



Kinetics of H₂O and CO₂ Splitting Chemistry on Reactive Structures Suitable for Concentrated Solar Power Application

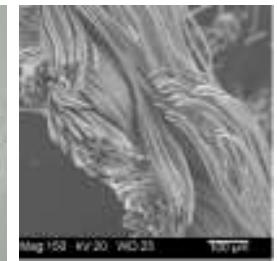
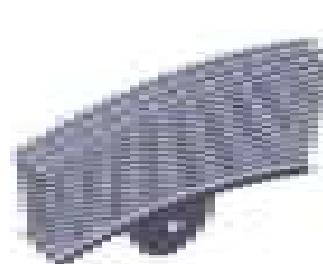
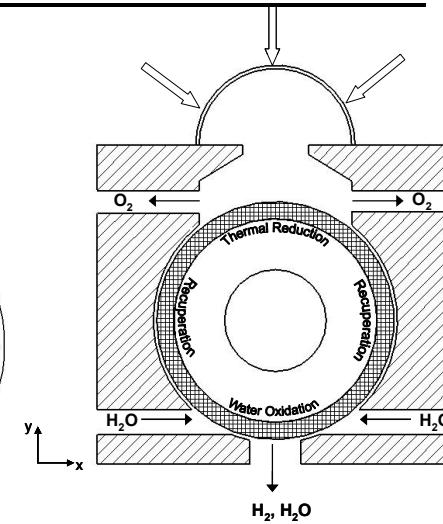
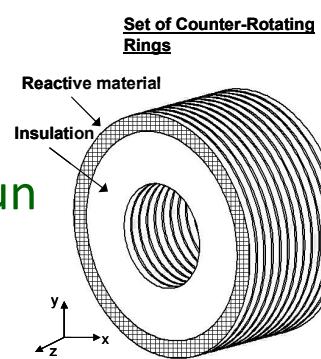
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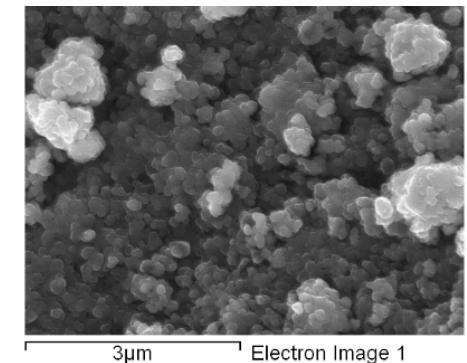
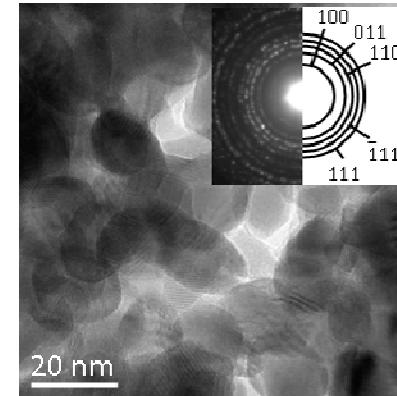
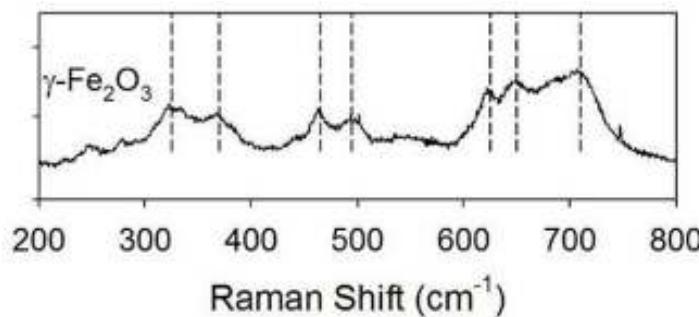
Non-volatile metal oxide reactive structures



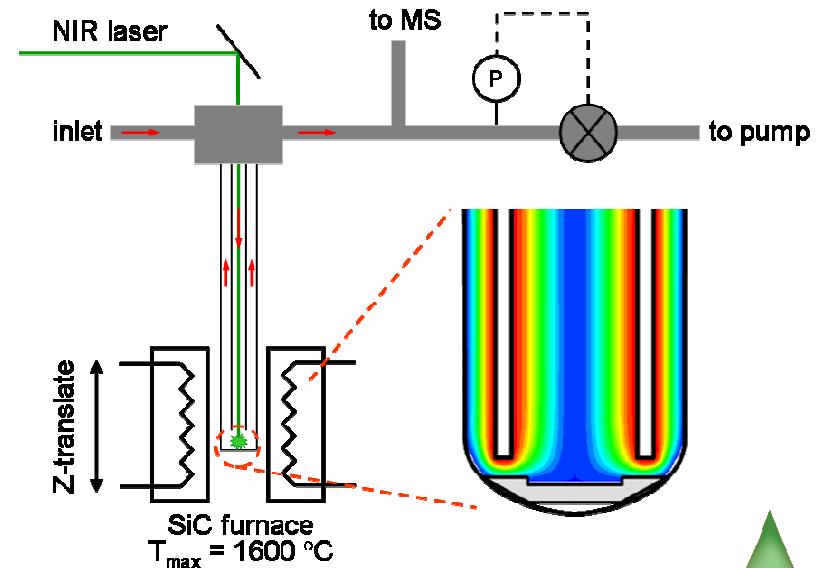
- Challenges imposed by performance goals
 - Continuous operation on-sun
 - Heat recuperation
 - Direct solar absorption
 - Chemical and mechanical durability
- Complex behavior
 - Surface/bulk reaction
 - Solid phase transport
 - Effects of dopants and supports



Experimental approach



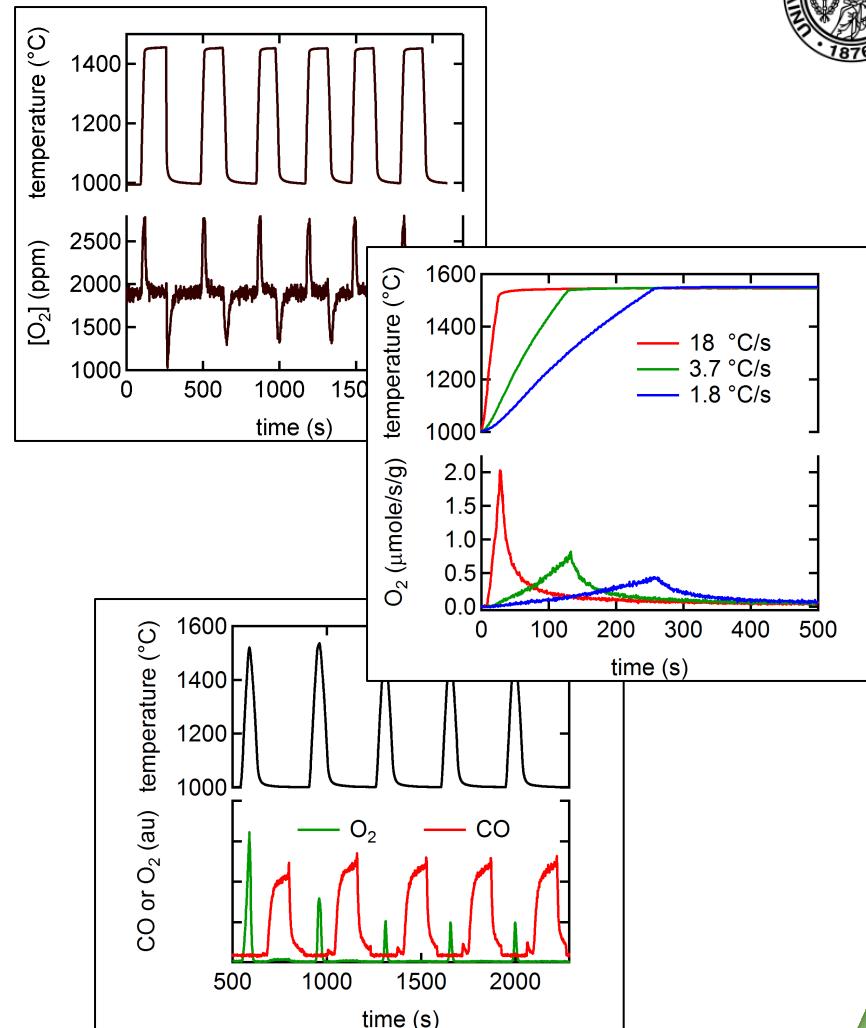
- Material properties
 - BET surface area
 - SEM-EDX, TEM-EELS, XRD
- Surface analysis
 - Surface Raman, XPS
- Kinetic measurements
 - Stagnation flow reactor
 - 500 W CW NIR laser heating
 - Modulated beam mass spectrometer



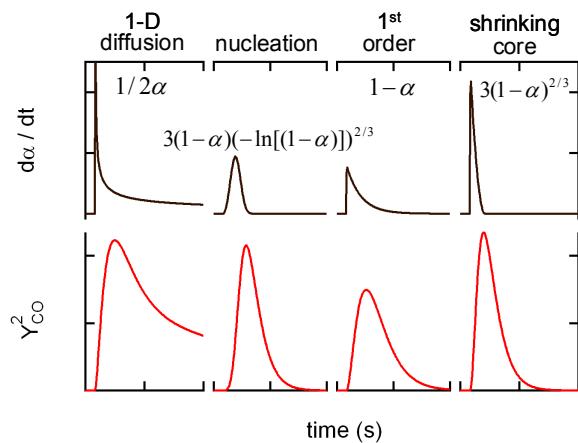
Evaluating oxidation and reduction behavior



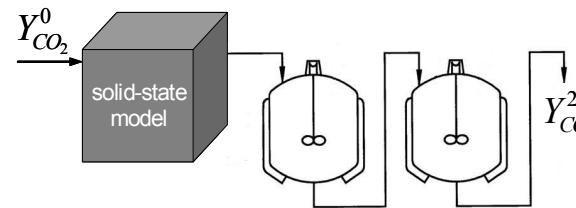
- Screen for O_2 uptake and release
 - System viability
- Resolve thermal reduction behavior
 - Variable heating rates
- Resolve gas splitting behavior
 - Variable T, P, [OX]
- Analysis
 - Rate limiting mechanisms
 - Kinetic models
 - Material stability
 - Cycle performance



Numerical approach to evaluating kinetic behavior



$$\frac{d\alpha}{dt} = k_0 [Y_{CO_2}^0 (t - t_{shift})]^\gamma \left(\frac{T}{T_0} \right)^\beta \exp[-E_a / RT] \cdot f(\alpha)$$

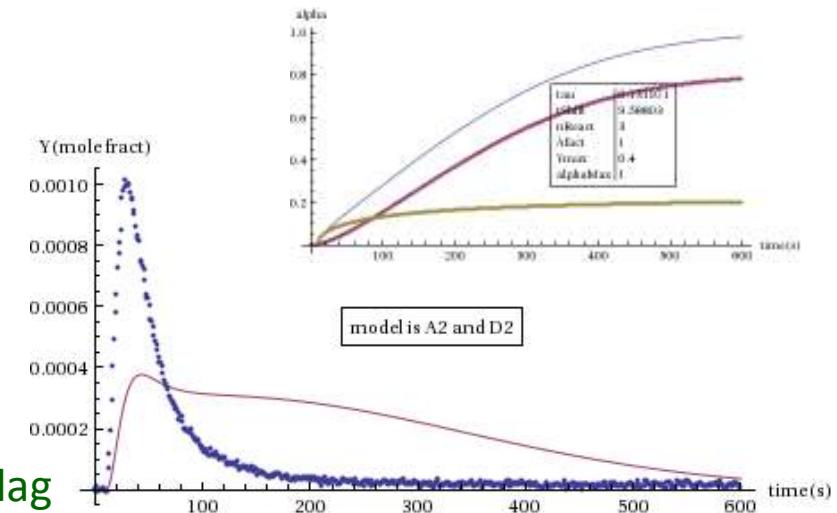


$$Y_{CO}^0 \propto \frac{d\alpha}{dt}$$

$$\frac{dY_{CO}^1}{dt} = \tau \cdot (Y_{CO}^0 - Y_{CO}^1)$$

$$\frac{dY_{CO}^2}{dt} = \tau \cdot (Y_{CO}^1 - Y_{CO}^2)$$

- Solid state kinetic theory
 - Concept applied to any measure of reaction extent (α)
 - Use 14 validated expressions for $f(\alpha)$
- Numerical procedure
 - Mathematica™ based
 - Stiff integrators
 - Global least squares optimization
 - Account for dispersion and detector lag
 - Resolve two competing, rate limiting mechanisms



Material systems currently under investigation

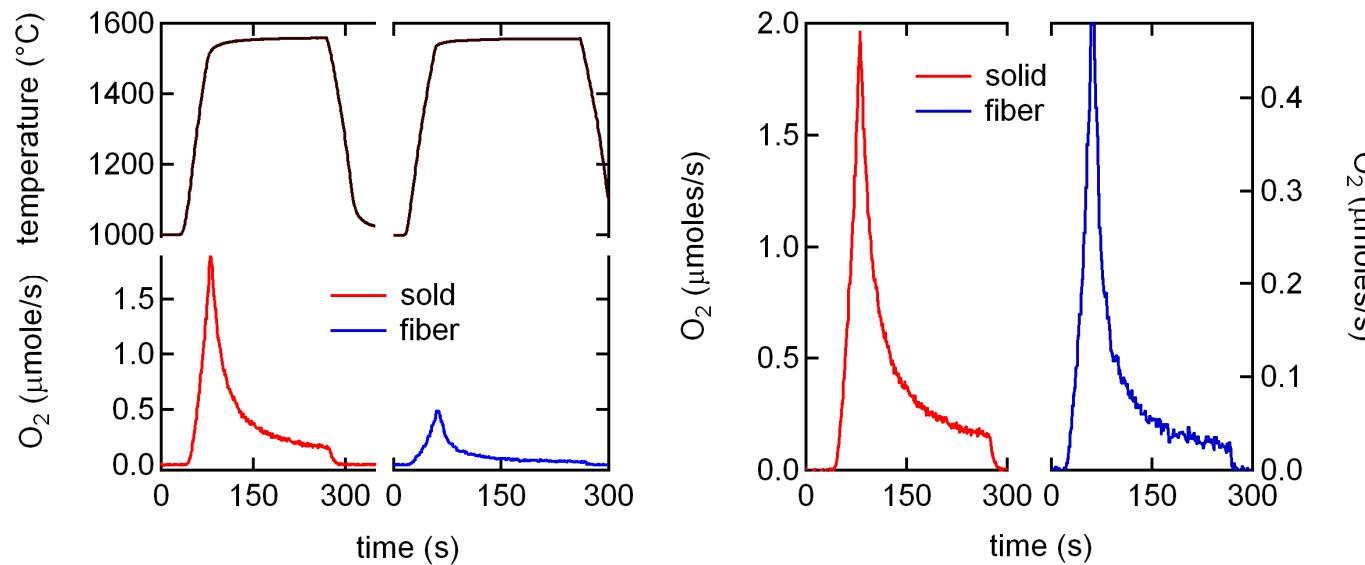


| Fe_2O_3 | CoFe_2O_4 | $\text{MO}_x:\text{CeO}_{2-\delta}$ | $\text{La}_{1-x}\text{Sr}_x\text{Cr}_{1-y}\text{Mn}_y\text{O}_{3-\delta}$ | |
|--------------------------------|--------------------------------|-------------------------------------|---|-----|
| YSZ | m-ZrO ₂ | | X | Y |
| m-ZrO ₂ | | | 0.9 | 0.5 |
| CeO ₂ | | 10 mol% Mn, Ni, Co, Mo, & Fe | 0.8 | |
| Al ₂ O ₃ | Al ₂ O ₃ | | 0.7 | |
| | | | 0.6 | |
| | | | 0.5 | |

- Redox cycle chemistries
 - Chemical systems 
 - $\text{M}^{+n}/\text{M}^{+(n+1)}$ redox couples
 - $\text{MO}_{n-\delta}$ non-stoichiometric oxides
 - CU “hercynite” 
- Supports 
- m-ZrO₂, YSZ, CeO₂, Al₂O₃

chemical and/or physical modification required to achieve performance goals

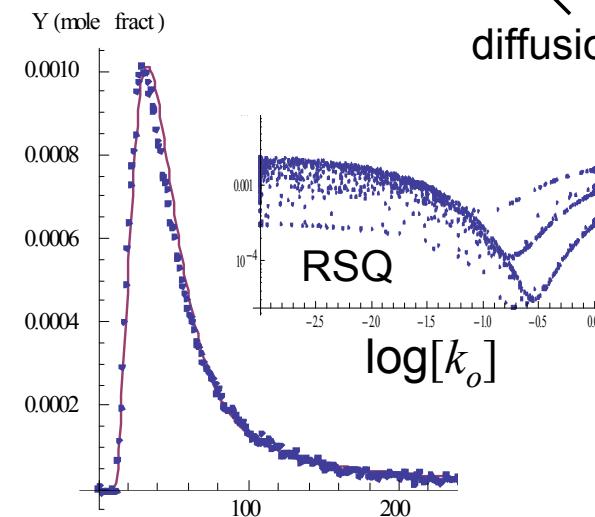
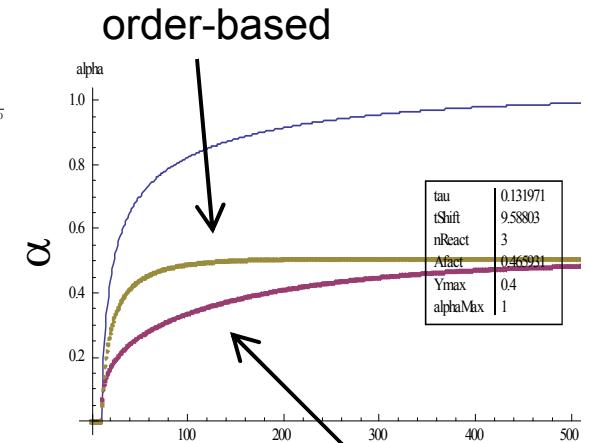
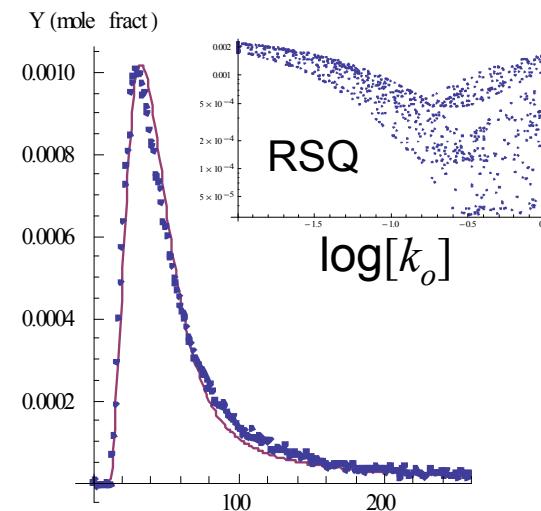
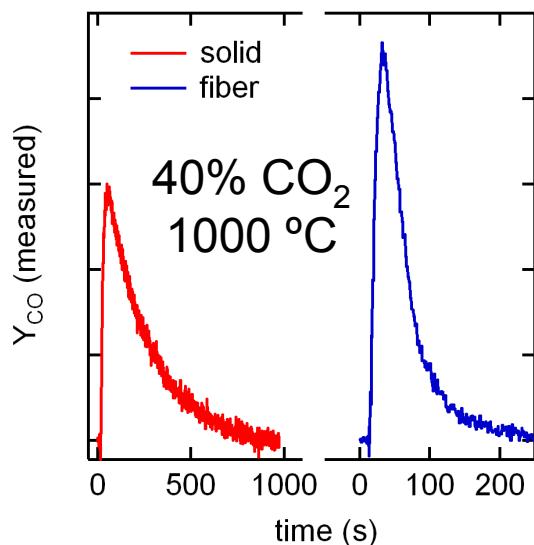
CeO₂ thermal reduction kinetics likely NOT limiting CSP chemistry



- Fiber diameter $\sim 10 \mu\text{m}$.
- Solid $1000 \mu\text{m}$ thick.
- Solid-state dynamics at *these length scales and heating rates* do not limit reduction kinetics.
 - Thermal conduction, vacancy diffusion, surface chemistry

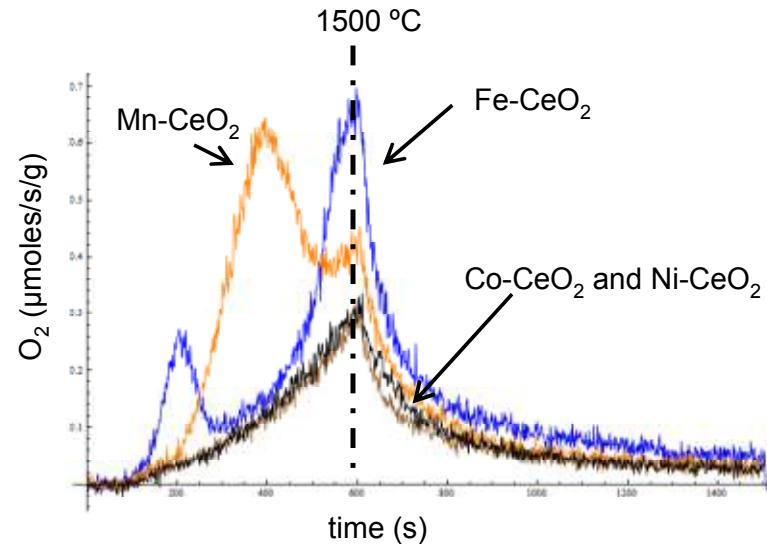
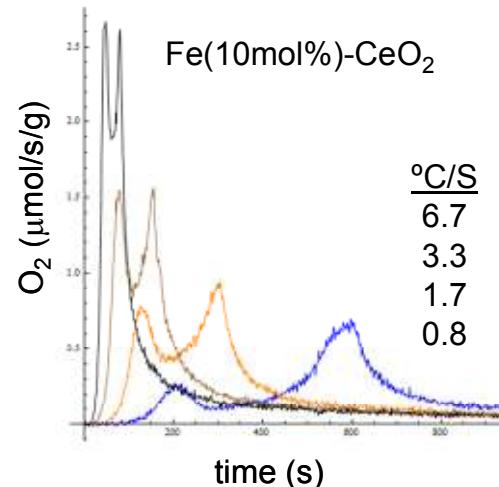
| mass (mg) | mole O ($\times 10^{-6}$) | δ |
|-----------|-----------------------------|----------|
| 960 | 220 | 0.0197 |
| 207 | 48 | 0.0199 |

Results for best fit to CO₂ splitting on fiber



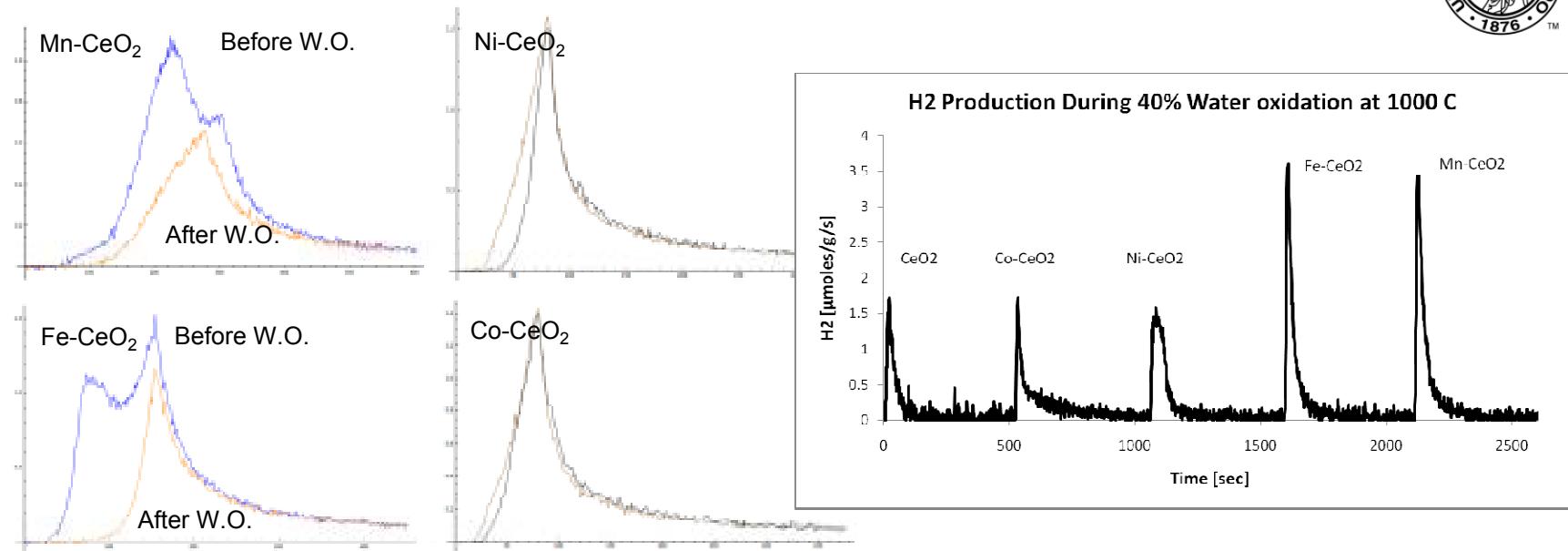
- Fibers oxidize faster than solids and achieve higher conversion
 - Surface area effects
- Fast initial “order-based” process followed by a slower “diffusion-based” process
 - Diffusion limitation more prevalent for lower surface area solids

O₂ redox behavior for transition-metal doped CeO₂ powders



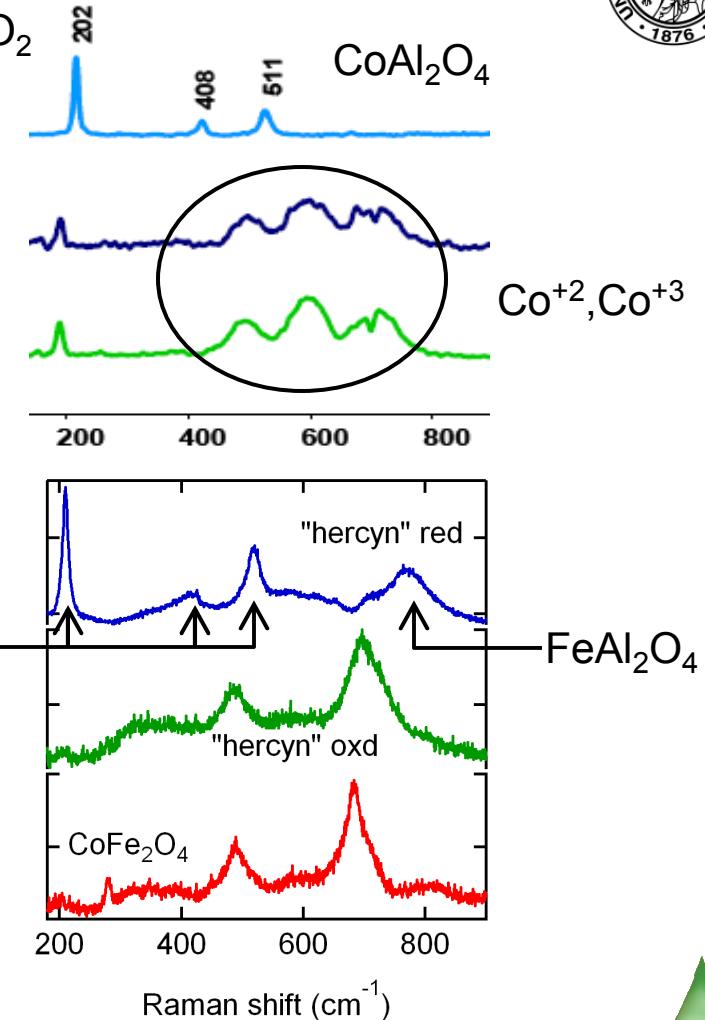
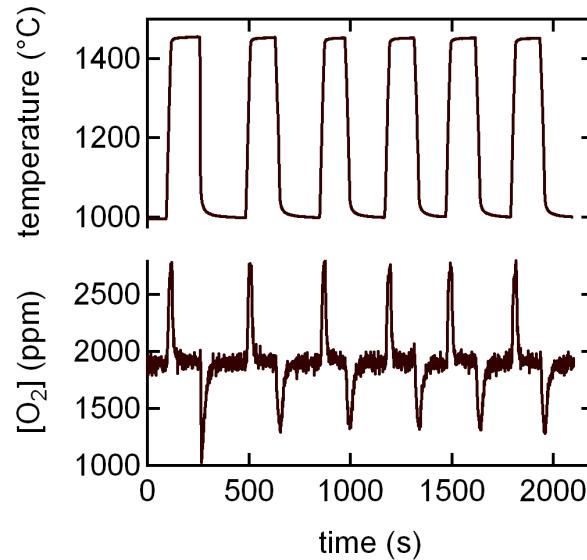
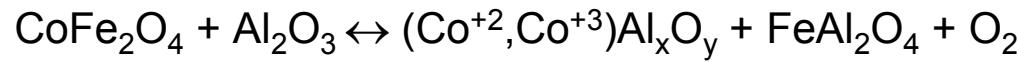
- Thermal reduction followed by O₂ oxidation
 - Kinetic model can be developed to describe reduction behavior
- O₂ evolution complex for Mn and Fe doped CeO₂
 - Possible phase segregation
 - More O₂ evolved per unit mass of material
 - Multiple valence states for Mn and Fe cations likely

H_2O redox behavior for transition-metal doped CeO_2 powders



- O_2 evolution post- H_2O oxidation reveals that active sites in system re-oxidize at different rates
- 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

Very interesting O₂ redox chemistry from thin film CoFeAl-spinsels



- Oxygen uptake and release remarkably facile
 - Chemistry requires rearranging multiple cations

Summary



- Solid-state kinetic models show promise for describing complex redox behavior
 - Multiple active centers, competing mechanisms
- Cerium oxide
 - Facile reduction kinetics
 - Complex redox chemistry evident when doped with various transitional metals (especially Fe and Mn)
- “Hercynite” oxide
 - Facile oxygen uptake and release observed for this unique thin-film system

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