Sunshine to Petrol

SAND2011-2553P

Materials for Sunshine to Petrol: Metal Oxides for Solar Fuels

Presented by:

James E. Miller

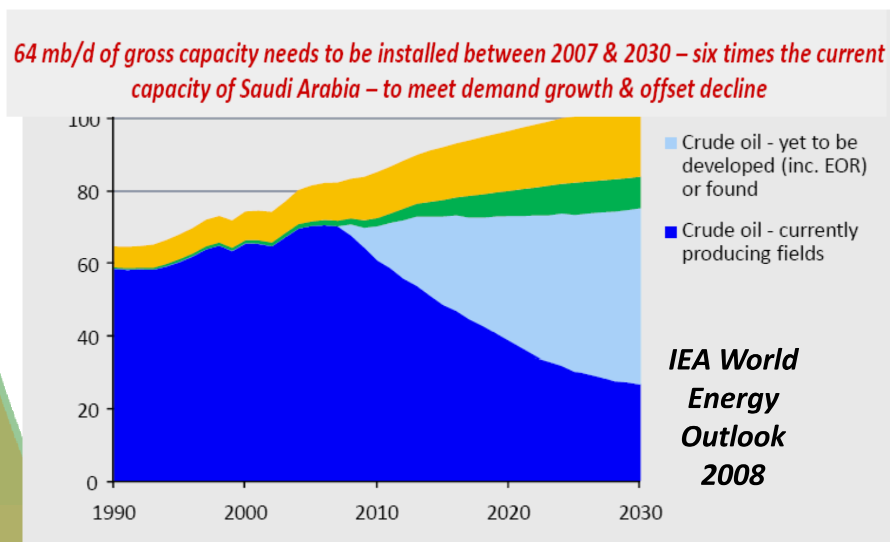
Sandia National Laboratories
Advanced Materials Laboratory
1001 University Blvd SE.
Albuquerque, NM 87106

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.

February 3, 2011

Assure Energy Security. Mitigate Climate Change Risk. Enhance Prosperity and Competiveness.

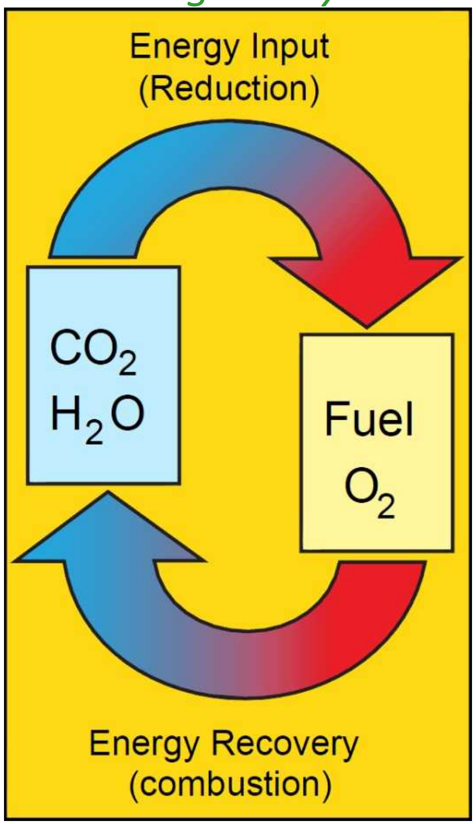
- *Energy consumption will continue to grow with development gains and population growth.*
- *Fossil fuels dominate energy picture and drive GHG emissions from energy sector.*
- *U.S. deeply dependent on foreign supplies of petroleum in the transportation sector.*
- *Energy and climate security are now a clear global priority.*



Significant resources will be expended even if we choose only to maintain the petroleum economy

Sunshine to Petrol

Closing the Cycle



For now and for transportation fuels, liquid hydrocarbons are the "Gold Standard"

Vision: Directly apply a solar thermal energy source to effectively reverse combustion and "energize" CO_2 and H_2O into hydrocarbon form in a process analogous to, but more efficient than, the one that produces bio- and fossil fuels, therefore achieving many of the benefits of hydrogen while preserving the advantages of the Hydrocarbon Economy.

$$\text{Sunlight} + CO_2 + H_2O \rightarrow \text{Fuel} + O_2$$

Direct Chemical Routes?

Capitalize on decades of Synfuel technology, e.g.

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

Focus on the following critical conversions:

$$4H_2O + \text{energy} \rightarrow 4H_2 + 2O_2 \text{ (water splitting)}$$

$$2CO_2 + \text{energy} \rightarrow 2CO + O_2 \text{ (carbon dioxide splitting)}$$

$$2CO_2 + 4H_2O + \text{energy} \rightarrow 2CO + 4H_2 + 3O_2$$

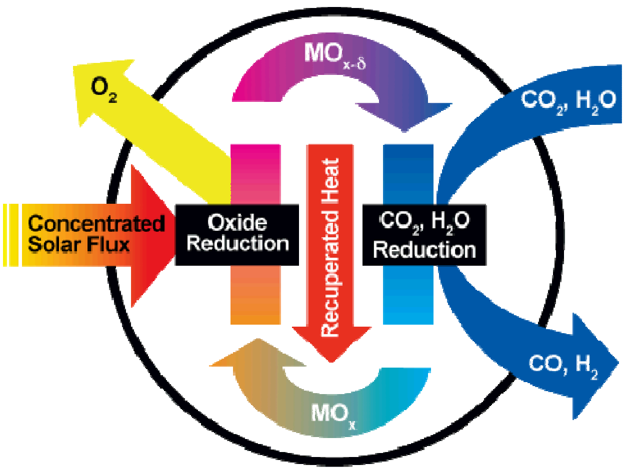
Note that WS and CDS are linked by the Water Gas Shift reaction

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

We are only <u>required</u> to carry out one reaction - WS or CDS

Direct Utilization of Thermal Energy

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



<u>*Without Recuperation*</u>

max efficiency = 36%

<u>*With Recuperation*</u>

max efficiency = 76%

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

In our case, the "working fluid" is a metal oxide (Ce- or Fe-based.)

High end temperatures of ~1500°C couple best with CSP.

Efficiency gains are possible as conversion to mechanical work and electricity are avoided.

Thermodynamics requires reactions be carried out at two temperatures.

Sunshine to Petrol

The CR5 is an Enabling Approach to Thermochemistry

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

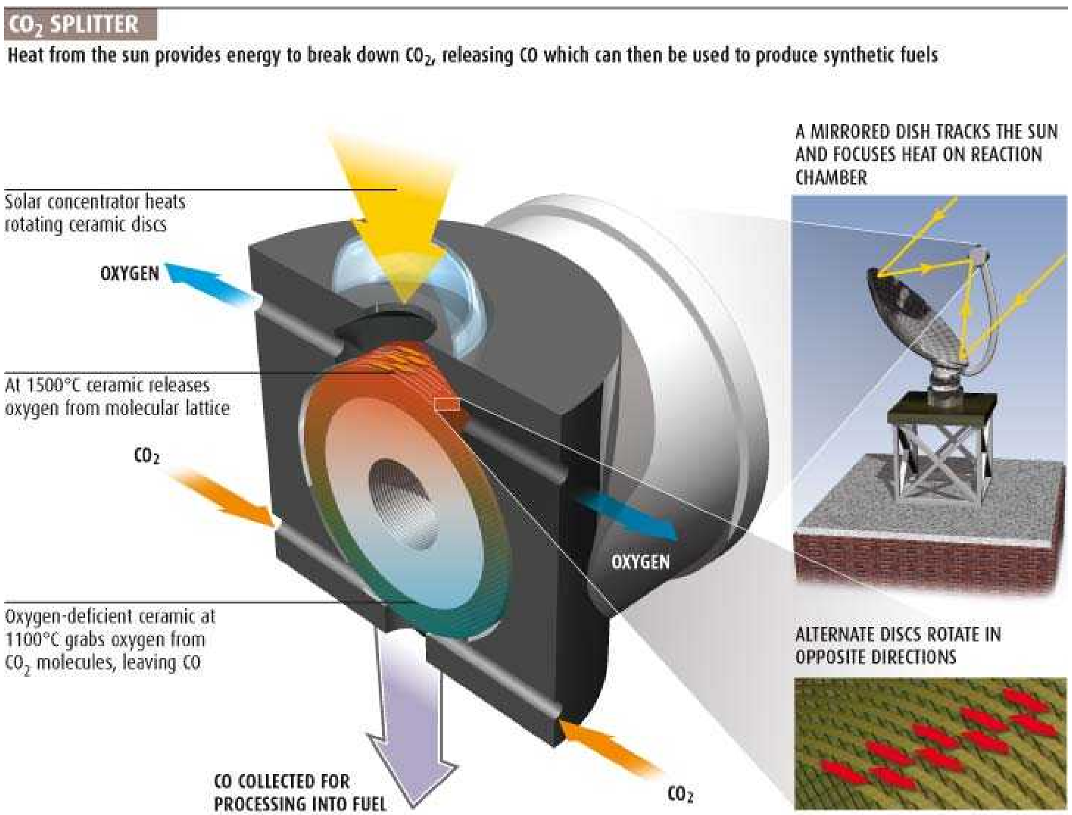
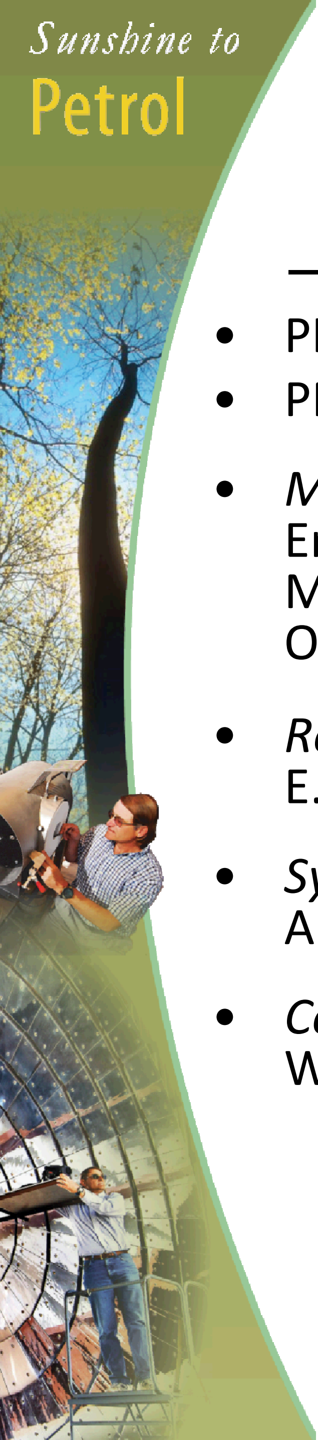


Figure Credit: Popular Science

Enabling Attributes:

- Continuous flow
- Spatial product separation
- Thermal Recuperation

"Reactorizing a Countercurrent Recuperator"



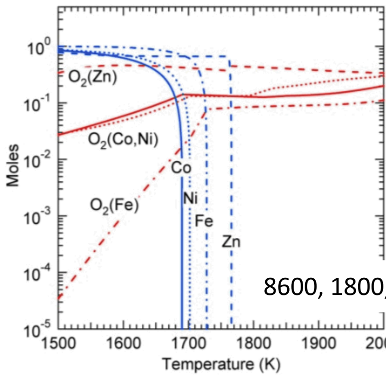
Success Built on an End to End Approach

- PI: James E. Miller
- PM: Ellen B. Stechel
- *Materials and Chemistry Focus:* James E. Miller, Andrea Ambrosini, Eric N. Coker, Mark A. Rodriguez, Gary L Kellogg, Ivan Ermanoski, Mark D. Allendorf, Anthony H. McDaniel, Terry J. Garino, Tony Ohlhausen
- *Reactor and Engineering Focus:* Richard B. Diver, Nathan P. Siegel, Roy E. Hogan, Ken S. Chen
- *Systems Engineering and Separations Focus:* Daniel E. Dedrick, Terry A. Johnson, Gregory H. Evans, Chad L. Staiger
- *Collaborations with:* Northwestern University, University of Wisconsin, Texas Tech University, and University of Colorado

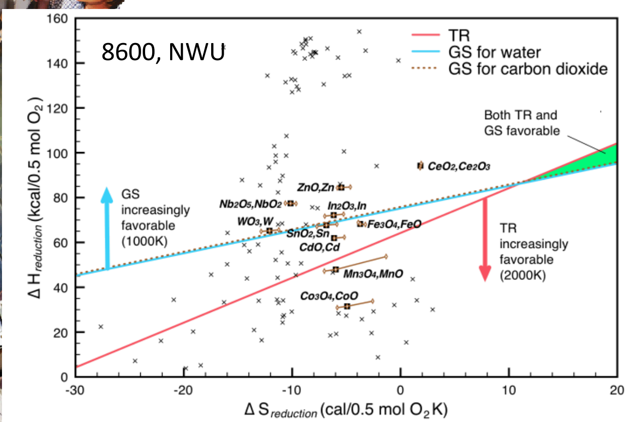
The Materials Focus supports the Engineering activities through the creation, production, and characterization of active materials and builds the science basis for the next generation of thermochemical materials.

Materials Thrusts

Thermodynamics

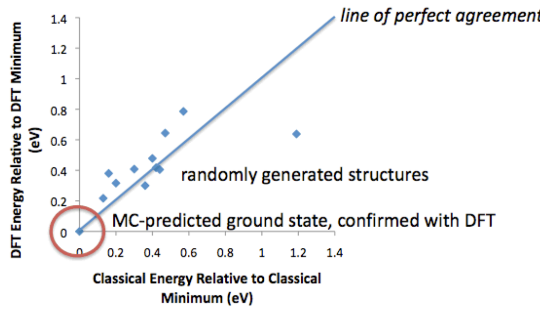


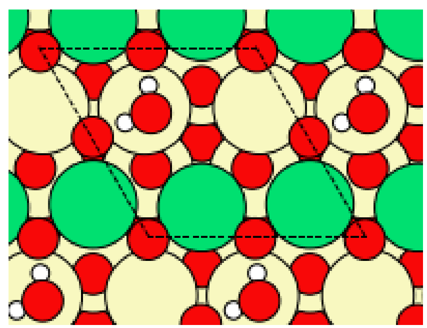
Energy & Fuels, **22** (2008), 4155



Physical Review B 80, 245119 (2009).

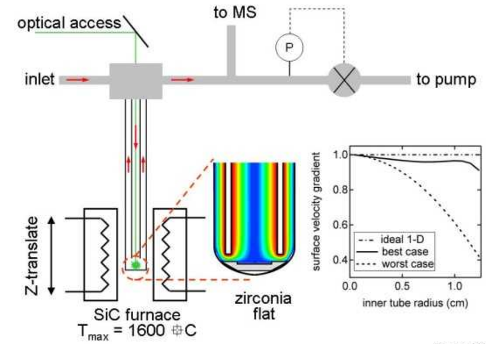
Computational Materials Science

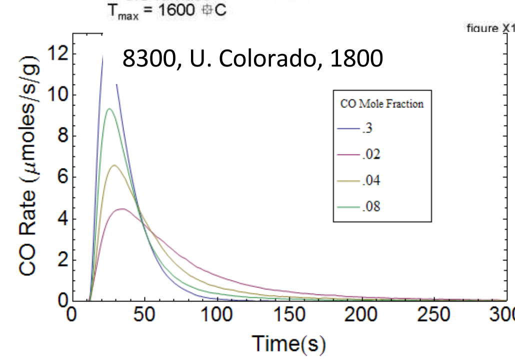


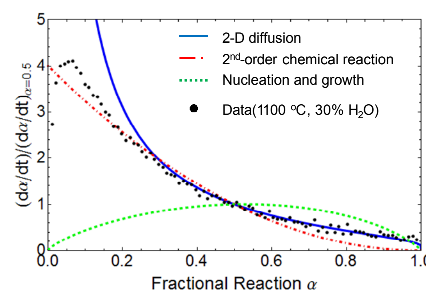


8600 in collaboration with Northwestern U.

Kinetics of Real & Model Systems

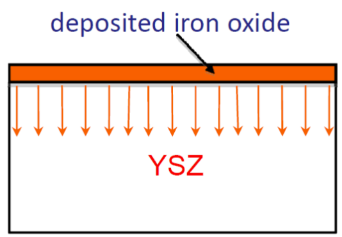


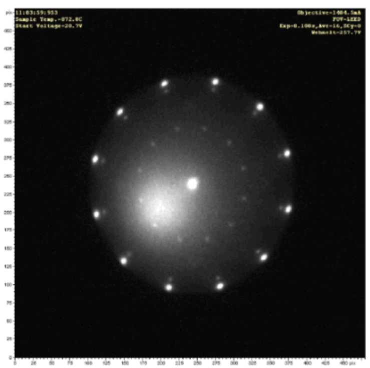




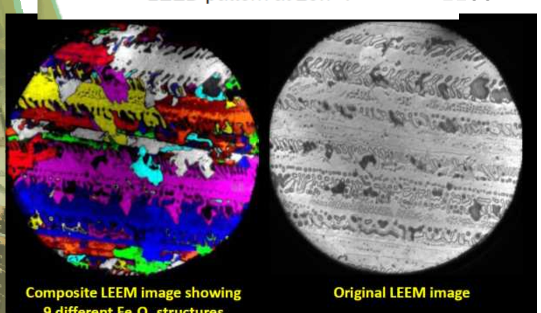
Materials Thrusts

Surface Science

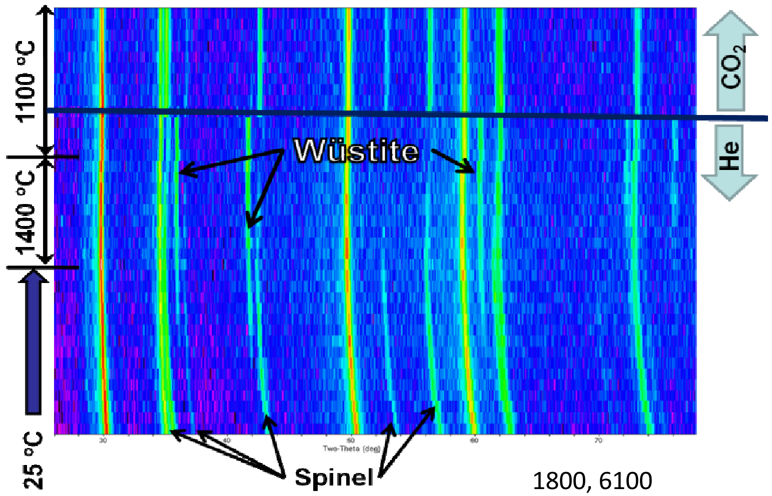




LEED pattern at 20.7 V 1100



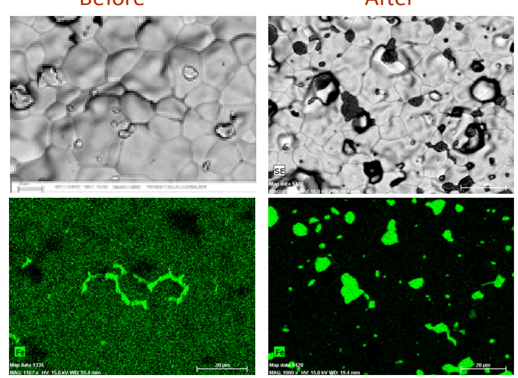
in situ, *ex situ* Characterization



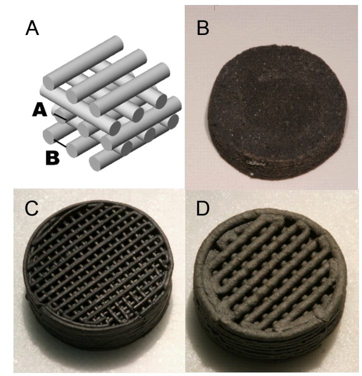
1800, 6100

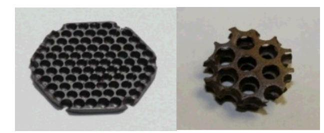
SEM of 10 wt.-% Fe_2O_3 /8YSZ before and after 3 thermochemical cycles (Ar/CO_2)

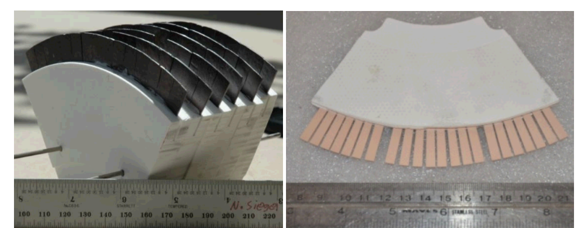
Before After

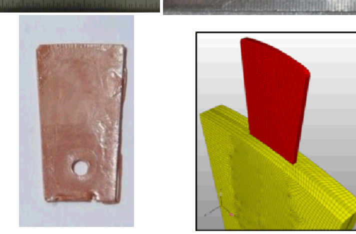


Fabrication and Testing







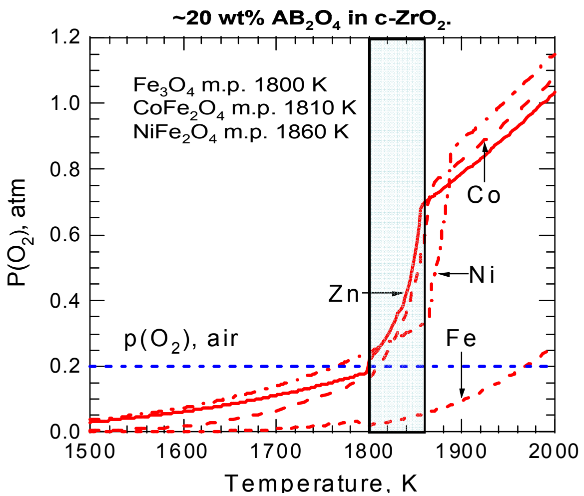


1800, 6100, 1500

Ferrites as an Example

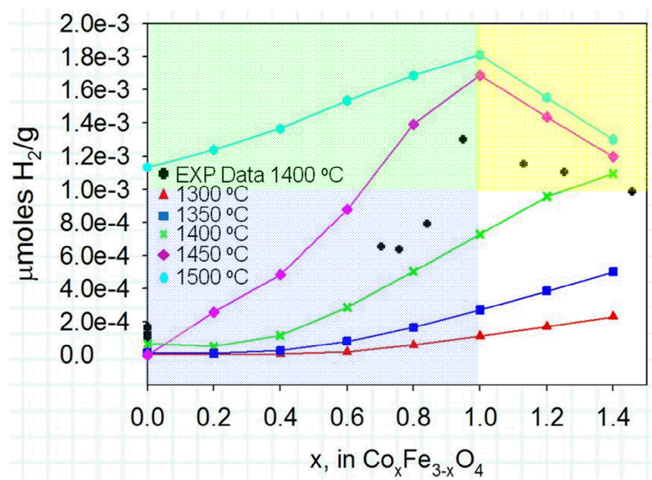
Idealized Chemistry

$$Fe_3O_4 \rightarrow 3FeO + \frac{1}{2} O_2$$
$$3FeO + H_2O \rightarrow Fe_3O_4 + H_2$$



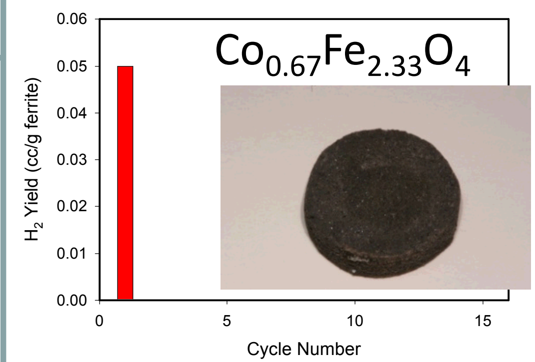
Favorable temperature range (thermodynamics) can be manipulated via metal substitutions in Fe_3O_4. Useful, e.g., to shift operating temperatures below the melting point.

The effect of composition on gas yields can be predicted.



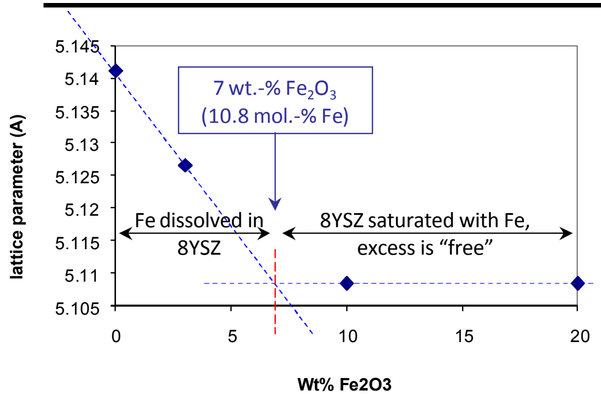
Modified Idealized Chemistry

$$A_xFe_{2-x}O_4 \rightarrow 3A_{x/3}Fe_{(2-x)/3}O + \frac{1}{2} O_2$$
$$3A_{x/3}Fe_{(2-x)/3}O + H_2O \rightarrow A_xFe_{2-x}O_4 + H_2$$

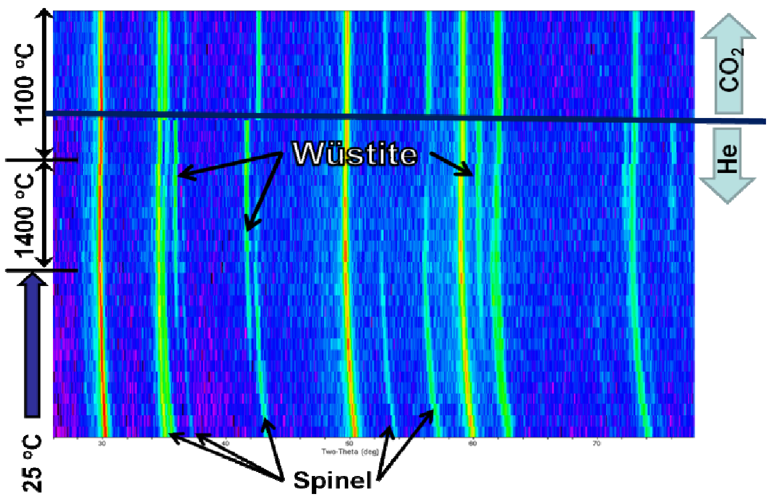


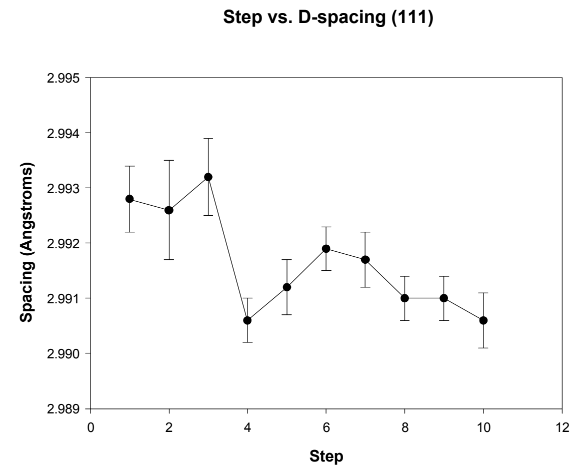
"Bulk" materials do not live up to their potential.

Monolithic composites with YSZ are cyclable – Why?



- Fe is soluble in 8YSZ
- Solubility is a function of both temperature and oxidation state.





In situ observation of phases and 8YSZ lattice parameters reflect complex migration of Fe in/out of solid solution.

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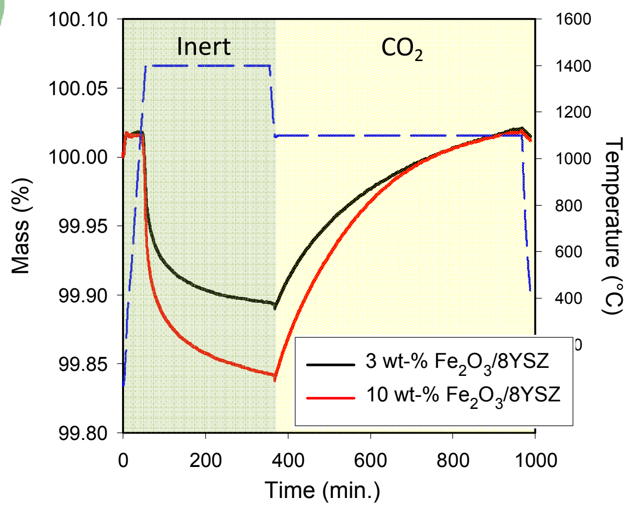
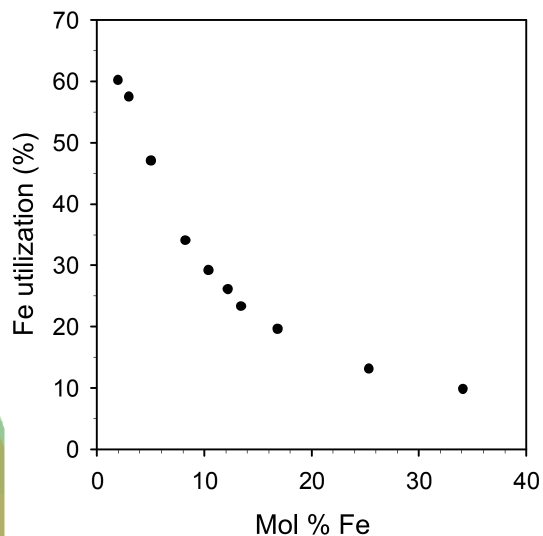
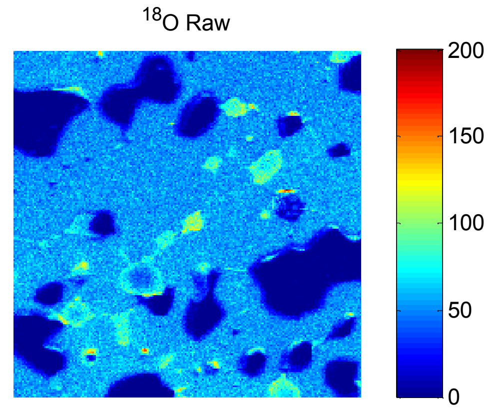
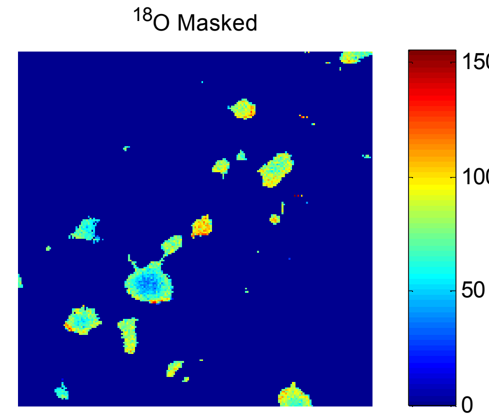
Monolithic composites with YSZ are cyclable – Why?



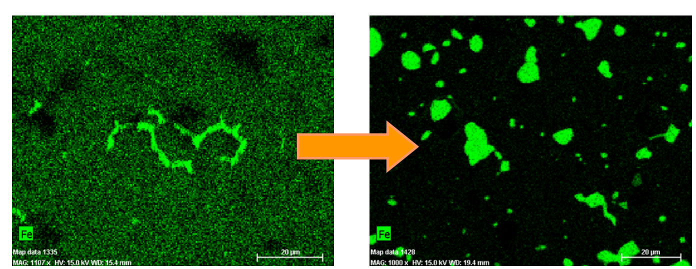


Beyond the solubility limit additional Fe contributes little to the overall gas yield.





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



Fe EDS

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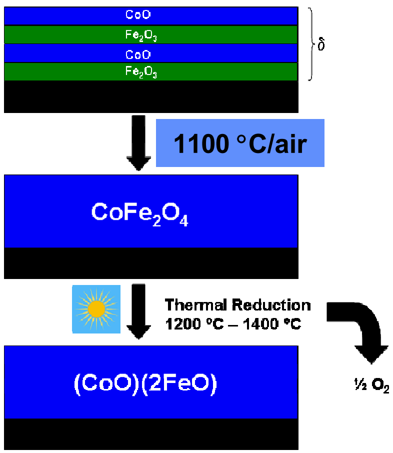
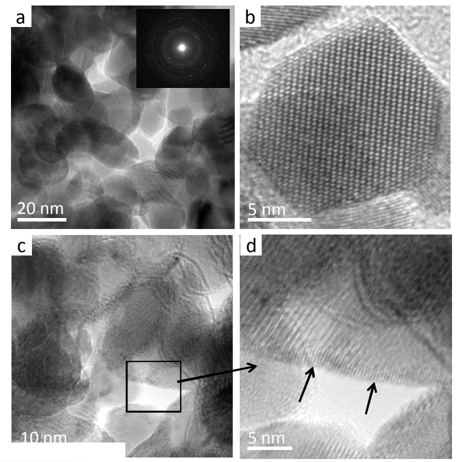
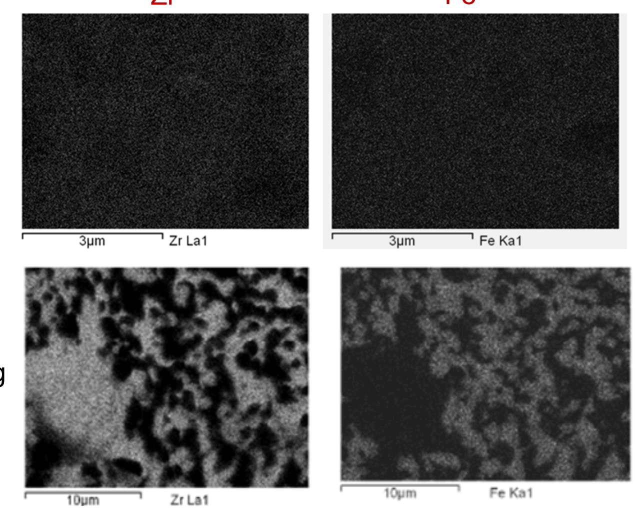
Structured Ferrites?

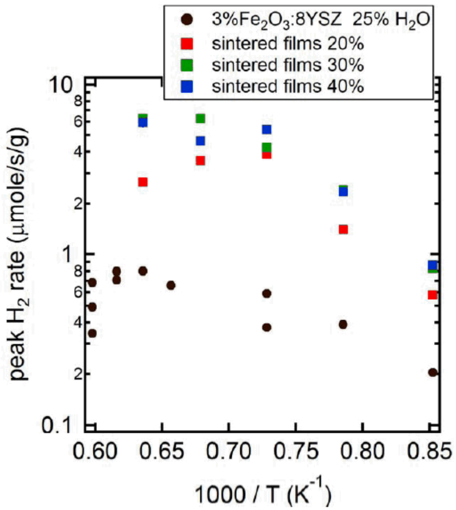


2 nm $CoFe_2O_4$ film after ALD synthesis



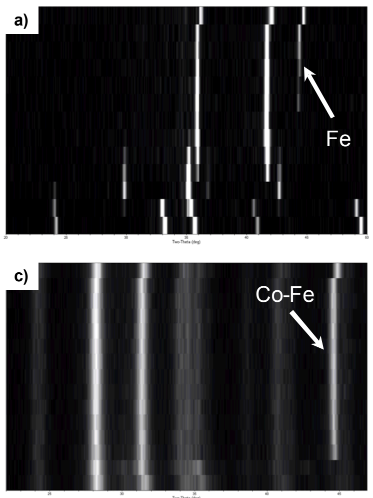
Phase Segregation





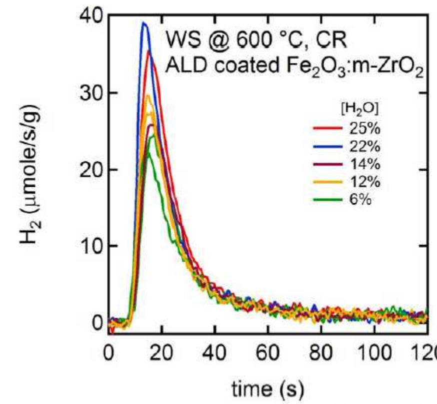
Aside from a higher surface area, after thermal reduction,
ALD films are chemically and physically similar to sintered structures.

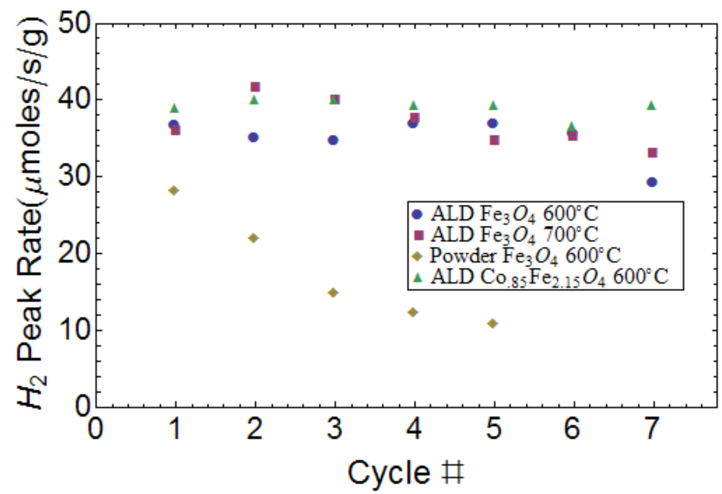
Structured Ferrites?



In situ XRD spectra of samples reduced in 1% H_2 / 1% CO_2 in He (500 sccm total) at 600 °C.

a) a- Fe_2O_3 nanoparticles
b) b) Fe_2O_3 on m-ZrO_2 (ALD/20.2% mass loading)
c) c) $Co_{0.85}Fe_{2.5}O_4$ on m-ZrO_2 (ALD/19% mass loading)

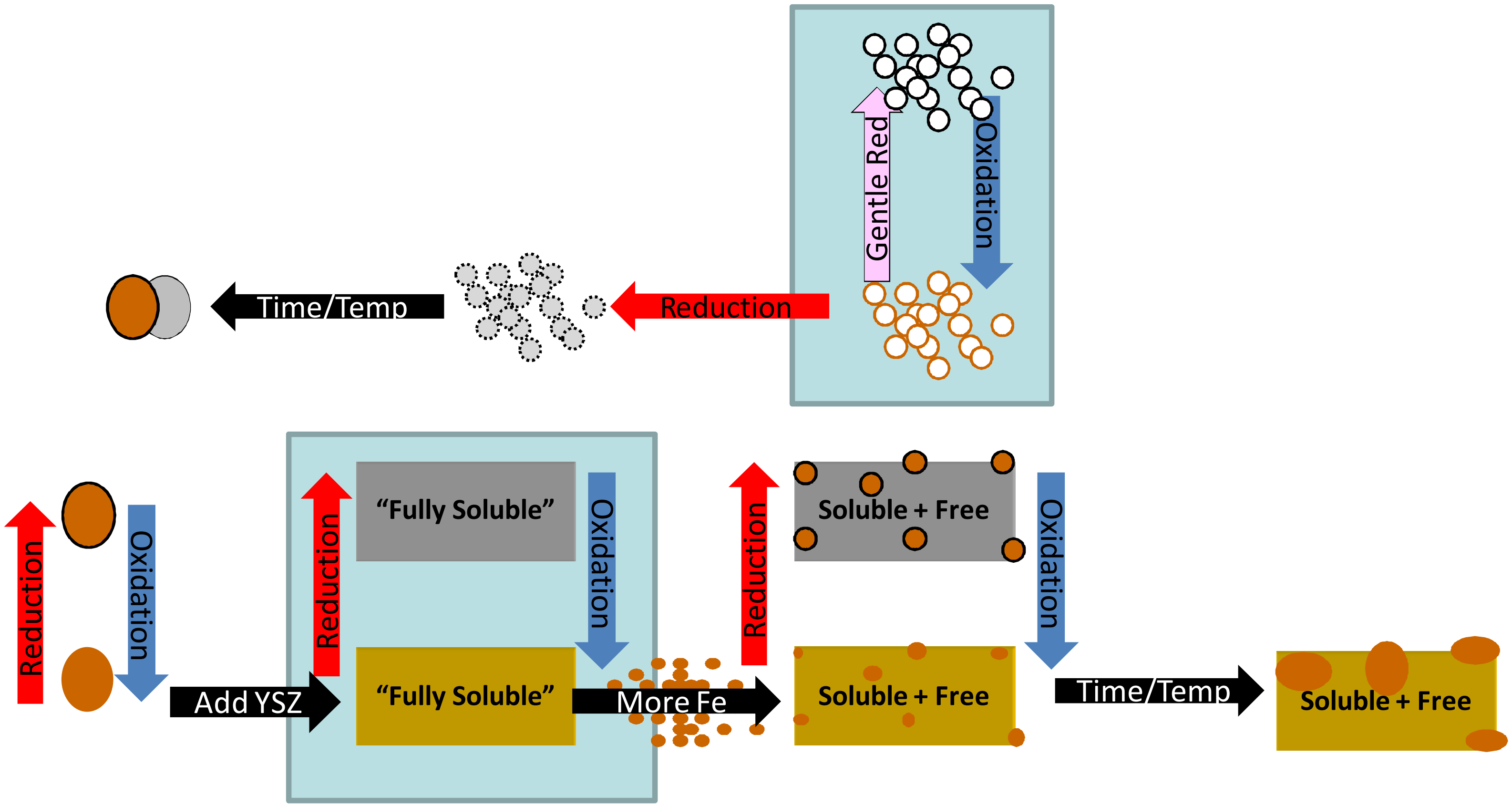




Development of a chemical reduction has allowed demonstration of rapid intrinsic kinetics for ferrites.

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

Ferrites Summary



Project Summary

Some Major Accomplishments:

- Demonstrated key operating features of the CR5 on-sun
  - continuous production of O_2 and CO from CO_2
  - recovery of O_2 and CO in separate streams
  - control over two distinct operating regions & temperatures
- Developed, for the first time, an in depth understanding of the dynamic Ferrite/YSZ composite system.
- Established credibility of high efficiency direct paths for solar fuels

Principal Goal for Remainder of the Year:

- Continuous steady state production of fuel intermediates at an average of at least 2% efficiency (chemical out/solar in).

Next?

- Apply lessons of materials science to design and development of next generation of materials.
- Design /development of next generation reactor/system (η=5 $\rightarrow$25%)
- Sustained resources on the decade time scale
- >10% full-system life-cycle sunlight-to-fuel efficiency