

Materials are challenging, but we have barely begin to explore the possibilities.


Thank You.