Materials for Sunshine to Petrol

BP Executive Visit

Albuquerque, NM

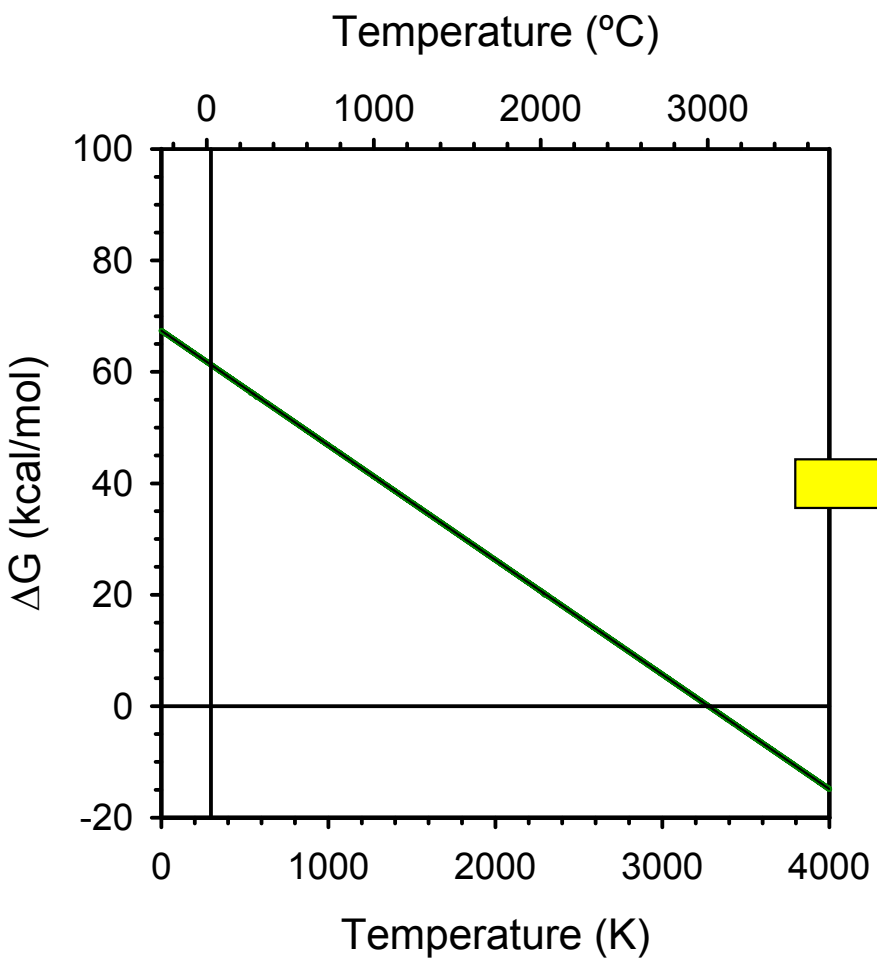
James E. Miller, Presenting

Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Three Themes

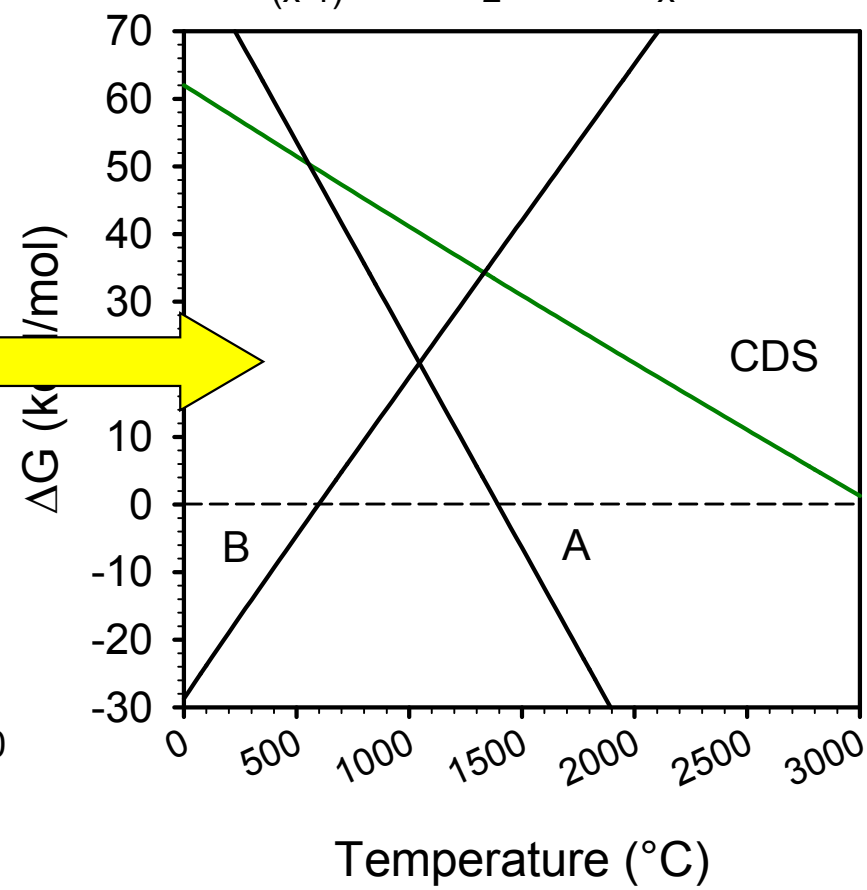
- What defines an ideal material and where are we?
- Aspects of our efforts in materials?
- A closer look at ferrites.

Thermodynamics – Operating Temperatures



$AO_x \rightarrow AO_{(x-1)} + ½O_2$

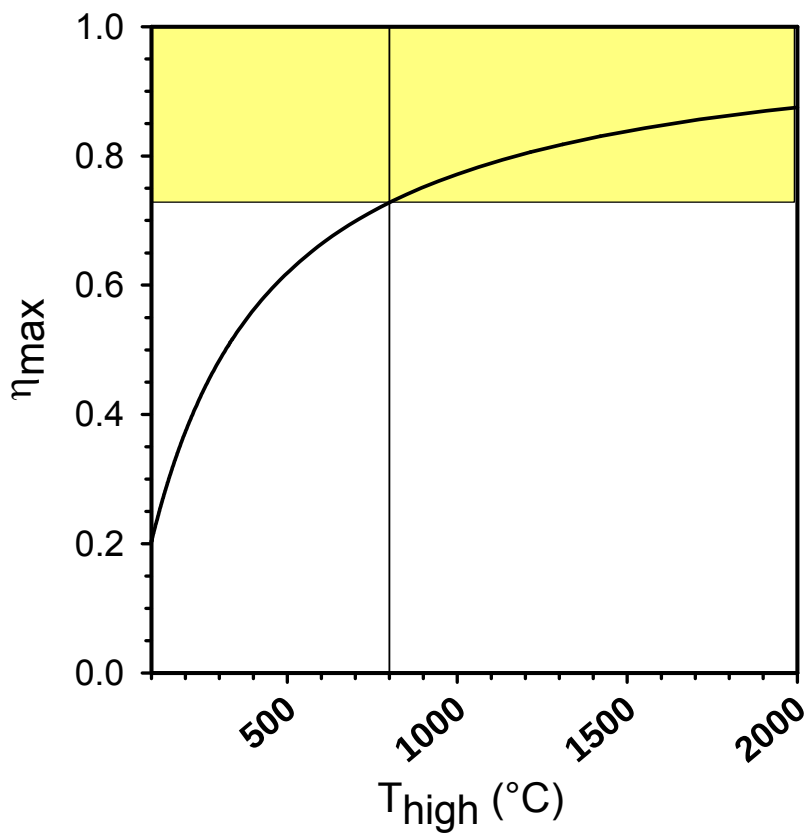
$AO_{(x-1)} + CO_2 \rightarrow AO_x + CO$

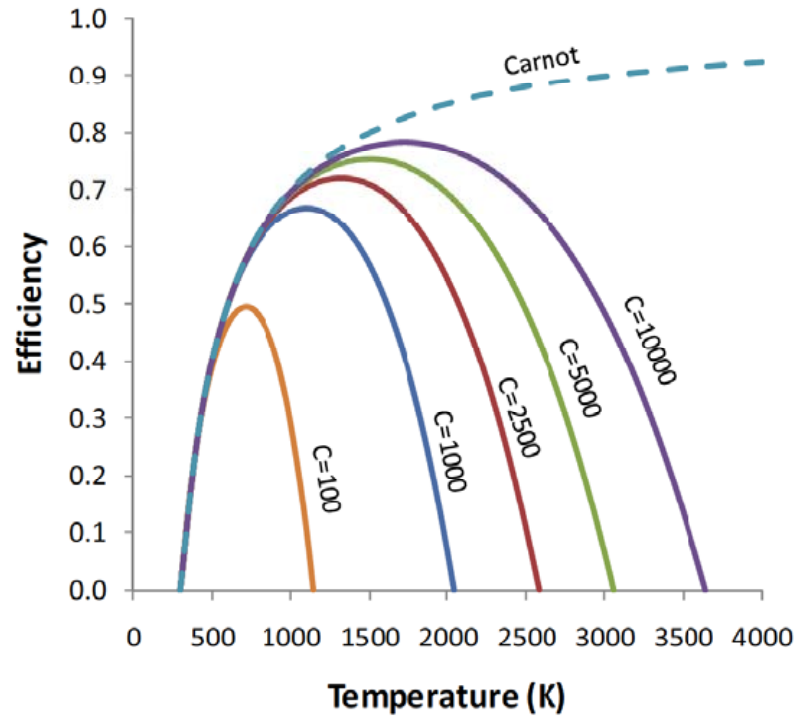


Assumptions: ΔH, $\Delta S \neq f(T)$, P=1 atm

Ideal Thermal Reduction 800-1500 °C

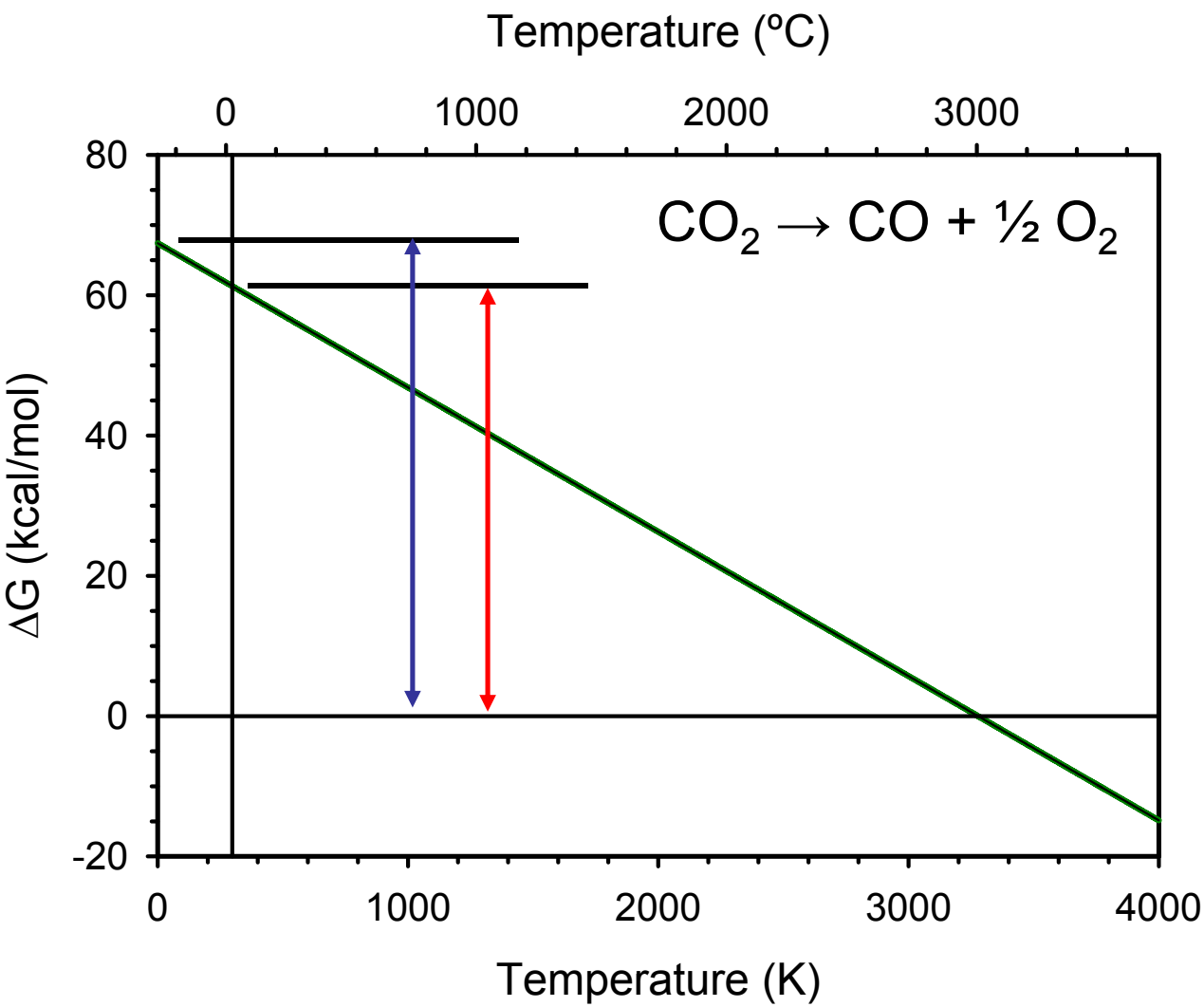
Carnot considerations suggest temperature should be as high as possible, but at least 800 °C





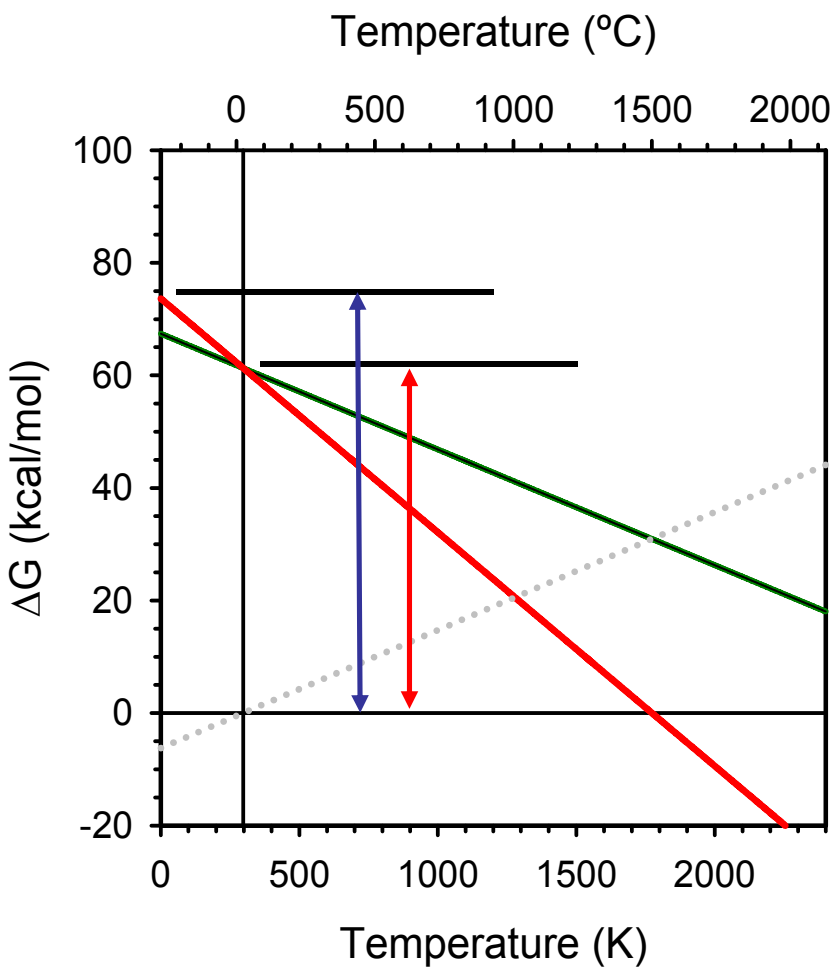
Radiation losses suggest temperature should be limited to < 1500 °C

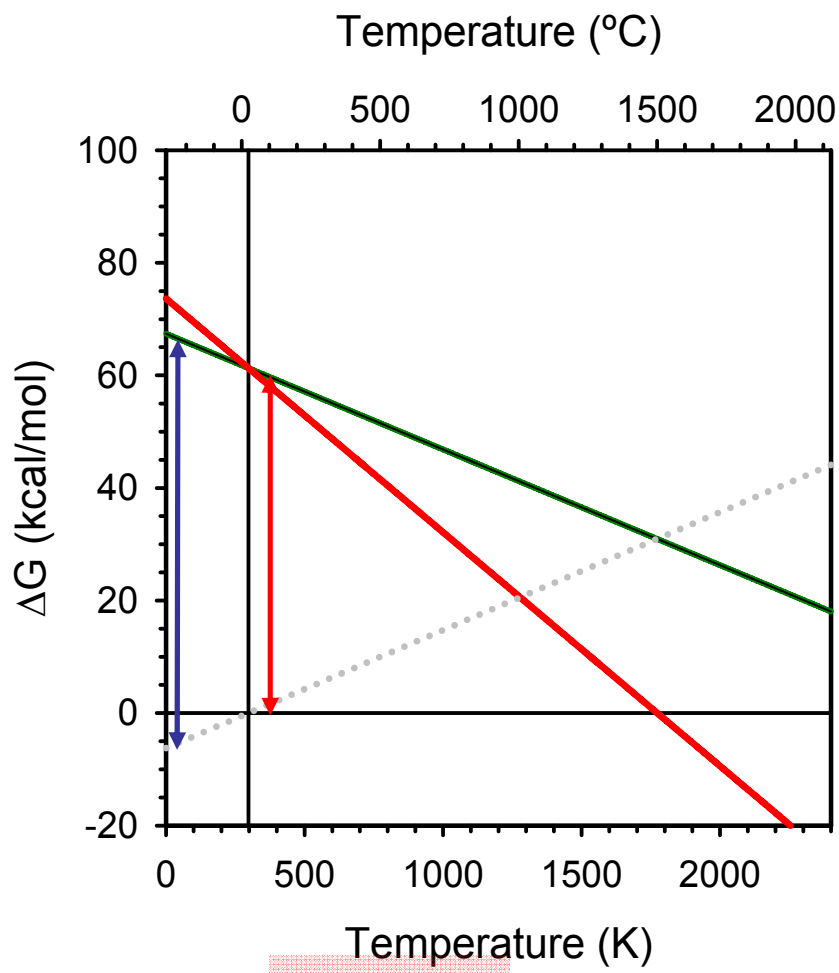
Efficiency Consideration



$$\eta = \frac{\Delta G_{CDS}^{298}}{\Delta H} = 0.91$$

Reduction @ 1500 °C
Oxidation @ 298 °C





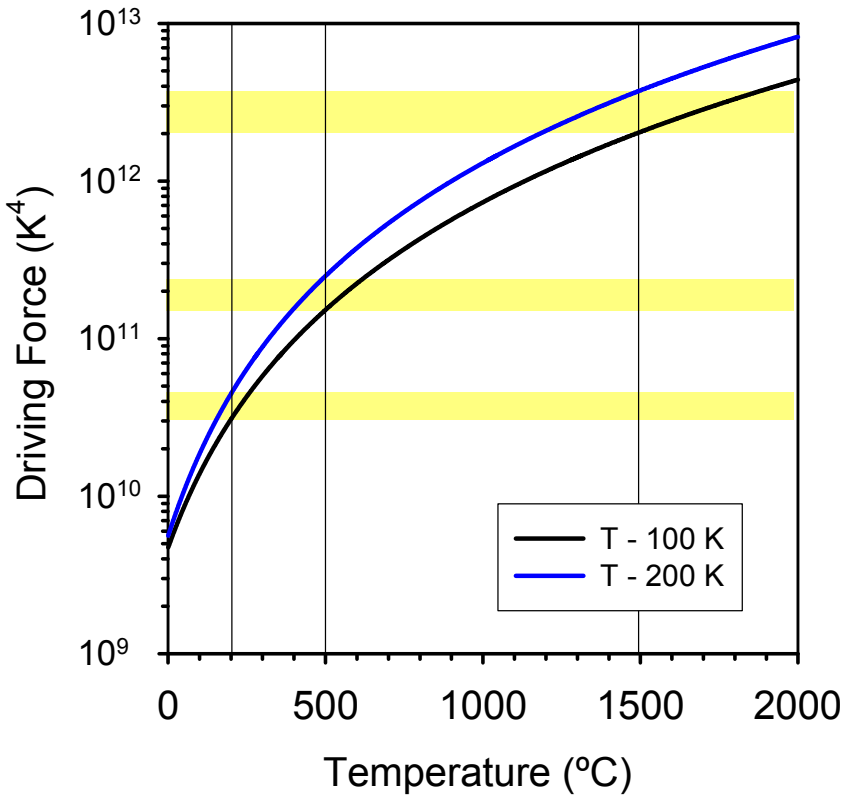
$$\eta = \frac{\Delta G^{298}_{CDS}}{\Delta H_{MOx\ Reduction}} = 0.83$$

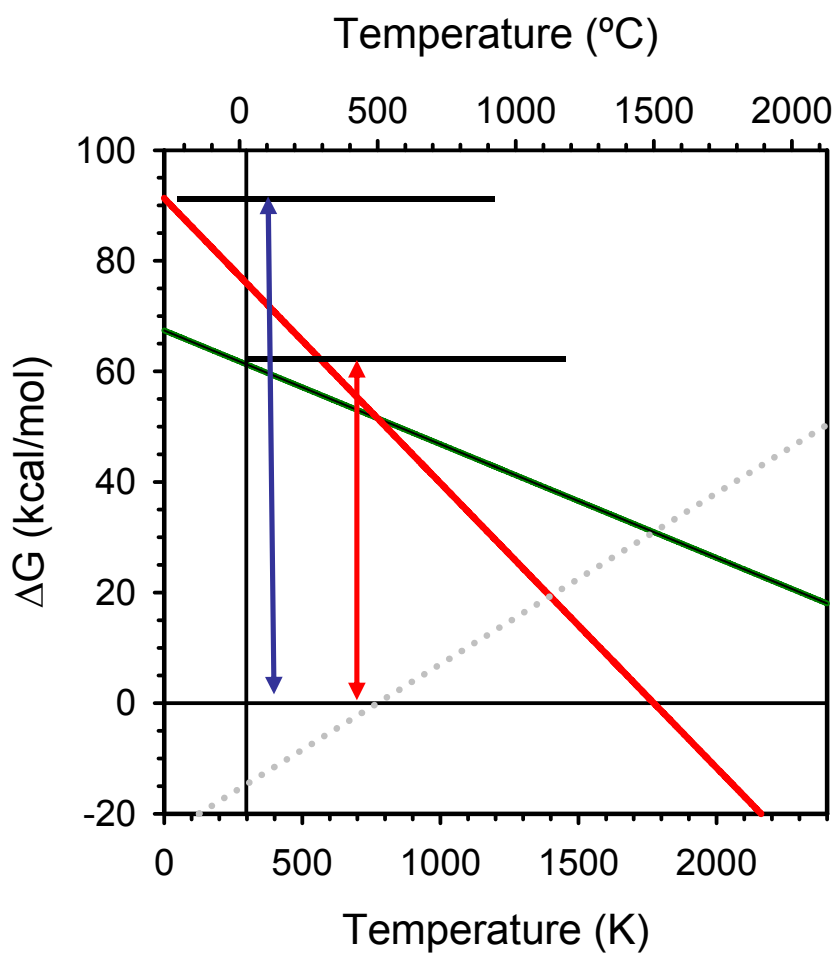
$$\eta = \frac{\Delta G^{298}_{CDS}}{\Delta H_{CDS} - \Delta H_{MOx\ Oxidation}} = 0.83$$

Ideal Oxidation

Reduction @ 1500, Oxidation @ 500 °C

$$Q_{12} = A_1 F_{12} \sigma \left(T_1^4 - T_2^4 \right)$$

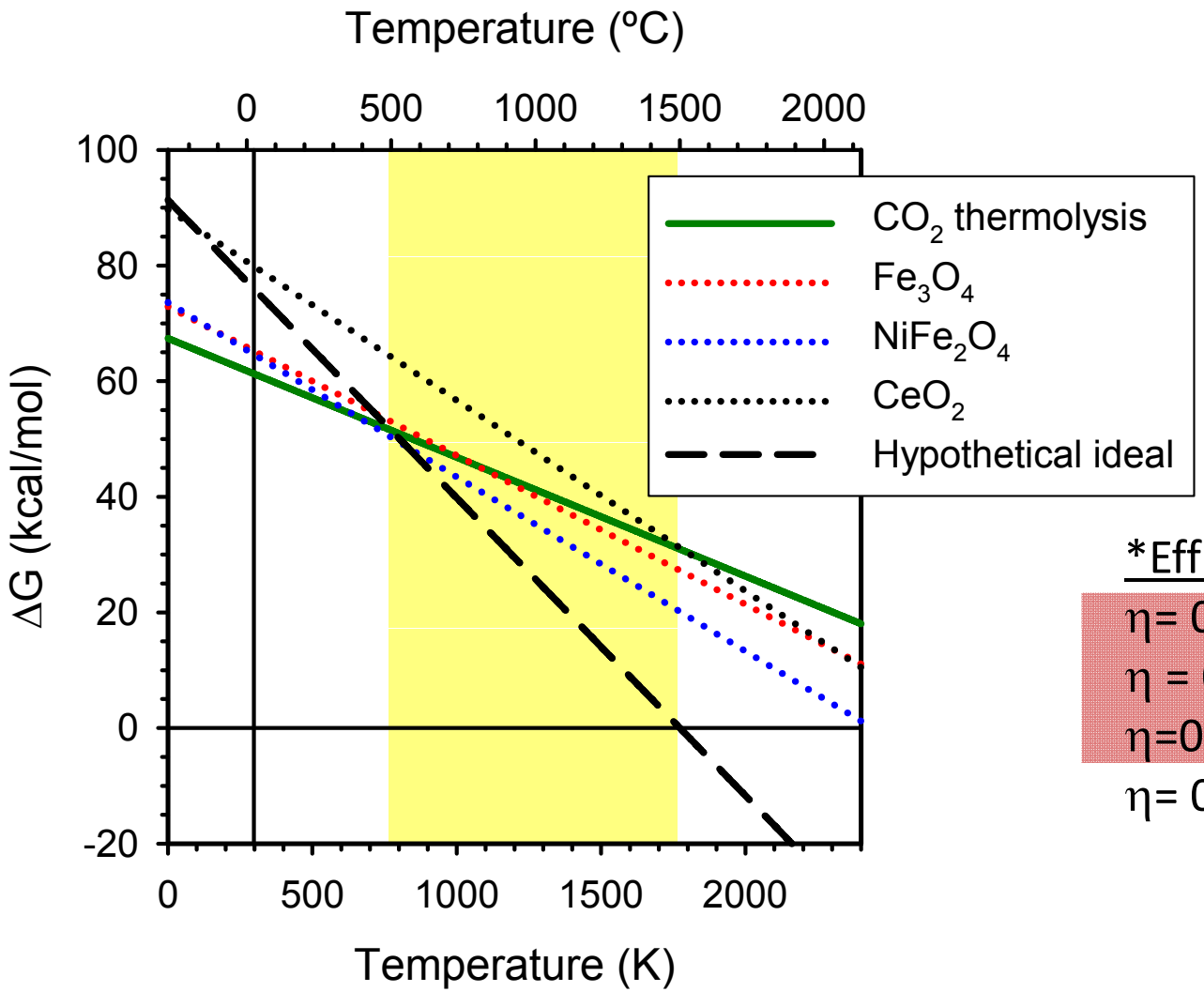




Oxidation should be at as low a temperature as possible, but need for recuperation suggests temperature limited to > ca. 500 °C

$$\eta = \frac{\Delta G_{CDS}^{298}}{\Delta H_{MOxReduction}} = 0.67$$

Current Materials?



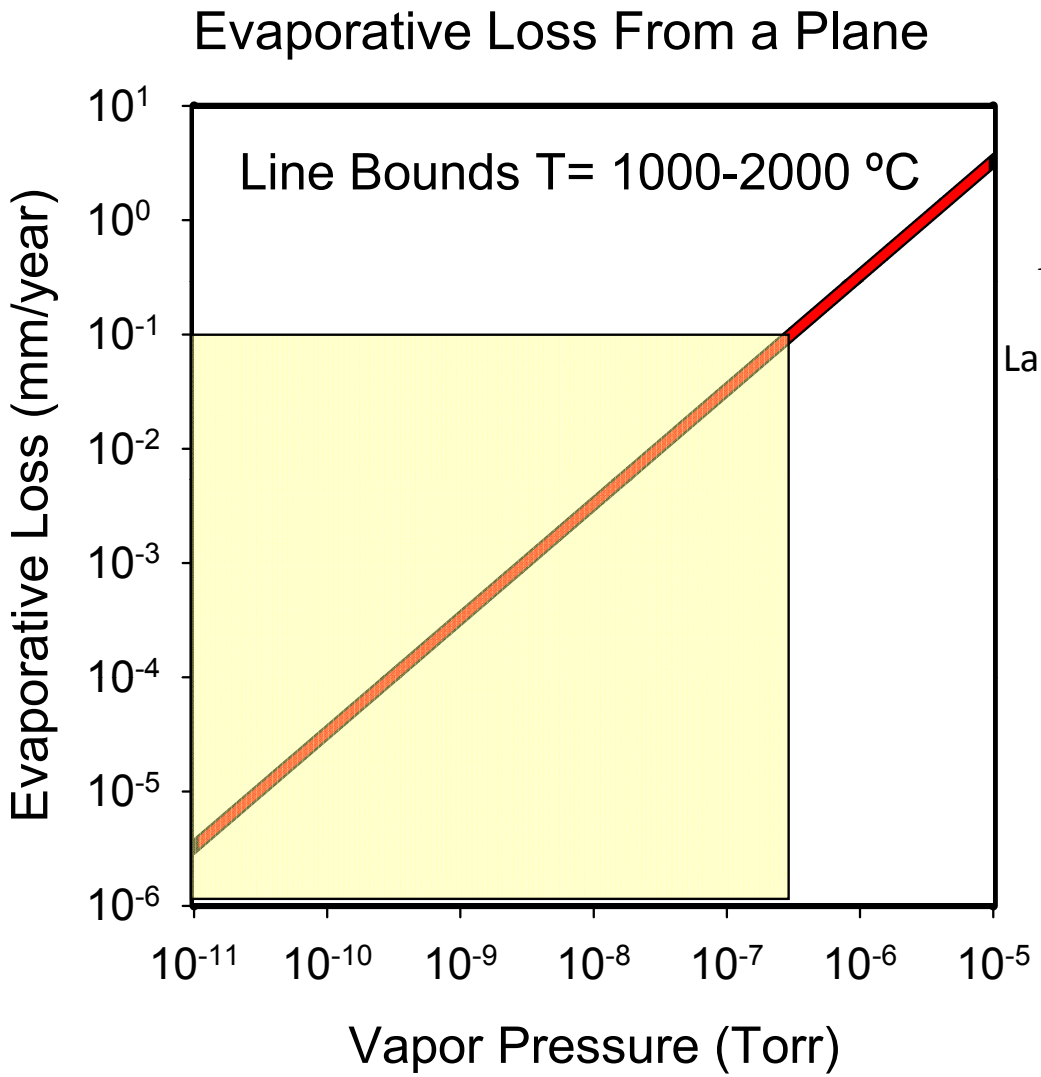
ΔH, ΔS values obtained by averaging tabulated values over 0-2000 ºC

*Efficiency based on ΔH

η= 0.83 Fe_3O_4
η = 0.84 $NiFe_2O_4$
η=0.68 CeO_2
η= 0.67 Hypothetical

Materials outside the window are usable, but put greater demands on recuperation due to low utilization

Volatility



$$Me = 5.85 \times 10^{-2} \cdot P \cdot \left(\frac{MW}{T}\right)^{\frac{1}{2}} \quad \frac{g}{cm^2 \cdot s}$$

Langmuir equations for sublimation rates.

<u>Hypothetical metal oxide</u>

ρ = 6 g/cm^3

MW = 175

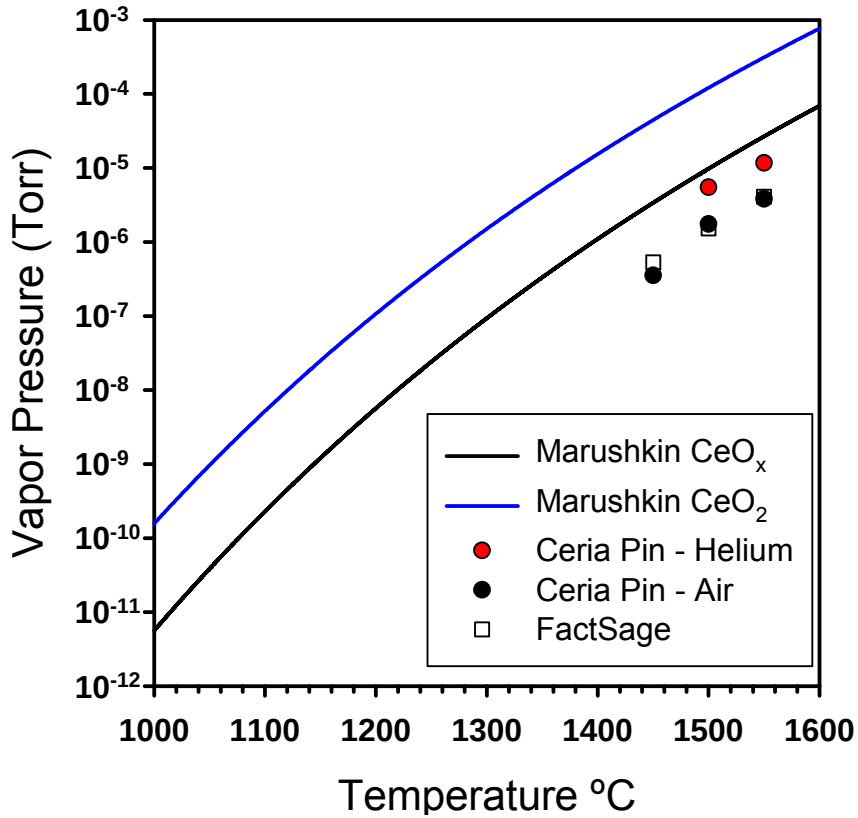
8 hours/day at Temperature

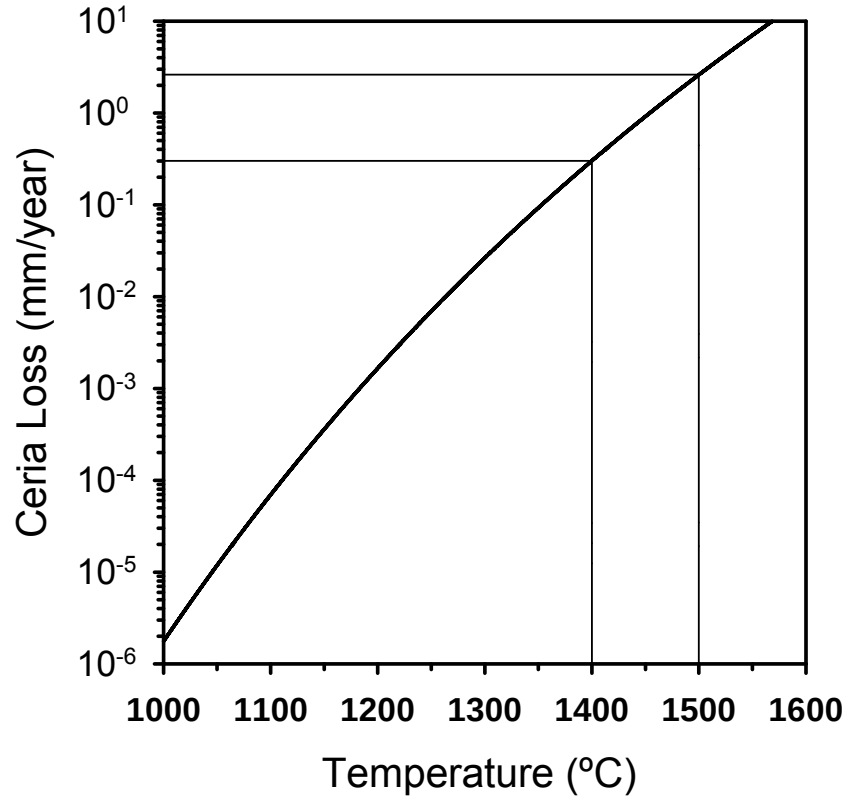
365 Days/year

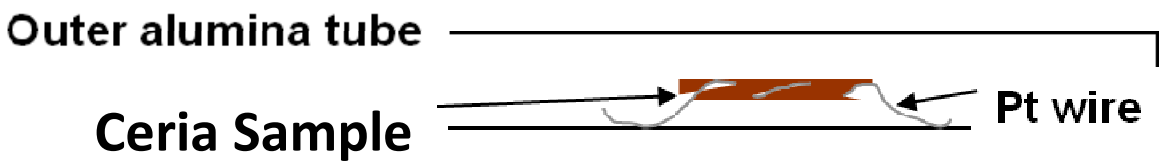
Loss < 0.1 mm/year if material V.P. is < 3×10^{-7} Torr

Ceria Loss Potentially Significant

Calculated using Marushkin et al. for CeO_x







Ferrites are also significantly challenged at T > 1400 °C

Cycling Limits Thermal Penetration & Hence Utilization

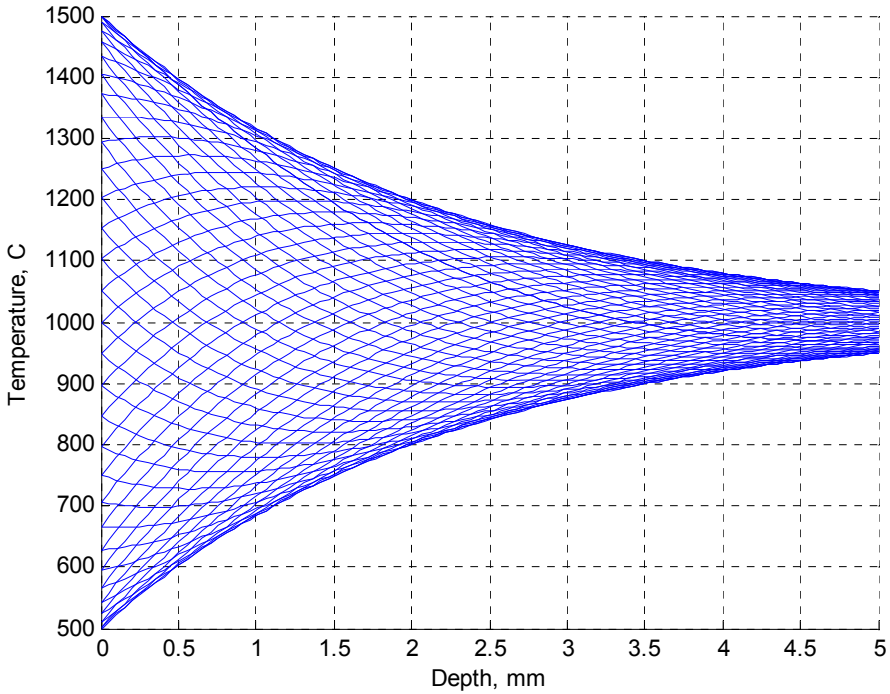
Utilization similar to rxn extent

Range of temperature waves over one cycle (60 secs @ 1 rpm)

Semi infinite material with sinusoidal varying surface temperature

Ce_2O_3 (thermal diffusivity ~2.5×10^{-7} m^2/sec)

Nominal ring speed 1 rpm (or 1 cycle/60 seconds)

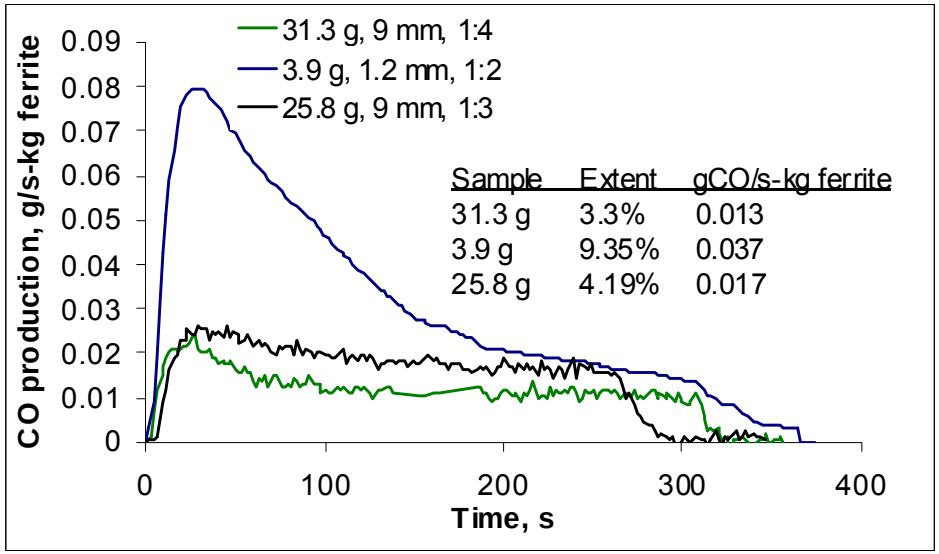


Material deeper than about 2mm will not see temperatures

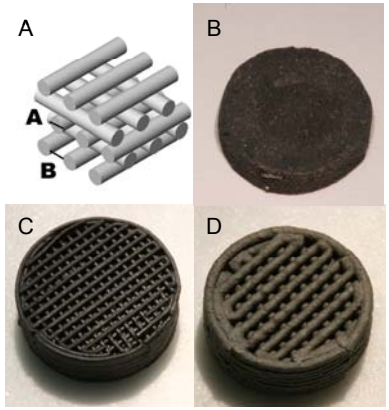
> 1200 °C and < 800 °C

Conduction of heat → Critical physical dimension

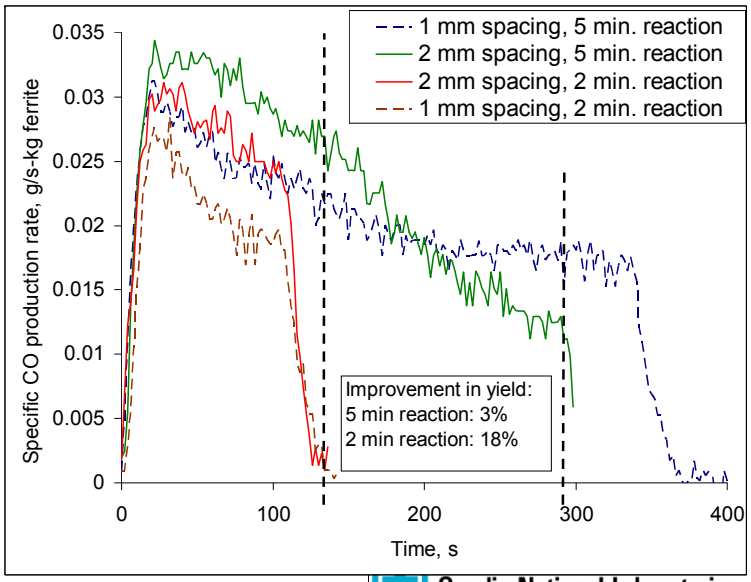
Direct Illumination is a key reactor attribute



Decreasing sample thickness improves utilization to >9%

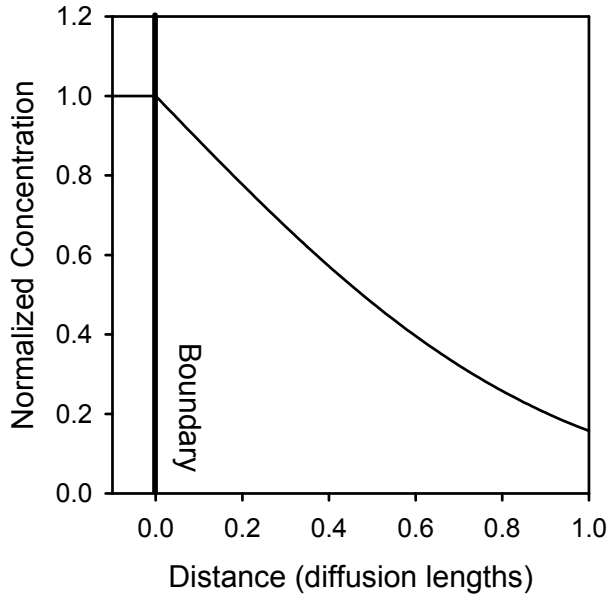


Doubling the lattice rod spacing improved CO production for 2 min. reaction by 18%.



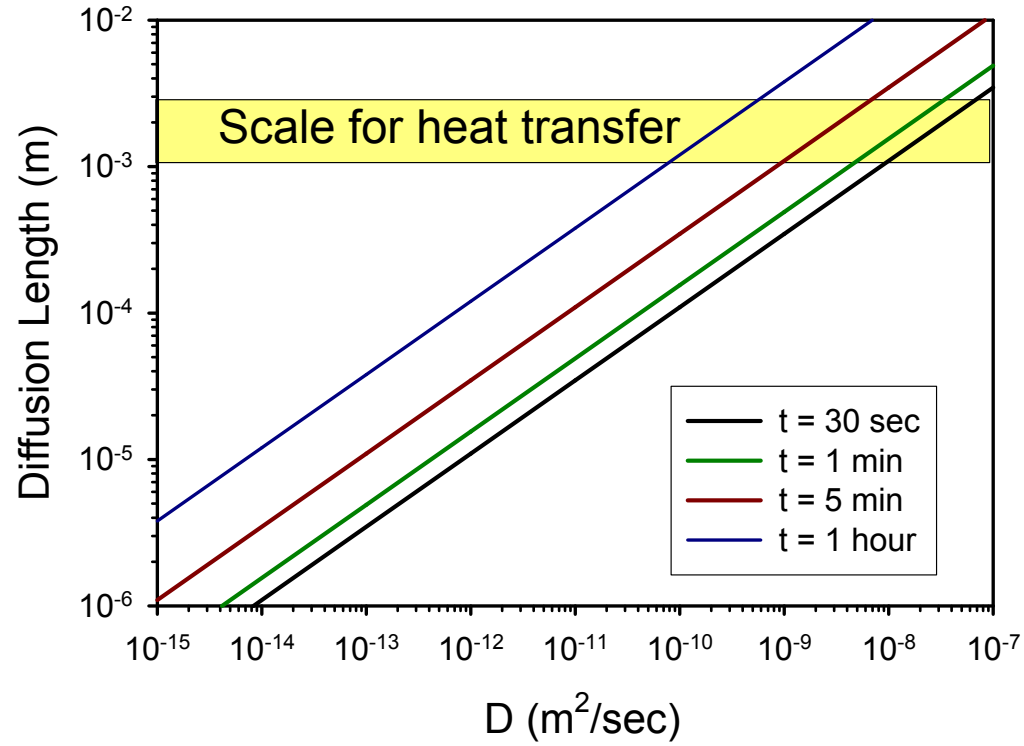
Utilization: Transport in the Oxide Bulk

Diffusion from a fixed concentration in one dimension



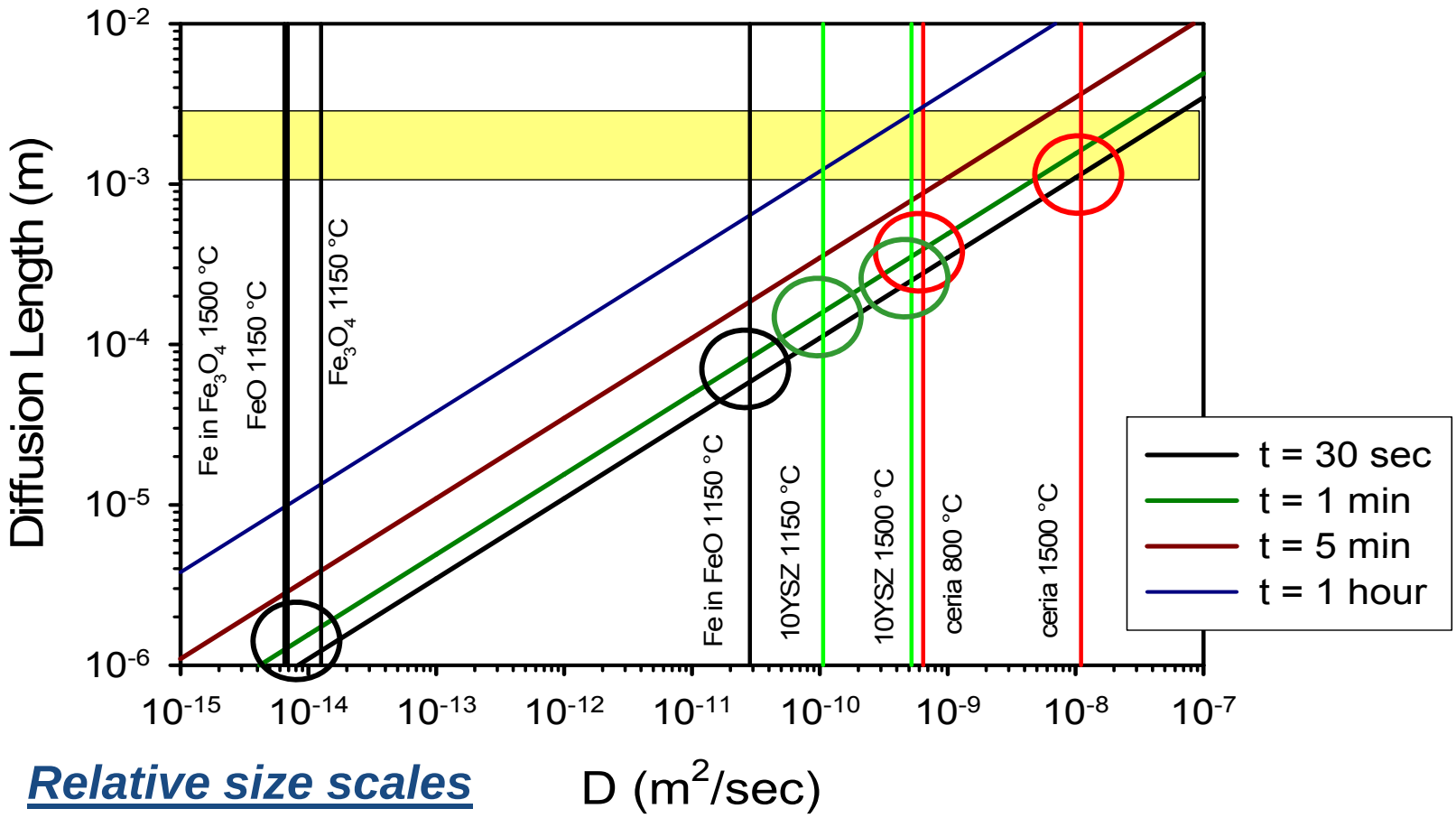
$$n(x,t) = n(0)\,erfc\left(\frac{x}{2\sqrt{Dt}}\right)$$

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



Defining D and *t* leads to a characteristic dimension

Where Do We Stand?



Relative size scales

Heat transfer: 1 mm

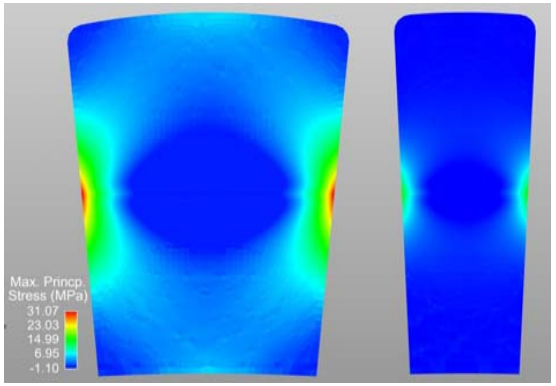
Ferrites: 1-100 μm

YSZ: 0.1 mm

Ceria: 0.1-1mm

Stability and Durability

- Bulk Melting Temperature (T_{mp})
- Tamman Temperature (T_T) = 0.5 T_{mp}
  Bulk to Surface Migration
- Hüttig Temperature (T_H) = 0.33T_{mp}
  2-d mobility, agglomeration on surfaces
- Sintering Rule of thumb – 0.4T_{mp}
- Creep – 0.3 T_{mp} for metals, 0.4-0.5 T_{mp} for ceramics



∴ If T_{high} = 1500 °C , T_{mp} is ideally > 3275 -5500 °C

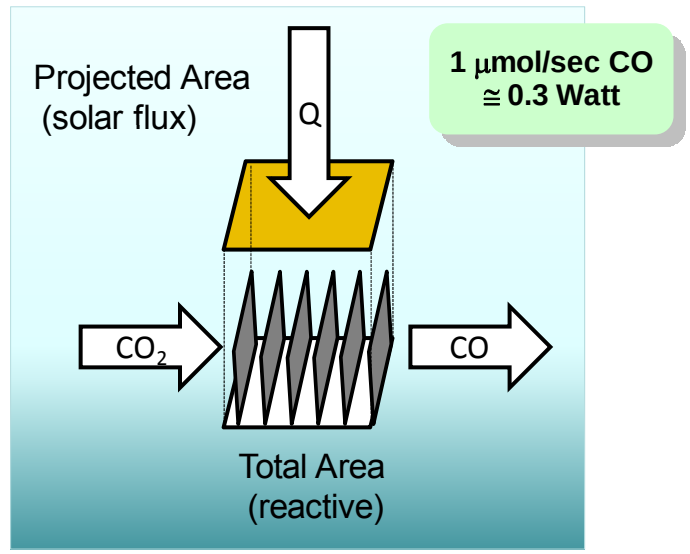
Kinetics Should be Matched to Solar Flux

$$\eta = \frac{Chemical\ Energy\ Out}{Solar\ Energy\ In} = \frac{\int_0^t \left(CO\ Flux \times HHV\right) dt}{\int_0^t Solar\ Flux\ dt}$$

$$CO\ Flux = 2\ O_2\ Flux$$

In order to achieve high efficiency the energy fluxes (solar and chemical) must match.

I.e. Reaction rates must be matched to the solar flux.



To the extent that the rates and flux do not match, heat is rejected.

Suitability of Current materials subject to surface area.

Attributes of Ideal Material are Linked to Device

Thermodynamic Operating Window 500-1500 °C

Vapor Pressure of Working Oxide < $3x10^{-7}$ Torr

Transport $\geq$ the characteristic dimension (thickness) of fabricated parts

High melting Points, Low thermal expansion, Characteristic dimensions small to relieve stress.

Reaction Kinetics/Material Loading matched to Flux

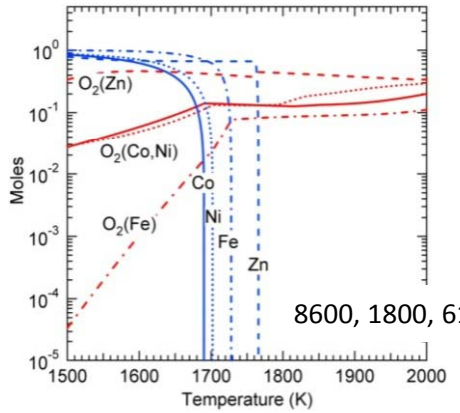
- Current Materials are appropriate for accomplishing our short term project goals, but fall short in one or more category.
- Improvements will be needed to meet long term targets as defined by systems, economics, and competing approaches.

Three Aspects to the Path Forward

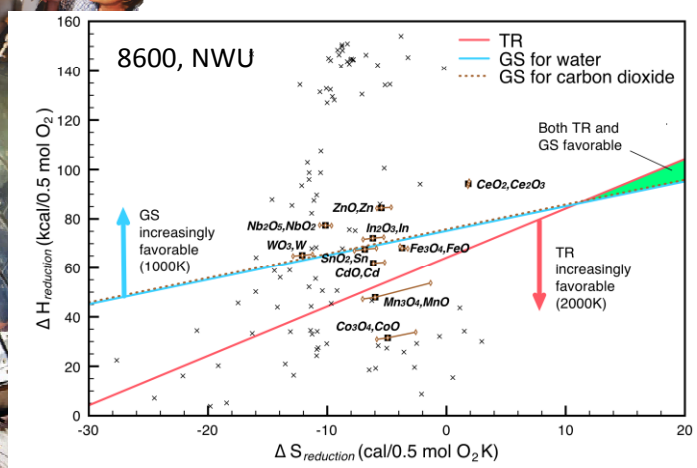
- Improved compositions – modification & discovery
- Structuring materials
- Matching the reactor to the material

Materials Thrusts

Thermodynamics

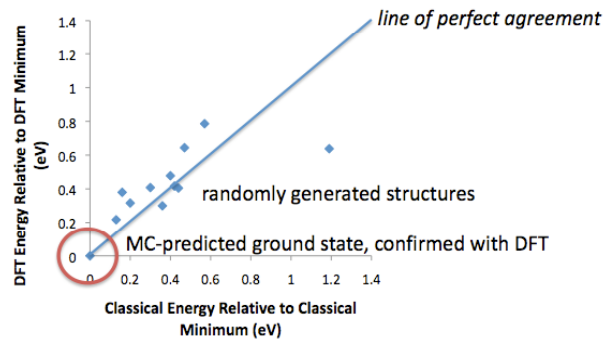


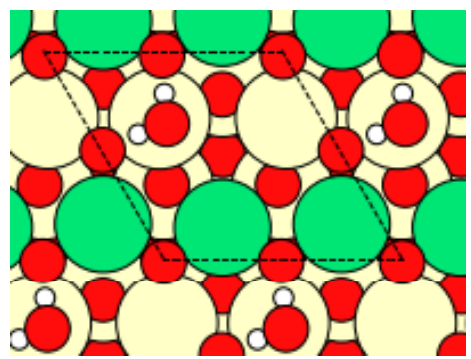
Energy & Fuels, **22** (2008), 4155



Physical Review B 80, 245119 (2009).

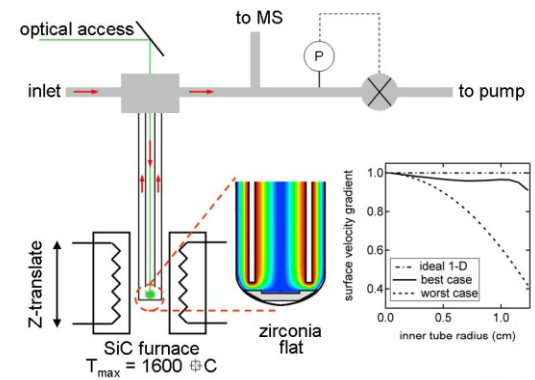
Computational Materials Science

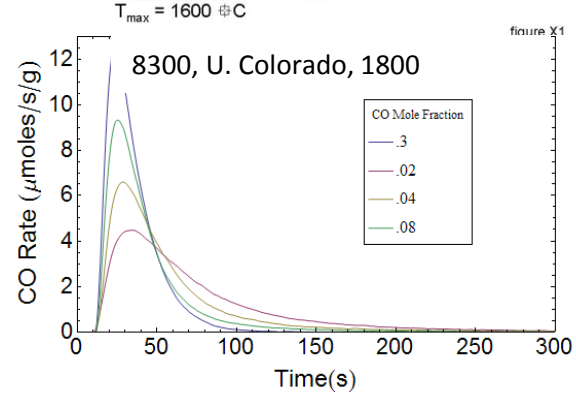


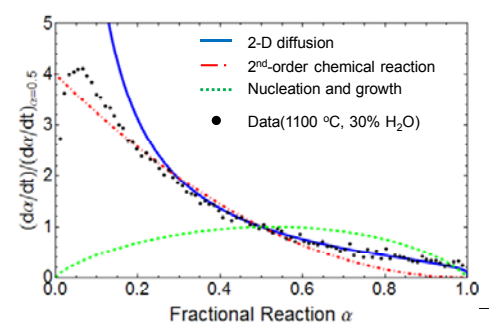


8600 in collaboration with Northwestern U.

Kinetics of Real & Model Systems

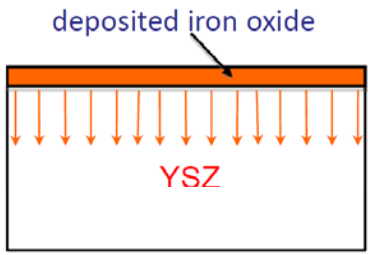


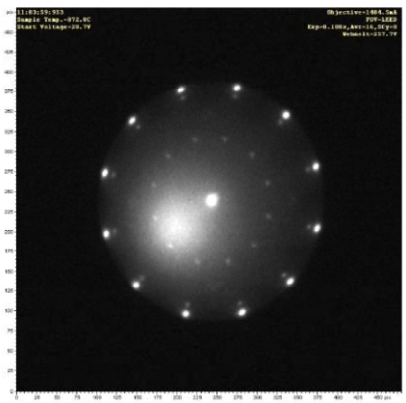




Materials Thrusts

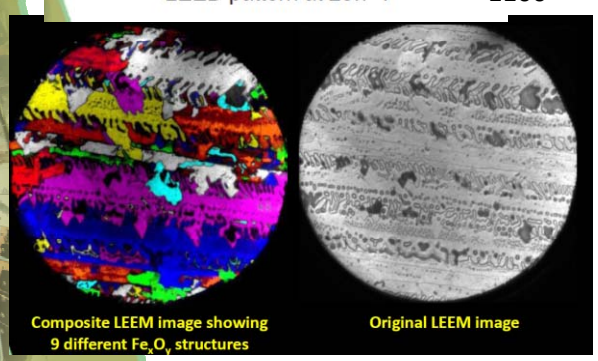
Surface Science



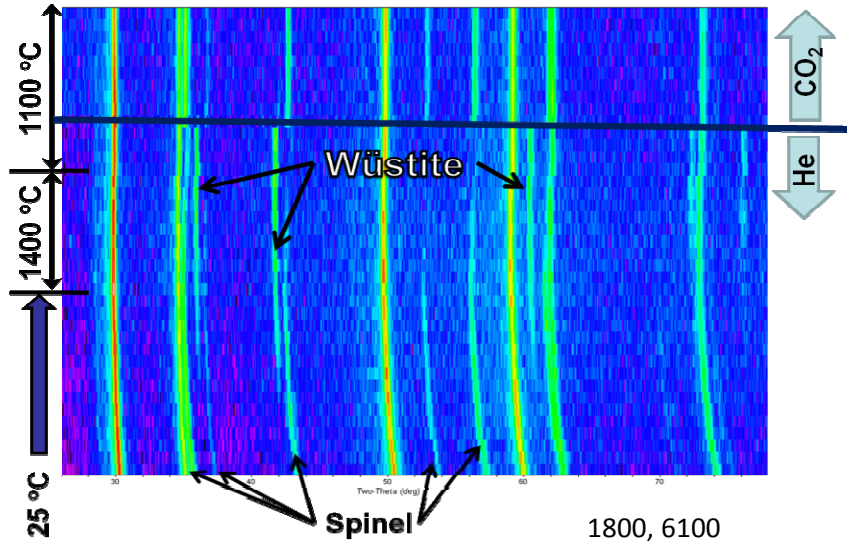


LEED pattern at 20.7 V

1100

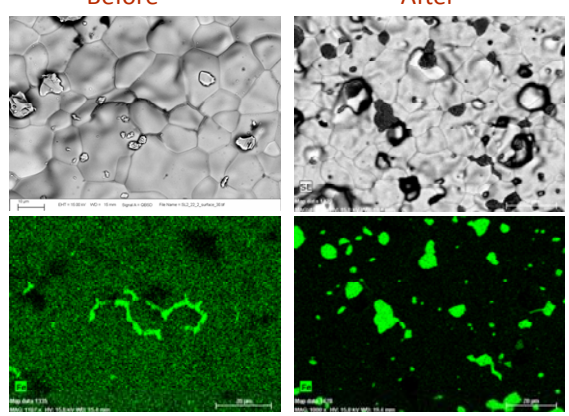


in situ, *ex situ* Characterization

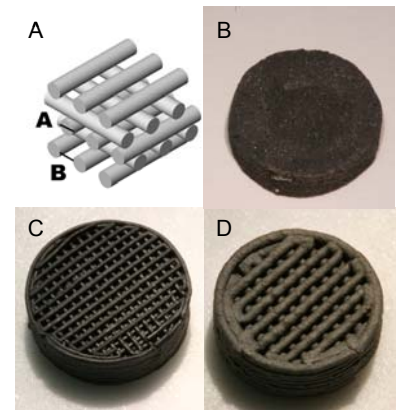


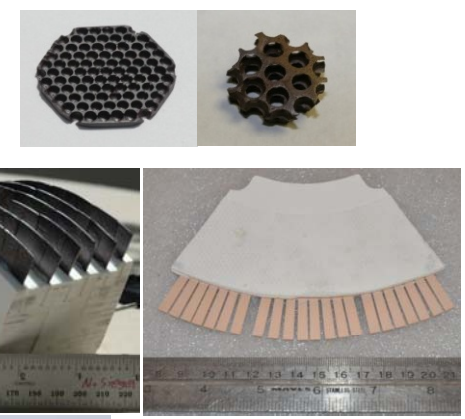
SEM of 10 wt.-% Fe_2O_3 /8YSZ before and after 3 thermochemical cycles (Ar/CO_2)

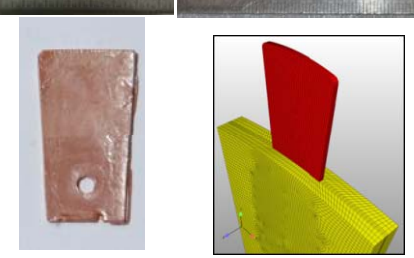
Before After



Fabrication and Testing





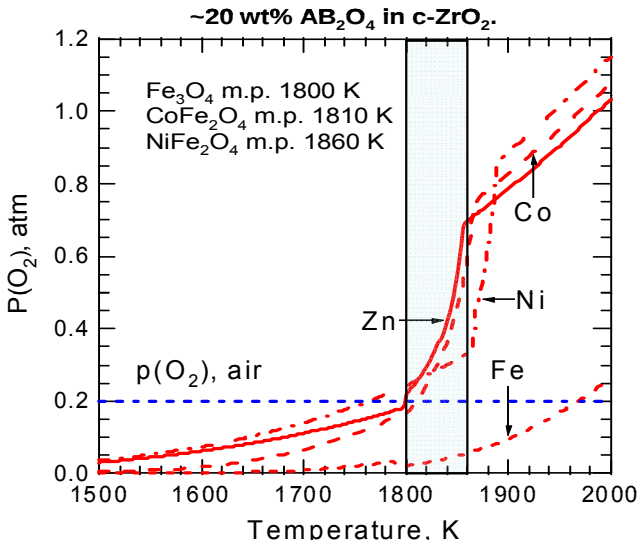


Ferrites as an Example

Idealized Chemistry

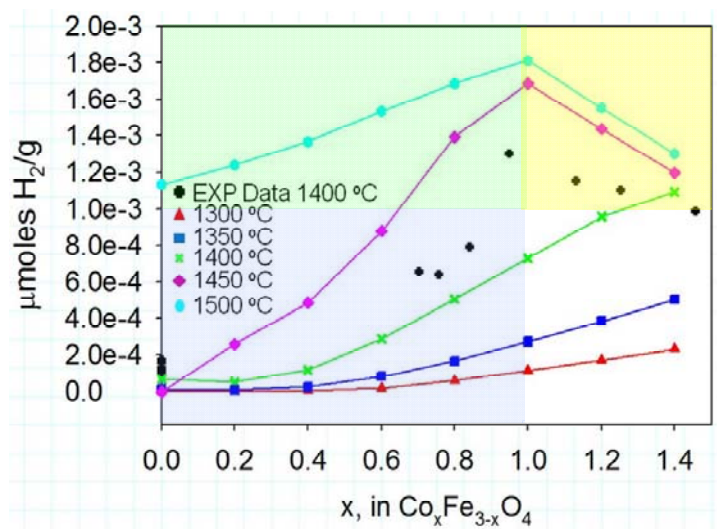
$$Fe_3O_4 \rightarrow 3FeO + \tfrac{1}{2} O_2$$

$$3FeO + H_2O \rightarrow Fe_3O_4 + H_2$$



Favorable temperature range (thermodynamics) can be manipulated via metal substitutions in Fe_3O_4. Useful, e.g., to shift operating temperatures below the melting point.

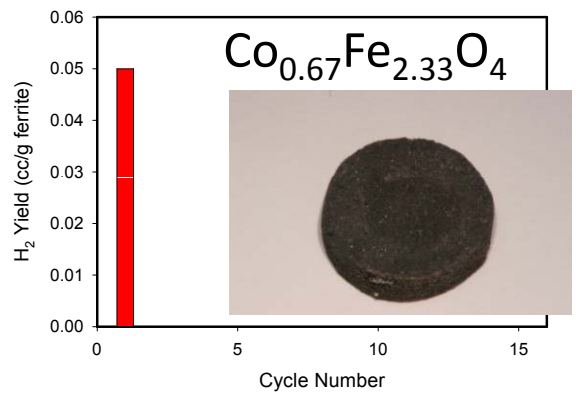
The effect of composition on gas yields can be predicted.



Modified Idealized Chemistry

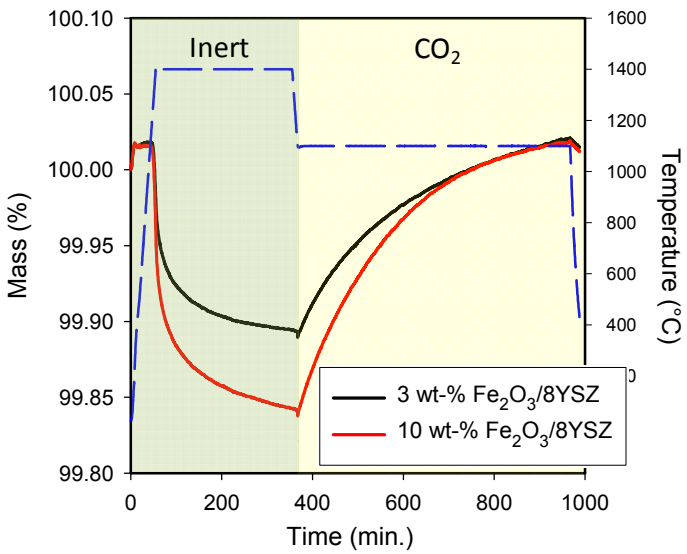
$$A_xFe_{2-x}O_4 \rightarrow 3A_{x/3}Fe_{(2-x)/3}O + \tfrac{1}{2} O_2$$

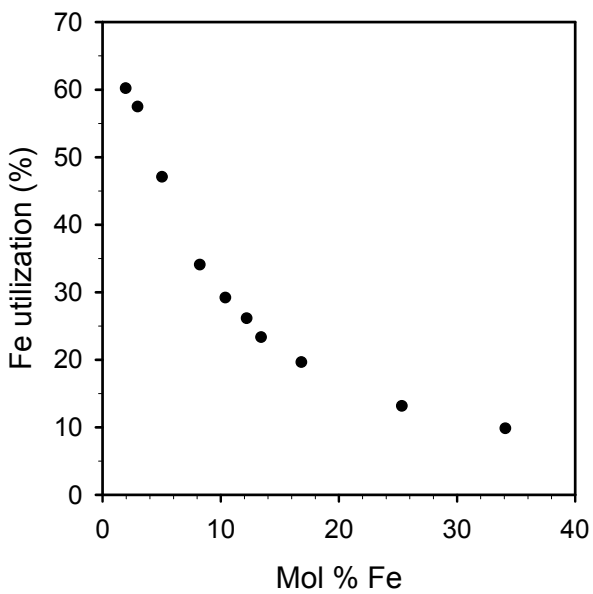
$$3A_{x/3}Fe_{(2-x)/3}O + H_2O \rightarrow A_xFe_{2-x}O_4 + H_2$$



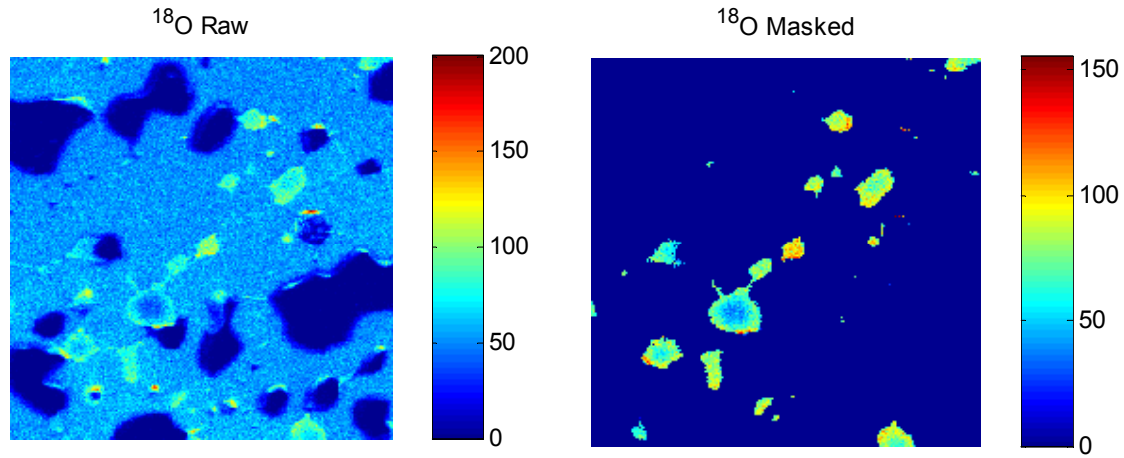
"Bulk" materials do not live up to their potential.

Monolithic Composites with YSZ are Cyclable – Why?

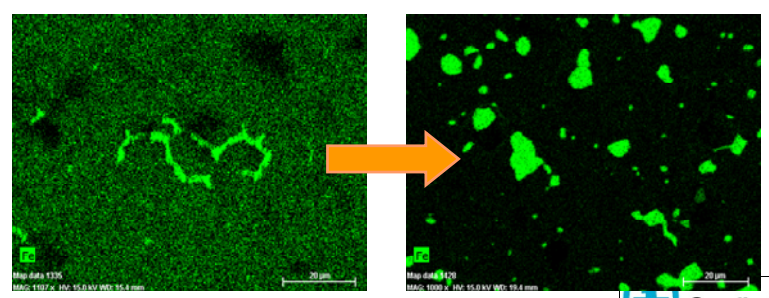




Beyond the solubility limit additional Fe contributes little to the overall gas yield.



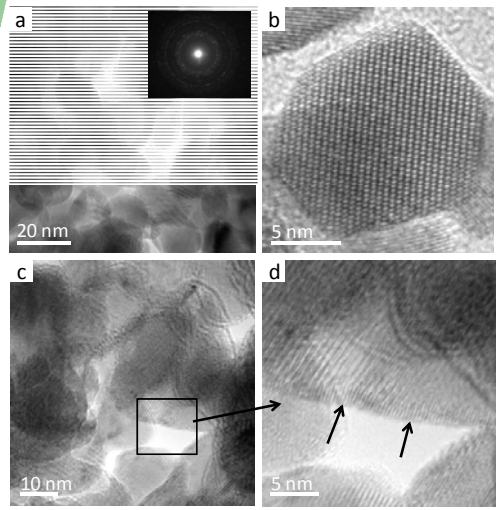
Reaction with ^{18}O-labelled CO_2 confirms limited utilization of bulk particles relative to Fe/YSZ.

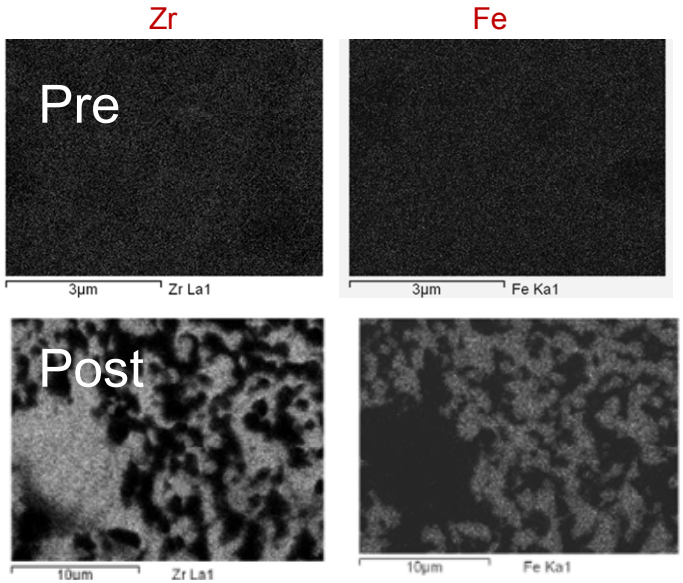


Fe EDS

Structured Ferrites?

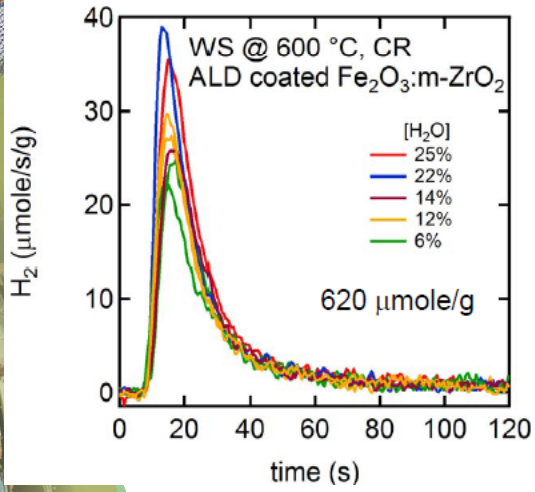
2 nm $CoFe_2O_4$ film after ALD synthesis



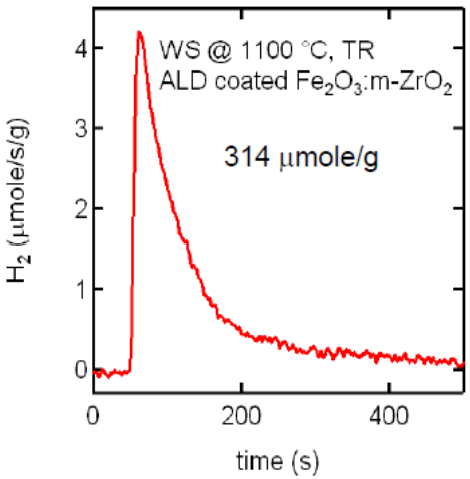


Development of a chemical reduction has allowed demonstration of rapid intrinsic kinetics for ferrites.

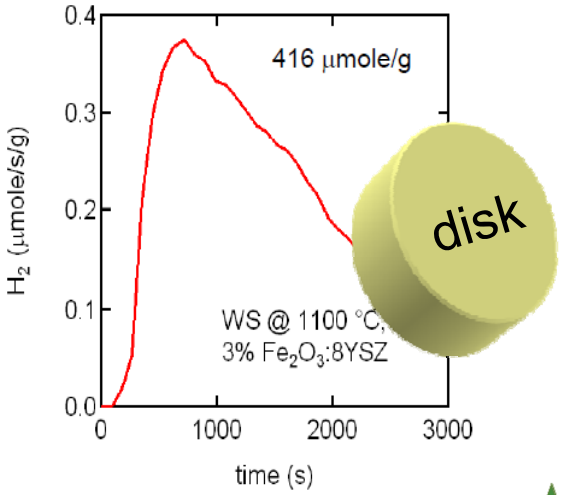
H_2 peak rates > 100x faster at 600 °C than Fe/YSZ at 1100 °C.



Chemically reduced ALD coated Fe:ZrO_2 nanoparticles

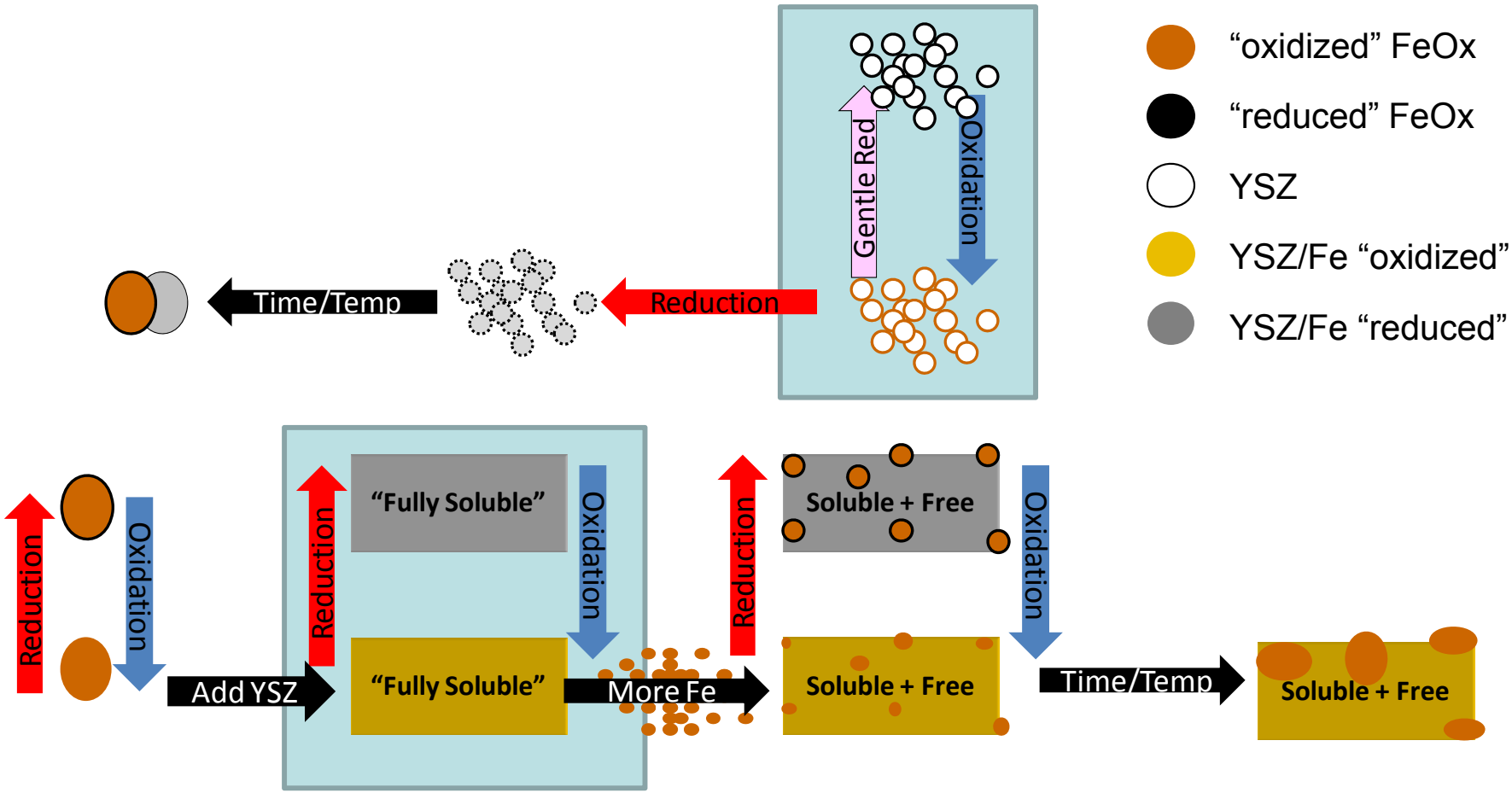


Thermally reduced ALD particles



Bulk Fe:YSZ

Ferrites Summary



Thank You
For Your Attention