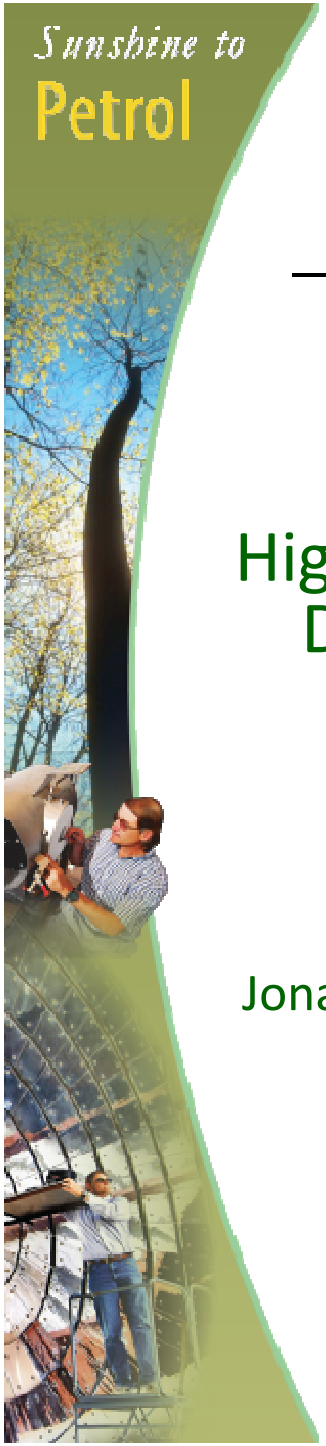


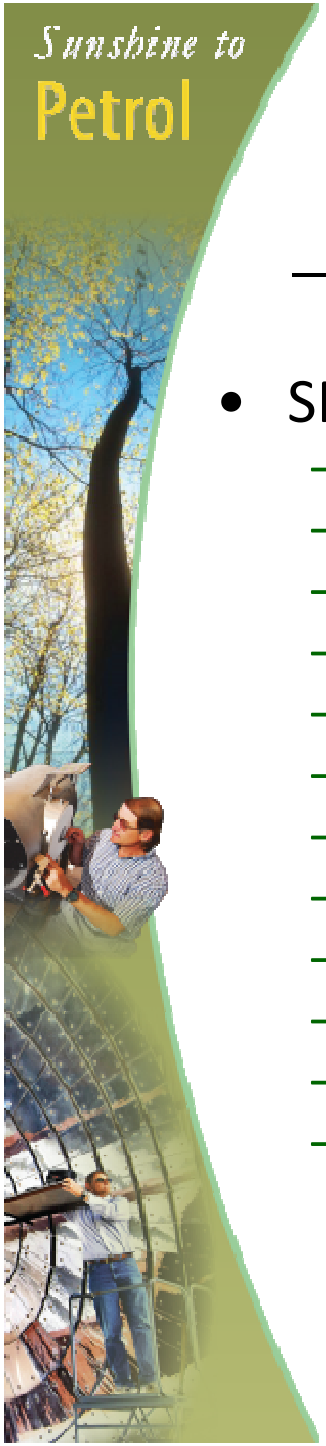
SAND2011-6244C

High Temperature Splitting Of Water And Carbon Dioxide Using Complex Oxides As A Route To Solar Fuels

Presented by Anthony McDaniel

Jonathan Scheffe, Victoria Aston, Darwin Arifin, Eric N. Coker, James Miller, Mark D. Allendorf, and Alan W. Weimer

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.



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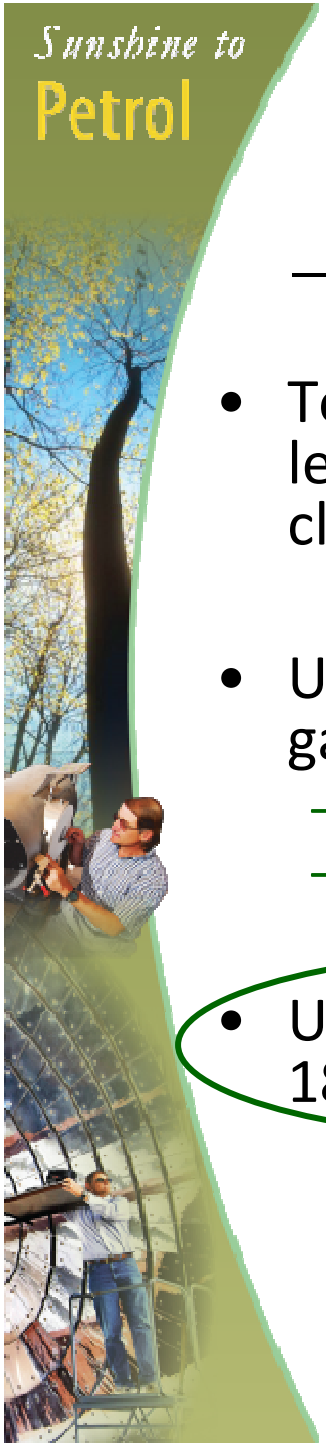


Energy security and climate change are intertwined

- To "stabilize" global CO_2 levels need > 10 TW of clean energy by 2050.
- US consumes 378 million gallons per day gasoline.
  - 0.58 TW annual average
  - Petroleum imports > 50%
- US land solar resource > 1800 TW.

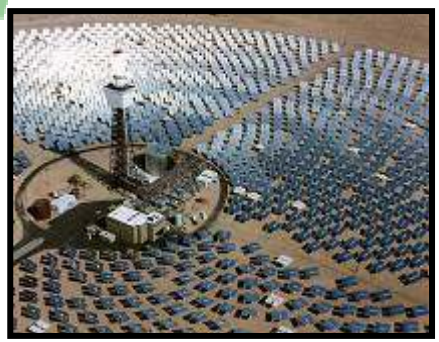
Leading Petroleum Importers in 2003 (mbpd*)	
United States	11.2
Japan	5.5
Germany	2.5
China	2.0
Leading Exporters	
Persian Gulf	18.7
Russia	5.5
Norway	3.3
Venezuela	2.2

*millions of barrels per day

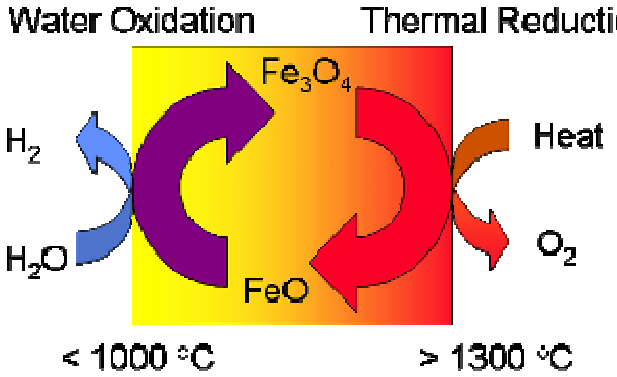
Roger Doyle, *Scientific American*, Sept. 2004.

Sunshine to Petrol

Concentrated solar power and thermochemical cycles



"no bugs, no wires"... and no membranes



$$MO_x \xleftrightarrow{+\Delta} MO_{x-\delta} + \frac{\delta}{2} O_2 \quad \text{TR}$$

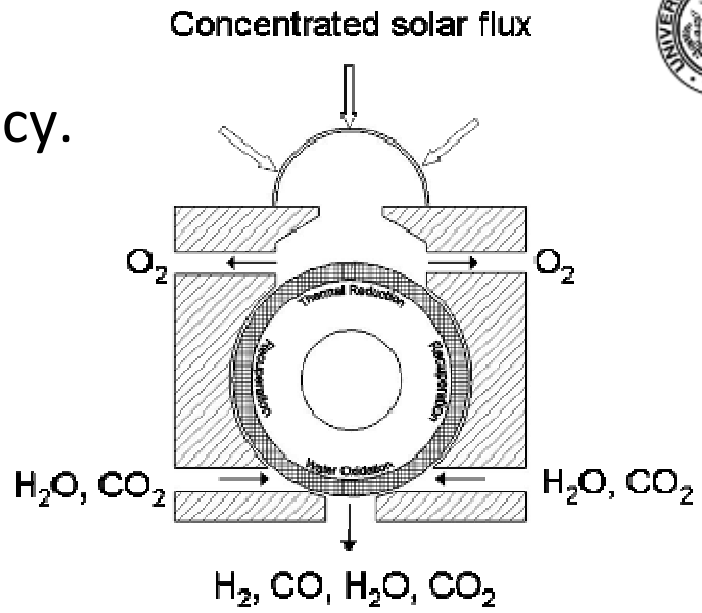
$$MO_{x-\delta} + H_2O \xleftrightarrow{-\Delta} MO_x + \delta H_2 \quad \text{WS}$$

- Concentrate solar energy using conventional technology.
  - 1000 suns = 100 W/cm^2
- Thermochemistry is a promising alternative to bio-fuels, PV-based electrolysis, photo-catalysis, or artificial photosynthesis.
  - Efficiency, simplicity, scalability
  - Dish Stirling engine currently holds world-record for peak efficiency (31.25% net solar-to-electric)

Sunshine to Petrol

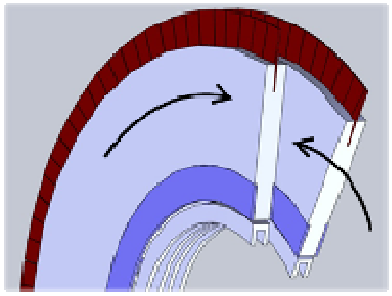
Key attributes of Sandia CR5 concept reactor

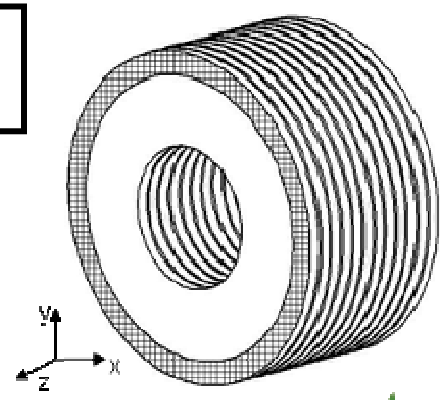
- Needed to achieve high efficiency.
  - Continuous operation on-sun.
  - Direct solar absorption.
  - Sensible energy recovery.
  - Minimal work input.
  - Intrinsic separation of products
    - H_2/CO from O_2



heat recuperation key to high efficiency

Design challenge to effectively balance incident solar flux, redox kinetics, and heat recuperation to yield an efficient thermochemical conversion cycle



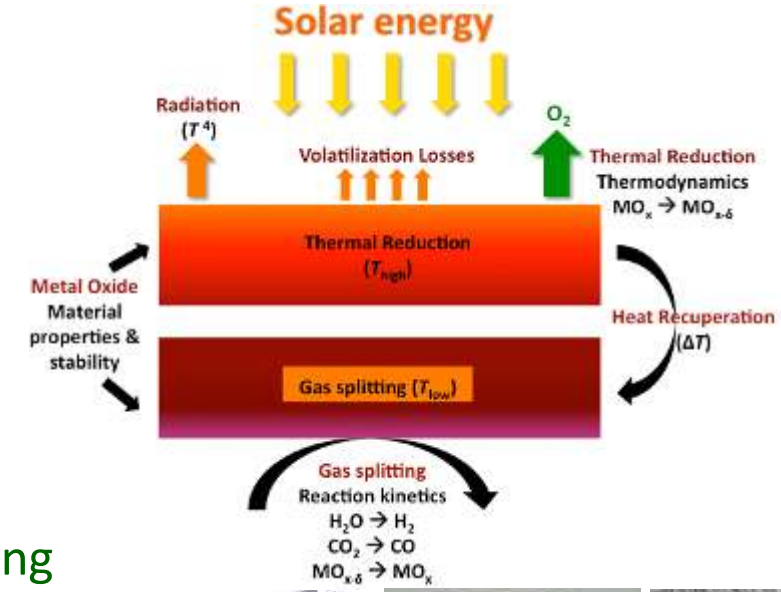


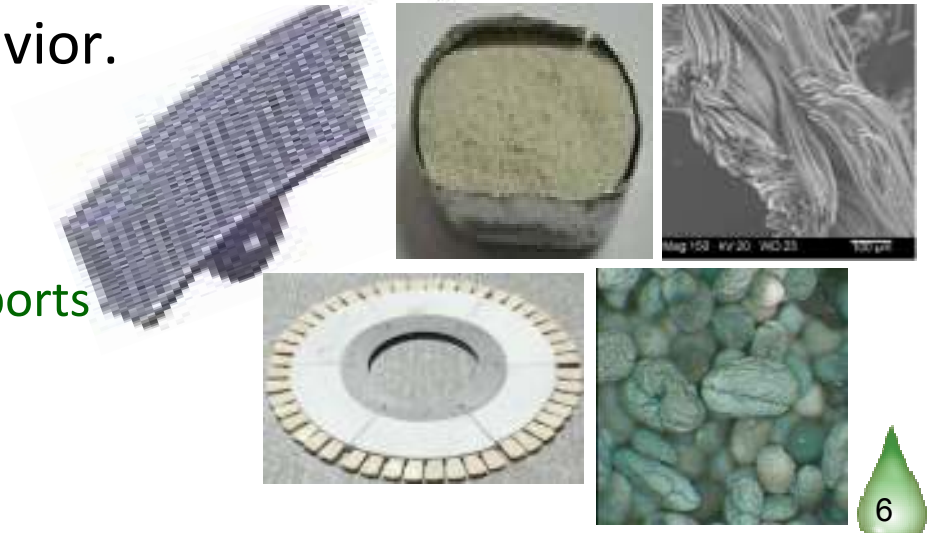
Counter-Rotating-Ring Receiver/Reactor/Recuperator (CR5)

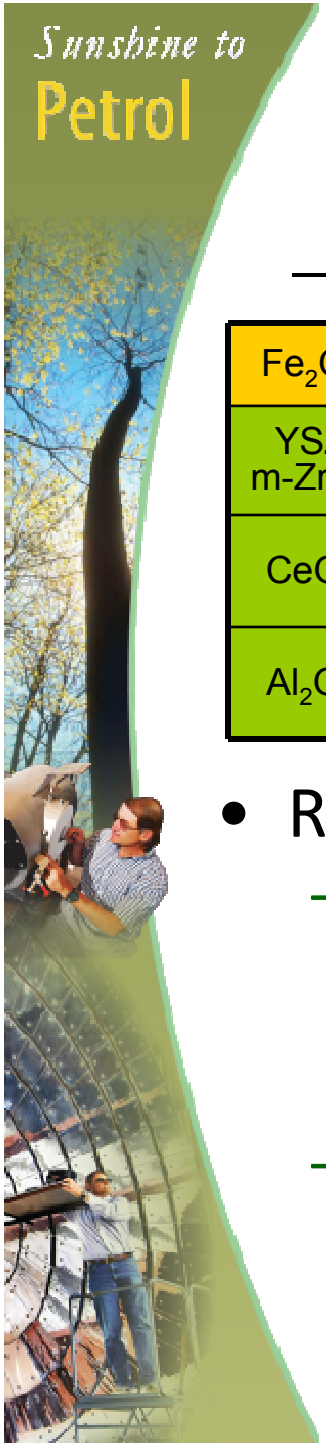
Sunshine to Petrol

Non-volatile metal oxide reactive structures

- Basic considerations.
  - Chemical composition
  - Macroscopic structure
    - Sunlight penetration
    - Gas transport
  - Microstructure
    - Reactive surface area
  - Structural stability and loading
- Understand complex behavior.
  - Surface/bulk reaction
  - Solid phase transport
    - Ionic species
  - Effects of dopants and supports
    - Reactivity/compatibility







Material systems currently under investigation

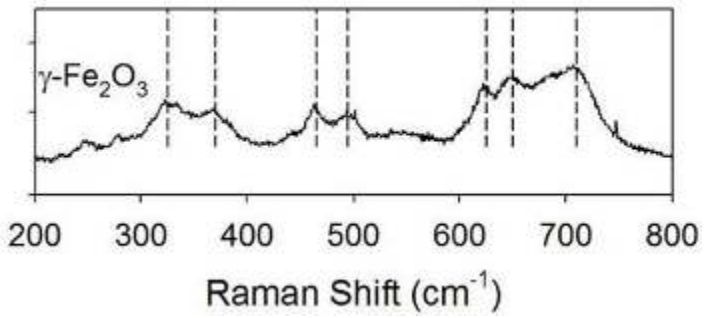
Fe_2O_3	$CoFe_2O_4$	MO_x:$CeO_{2-\delta}$	$La_{1-x}Sr_xCr_{1-y}Mn_yO_{3-\delta}$	
			X	Y
YSZ m-ZrO_2	m-ZrO_2	10 mol% Mn, Ni, Co, Mo, & Fe	0.9 0.8 0.7 0.6 0.5	0.5
CeO_2				
Al_2O_3	Al_2O_3			

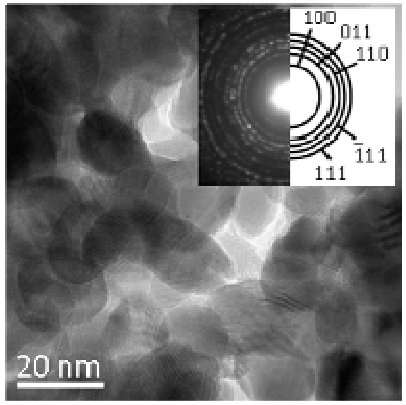
- Redox cycle chemistries.
  - Chemical systems
    - $M^{+n}/M^{+(n+1)}$ redox couples
    - $MO_{n-\delta}$ non-stoichiometric oxides
    - CU “hercynite”
  - Supports
    - m-ZrO_2, YSZ, CeO_2, Al_2O_3

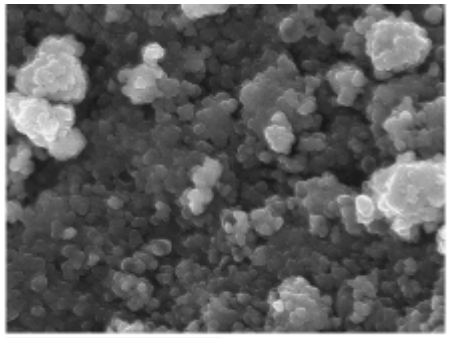
chemical and/or physical modification required to achieve performance goals

Sunshine to Petrol

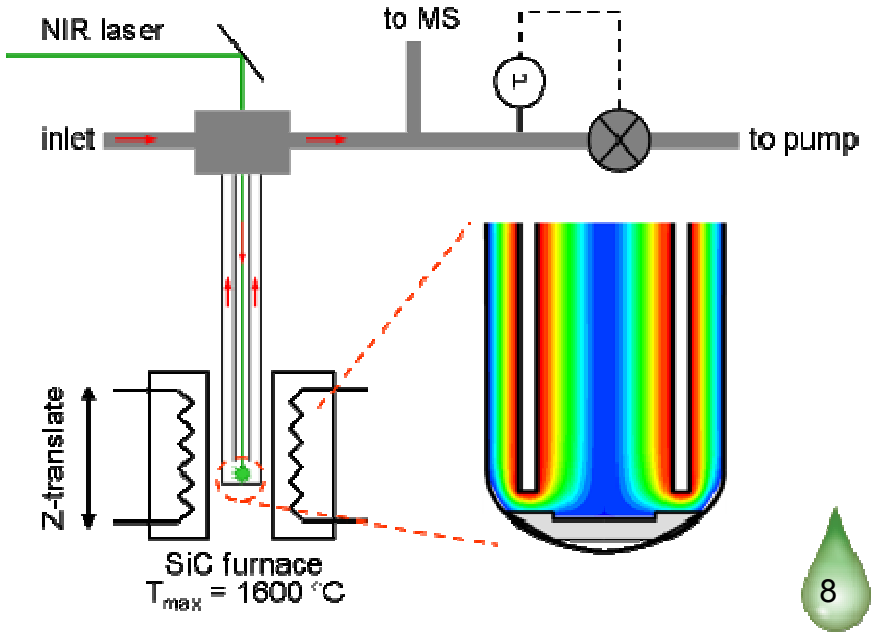
Experimental approach







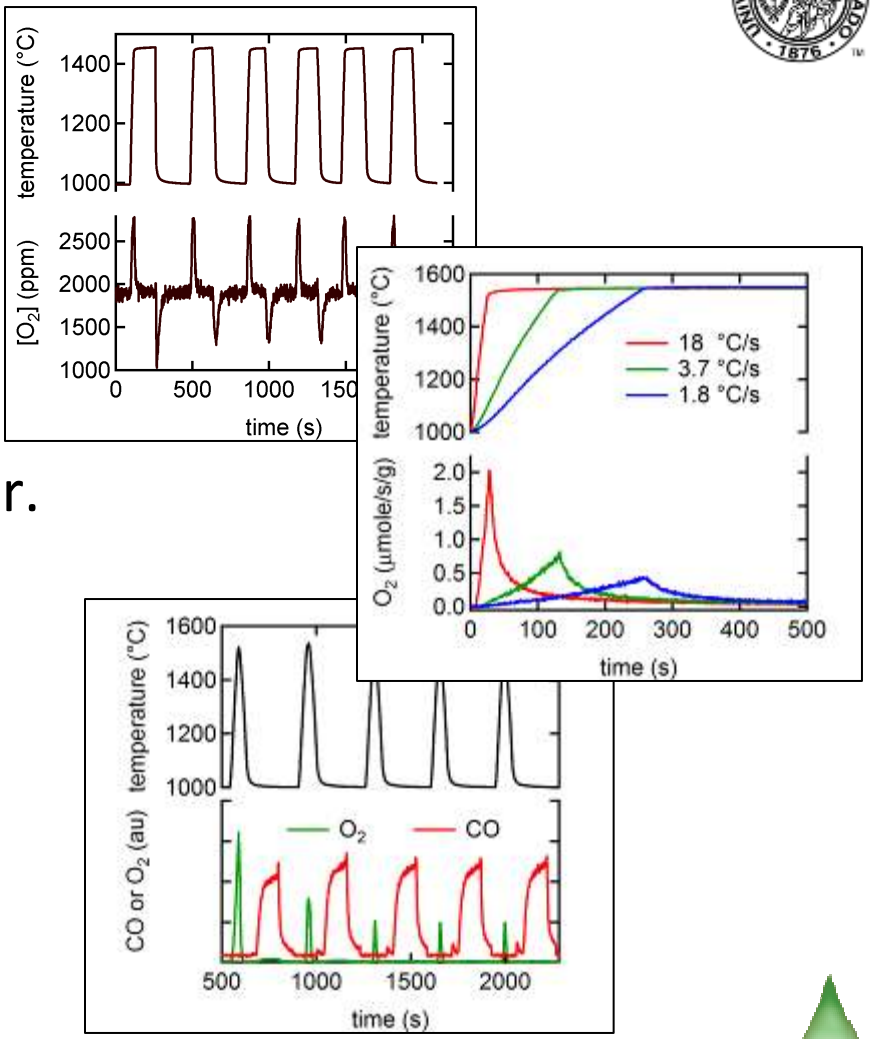
- Material properties.
  - BET surface area
  - SEM-EDX, TEM-EELS, XRD
- Surface analysis.
  - Surface Raman, XPS
- Kinetic measurements.
  - Stagnation flow reactor
    - 500 W CW NIR laser heating
    - Modulated beam mass spectrometer



Sunshine to Petrol

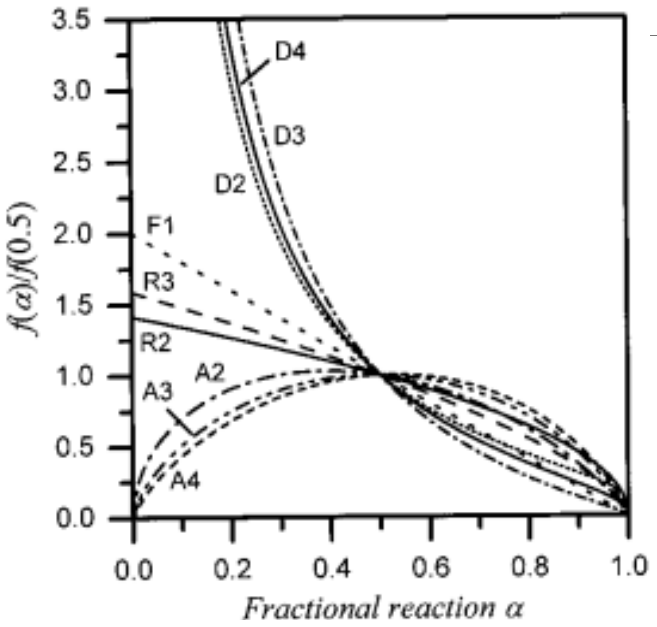
Oxidation and reduction behavior

- Screen for O_2 uptake and release.
  - System viability
- Resolve thermal reduction behavior.
  - Variable heating rates
- Resolve gas splitting behavior.
  - Variable T, P, [OX]
- Analysis.
  - Rate limiting mechanisms
  - Kinetic models
  - Material stability
  - Cycle performance



Sunshine to Petrol

Solid-state kinetic theory

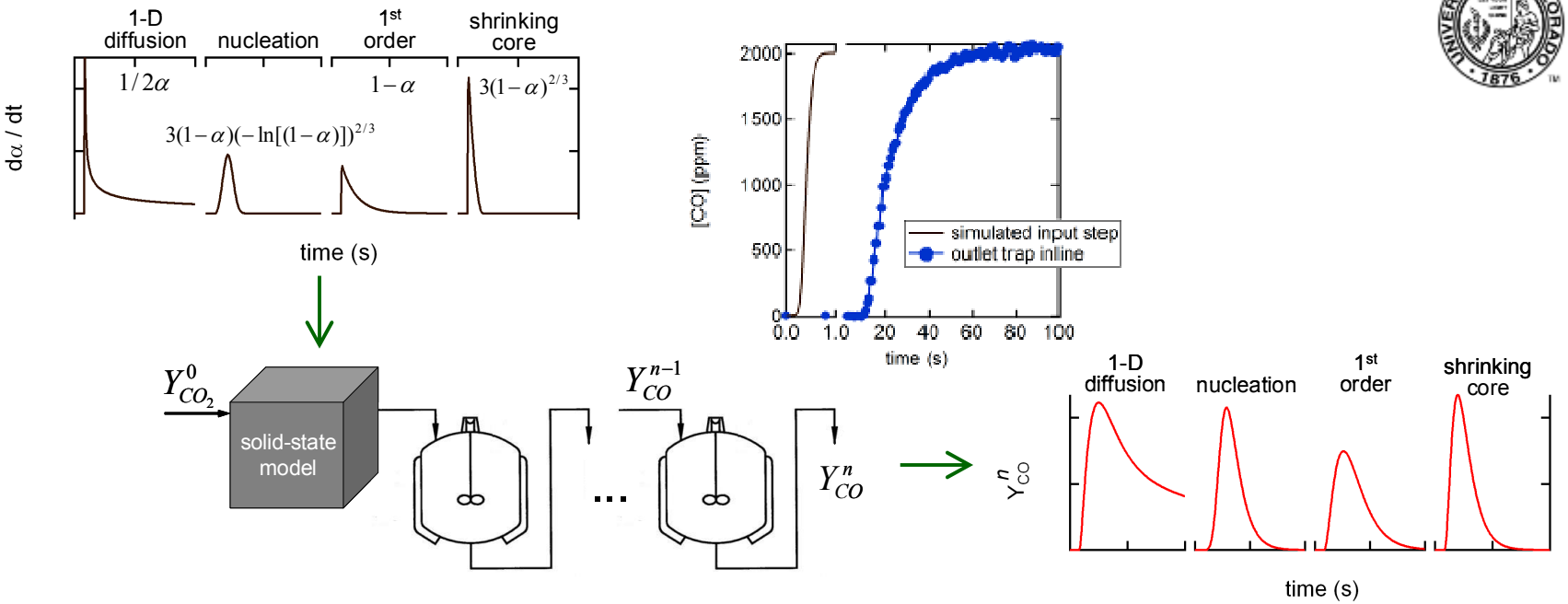


Khawam and Flanagan, *J. Phys. Chem. B*, **110**, 17315 (2006)

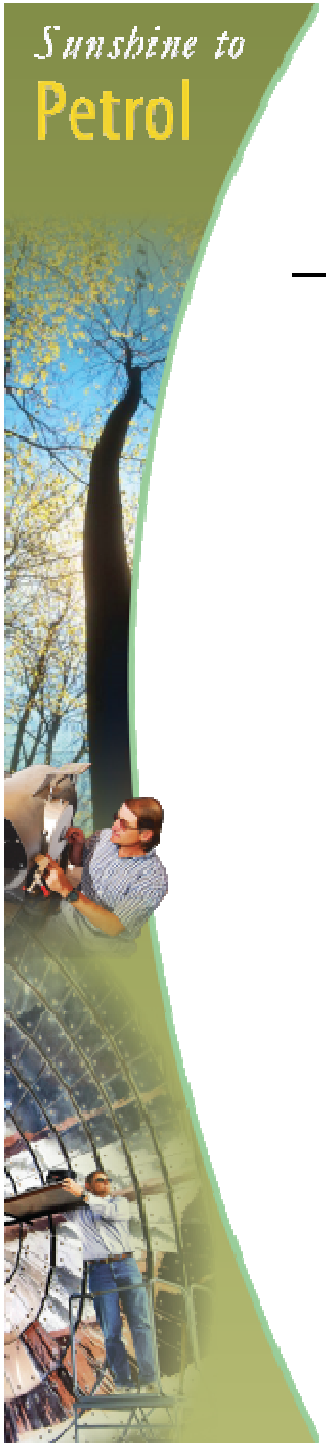
model	differential form $f(\alpha) = 1/k\ d\alpha/dt$	integral form $g(\alpha) = kt$
nucleation models		
power law (P2)	$2\alpha^{1/2}$	$\alpha^{1/2}$
power law (P3)	$3\alpha^{2/3}$	$\alpha^{1/3}$
power law (P4)	$4\alpha^{3/4}$	$\alpha^{1/4}$
Avrami–Erofeyev (A2)	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
Avrami–Erofeyev (A3)	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
Avrami–Erofeyev (A4)	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
Prout–Tompkins (B1)	$\alpha(1-\alpha)$	$\ln[\alpha/(1-\alpha)] + c^a$
geometrical contraction models		
contracting area (R2)	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
contracting volume (R3)	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$
diffusion models		
1-D diffusion (D1)	$1/(2\alpha)$	α^2
2-D diffusion (D2)	$-[1/\ln(1-\alpha)]$	$((1-\alpha)\ln(1-\alpha)) + \alpha$
3-D diffusion–Jander (D3)	$[3(1-\alpha)^{2/3}]/[2(1-(1-\alpha)^{1/3})]$	$(1-(1-\alpha)^{1/3})^2$
Ginstling–Brounshtein (D4	$3/[2((1-\alpha)^{-1/3}-1)]$	$1-(2/3)\alpha-(1-\alpha)^{2/3}$
reaction-order models		
zero-order (F0/R1)	1	α
first-order (F1)	$(1-\alpha)$	$-\ln(1-\alpha)$
second-order (F2)	$(1-\alpha)^2$	$[1/(1-\alpha)]-1$
third-order (F3)	$(1-\alpha)^3$	$(1/2)[(1-\alpha)^{-2}-1]$

- Master Plot used to screen rate controlling mechanism(s).
  - Applied to any measure of the extent of reaction (α).
- Extract kinetic parameters from isoconversion analysis.
  - Model independent

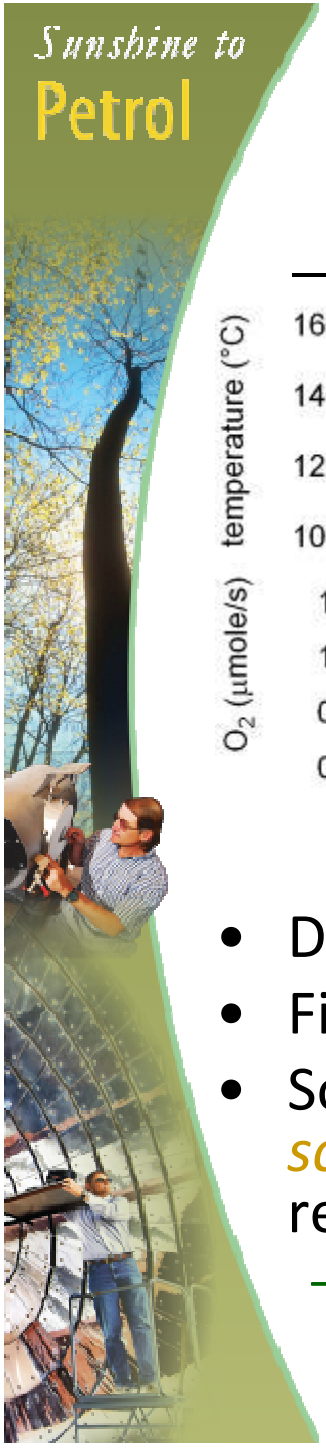
Model-based approach to evaluating kinetic behavior



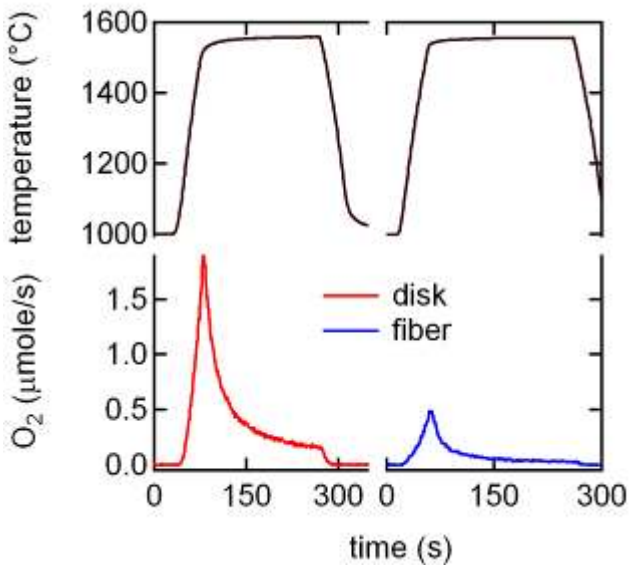
- CSTR model accounts for dispersion and detector lag.
  - Deconvolute experimental effects from O_2, H_2, and CO signals
- Governing equations constitute a system of DAEs.
- Mathematica™ based optimization.
  - Least squares objective function
  - Stochastic algorithms search for best fit model and kinetic parameters
    - Differential Evolution, Simulated Annealing

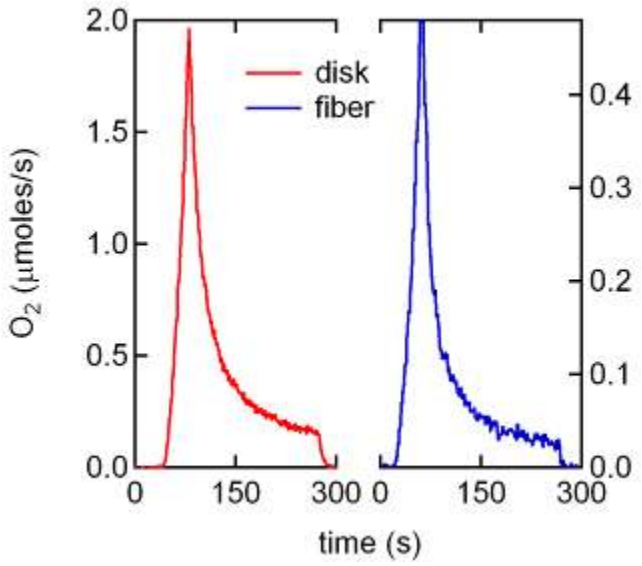


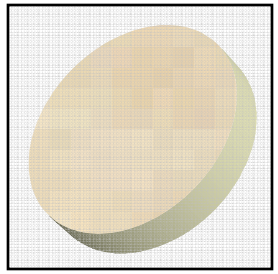
Transition metal doped CeO_2

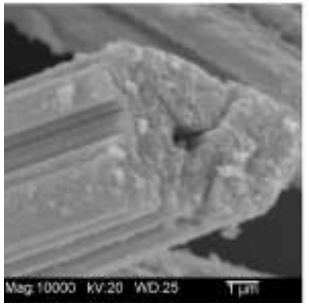


Thermal reduction of CeO_2 very rapid









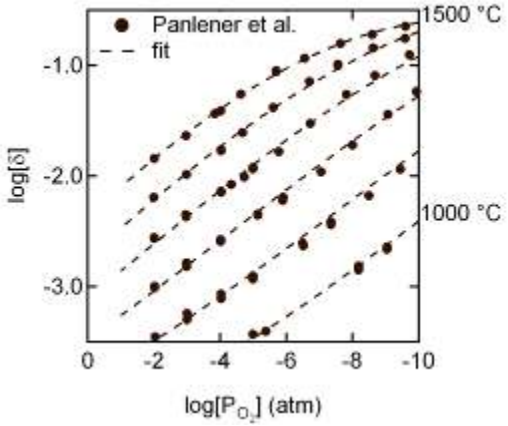
- Disk 1000 μm thick.
- Fiber diameter ~ 10 μm.
- Solid-state dynamics at *these length scales and heating rates* do not limit reduction kinetics.
  - Thermal conduction, vacancy diffusion, surface chemistry

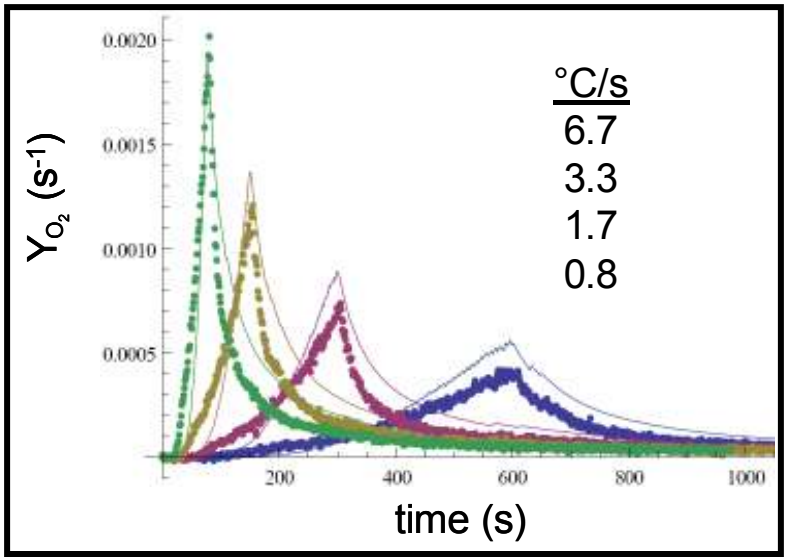
mass (mg)	mole O ($\times 10^{-6}$)	δ
960	220	0.039
207	48	0.039

Relatively simple kinetic model for CeO_2 reduction

$$\frac{d\delta}{dt} = k_1\left(\frac{T}{T_1}\right)^{\beta_1} \exp\left[-E_1/RT\right]\cdot(\delta_{eq}-\delta)^{m_1}$$

$$\delta_{eq} = f(\mathrm{Log}[P_{O_2}], T)$$





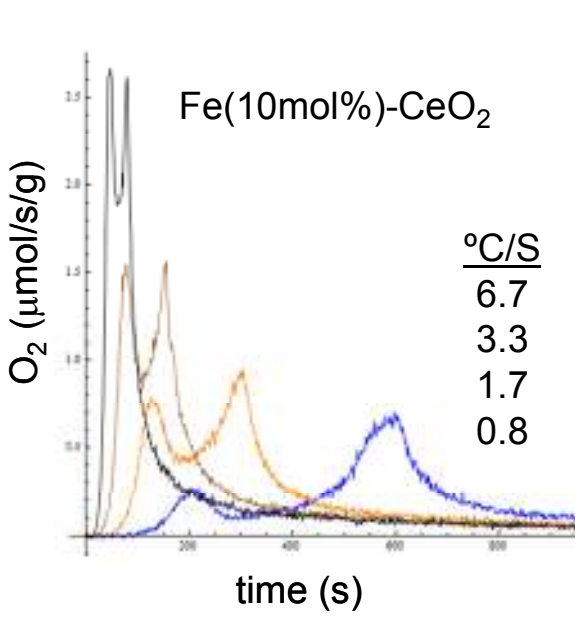
δ = 0.048

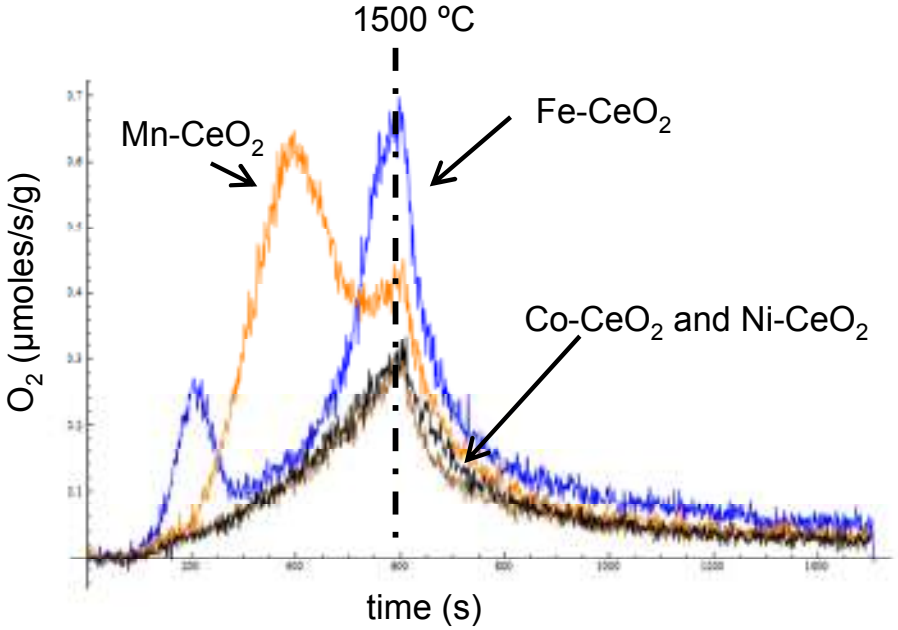
- Incorporated into engineering models to predict CR5 performance

"mass"	"temp"	"[oxid]"	"total O2"
0.4129	1503.67	0	140.244
0.4129	1500.74	0	137.743
0.4129	1503.79	0	141.993
0.4129	1503.75	0	143.211

Sunshine to Petrol

Reduction behavior of transition-metal doped CeO_2 powders

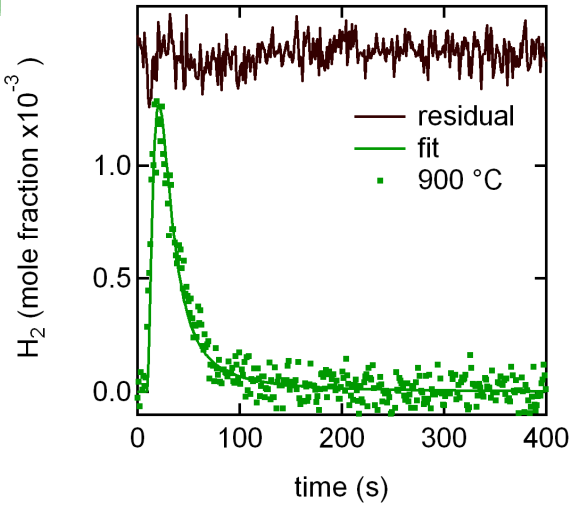


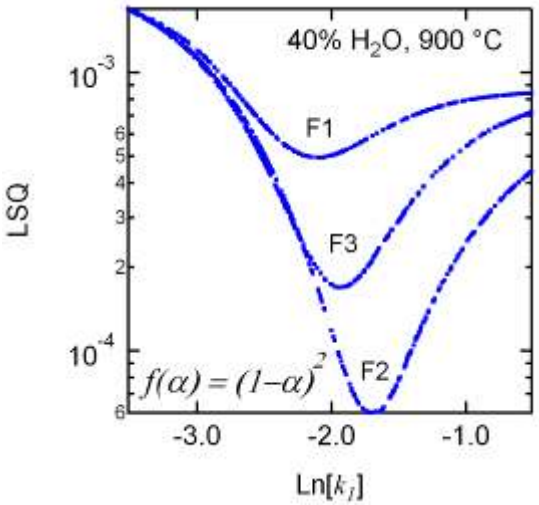


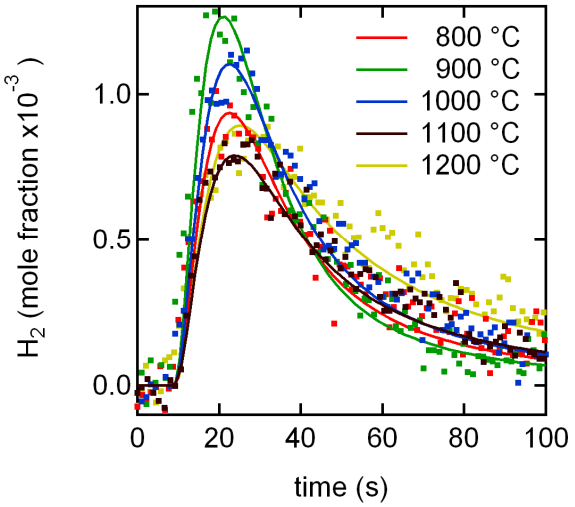
- Goal is to lower the thermal reduction temperature.
  - Destabilize the fluorite crystal structure
- O_2 evolution complex for Mn and Fe doped CeO_2.
  - Compound formation and phase segregation possible
- Significantly more O_2 evolved per unit mass of material.
  - Mn and Fe variants at 10 mol% but O_2 capacity > 2×

Sunshine to Petrol

H_2O oxidation of CeO_2 exhibits 2nd order behavior





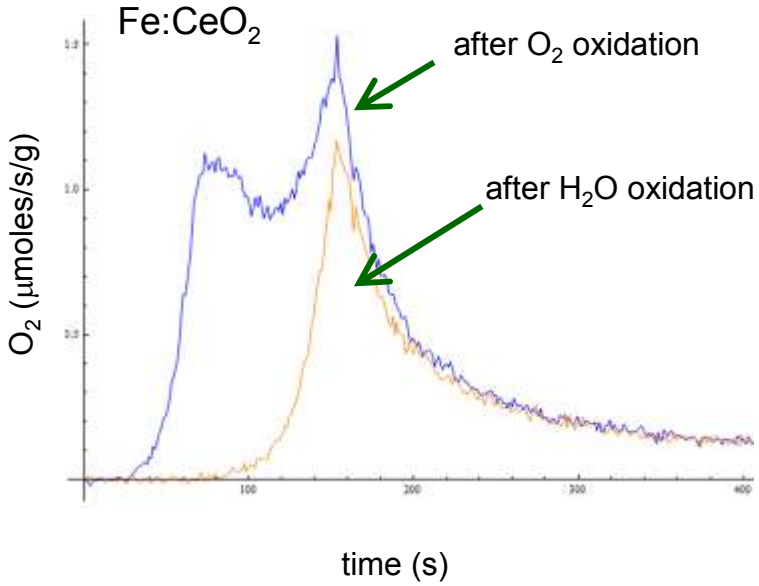


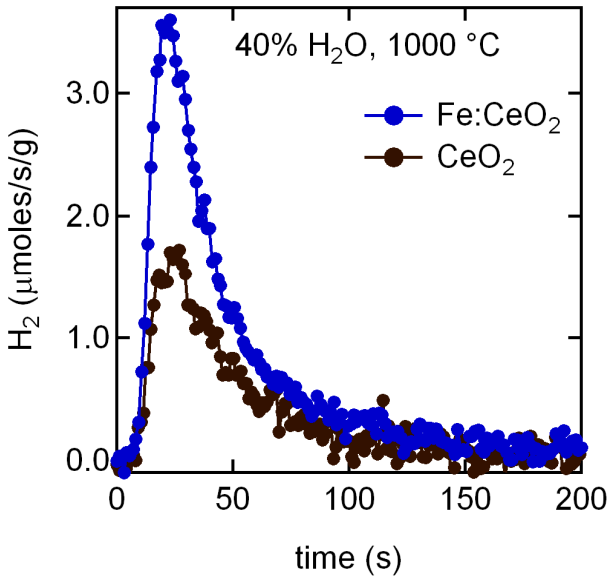
$$\frac{d\alpha_1}{dt} = k_1[Y^0_{CO_2}(t - t_{shift})] \cdot f(\alpha_1)$$

- H_2 production rate peaks at 900 °C.
- Well defined LSQ minimum for the F2 model over all T.

H_2O splitting on Fe-doped CeO_2

TR to 1500 °C @ 3.3 °C/s

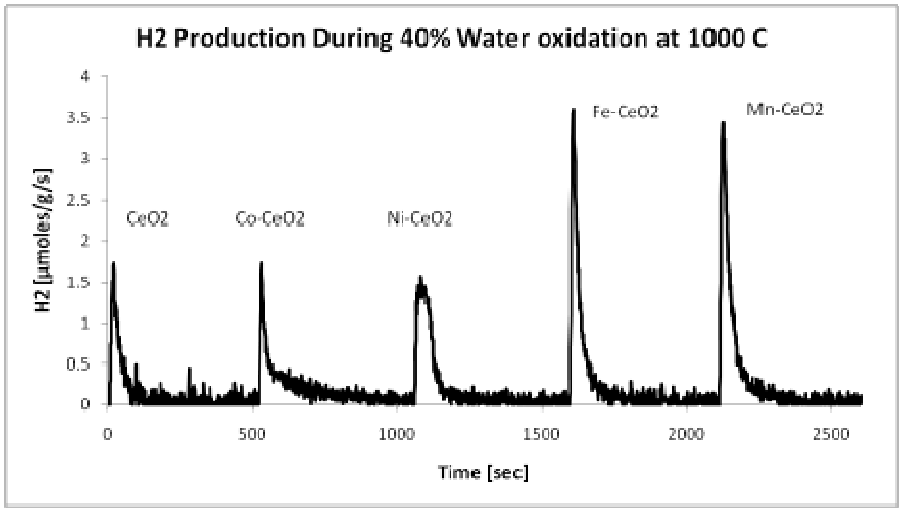


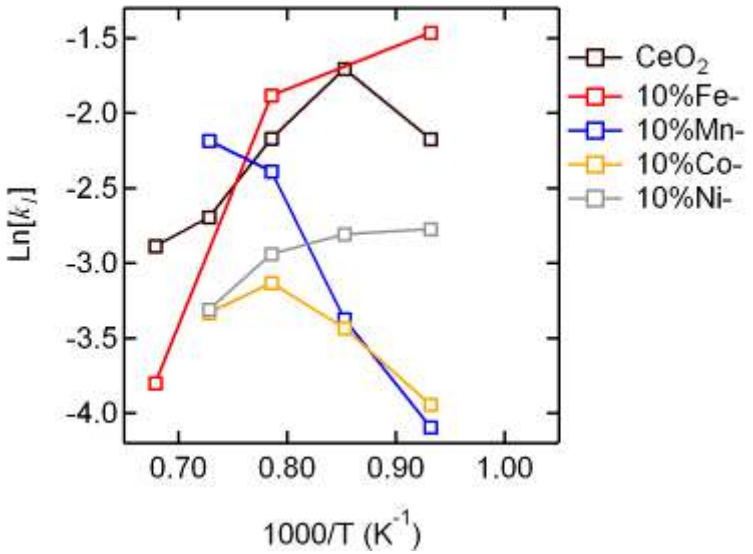


- O_2 evolution post-H_2O oxidation reveals that active sites in doped system re-oxidize at different rates.
- Presence of 10mol% Fe increases net H_2 production.

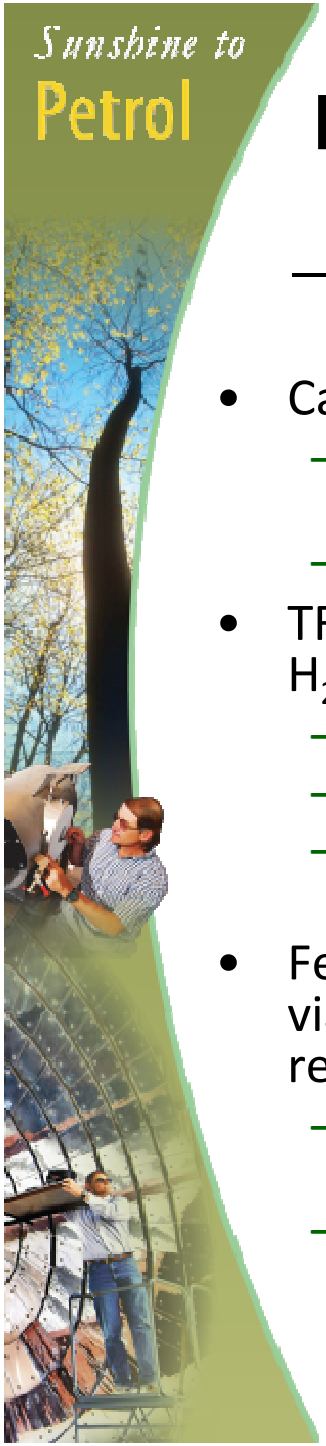
Sunshine to Petrol

Dopants have a dramatic effect on H_2 production rates



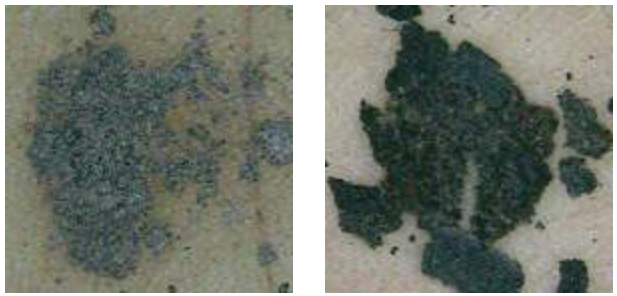


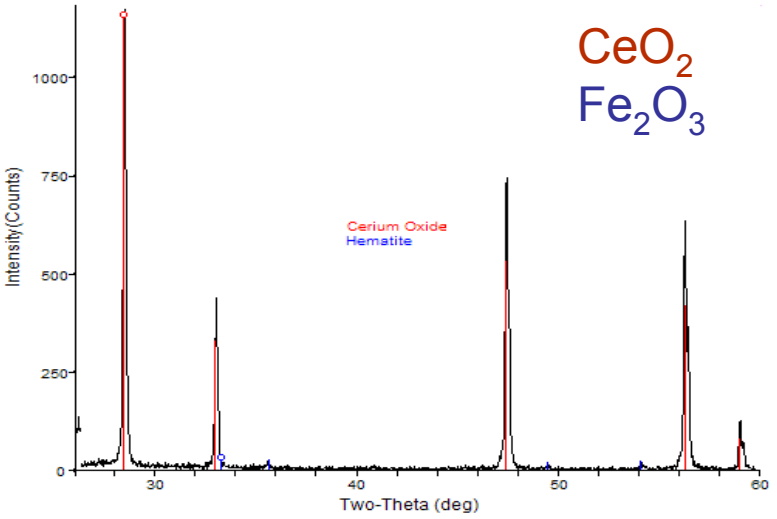
- Peak temperature in volcano plot shifts.
- Effect on net hydrogen production varies.
- Trends not obvious.
  - All multivalent (2^+– 4^+, or 2^+– 6^+ for Mn)
  - All have effective ionic radii << Ce^{3+} and Ce^{4+}

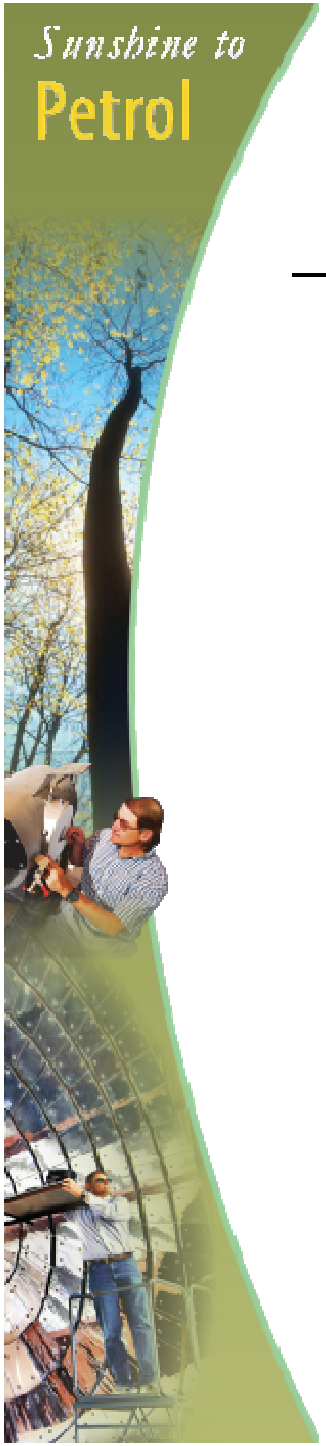


Fe and Mn enhance sintering of powders during redox

- Calcine in air @ 1400 °C for 36 hrs.
  - XRD patterns show little evidence of other phases
  - Material is a loose packed powder
- TR in He at 1500 °C followed by H_2O oxidation at 1000 °C.
  - Color darkens
  - Material sinters
  - Need to complete analysis
    - Composition and morphology
- Fe and Mn-doped ceria not likely a viable strategy despite greater redox capacity.
  - Slow kinetics on “low energy” O-site
  - Severe problems with sintering/reactivity with ceramics

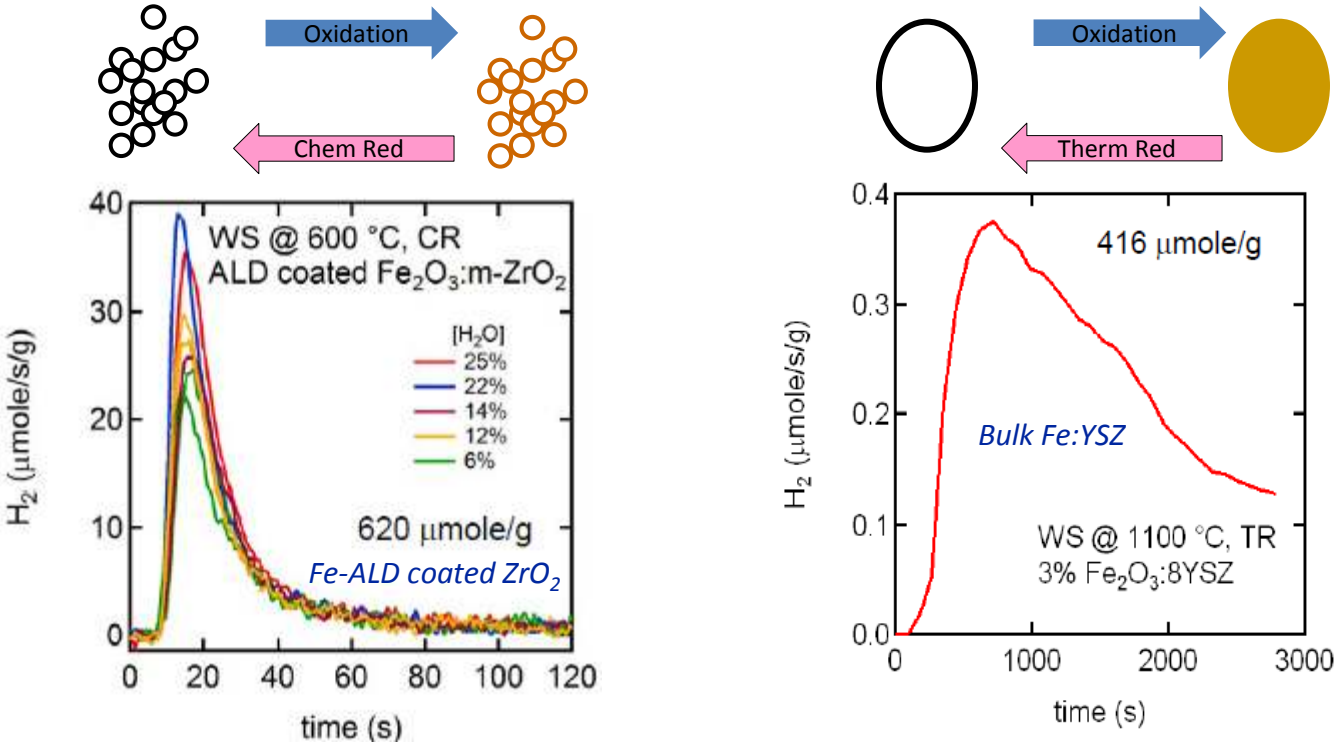






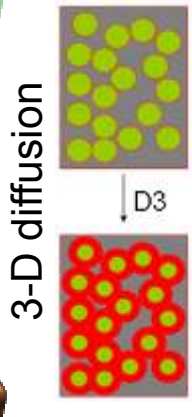
Fe in YSZ

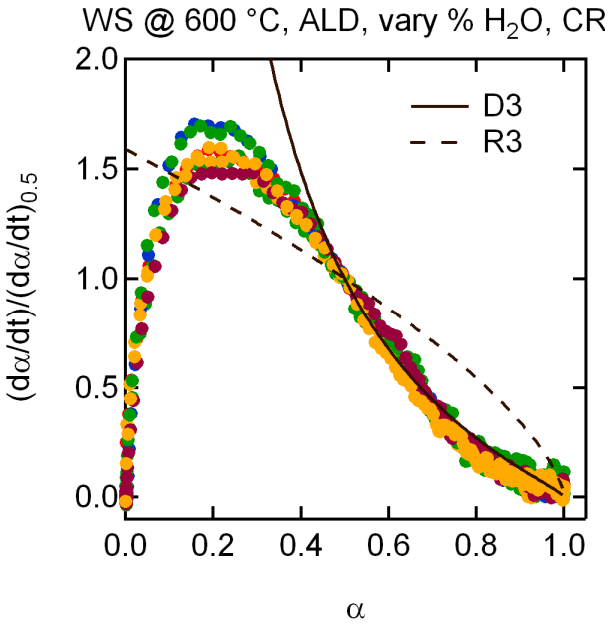
High surface area/small dimension structures desirable

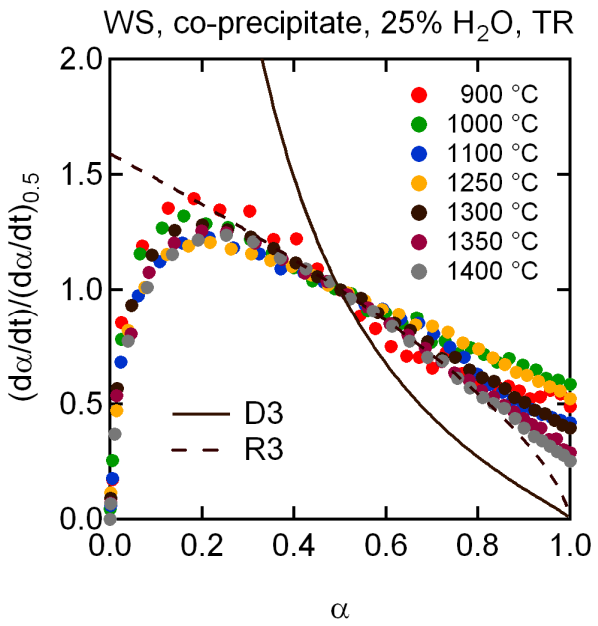


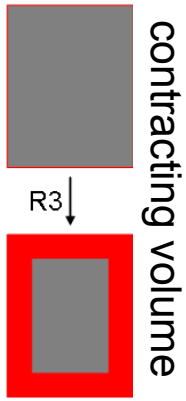
- Rates for water oxidation highly dependent on reactive structure.
  - Different manifestations of Fe^{2+}/Fe^{3+} redox couple
  - ALD thin film peak H_2 production rate 100× faster than Fe dissolved in YSZ

Rate controlling mechanisms revealed through MP analysis





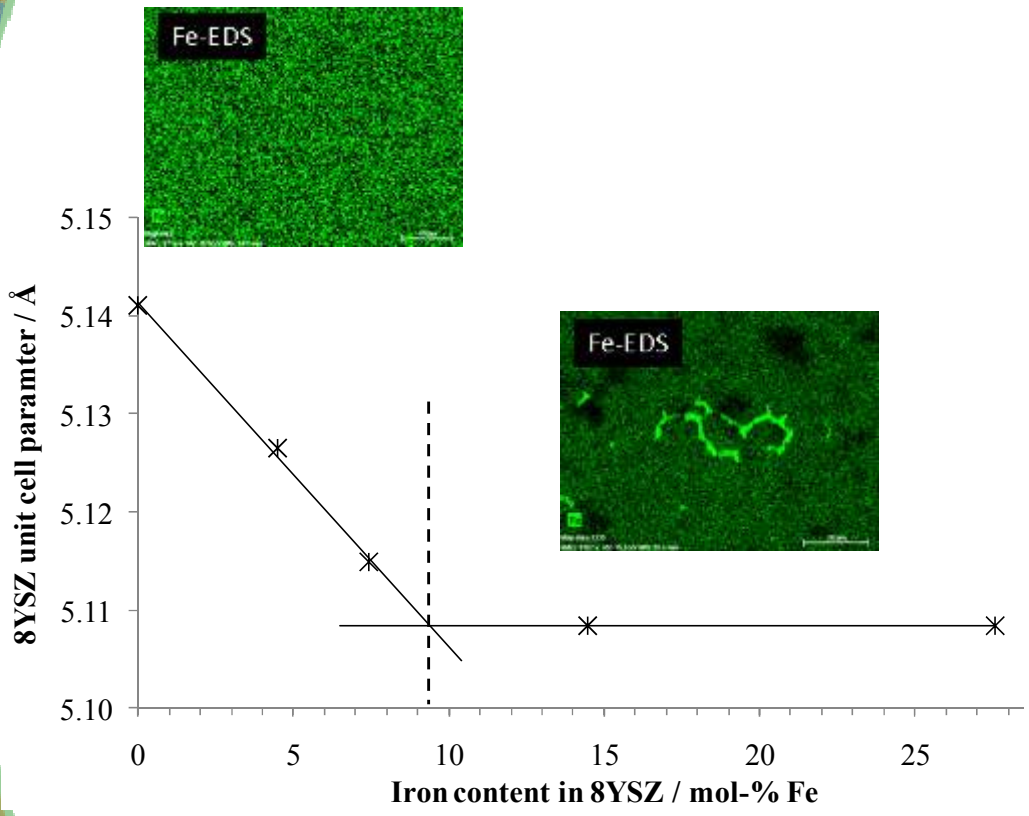


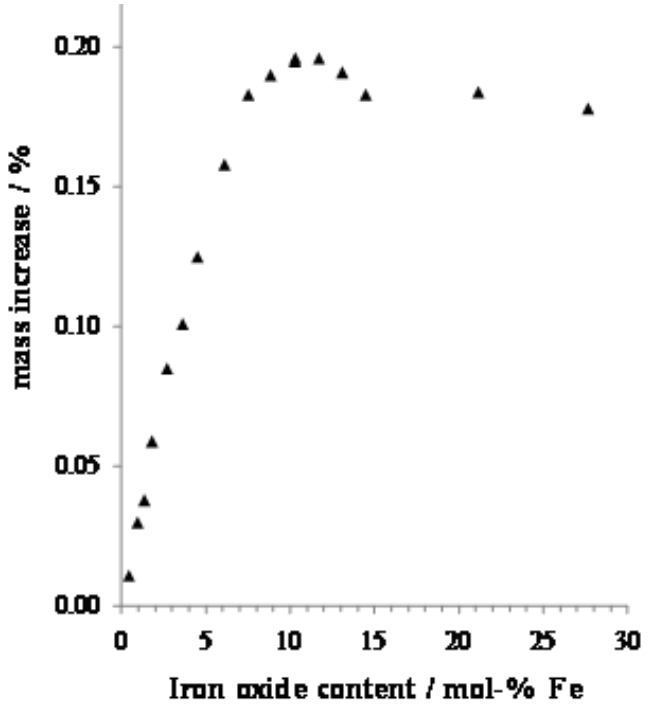


- Thin film structure results from ALD films.
  - Expect diffusion limited behavior (D3)
- Homogenous structure results from co-precipitate.
  - Uniform dispersion of Fe cation
  - Expect contracting volume behavior (R3)

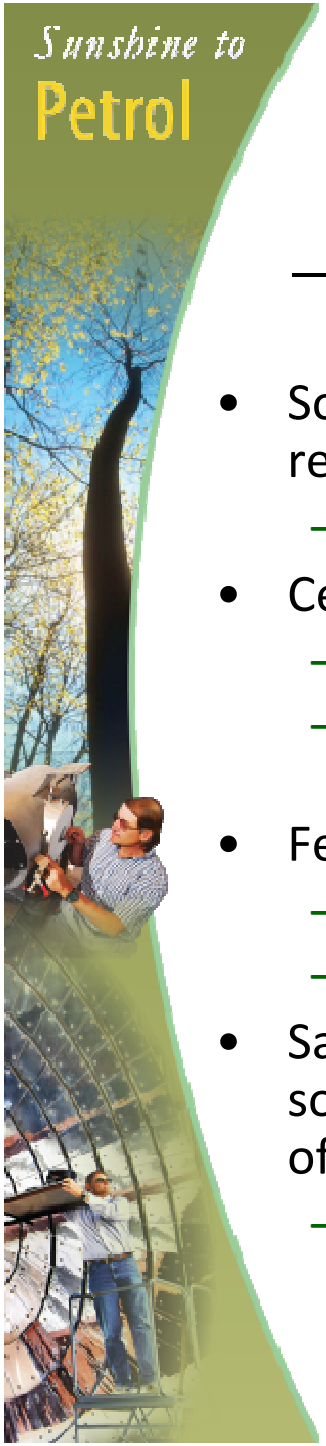
Sunshine to Petrol

Iron solubility in 8YSZ limits performance



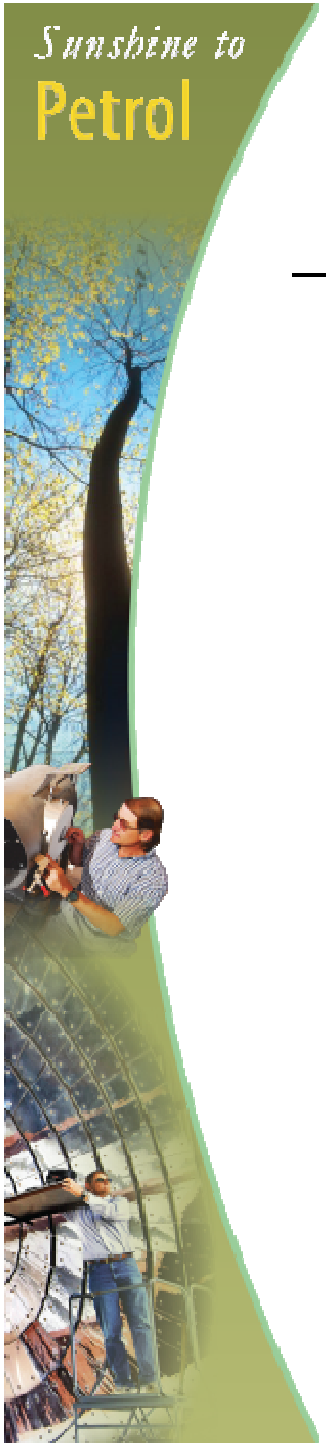


- Ferrite cycle desirable due to greater redox capacity compared to ceria.
  - Higher efficiency if iron utilization can be improved



Summary

- Solid-state kinetic models show promise for describing oxidation and reduction behavior.
  - Redox models incorporated into CR5 simulation tools
- Cerium oxide cycle.
  - Facile reduction kinetics
  - Complex redox chemistry evident when doped with various transitional metals (especially Fe and Mn)
- Ferrite cycle.
  - More desirable than ceria if higher effective mass loading can be realized
  - Oxidation rates can be manipulated by choice of reactive structure
- Sandia remains committed to demonstrating greater than 2% net solar-to-fuel conversion efficiency in the CR5 testbed before the end of 2011.
  - 18 KW system with continuous CO production



Thank you for your attention.

Questions?