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Sunshine to petrol: Thermochemistry for solar fuels

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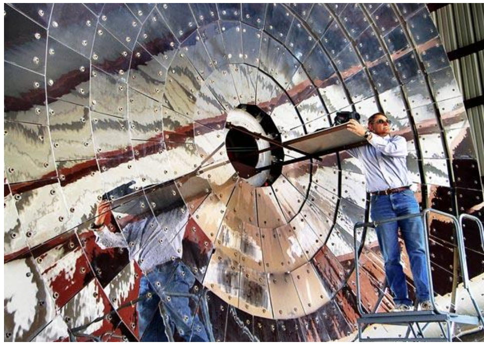

SUNSHINE TO PETROL: THERMOCHEMISTRY FOR SOLAR FUELS

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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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% Annual Average) 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.

Solar Thermal Heat In, Fuel Out

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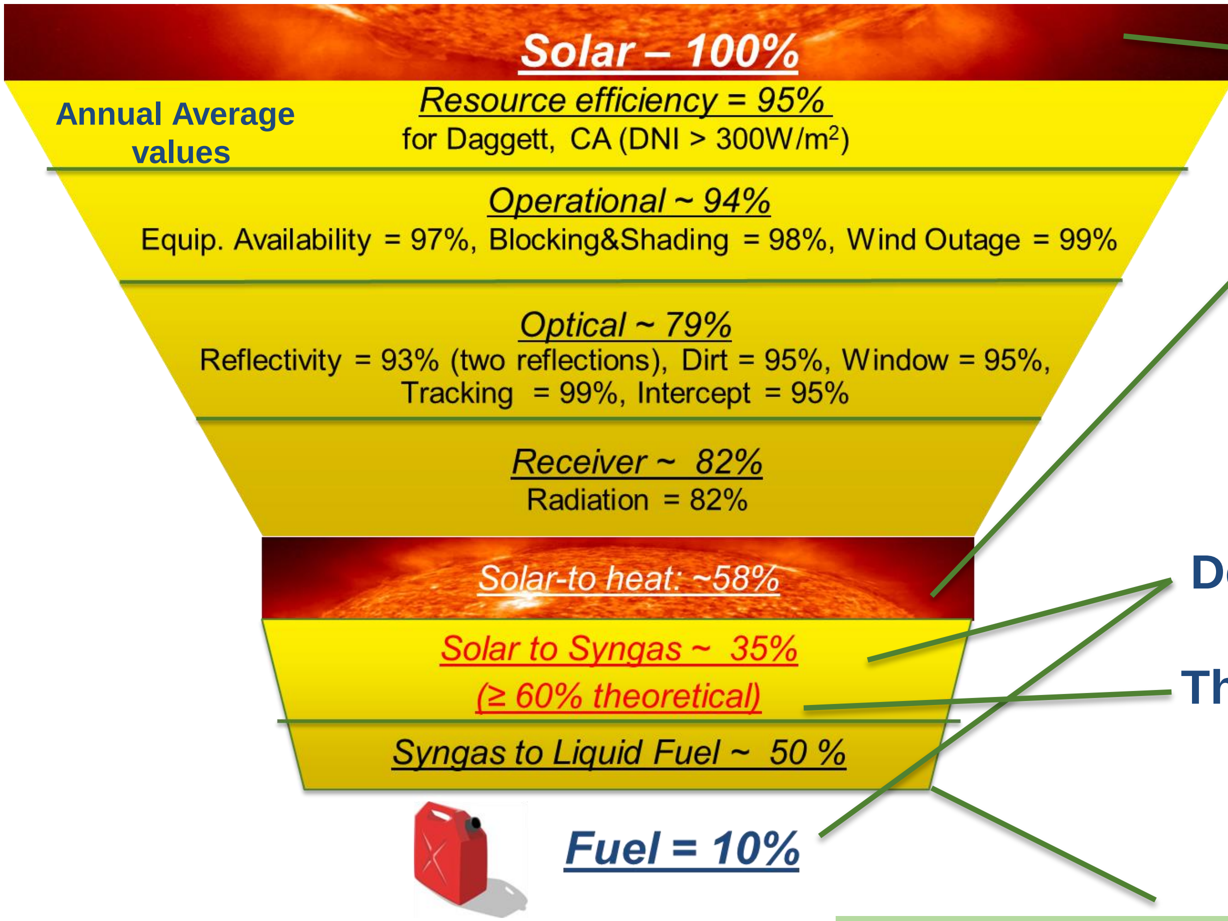


Use entire solar spectrum

Convert heat directly to chemical energy. Avoid conversion to mechanical or electrical work.

Desired outcome defines minimum efficiency. Theoretical value must be higher to account for losses.

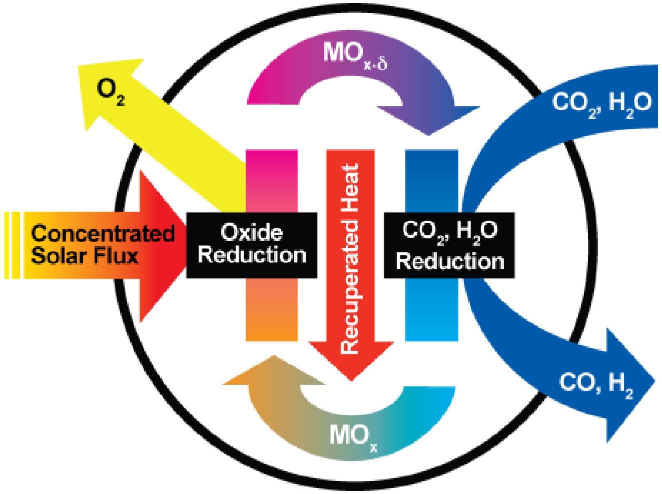
Capitalize on decades of Synfuel technology, e.g.

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

Siegel, Miller, Ermanoski, Diver, Stechel, Ind. Eng. Chem. Res., 2013, 52 , 3276.

A Simple Concept: Heat in, Fuel Out

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



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

3) $CO_2 \rightarrow CO + ½\ O_2$

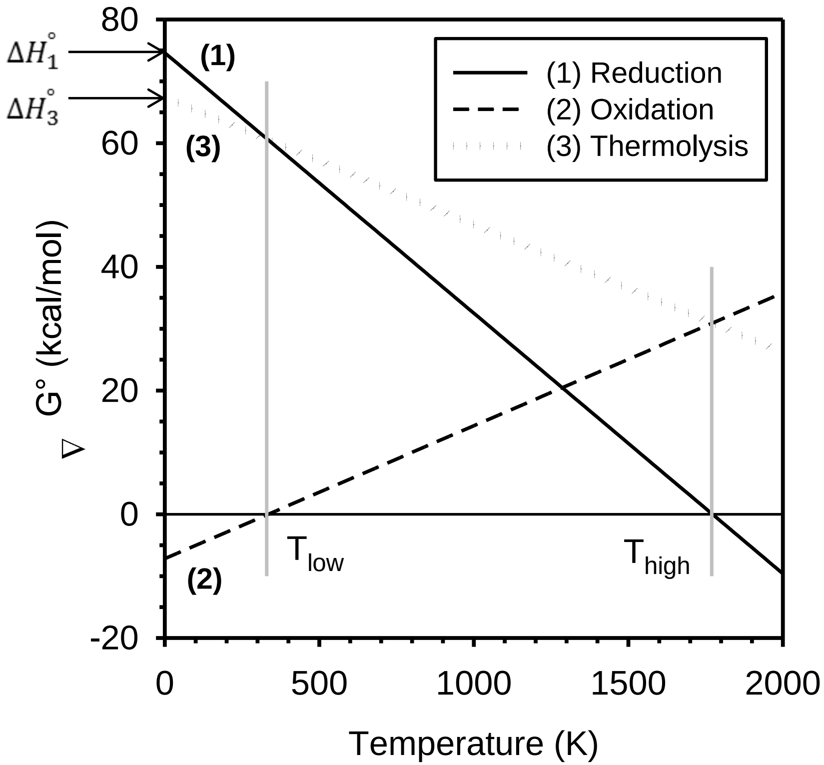
A thermochemical cycle is essentially an engine that converts heat into work in the form of stored chemical energy. ***Efficiency gains are possible as initial conversion to mechanical work and electricity are avoided.***

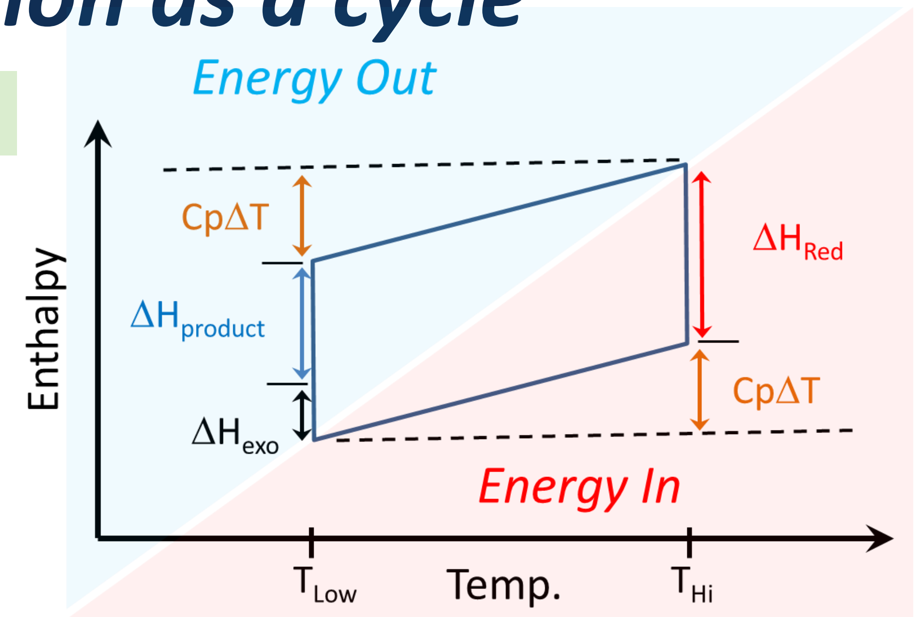
Of interest here are two-step, metal oxide-based processes.

Divide an unfavorable endothermic reaction
($H_2O \rightarrow H_2 + ½\ O_2$, or $CO_2 \rightarrow CO + ½\ O_2$)
into two thermodynamically favorable reactions.

The thermodynamic cost implementing a reaction as a cycle

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



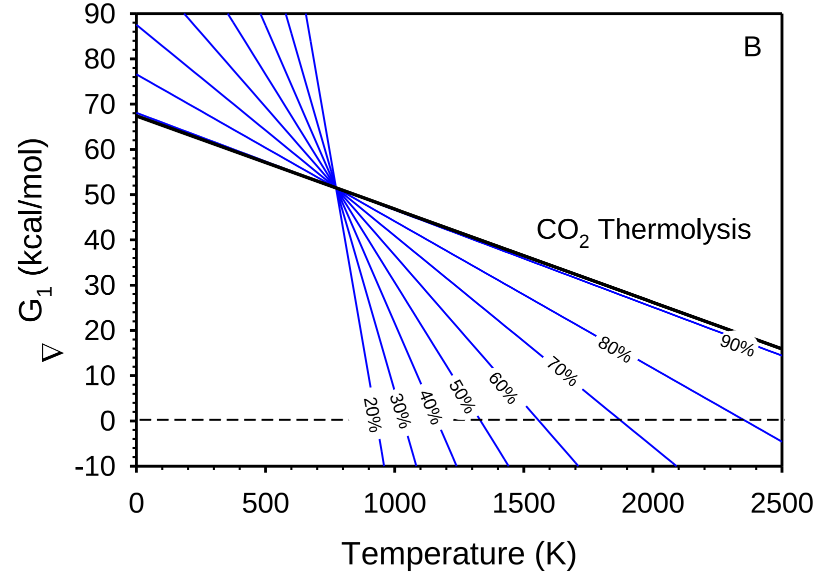


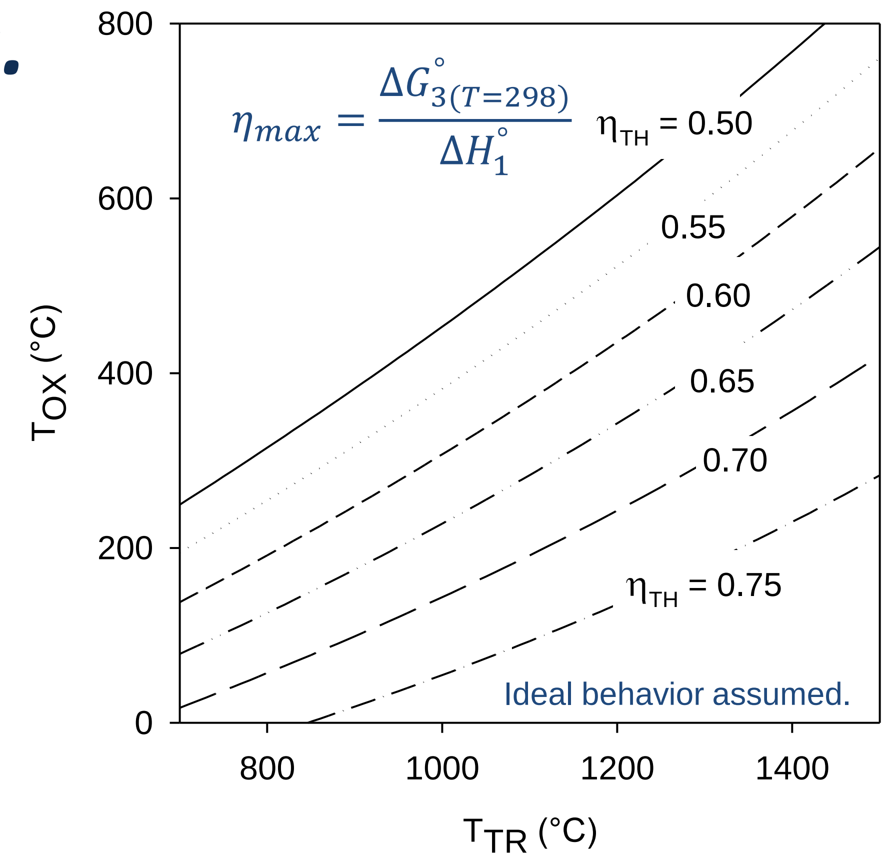
$$\frac{\Delta H_{\text{fuel product}}}{\Delta H_{red} + C_p \Delta T_{net}} = \text{Max. thermal eff.}$$

- *Each reaction favorable at a different temperature*
- *Some heat will be rejected as an exotherm*
- *Temperature gap and exotherm are a function of the active material*

Heat of reaction and thermodynamically defined temperatures.

Materials with high reduction temperature, low oxidation temperature (wide spread) minimize reduction enthalpy. Sensible heat considerations favor a narrow 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

Miller, Ambrosini, Coker, McDaniel, Allendorf, Energy Procedia, 2014, 49, 2019.

Reaction Extent and the Utilization Factor

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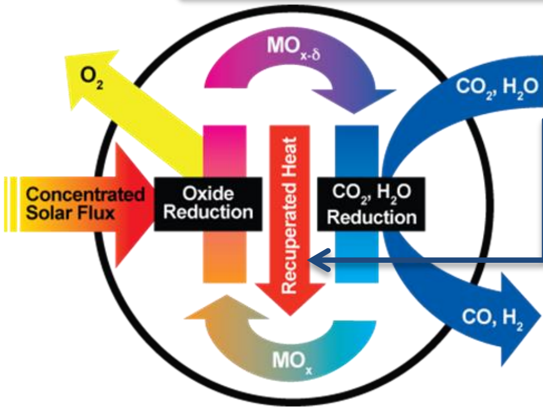
$MO_x \rightarrow MO_{x-\delta} + \delta/2\ O_2$ (ΔH_1, T_{high}, e.g. 1500 °C)



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

T_{low}, e.g. 800 °C

<u>Efficiency is a function of:</u>

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

Kinetics: δ

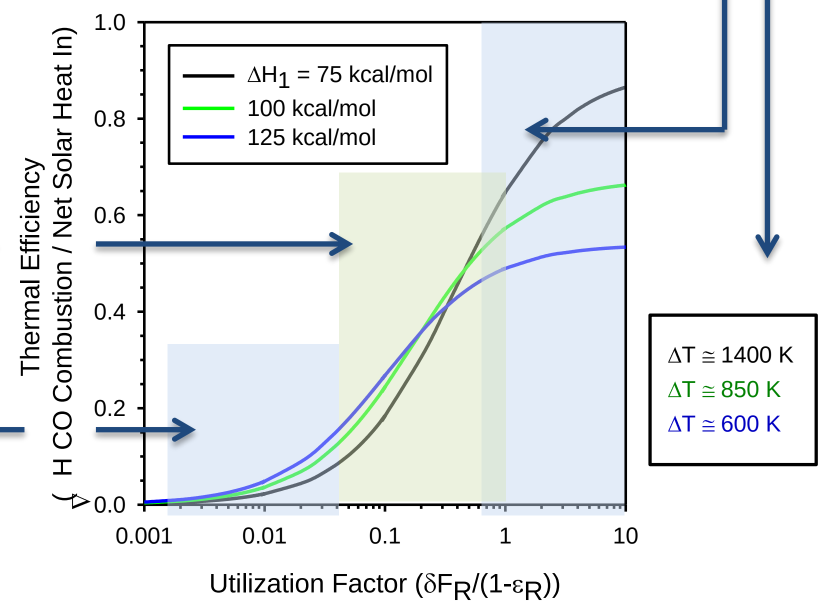
The reactor: recuperation effectiveness & Pressures, sweep etc. (work input

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.



Siegel, Miller, Ermanoski, Diver, Stechel,
Ind. Eng. Chem. Res., 2013, 52 (9), 3276–3286.

"Non-thermodynamic "Temperatures?

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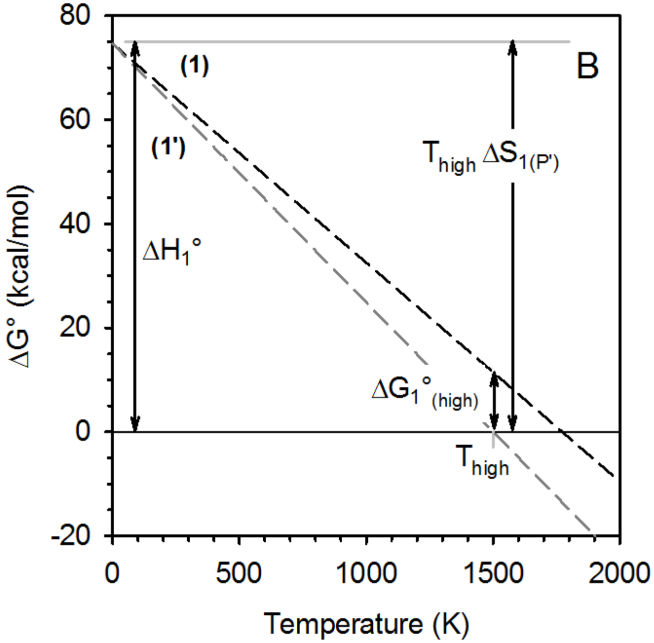
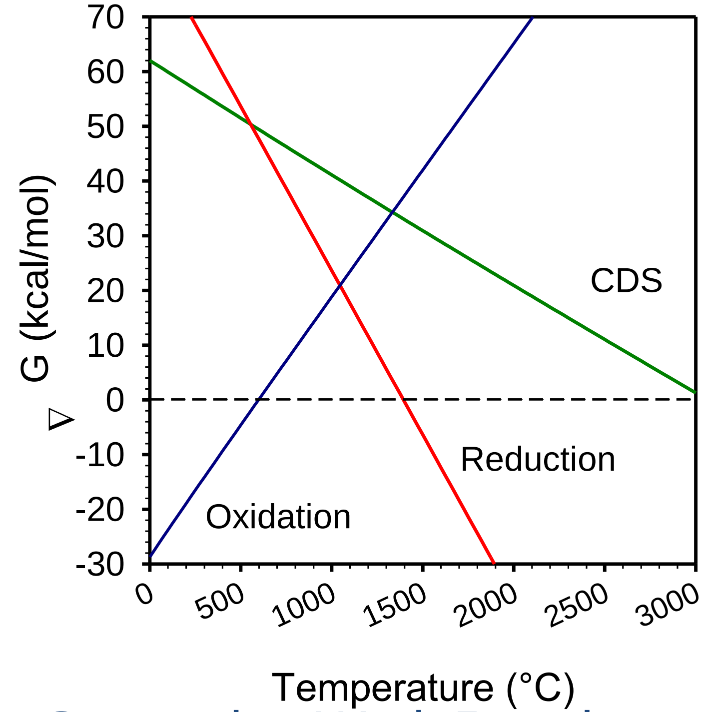
Reduction: Work in the form of Pumping or sweep gas shifts reduction temperature.



Heat to Work Conversion Penalty

Oxidation:

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



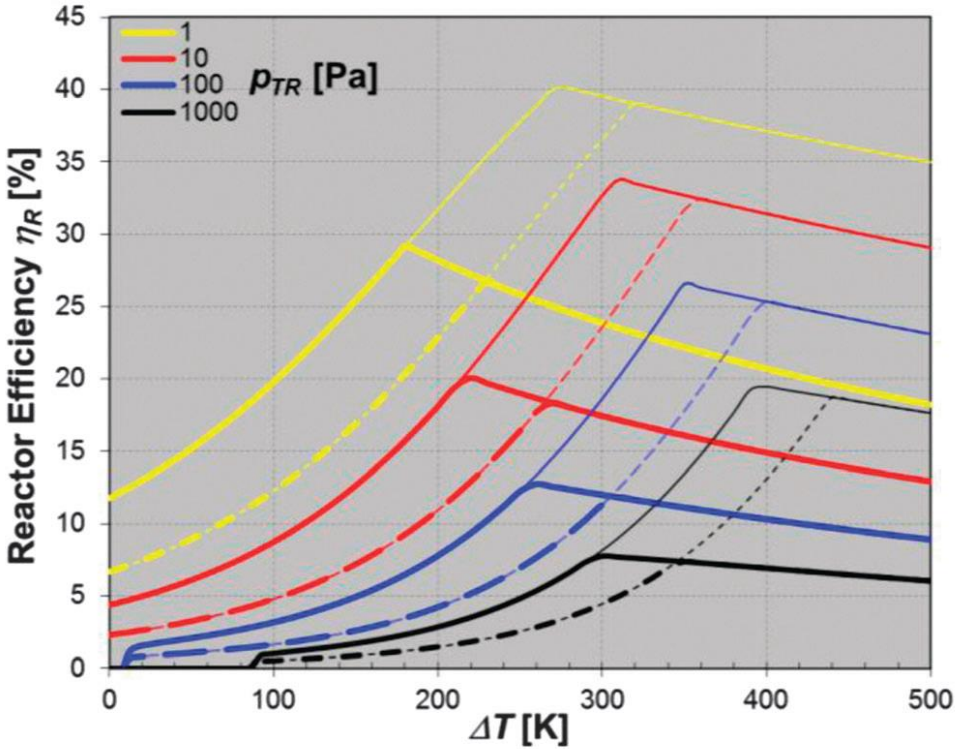
Separation Work Requirement

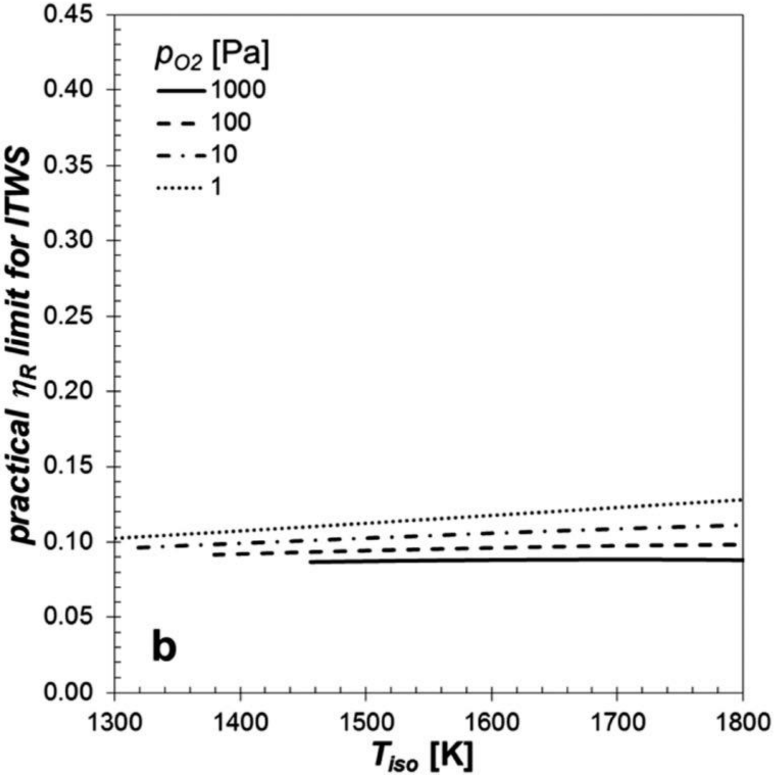
Yes, but at a price!

$$\frac{\Delta H_{\text{fuel product}}}{\Delta H_{red} + C_p\Delta T_{net} + Q_{parasitic} + W/\eta} = \text{Thermal eff.}$$

Optimum Temperature Swing

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



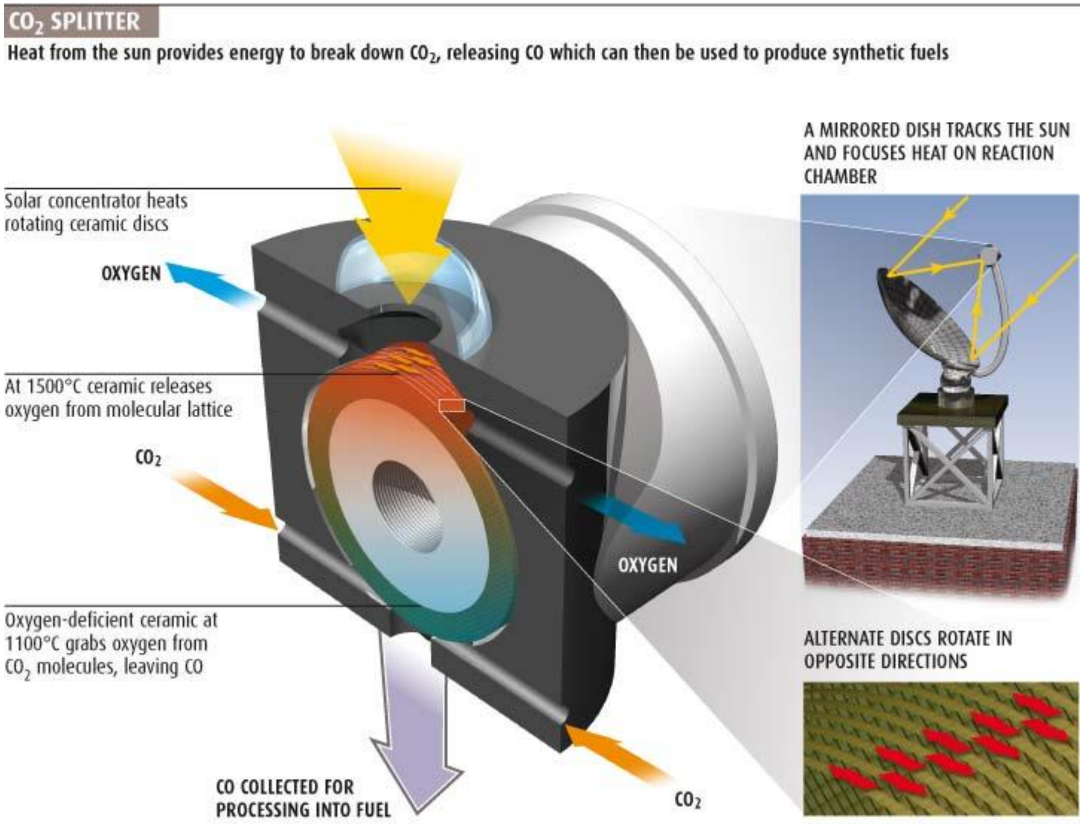


Isothermal is possible, but in my opinion inadvisable – can we use that electricity to better advantage?

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

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

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



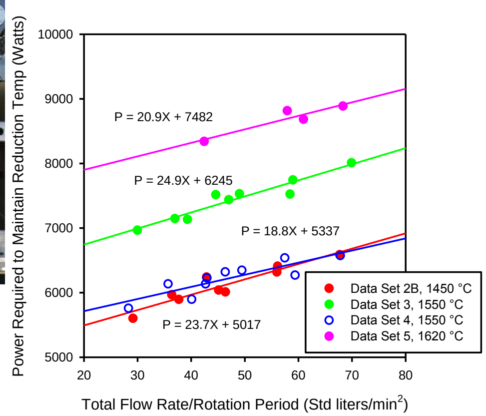
"Reactorizing a Countercurrent Recuperator"

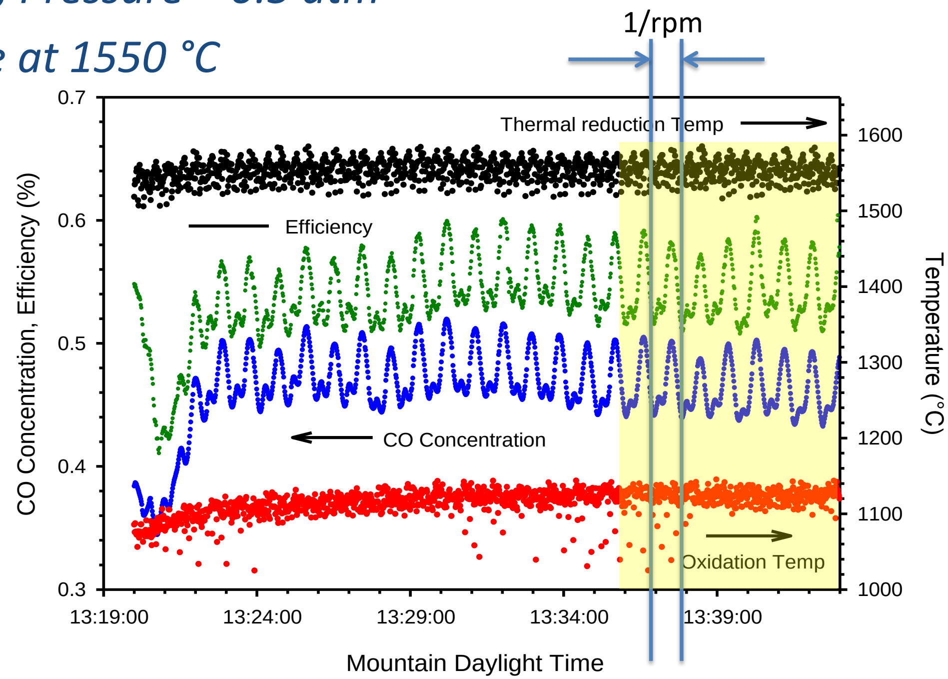
Continuous flow, Spatial separation of products, Thermal recuperation

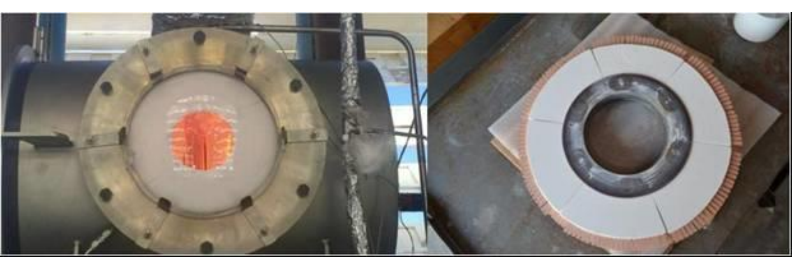
Performance Map of Gen-1 Prototype

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*







Miller, Allendorf, Ambrosini, Coker, Diver, Ermanoski, Evans, Hogan, 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

Materials Challenges

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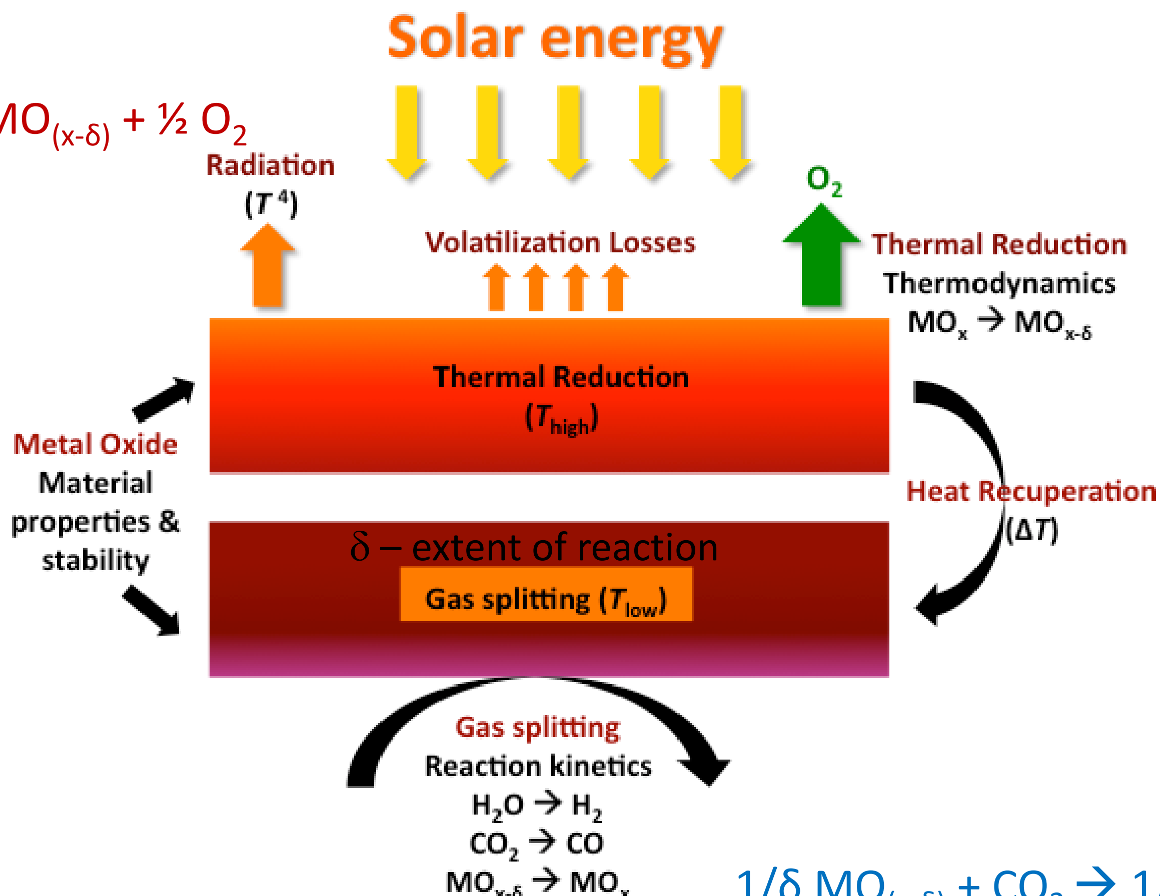
$1/\delta\ MO_x \rightarrow 1/\delta\ MO_{(x-\delta)} + ½\ O_2$

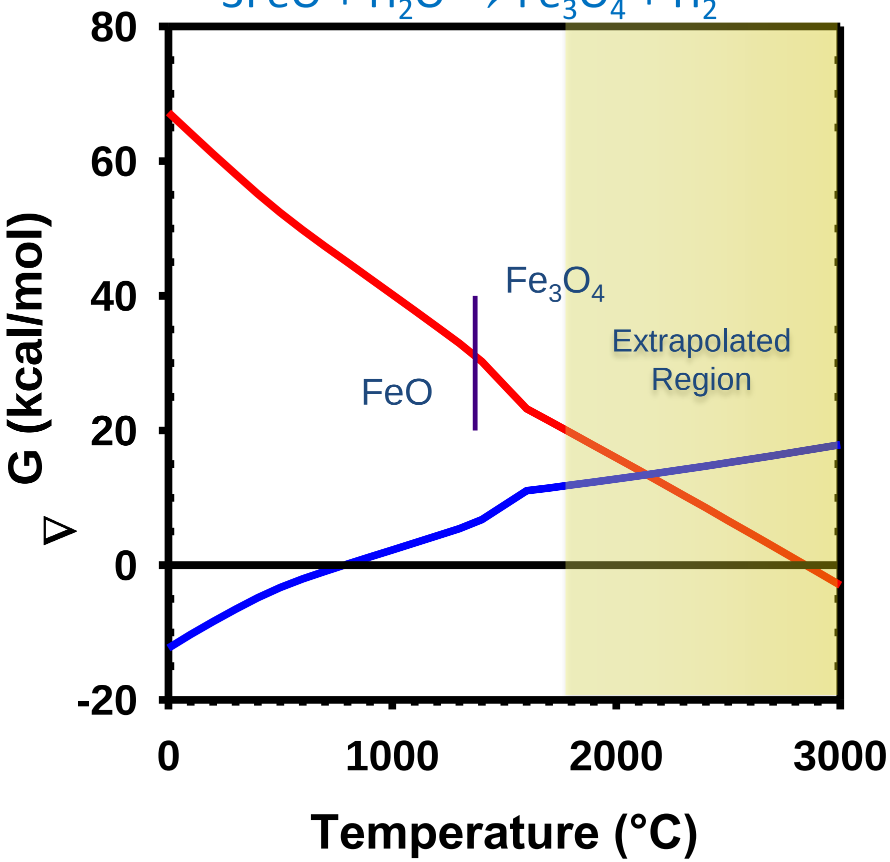


$1/\delta\ MO_{(x-\delta)} + CO_2 \rightarrow 1/\delta\ MO_x + CO$

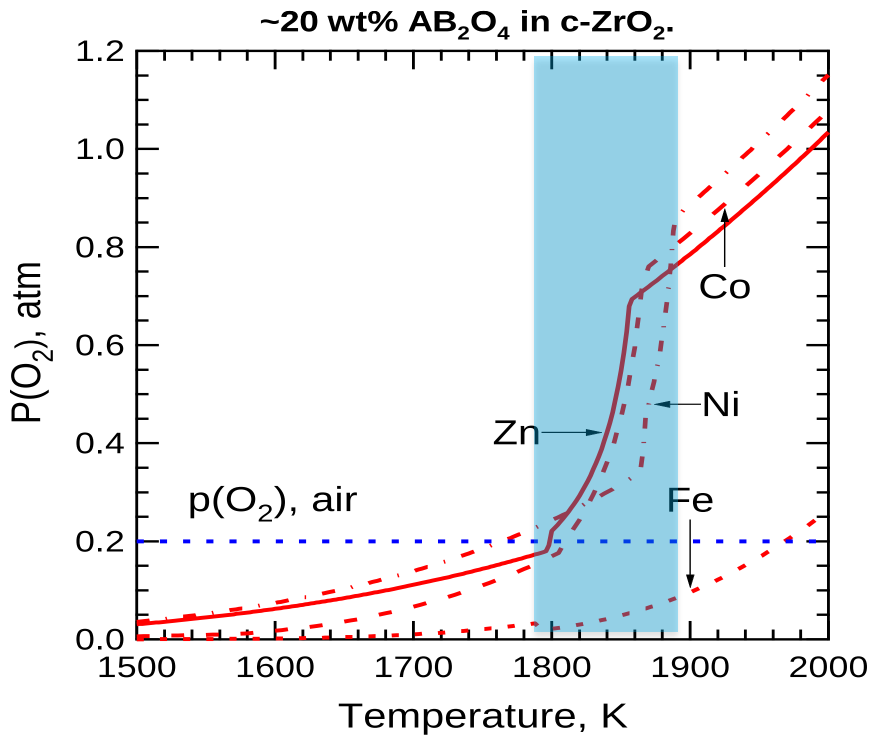
Metal Oxide TC Begins with Ferrites

$Fe_3O_4 \rightarrow 3FeO + ½ O_2$

$3FeO + H_2O \rightarrow Fe_3O_4 + H_2$



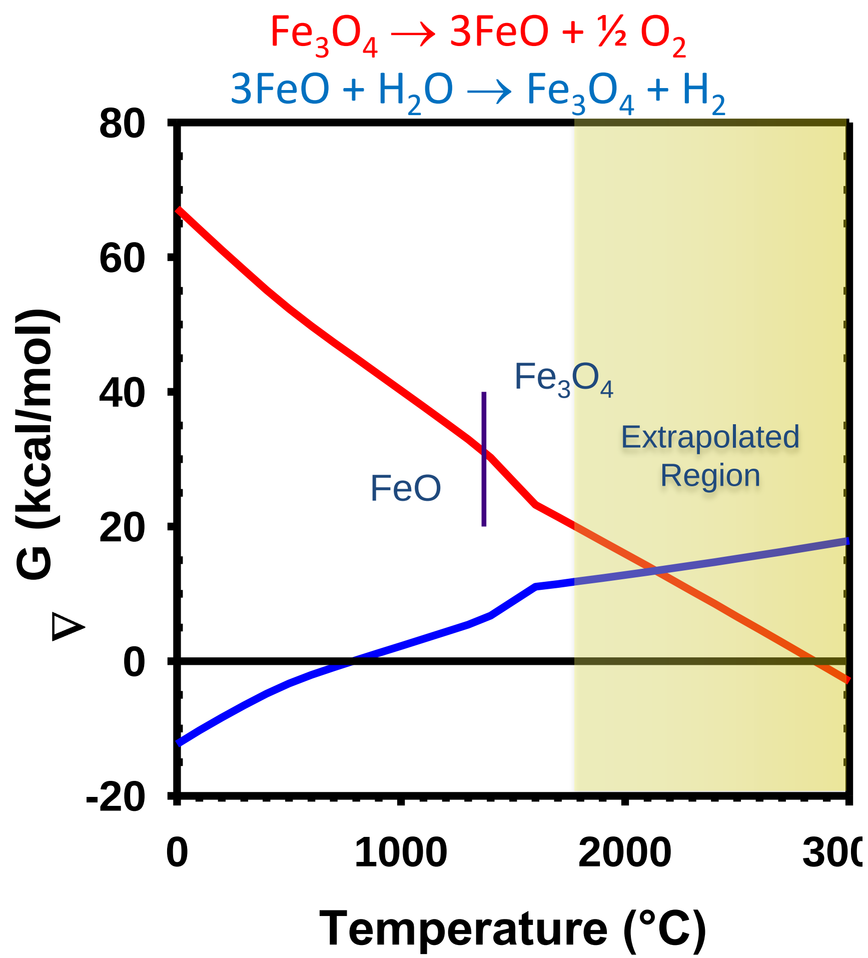
Ferrite metal oxide cycle (Nakamura 1977).



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

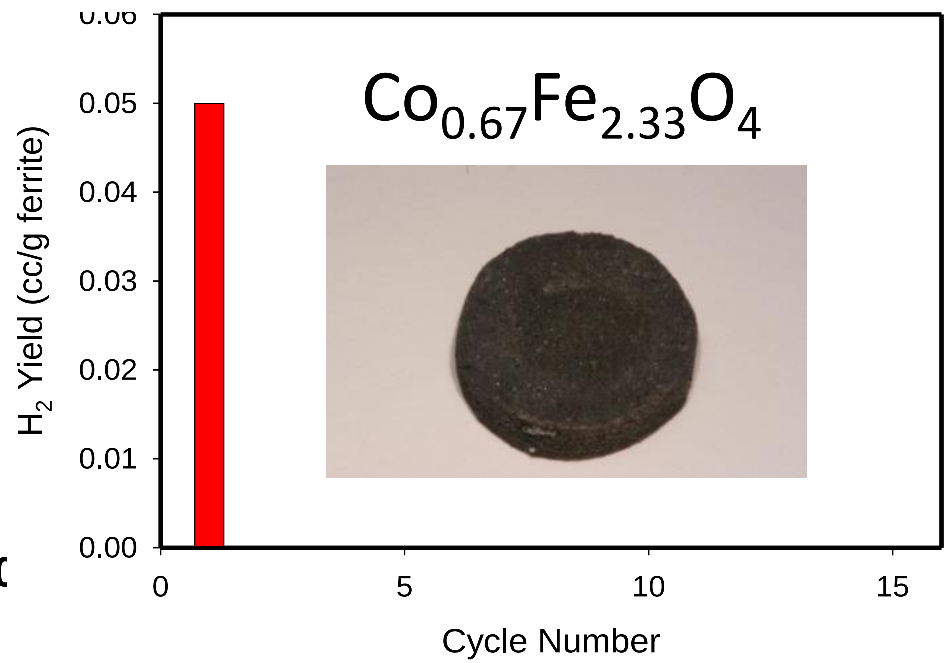
Partial conversion now possible.

Metal Oxide TC Begins with Ferrites



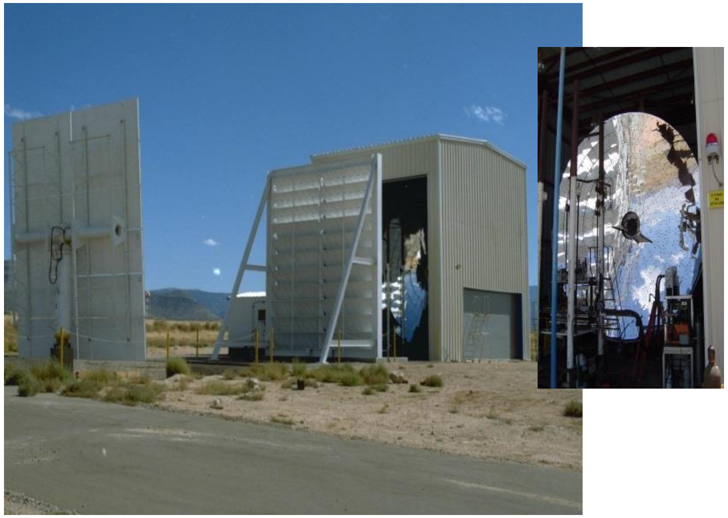
Ferrite metal oxide cycle (Nakamura 1977).

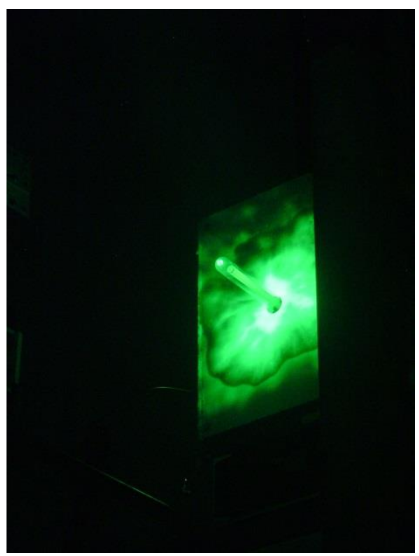
"Bulk" doped ferrites do not live up to thermodynamic expectations



Porous disk of cobalt ferrite produced small amount of H_2 for only one cycle.

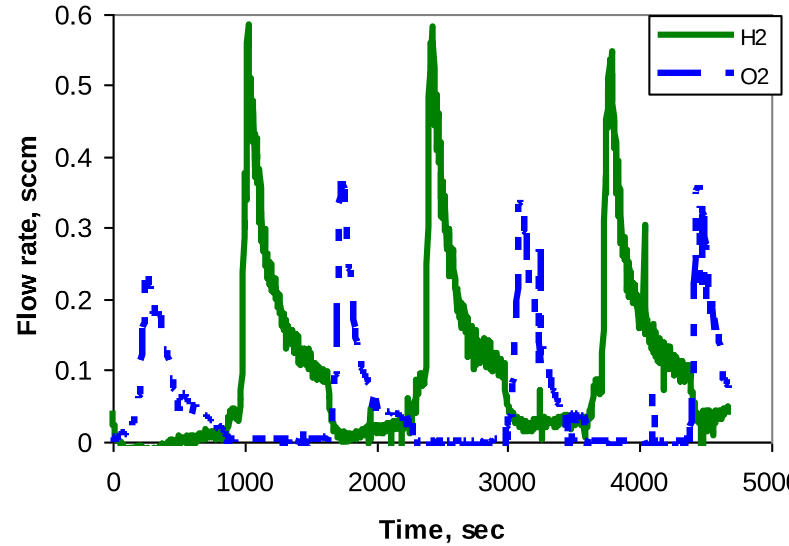
Ferrites work … when you add Zirconia





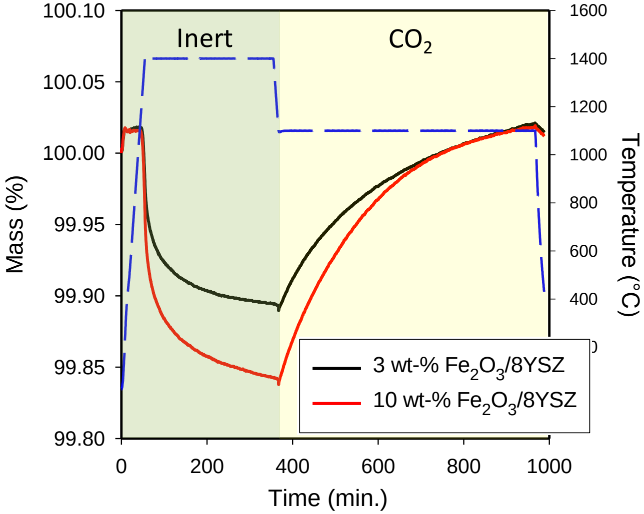
On-Sun Test:
$Co_{0.67}Fe_{2.33}O_4$/YSZ (1:4)

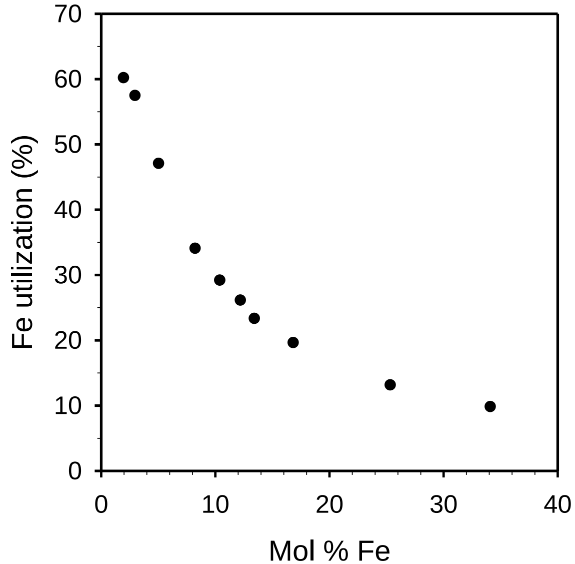
T_{TR} 1580 °C, T_{OX} 1050 °C
H_2 = 3.5-4 scc/g ferrite each cycle



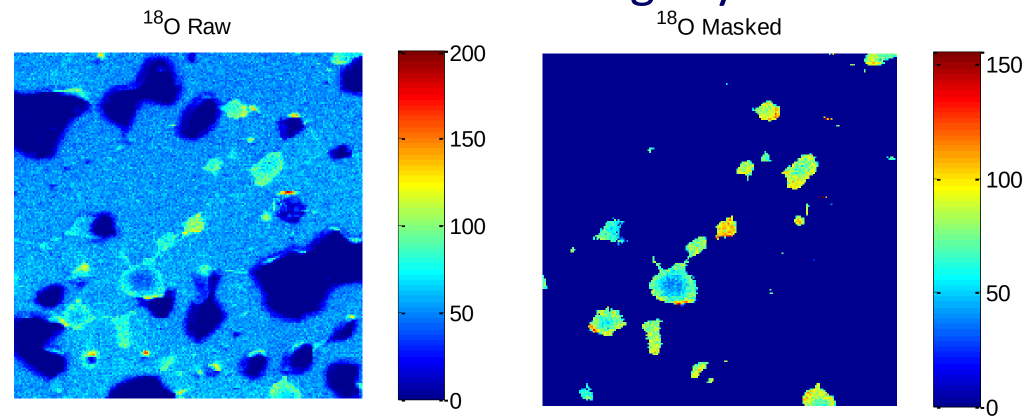
Pioneered by Kodama et. al. (ISEC) 2004, ISEC2004-65063, Portland, OR.

Fe dissolution and oxygen transport are the keys

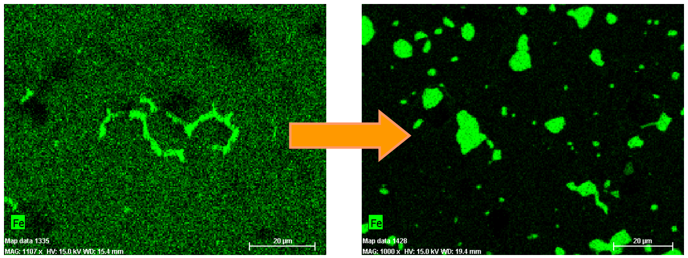




Beyond the solubility limit additional Fe contributes little to the overall gas yield.



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



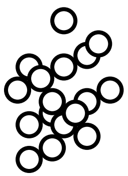
Fe EDS

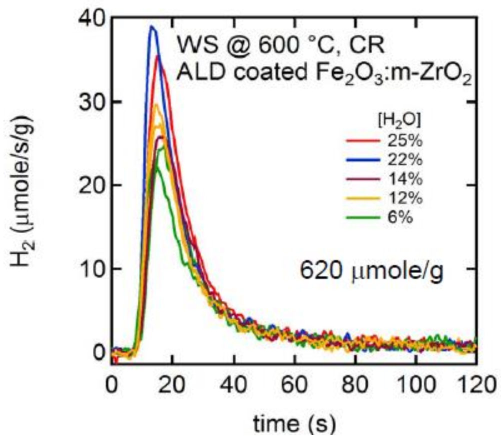
E.N. Coker, J.A. Ohlhausen, A. Ambrosini, and J.E. Miller J. Mater. Chem., 2012, 22, 6726. DOI:10.1039/C2JM15324F.

Sunshine to
Petrol

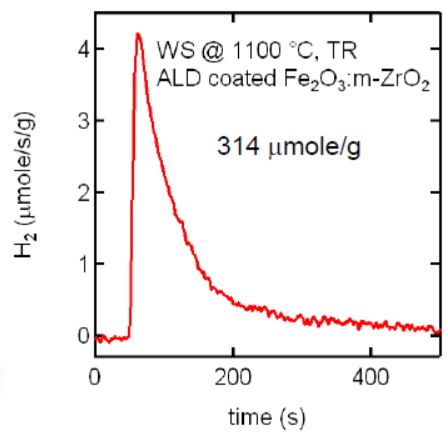
Small Dimension Structures

ALD thin film peak production rate ~ 100X faster than bulk

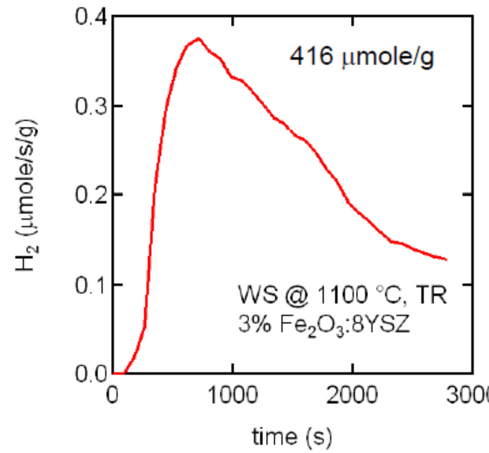




Chemically reduced ALD $Fe:ZrO_2$ nanoparticles

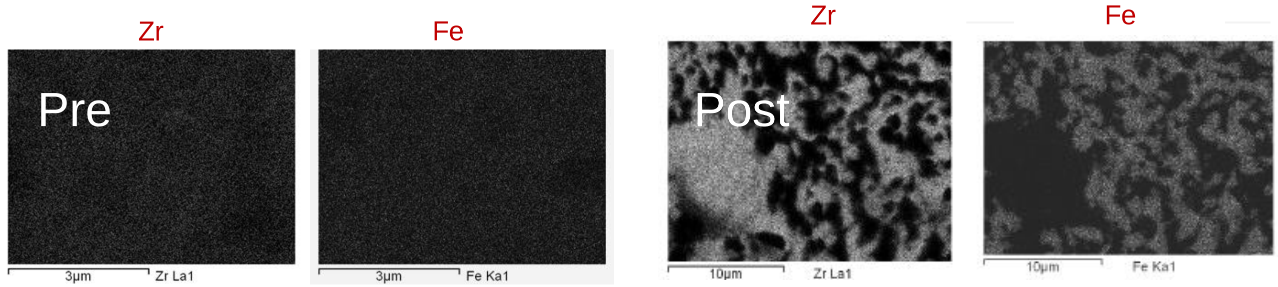


Thermally reduced ALD particles



Bulk Fe:YSZ

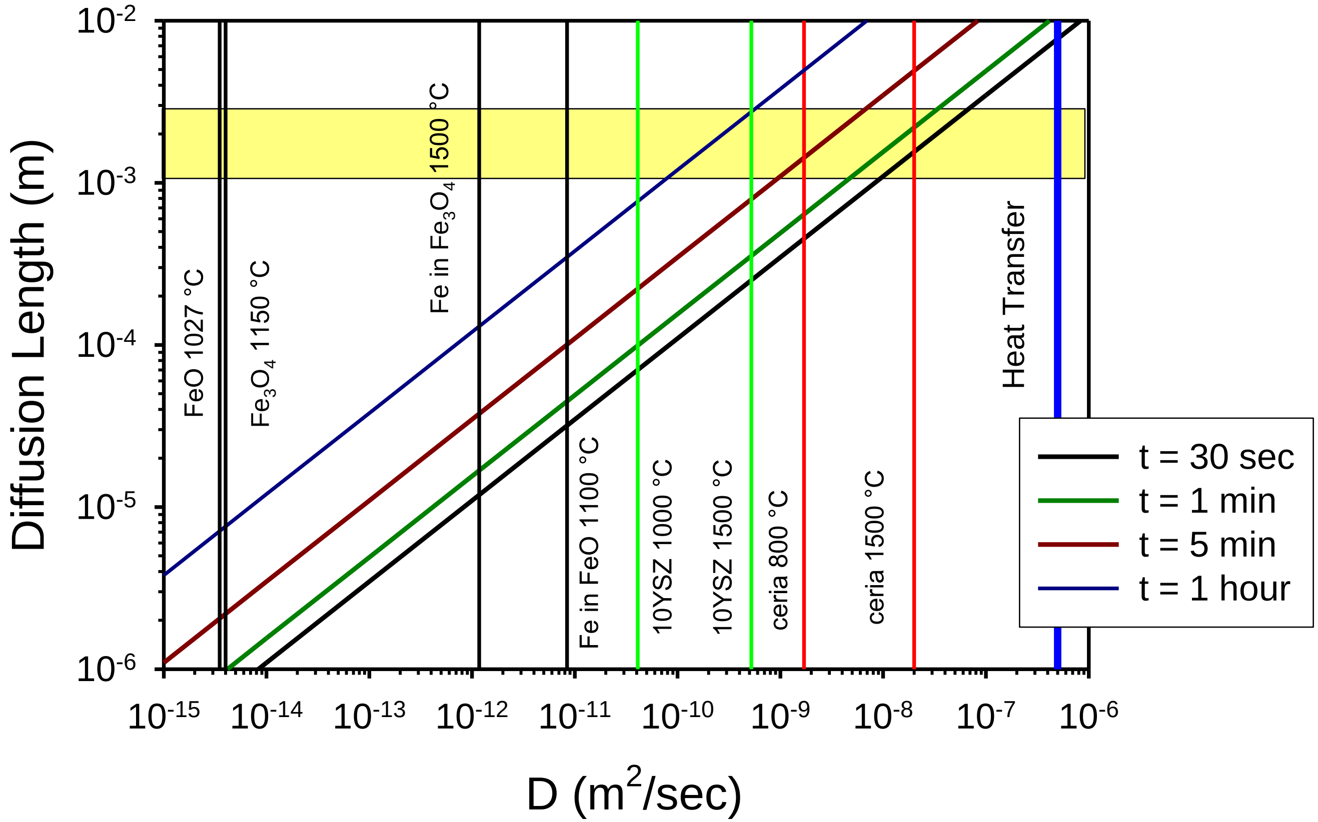
- CO_2-splitting activity improves dramatically for particles of ZrO_2 coated with *nanometer scale* layers of Fe_2O_3



JR Scheffe, MD Allendorf, EN Coker, BW Jacobs, AH McDaniel, AW Weimer
Chemistry of Materials 23 (8), 2030-2038.

Perspective on Ion Transport

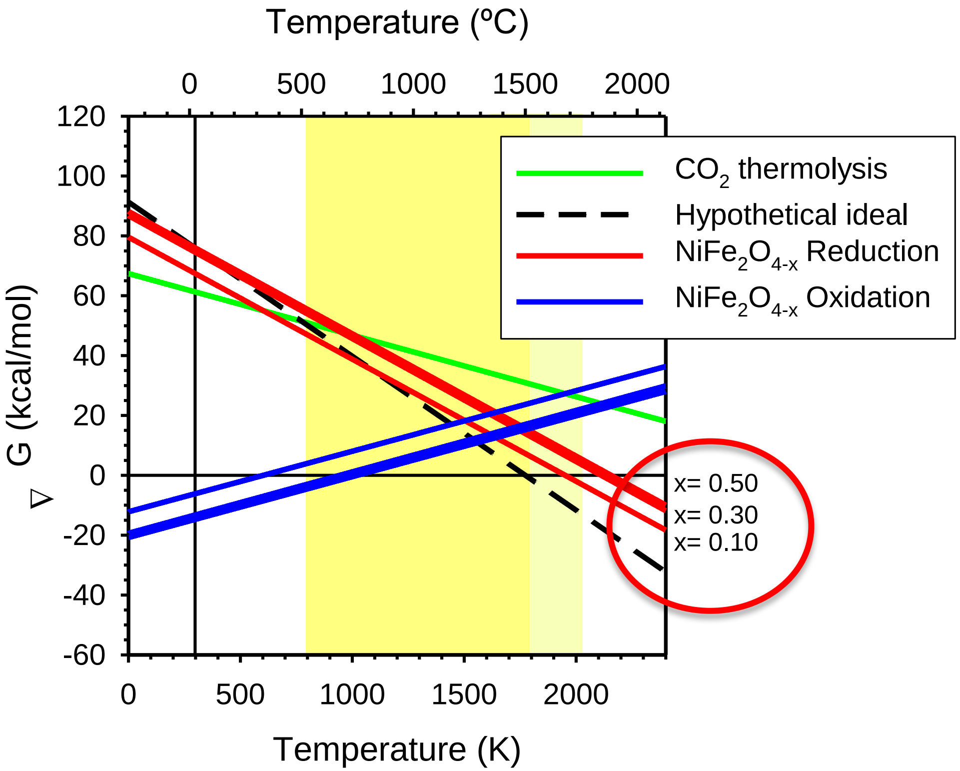
$$diffusion\ \ length = 2\sqrt{Dt}$$



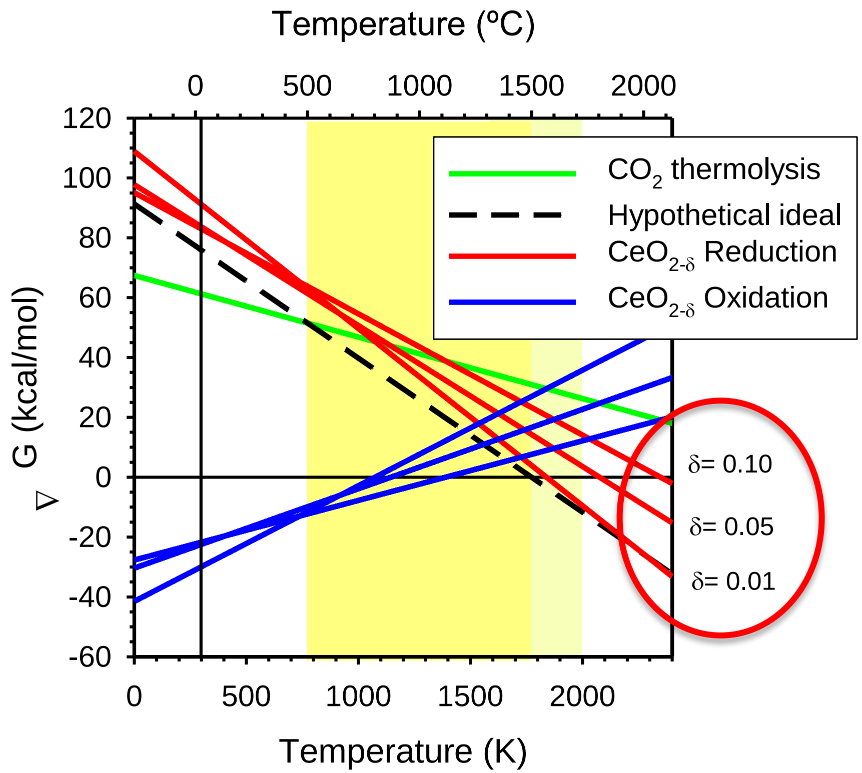
Heat> Ceria > YSZ >> Fe_3O_4

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

The problem with ceria – reaction extent



ΔH and ΔS (ΔG) are functions of redox state (δ or x). With each increment of reduction, materials become harder to reduce, easier to oxidize.



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

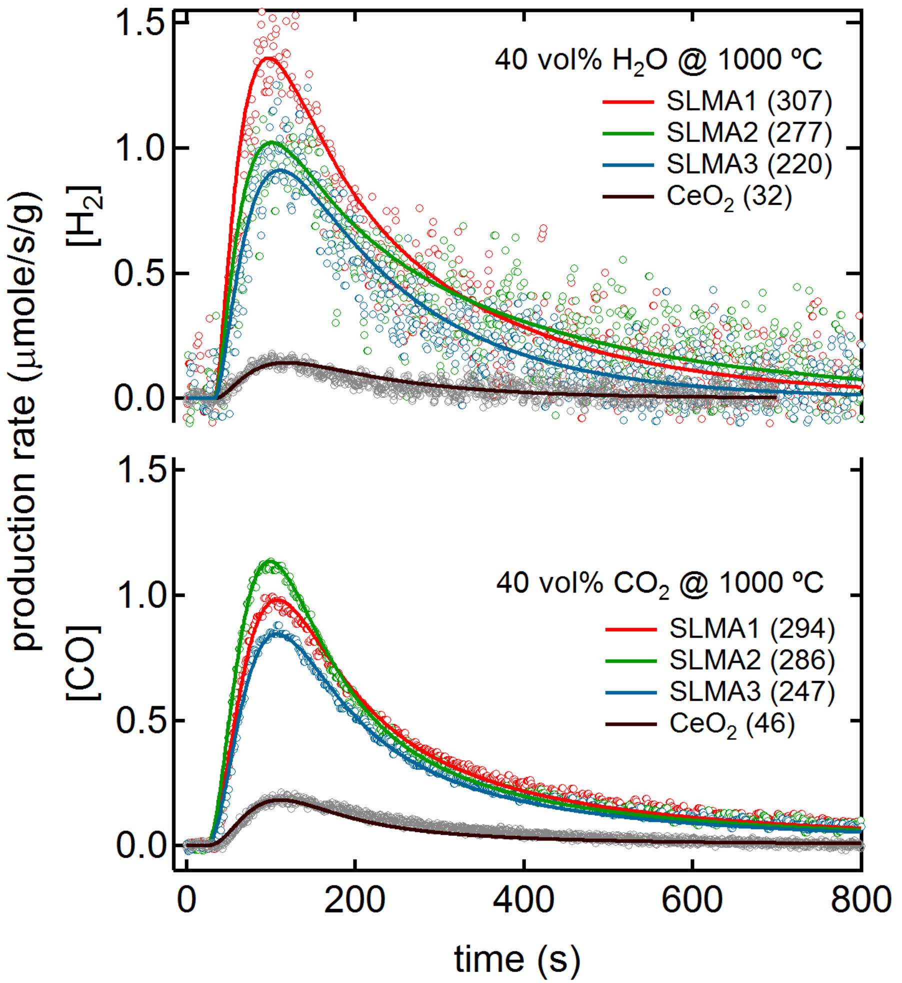
Miller, McDaniel, Allendorf *Adv. Energy Mater 2013.*

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.

Take-home points

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- 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.