SAND2012-5571P

Metal Oxide Cycles: Introduction and Material Development

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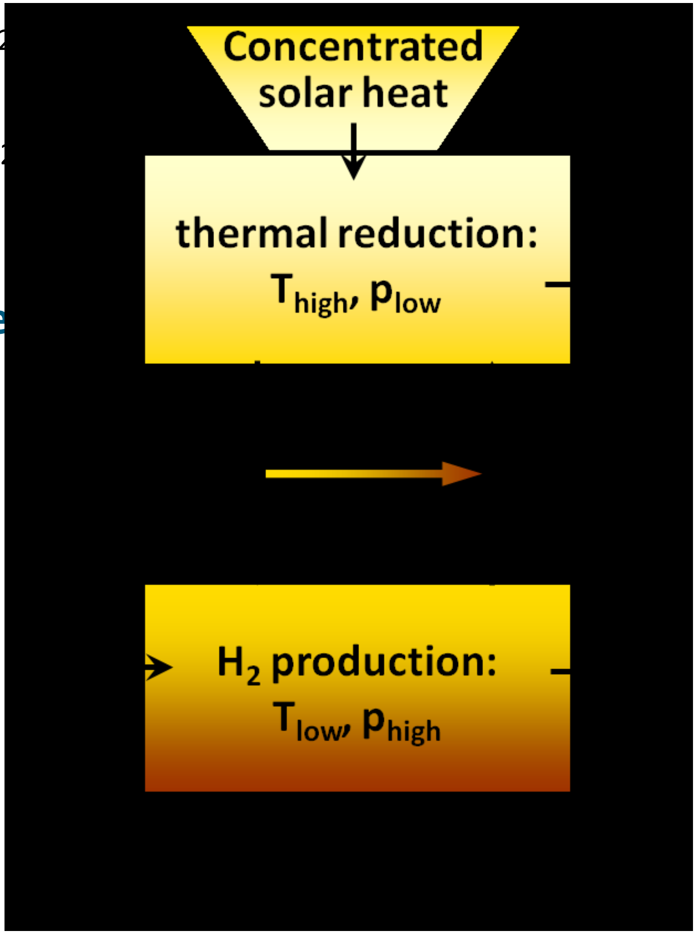
Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

The Two-step Non-volatile Metal Oxide Cycle

$$CeO_2 \rightarrow CeO_{2-\delta} + \frac{\delta}{2} O_2$$ STEP 1 @ T_{high}, low γ_{O2}

$$CeO_{2-\delta} + \delta \cdot H_2O \rightarrow CeO_2 + \delta \cdot H_2$$ STEP 2 @ T_{low}, high γ_{O2}



GOAL:

- **Develop hydrogen-producing thermochemical (TC) cycle and efficient solar-powered reactors.**

OBJECTIVE:

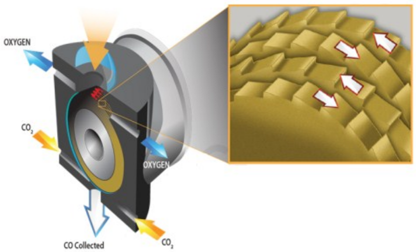
- **Identify and characterize viable reactant materials.**
  - Non-volatile metal oxides
- **Design and demonstrate highly-efficient reactors.**
  - Continuous H_2 production at annual average $\eta_{solar} > 25\%$
  - Avoid energy penalties going from solar → e- → H_2

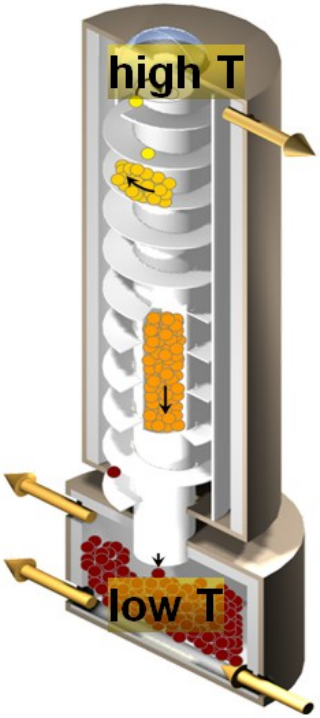
CHALLENGE:

- **Meet or exceed DOE cost targets for H_2 production.**
  - Need to operate at a system efficiency GREATER than PV – cold electrolysis (existing technology)
  - Annual average $\eta_{solar} \approx 15\% - 20\%$

Approach: Identify Key Design Attributes That Impact Efficiency

Reactor	Direct Irradiance	Efficient Recuperation	Continuous Operation	H_2/O_2 Spatial Separation	Pressure Separation	Institute
CR5	X	X	X	X		SNL
moving particle bed	X	X	X	X	X	SNL
rotary reactor	X		X	X		Tokyo Inst. Tech.
lined cavity	X				X	ETH, CalTech
tubular packed bed					X	U. Colorado
tubular flow			X	X	X	U. Colorado
Hydrosol	X				X	DLR
fluidized bed	X		X	X		U. Niigata
rotary reactor	?	?	?	?	?	U. Minn., CalTech
magnetized fluidized bed	?	?	?	?	?	U. Florida





Key efficiency attributes:

- DIRECT solar absorption by working material
- EFFICIENT heat recovery between T_H & T_L
- CONTINUOUS on-sun operation
- INTRINSIC gas and pressure separation

Reactor design and material performance are critically linked.

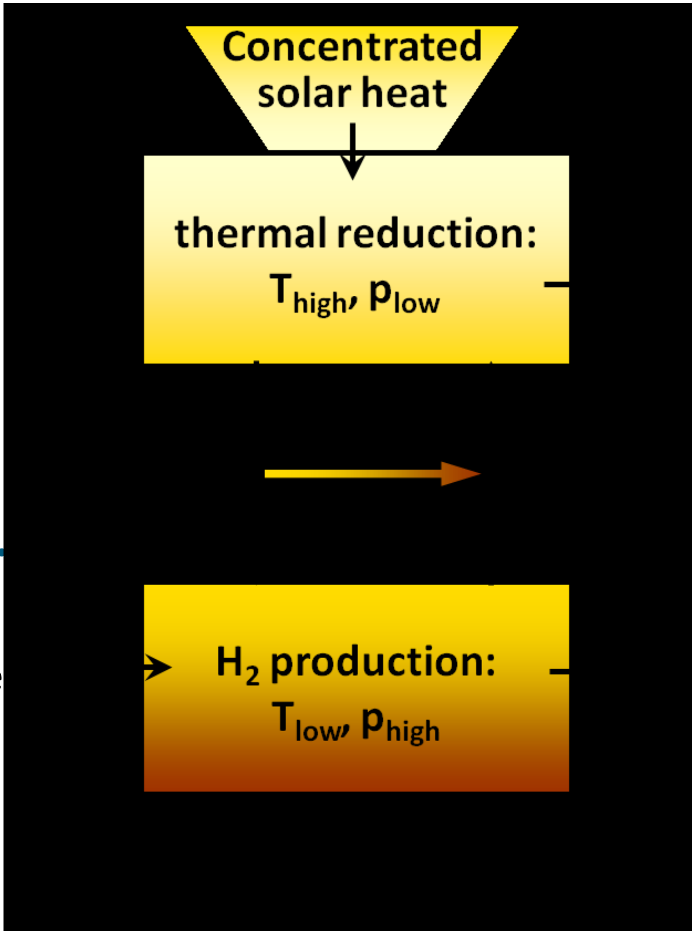
Reducing To Practice: Technological Challenges For Materials

CHALLENGE:

- **Stability and long-term durability of redox active ceramic structures.**
  - Thermal and mechanical stresses
    - phase change, volatility
    - heating rates (1000°C/min), cycling
  - Compatibility with materials of construction
- **Oxidation/reduction kinetics and oxygen capacity.**
  - Residence time depends on rates
    - comparable oxidation and reduction kinetics desirable
  - Mass throughput depends on oxygen capacity
- **Earth abundant and easy to manufacture.**

APPROACH:

- **Use particles.**



Recent Progress: Search For Suitable Materials

CHALLENGE:

- **Very large number of possible redox active compounds.**
- **Many different ways to modify compounds to improve performance.**
  - Nano-engineering, doping, catalyzing

ferrites		ceria compounds		perovskites	
Fe_2O_3	$CoFe_2O_4$	$MO_x:CeO_{2-\delta}$	MO_x:CeZr	$(La_{1-x}Sr_x)([Al,Cr]_{1-y}Mn_y)O_{3-\delta}$	
YSZ m-ZrO_2	m-ZrO_2	10 mol% Mn, Ni, Co, Mo, & Fe	various quaternary compositions	X	Y
CeO_2				0.9	0.25
Al_2O_3	Al_2O_3			0.8	0.50
				0.7	0.75
				0.6	
				0.5	

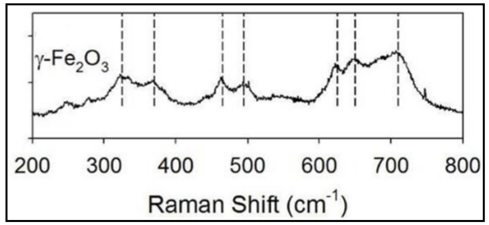
property	ferrite (Fe_2O_3)	ceria (CeO_2)	hercynite ($FeAl_2O_4$)	perovskite (ABO_3)	MO_x:CeZr $MO_x:CeO_2$	ideal
redox kinetics	SLOW	FAST	SLOW/MED	?	?	FAST
redox capacity	HIGH	LOW	MEDIUM	HIGH	?	HIGH
reduction T_H	MED/HIGH	HIGH	MEDIUM	LOW	MEDIUM	LOW
durability	MEDIUM	HIGH	HIGH	?	HIGH	HIGH
earth abundance	HIGH	LOW/MED	HIGH	?	LOW/MED	HIGH

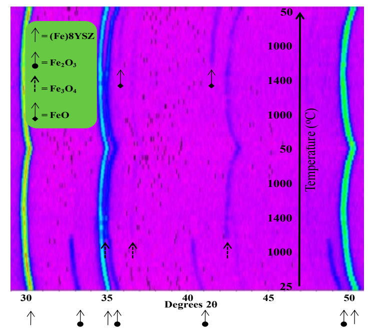
APPROACH:

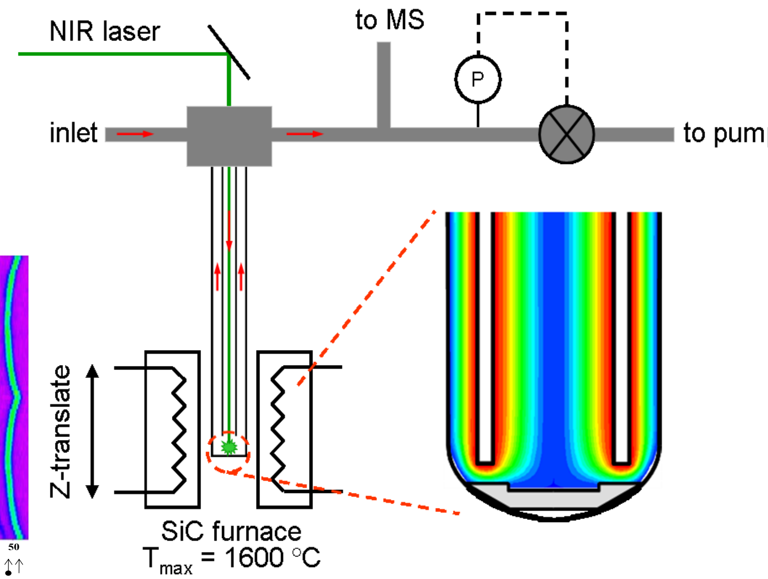
- **Chemical intuition and simple thermodynamic assessments.**
  - Developing a knowledge base that may provide descriptors for composition-performance mapping
- **"Rapid" synthesis and screening.**
  - 5-10 compounds per month

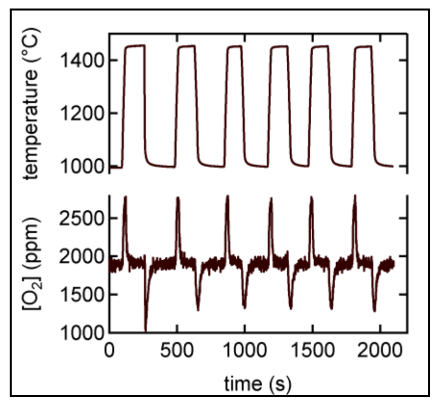
Experimental Methods For Characterizing Redox Materials

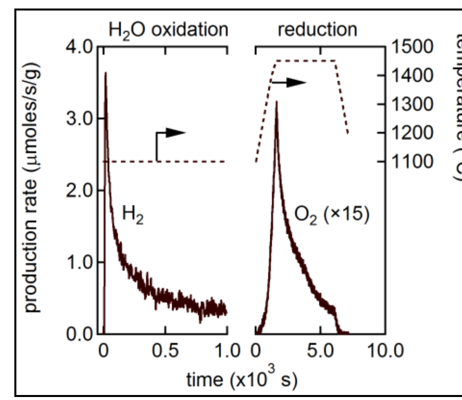
- **Surface analysis.**
  - Surface Raman, XPS
- **Material properties.**
  - BET surface area
  - SEM-EDX, TEM-EELS, in-situ XRD
- **Kinetic measurements.**
  - Stagnation flow reactor
    - 500 W CW NIR laser heating
    - Modulated beam mass spectrometer
- **Screen for O_2 uptake and release.**
  - Assess redox viability
- **Resolve thermal reduction behavior.**
- **Resolve water splitting behavior.**
  - Variable T, P, $[H_2O]$
- **Analysis.**
  - Resolve rate limiting mechanisms
  - Develop kinetic models
  - Evaluate material stability
  - Test cycle performance







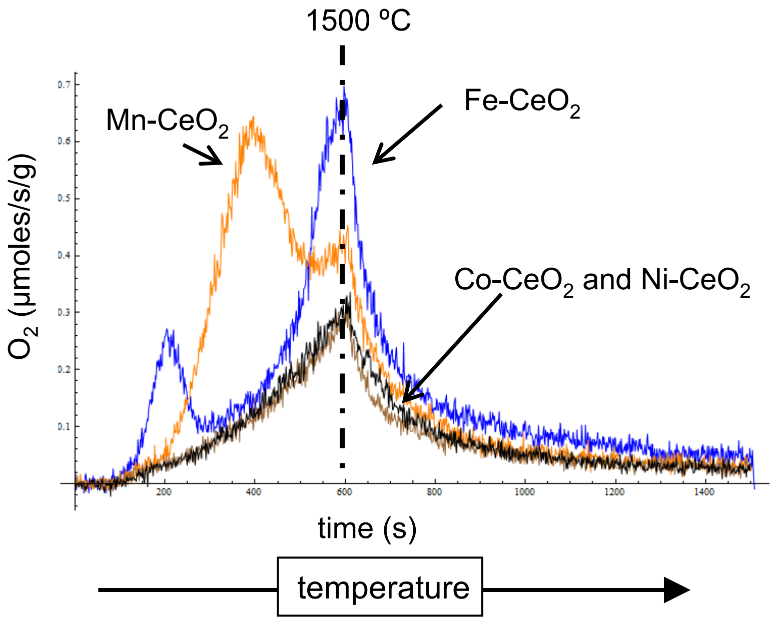




Assess material behavior at heating rates > 10°C/s.
Expose material to many rapid heating cycles.

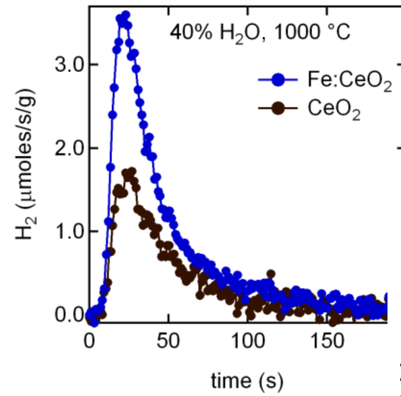
Recent Progress: TM Doping Of Ceria

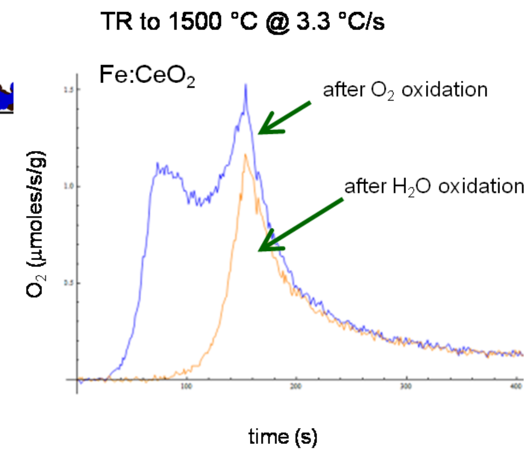
thermal reduction @ 1500°C



- **O_2 evolution complex for Mn and Fe.**
  - More O_2 evolved per unit mass of material than undoped CeO_2
  - Multiple valence states for Mn and Fe cations likely in doped system

H_2O oxidation @ 1000°C

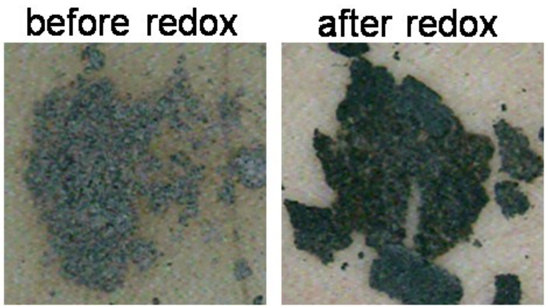


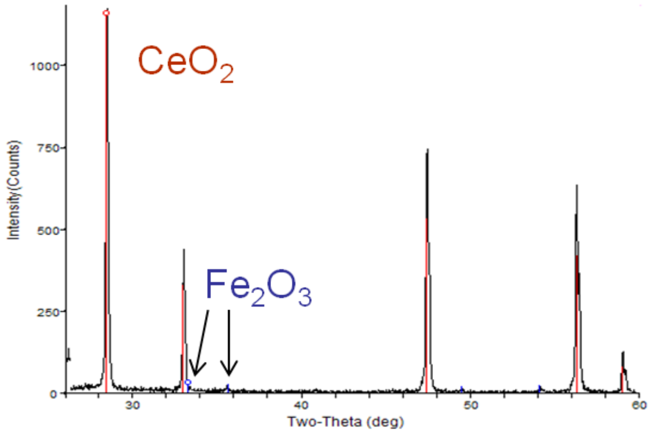


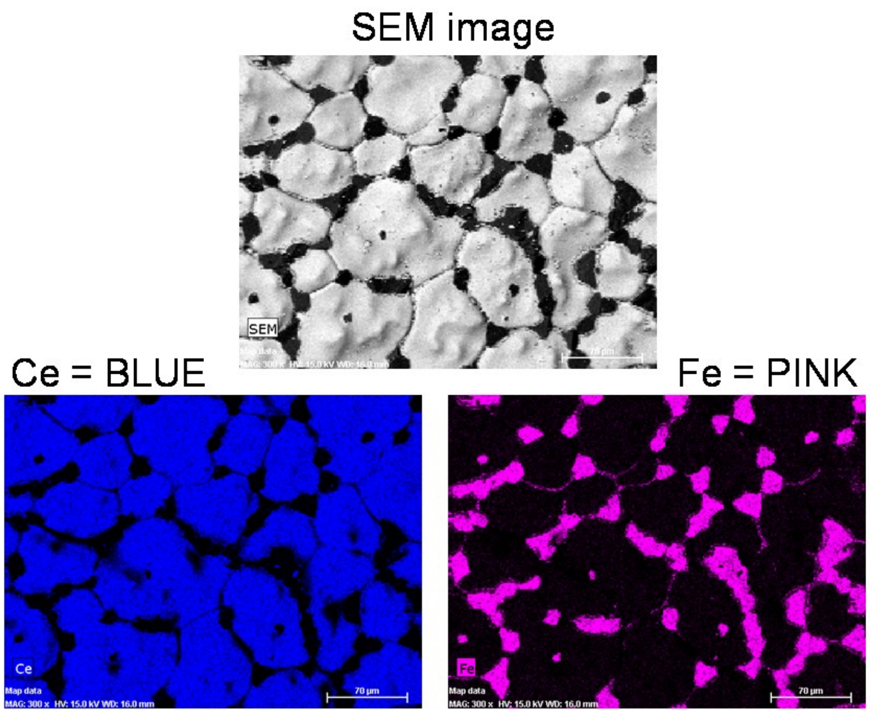
- **FeO_x doping increases net H_2 production.**
- **Active sites in Fe-doped CeO_2 oxidize at different rates.**

Fe and Mn change material behavior but difficult to re-oxidize added with water.

Recent Progress: Why Fe Doped Ceria Will Not Work





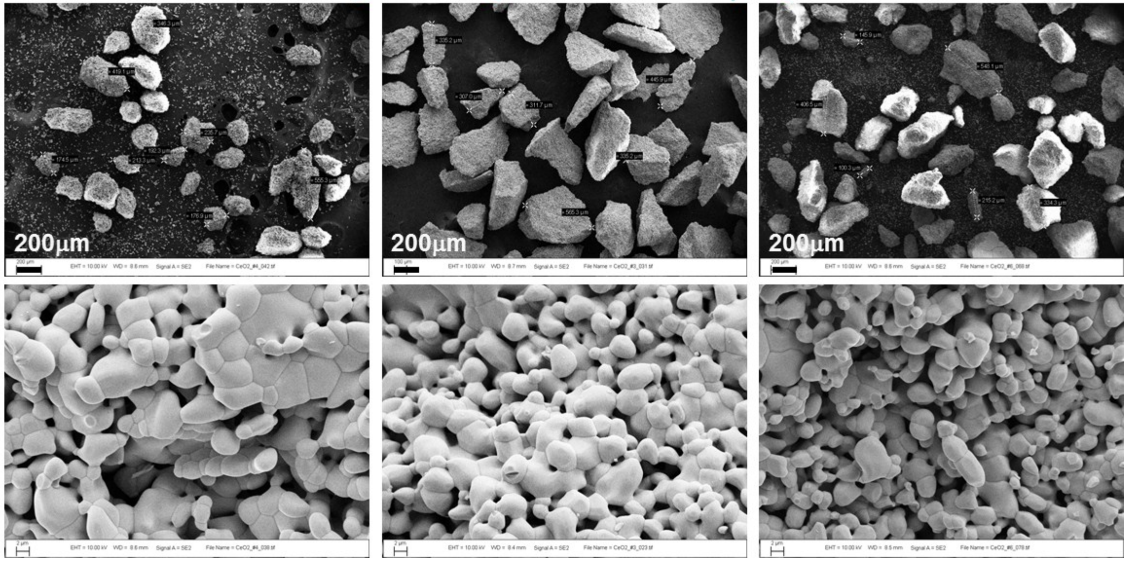


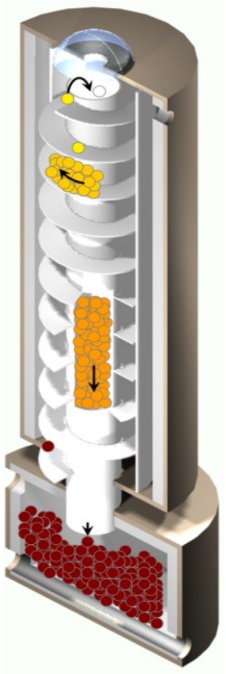
- **Reduction in helium at 1500°C followed by H_2O oxidation at 1000°C.**
  - Severe problems with sintering and reactivity with other ceramics
  - Fe phase segregation evident in SEM-EDS despite lack of evidence in XRD
  - Slow kinetics on "low temperature" O-site

Fe doping not a viable strategy but other modifications might work.

Recent Progress: Particle Design And Manufacturability

Ceria particles synthesized from 5µm powder





CHALLENGE:

- Optimize particle transport in conveyor.

APRROACH:

- Determine optimal particle size for mass throughput and permeability.
- Develop and scale up a synthesis method.
- Test chemical and mechanical durability.

Efficient conveying depends on shape, size, density, cohesive strength, etc.
Low gas permeability is key to pressure separation and high efficiency.

Materials R&D: Current Status FY12

ACTIVITY	MILESTONE	COMPLETE
Develop a protocol for material characterization	evaluated oxidation behavior (water splitting) of ferrite, ceria, and hercynite cycles	**50%**
Develop and validate a kinetic model for ceria	model used to establish theoretical cycle performance metrics for ceria in Sandia reactors	**100%**
Synthesize and characterize doped ceria materials	decreased thermal reduction temperature for ceria (T_H) below 1450°C	**50%**

Publications:

1. Scheffe, J. R.; McDaniel, A. H.; Allendorf, M. D.; Weimer, A. W. "Kinetic analysis of the oxidation of $Co_{0.9}Fe_{2.1}O_4/ZrO_2$ for thermochemical H_2 production." In review at E&ES. (2012)
2. Arifin, D.; Aston, V.A.; Liang, X.; McDaniel, A.H.; Weimer, A.W. "$CoFe_2O_4$ on porous Al_2O_3 nanostructure for solar thermochemical CO_2 splitting." In revision at E&ES. (2012)

Remainder of FY12:

- **Characterize the redox kinetics of MO_x:CeZr.**
  - Small number of doped variants using transition metals (8 samples)
- **Characterize the redox kinetics of (SrLa)(AlMn)O_3 perovskite.**
  - Small number of compositional variants within family (5-10 samples)

Materials R&D: 2020 Performance Projections

property	compared to...	metric	ideal
redox kinetics	$\geq CeO_2$	90% utilized < 1 min	**FAST**
redox capacity	$\geq Fe_3O_4$	$\geq$ 6.9%-mass	**HIGH**
reduction T_H	$\leq Fe_3O_4$	$\leq$ 1300°C	**LOW**
durability	?	1,000,000 cycles	**HIGH**
earth abundance	?	availability ($) of ore	**HIGH**

- **Compare material performance to end member compounds CeO_2 and Fe_3O_4.**
  - Ceria kinetics with ferrite capacity to attain annual average η_{solar} > 25%
- **Other design considerations:**
  - Manufacturability, density, permeability, chemical and mechanical stability
- **Output of brainstorming session will define staged performance projections.**

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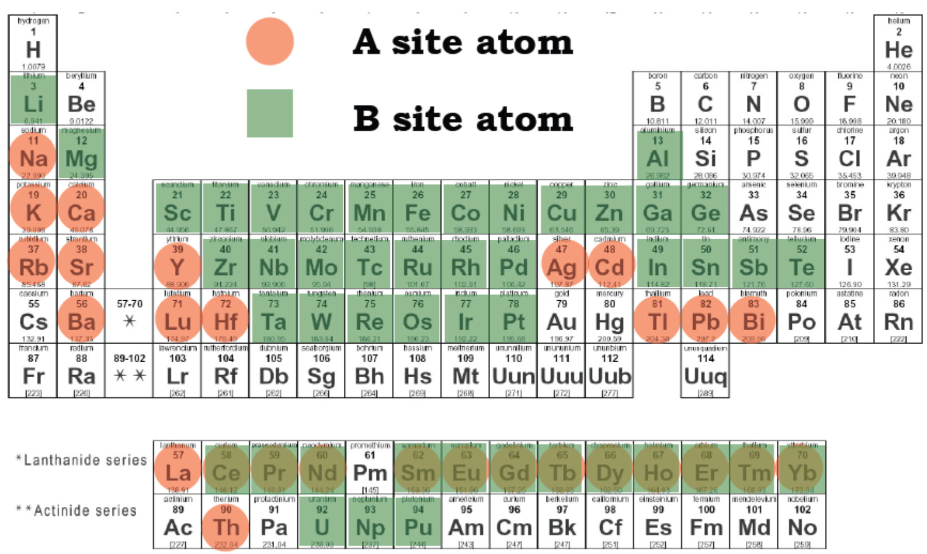
Materials R&D Plan

- **Focus on ABO_3 perovskite-type oxides.**
  - High oxygen vacancy concentration, oxygen vacancy diffusivity, and surface exchange = FAST KINETICS
  - Structurally stable with large range of oxygen nonstoichiometry = HIGH CAPACITY and HIGH DURABILITY
  - Large number of possible ABO_3 compositions = HIGH ABUNDANCE

Structure, Properties, Applications of Perovskite-type Oxides



Materials R&D Plan

- **Formulate two methodologies for theoretically screening perovskites.**
  - 100's – 1000's of compositions
  - DFT-based computational chemistry using simple descriptors
    - Demonstrated by Prof. Christopher Wolverton, NWU
  - Choose A, B elements based on heuristic rules (binary phase thermodynamics, abundance, tolerance factors, aliovalence, etc.)
    - Demonstrated by Prof. Jianhua Tong, CSM
- **Downselect and synthesize most promising theoretical candidates via sol-gel or solid-state synthesis reaction (SSR).**
- **"Rapidly" characterize redox behavior.**
  - Two-environment TGA screening
    - throughput limited to 1 sample per day per TGA
  - Laser-heated modified stagnation flow reactor
    - throughput limited to 5-10 samples per day
- **Experimental feedback to theoretical selection protocol.**
  - Improve and refine method(s).
- **Downselect final candidate(s) based on material characteristics.**
  - Redox behavior, manufacturability, density, permeability, chemical and mechanical stability

Materials R&D Plan

- **Scale and scope of project plan depends on available funding.**

	PY1	PY2	PY3	PY4	PY5
Theoretical Method	comp. chem. heuristic	downselect method			
Synthesis	composition Go/No-Go's based on feedback				
Redox Characterization	composition Go/No-Go's based on feedback				
Material Properties					Final Selection

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