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# Kinetics of H<sub>2</sub>O and CO<sub>2</sub> Splitting Chemistry on Reactive Structures Suitable for Concentrated Solar Power Application

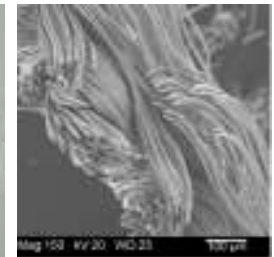
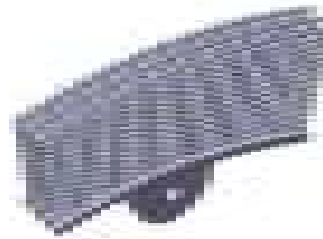
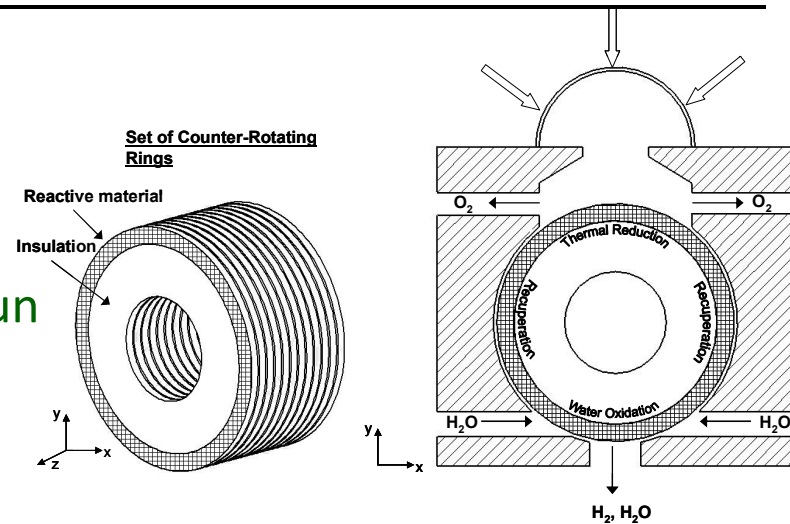
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Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

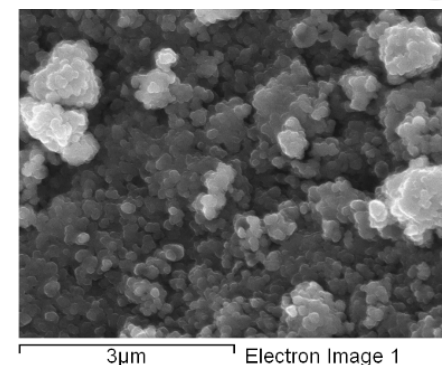
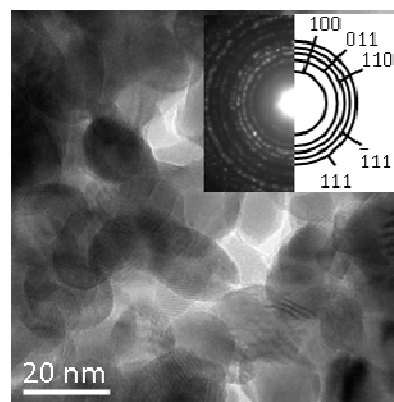
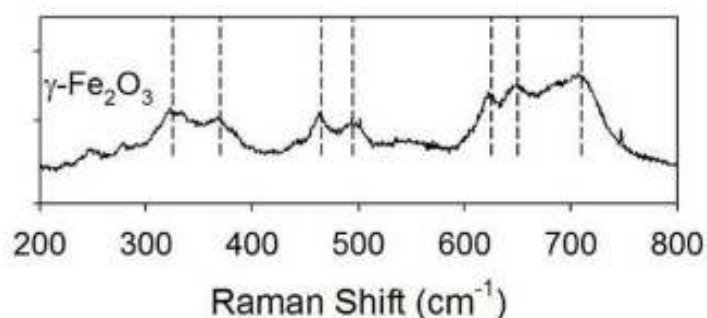
# Non-volatile metal oxide reactive structures



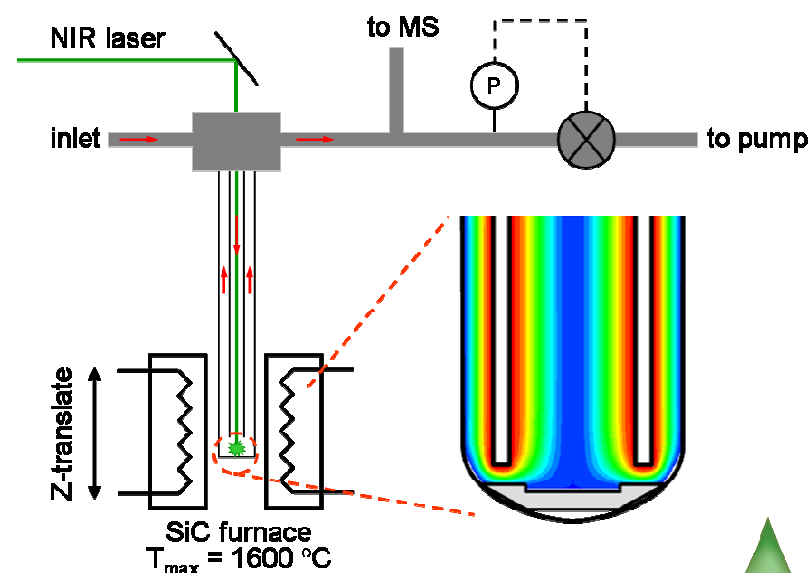
- Challenges imposed by performance goals
  - Continuous operation on-sun
  - Heat recuperation
  - Direct solar absorption
  - Chemical and mechanical durability
- Complex behavior
  - Surface/bulk reaction
  - Solid phase transport
  - Effects of dopants and supports



# Experimental approach



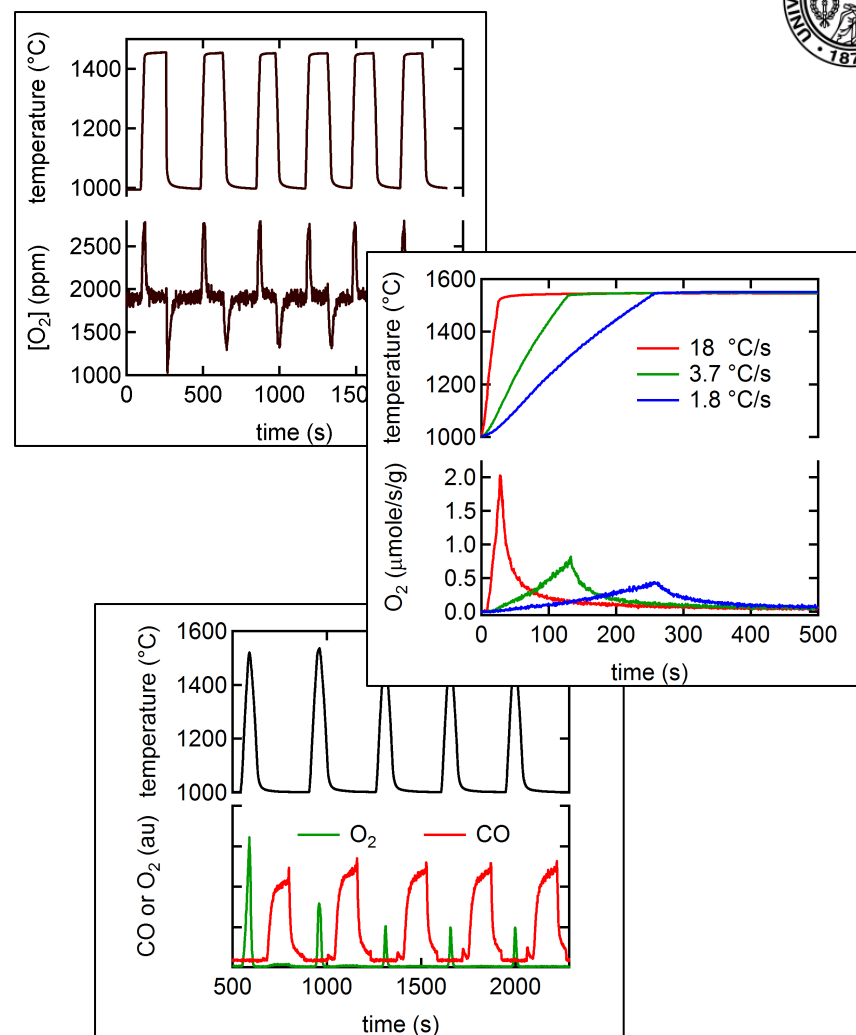
- Material properties
  - BET surface area
  - SEM-EDX, TEM-EELS, XRD
- Surface analysis
  - Surface Raman, XPS
- Kinetic measurements
  - Stagnation flow reactor
    - 500 W CW NIR laser heating
    - Modulated beam mass spectrometer



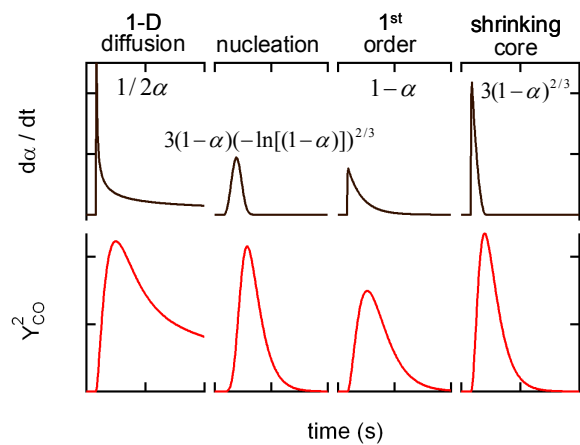
# Evaluating oxidation and reduction behavior



- Screen for O<sub>2</sub> 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

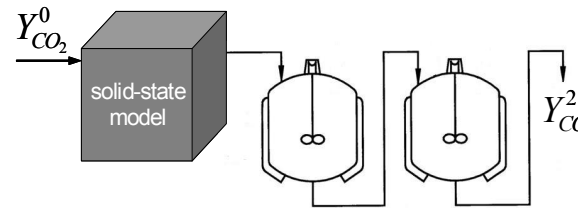


$$\frac{d\alpha}{dt} = k_0 [Y_{CO_2}^0 (t - t_{shift})]^\gamma \left( \frac{T}{T_0} \right)^\beta \exp[-E_a / RT] \cdot f(\alpha)$$

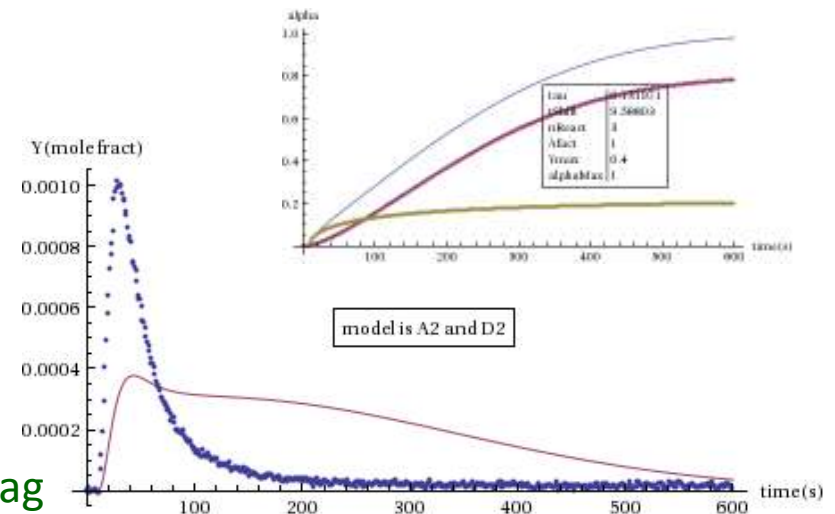
$$Y_{CO}^0 \propto \frac{d\alpha}{dt}$$

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

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



- Solid state kinetic theory
  - Concept applied to any measure of reaction extent ( $\alpha$ )
  - 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

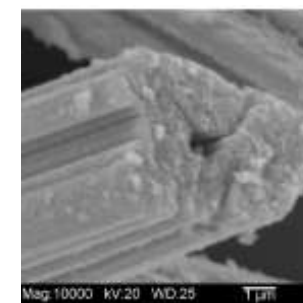
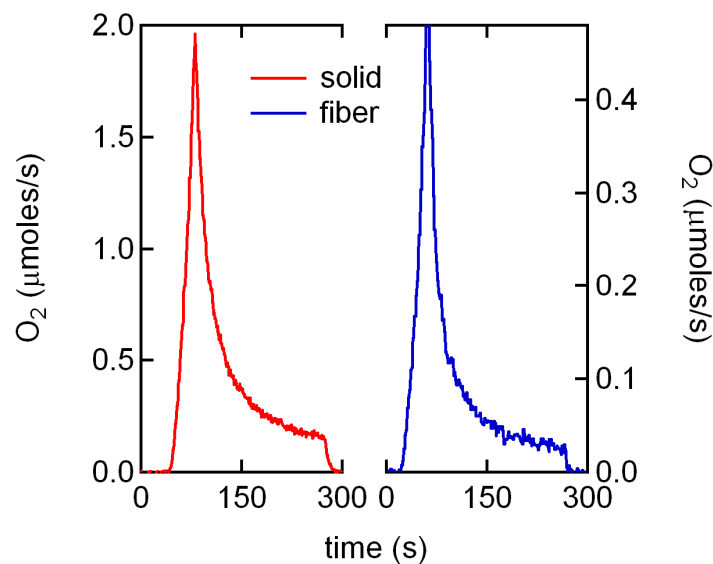
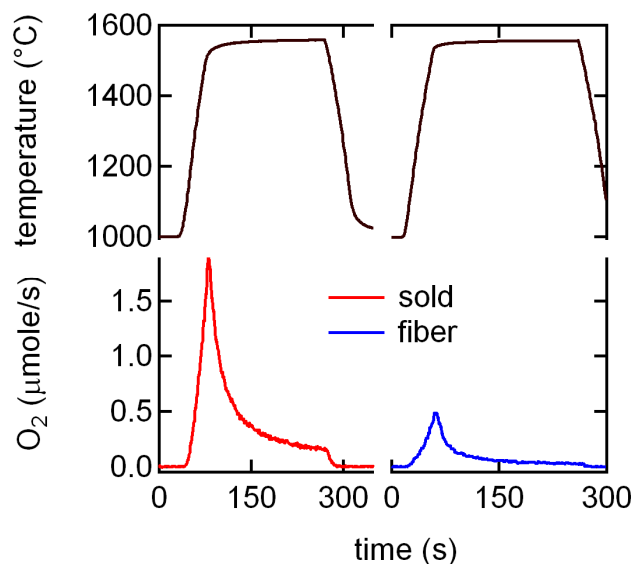


$\text{Fe}_2\text{O}_3$	$\text{CoFe}_2\text{O}_4$	$\text{MO}_x:\text{CeO}_{2-\delta}$	$\text{La}_{1-x}\text{Sr}_x\text{Cr}_{1-y}\text{Mn}_y\text{O}_{3-\delta}$	
YSZ	m-ZrO <sub>2</sub>	10 mol% Mn, Ni, Co, Mo, & Fe	$\underline{\text{X}}$	$\underline{\text{Y}}$
m-ZrO <sub>2</sub>			0.9	0.5
CeO <sub>2</sub>			0.8	
Al <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>		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-ZrO<sub>2</sub>, YSZ, CeO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>

chemical and/or  
physical modification  
required to achieve  
performance goals

# CeO<sub>2</sub> thermal reduction kinetics likely NOT limiting CSP chemistry

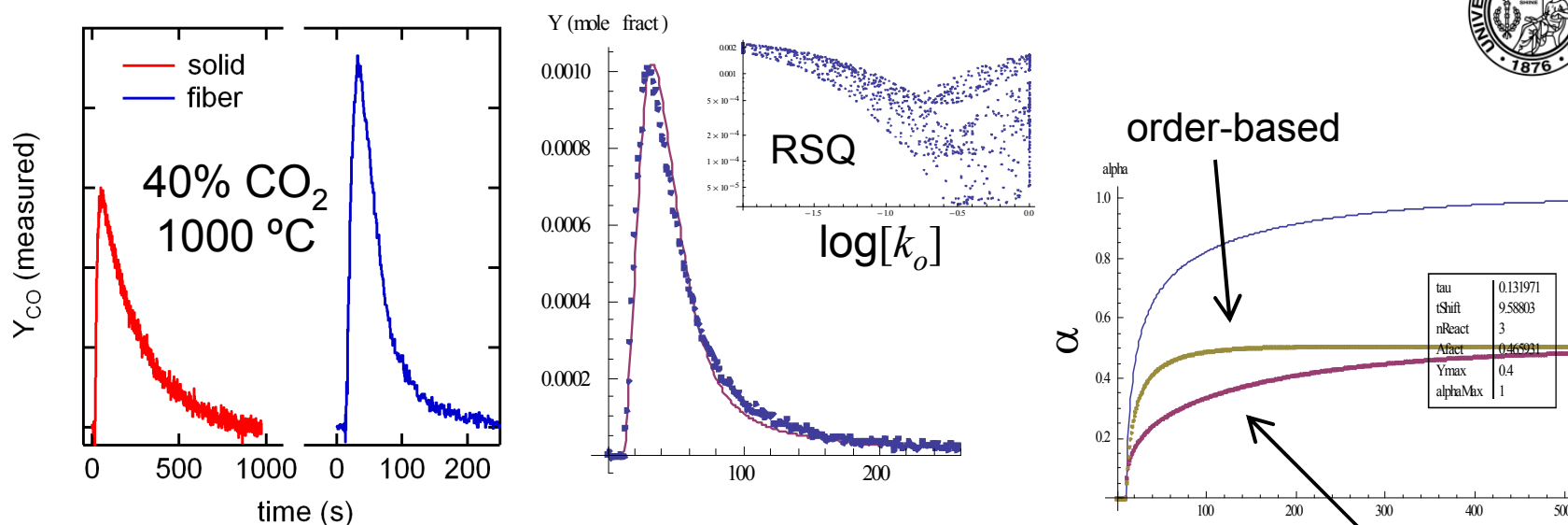


- Fiber diameter ~ 10 μm.
- Solid 1000 μm thick.
- Solid-state dynamics at *these length scales and heating rates* do not limit reduction kinetics.
  - Thermal conduction, vacancy diffusion, surface chemistry

mass (mg)	mole O (×10 <sup>-6</sup> )	δ
960	220	0.0197
207	48	0.0199



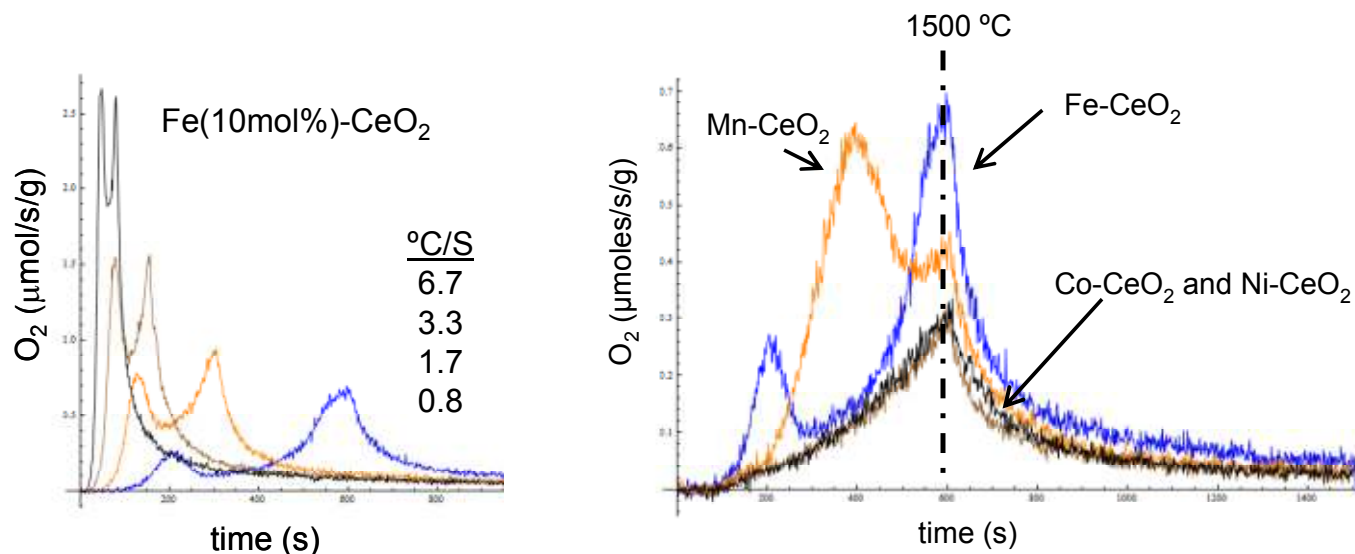
# Results for best fit to CO<sub>2</sub> splitting on fiber



- 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

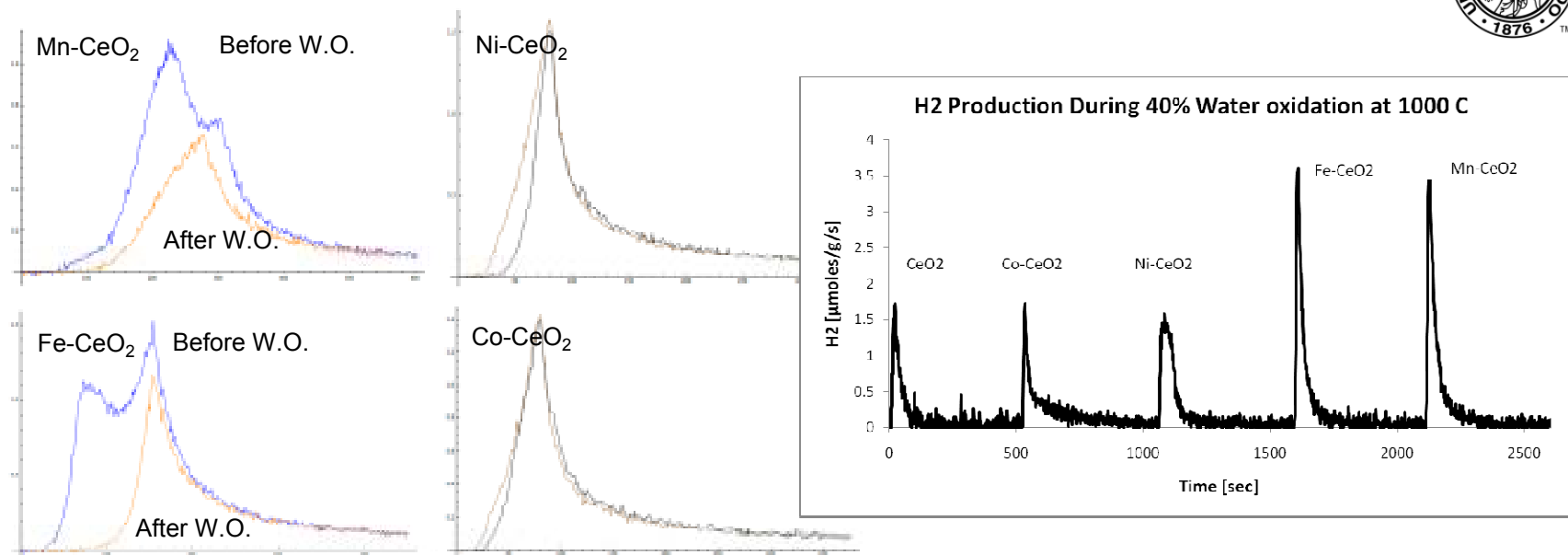


# O<sub>2</sub> redox behavior for transition-metal doped CeO<sub>2</sub> powders



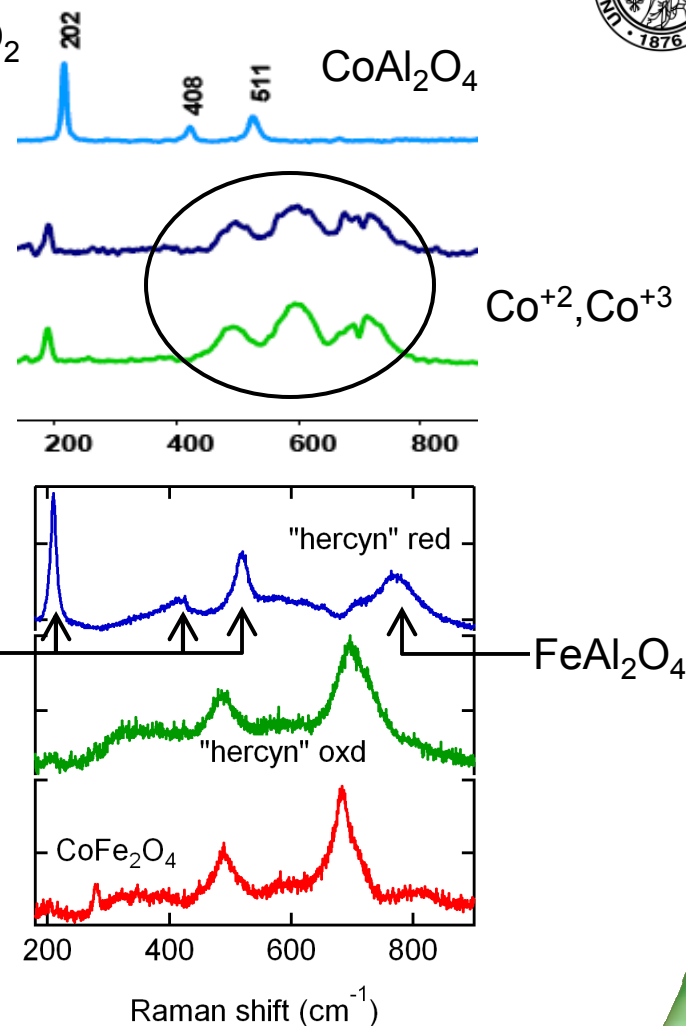
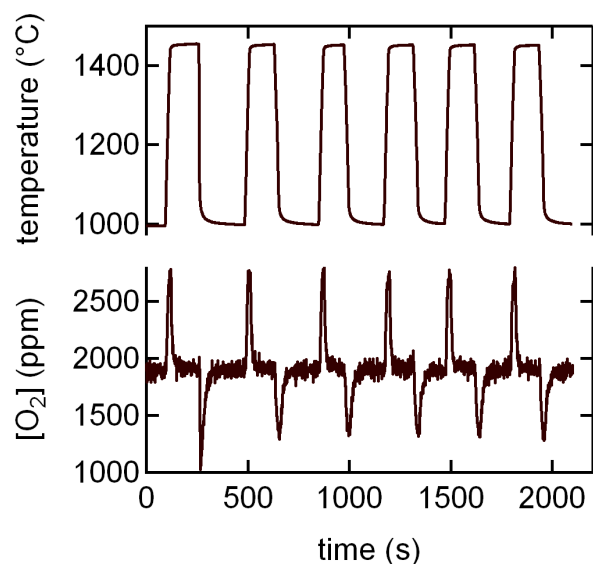
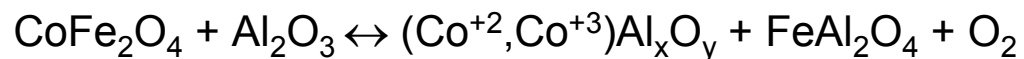
- Thermal reduction followed by O<sub>2</sub> oxidation
  - Kinetic model can be developed to describe reduction behavior
- O<sub>2</sub> evolution complex for Mn and Fe doped CeO<sub>2</sub>
  - Possible phase segregation
  - More O<sub>2</sub> evolved per unit mass of material
    - Multiple valence states for Mn and Fe cations likely

# H<sub>2</sub>O redox behavior for transition-metal doped CeO<sub>2</sub> powders



- O<sub>2</sub> evolution post-H<sub>2</sub>O 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 O<sub>2</sub> redox chemistry from thin film CoFeAl-spinels



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

# Summary

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- 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

# Funding and support

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