Solar-thermal ALD Ferrite-Based Water Splitting Cycles

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Project ID No. PD028

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Overview

Timeline

- 6-1-2005
- 9-30-2012
- 80% completed

Budget

•Total Project Funding

2005-2010: $900K DOE

$270,000 Cost Share

•Funds received in FY11

$310,000 (subcontract from SNL)

$ 77,500 Cost Share

•Planned FY2012 Funding

$217,000 (subcontract from SNL)

Barriers

U. High-Temperature Thermochemical Technology

V. High-Temperature Robust Materials

W. Concentrated Solar Energy Capital Cost

X. Coupling Concentrated Solar Energy and Thermochemical cycles

Partners

National Renewable Energy Laboratory (NREL)
Sandia National Laboratories (SNL)

Objective

- Develop and demonstrate robust materials for a two-step thermochemical redox cycle that will integrate easily into a scalable solar-thermal reactor design and will achieve the DOE cost targets for solar hydrogen*:

  ($6/gge H_2 in 2012; $3/gge H_2 in 2017)

  * Cost targets being updated by DOE in FY2012

Process Overview

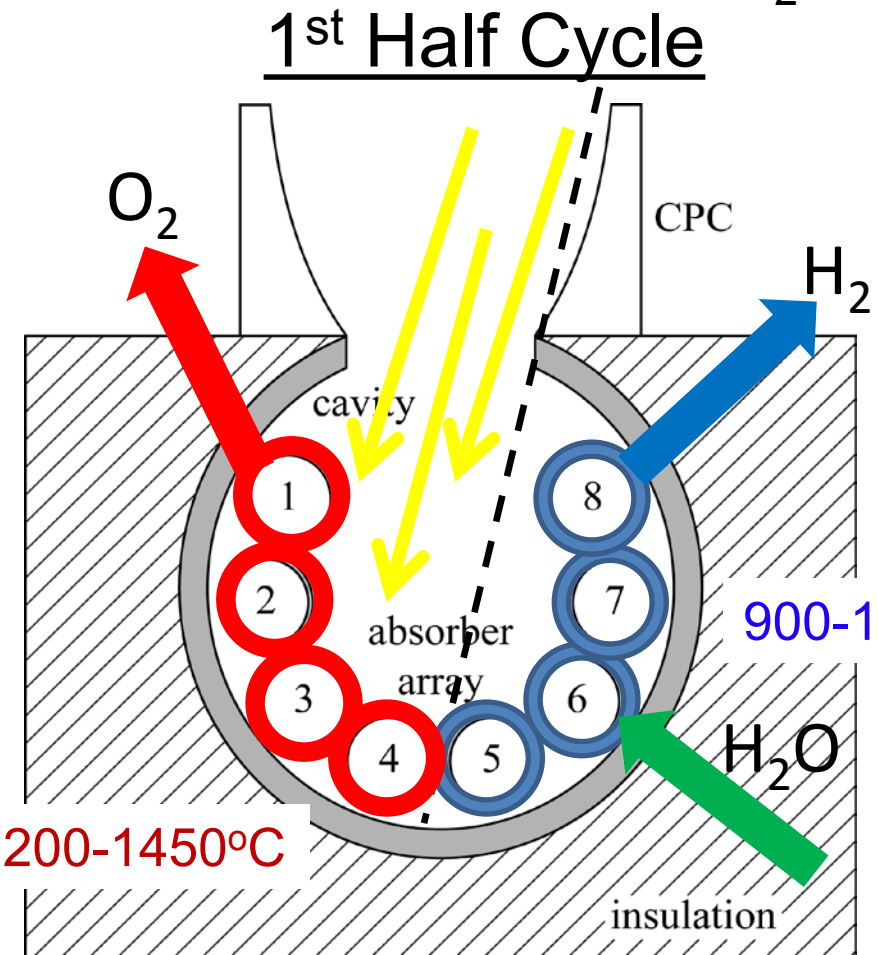
- Chemistry & Reactor Configuration
- Materials Requirements
- Thermodynamics Predicted Robustness

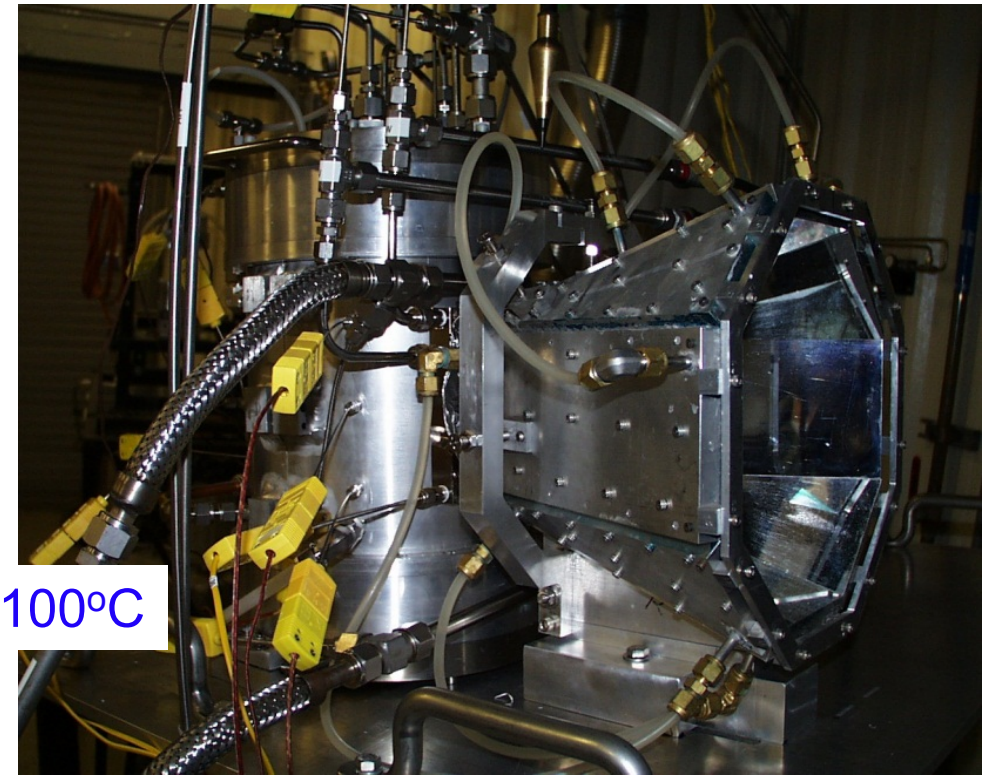
SurroundSun™ Multi-tubular Switching Redox Reactor/Receiver

(R): $CoFe_2O_4 + 3\ Al_2O_3 \rightarrow [CoAl2O4{:}2Fe2AlO4] + 1/2O_2$

(O): $[CoAl_2O_4{:}2Fe_2AlO_4] + H_2O \rightarrow CoFe_2O_4 + 3\ Al_2O_3 + H_2$

$H_2O \rightarrow H_2 + 1/2O_2$

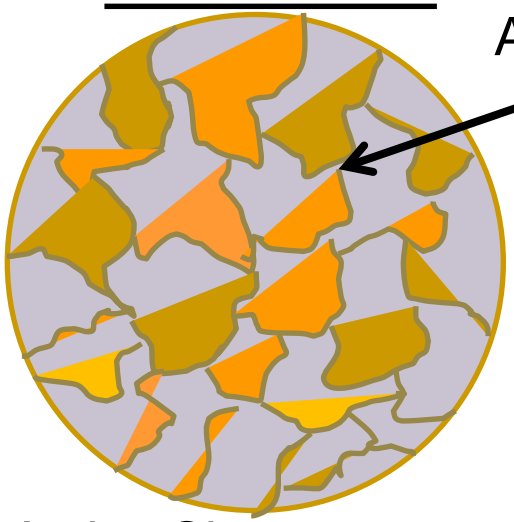




University of Colorado
Multi-tube Solar Receiver/Reactor

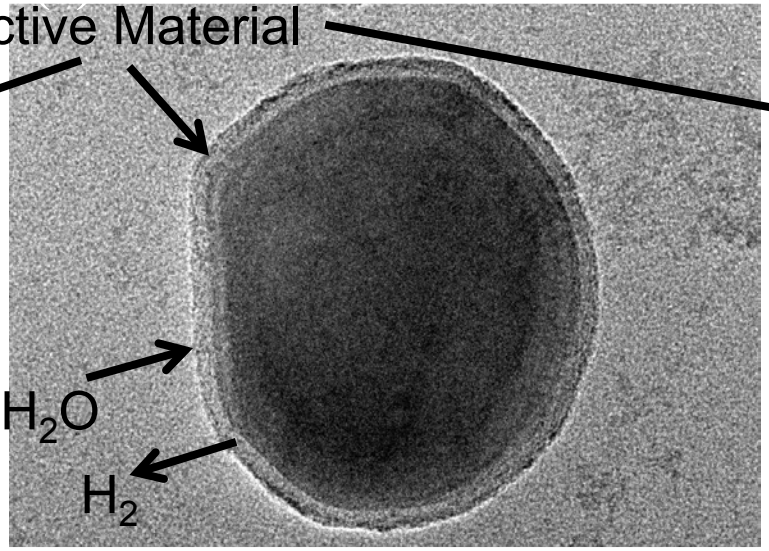
Active Material Types

Bulk/Solid



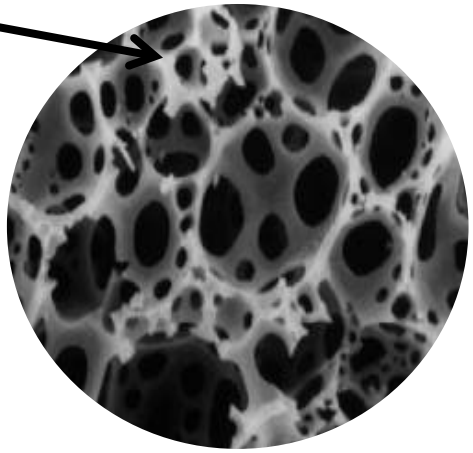
Active Sites Scattered, but Near Surface; Rates Limited by Heat Conduction & Diffusion; Sensible Heat Losses

Coated/Solid



Reaction at Surface; Diffusional Resistances Eliminated; Rates Limited by Heat Conduction; Sensible Heat Losses

Coated/Porous



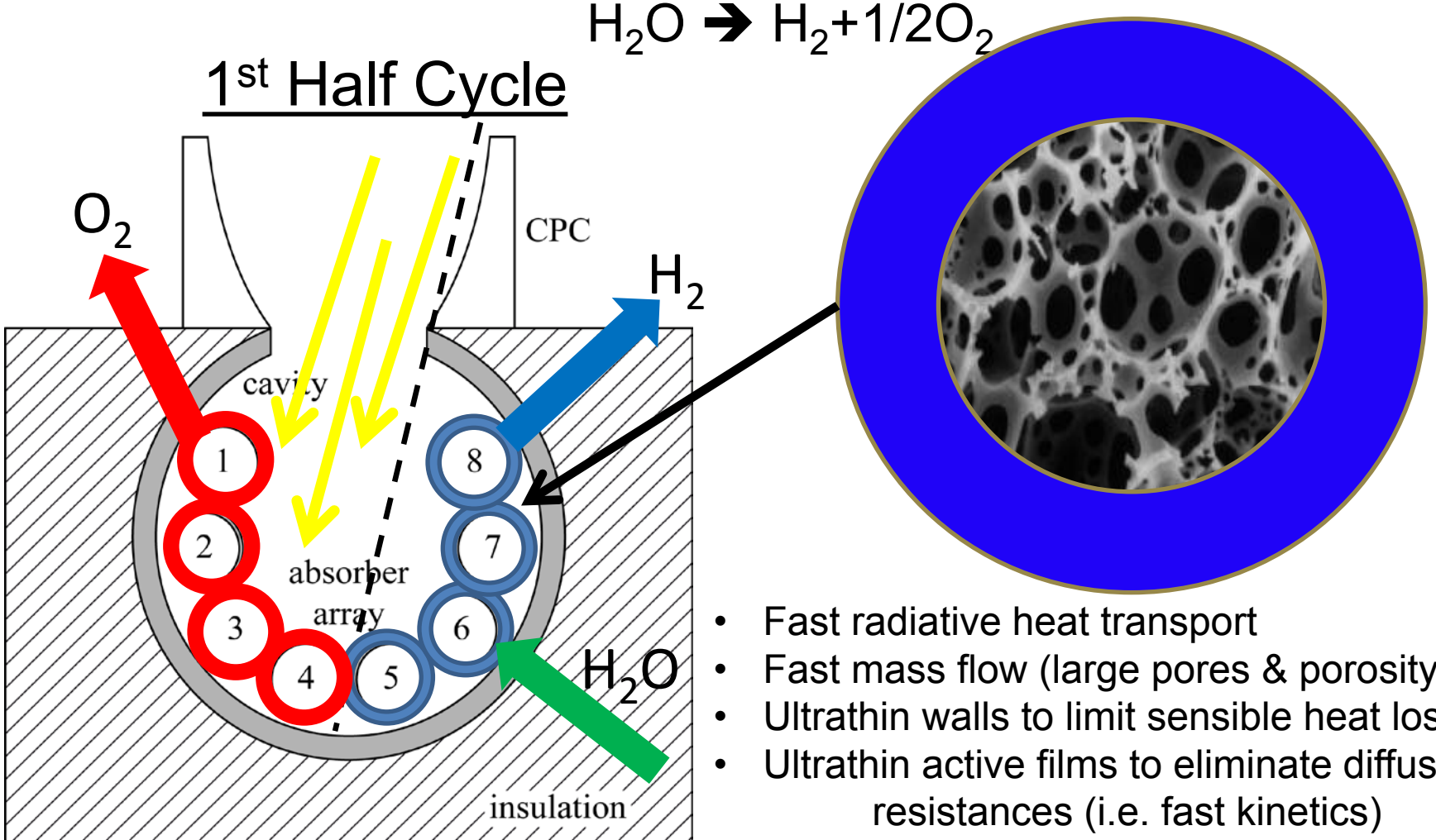
Reaction Throughout; Diffusional Resistances Eliminated; Radiation Drives Heat Transfer; No Sensible Heat Losses

Nanostructured Materials Design is Key for Optimal Performance

(R): $CoFe_2O_4 + 3\ Al_2O_3 \rightarrow [CoAl2O4{:}2Fe2AlO4] + 1/2O_2$

(O): $[CoAl_2O_4{:}2Fe_2AlO_4] + H_2O \rightarrow CoFe_2O_4 + 3\ Al_2O_3 + H_2$

$H_2O \rightarrow H_2 + 1/2O_2$

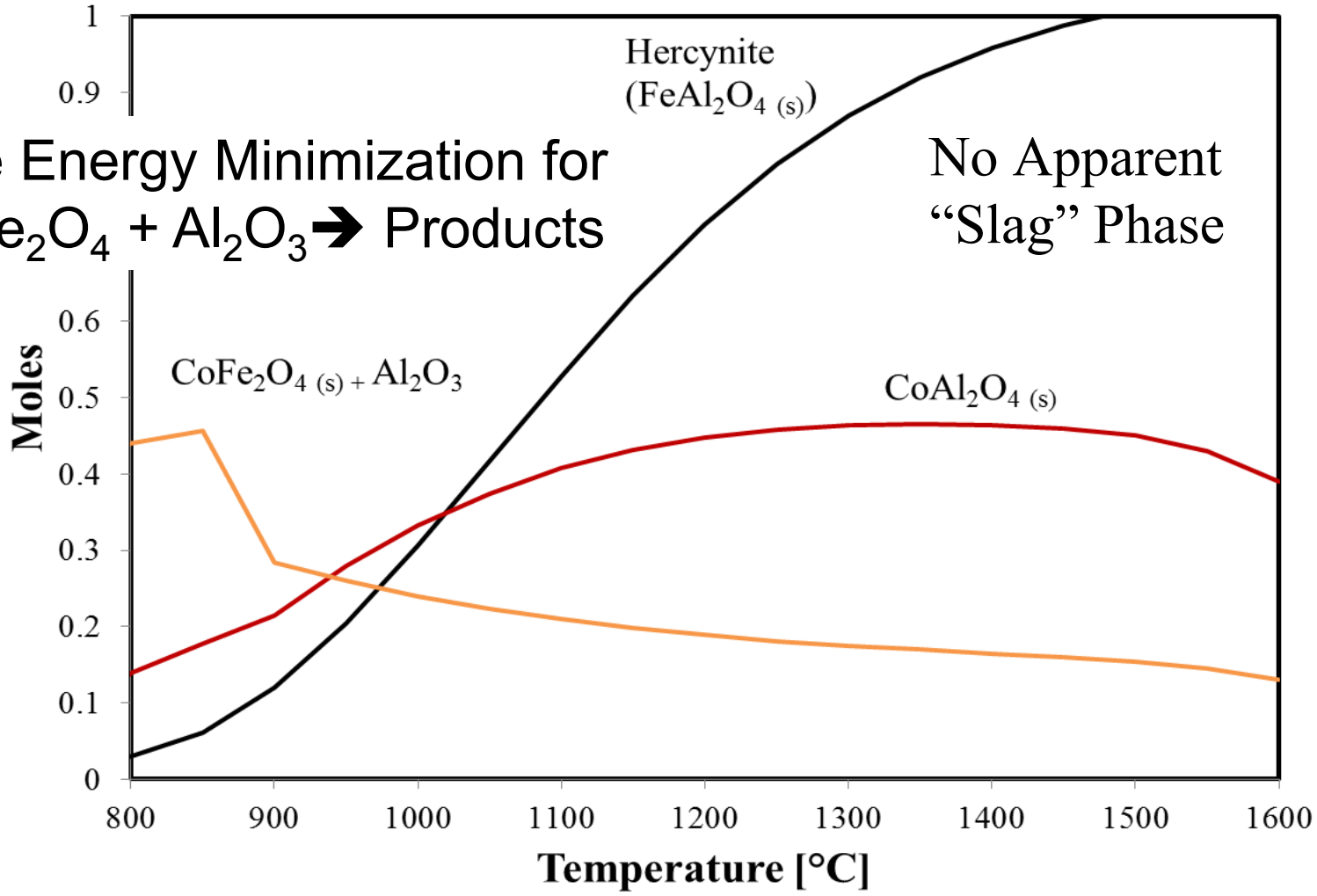


- Fast radiative heat transport
- Fast mass flow (large pores & porosity)
- Ultrathin walls to limit sensible heat loss
- Ultrathin active films to eliminate diffusional resistances (i.e. fast kinetics)

"Hercynite Cycle" is Predicted Thermodynamically to be Robust

Free Energy Minimization for $CoFe_2O_4 + Al_2O_3$ ➔ Products

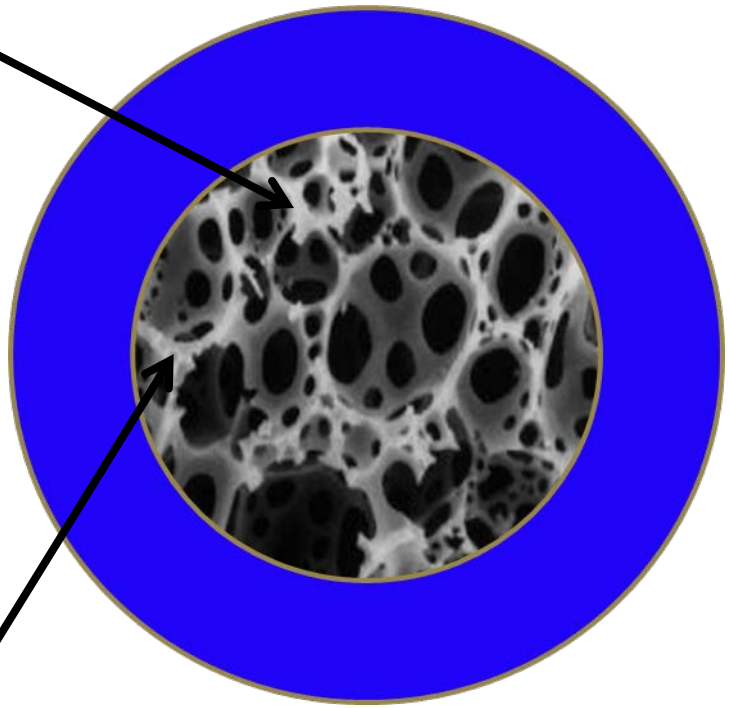
No Apparent "Slag" Phase



Scheffe J.R., J. H. Li and A. W. Weimer, International J. of Hydrogen Energy, 35, 3333, 2010

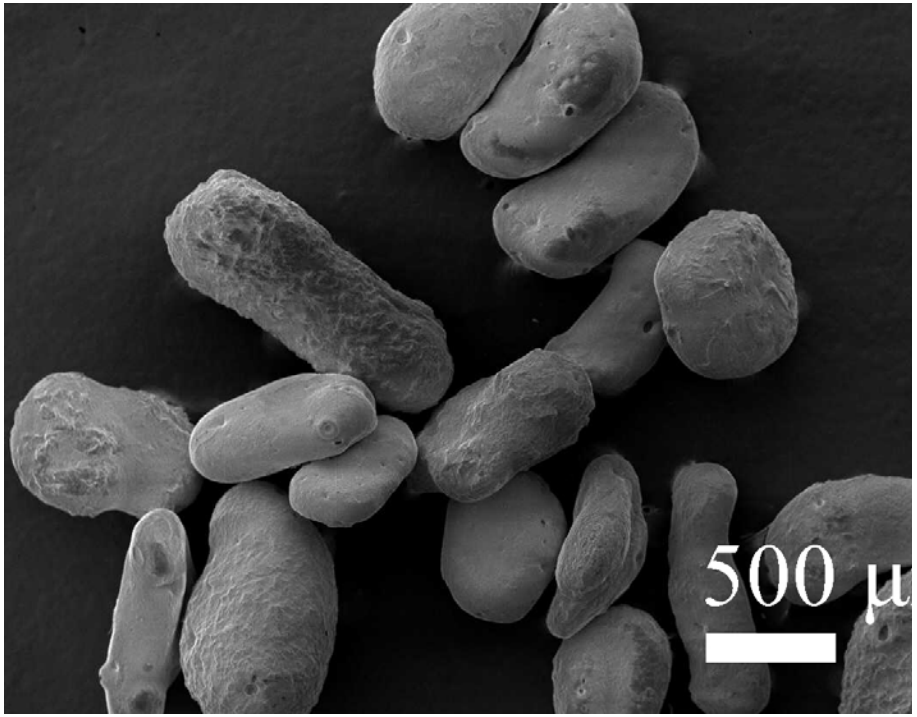
Designed Active Materials Fabrication

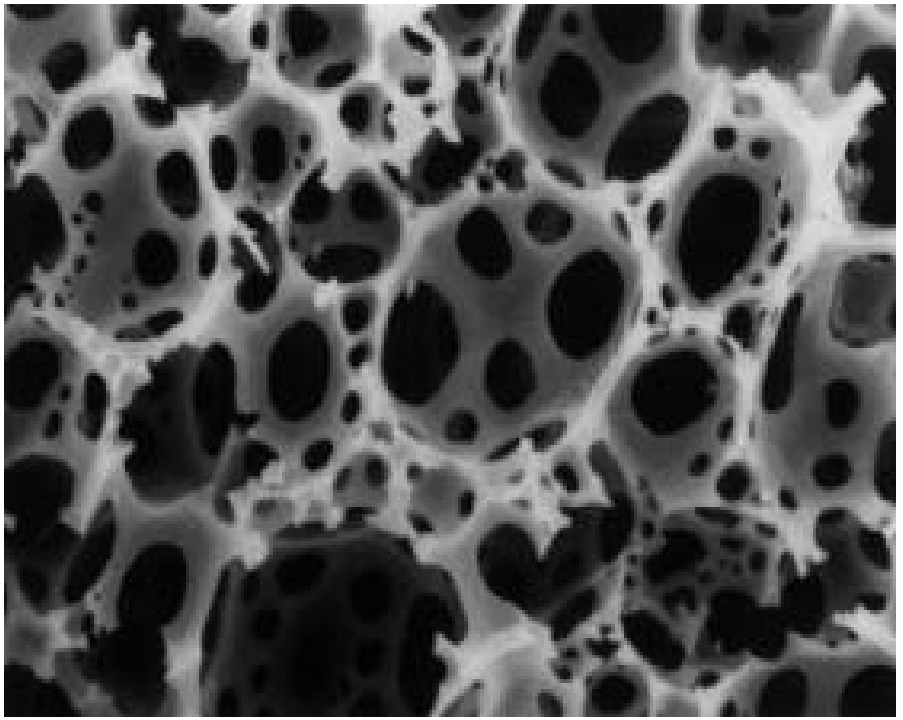
- Sacrificial Polymer Template is used for achieving desired porosity and pore diameter



- Atomic Layer Deposition (ALD) used to Synthesize Designed Nanostructure of Active Materials

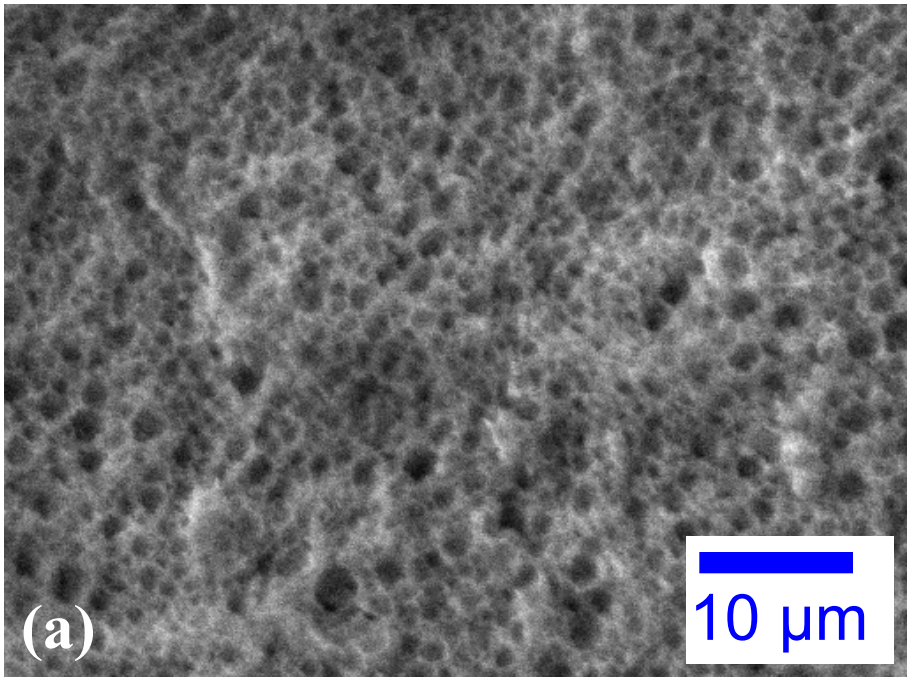
Uncoated poly(styrene-divinylbenzene) particles (Dowex™ or Cavilink™)



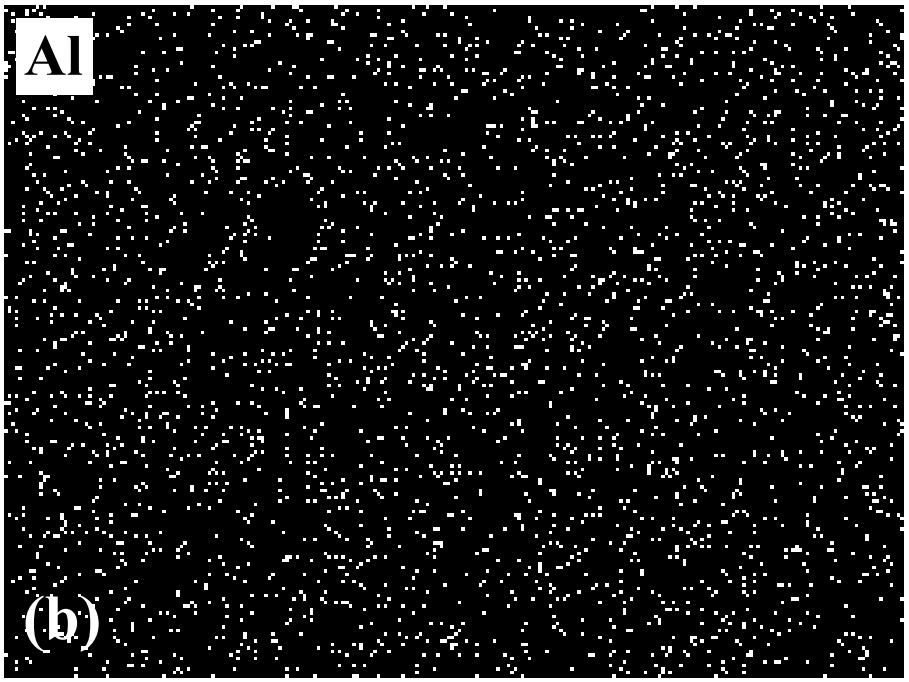


Particle size of ~600 µm, a porosity of 85%, a pore volume of 8-10 cm^3/g, a surface area of 43.5 m^2/g, and a density of 70 kg/m^3

Alumina films were coated throughout the inner surface of the particles

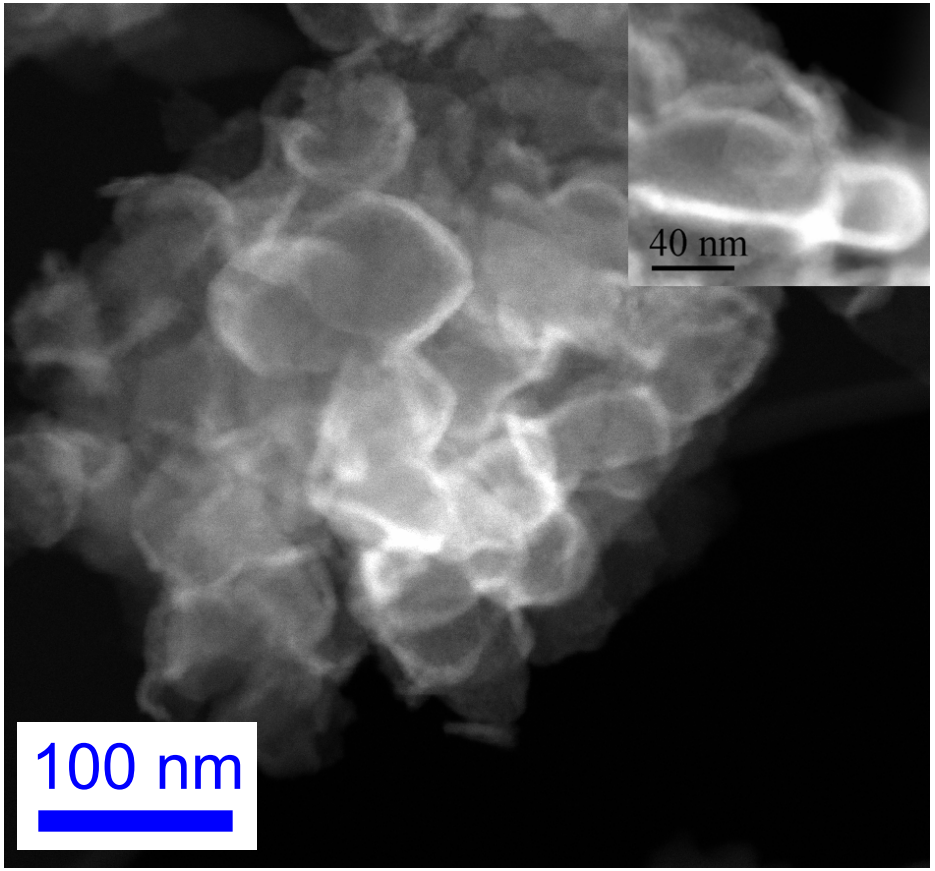


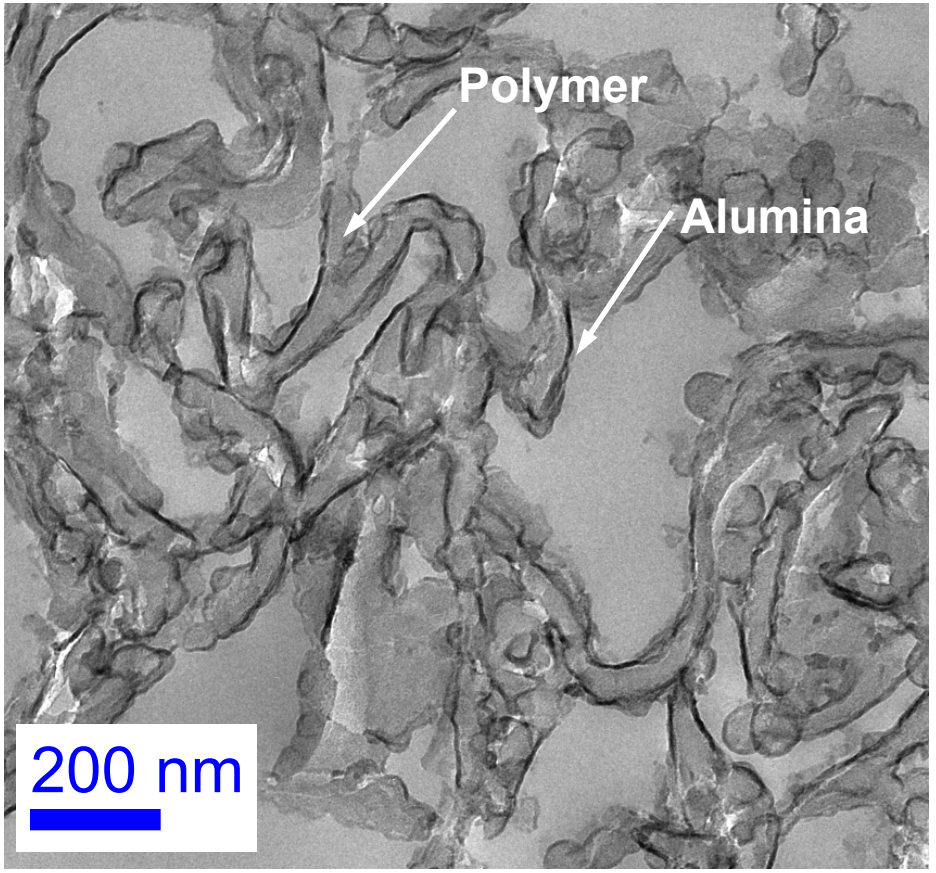
FESEM of cross sectional surface after 25 cycles of Al_2O_3 coating



Al EDS mapping

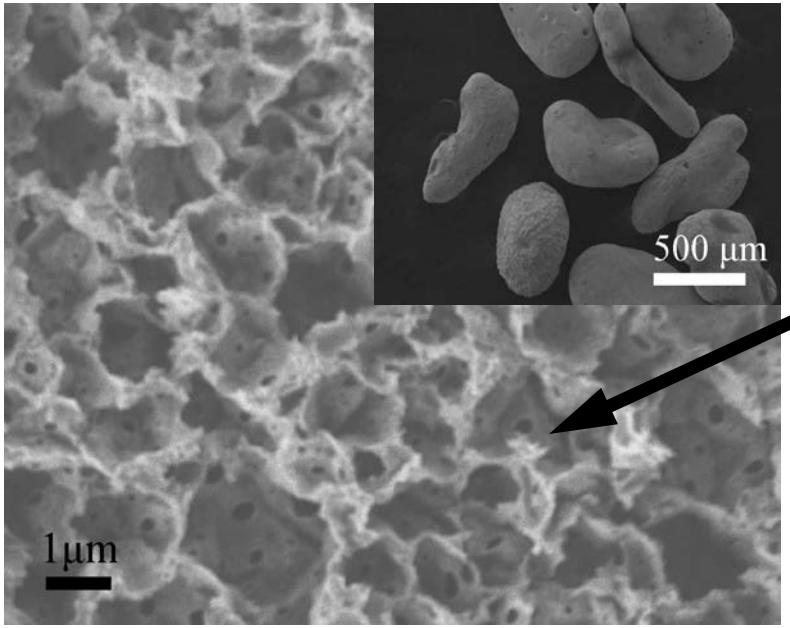
Conformal Al_2O_3 films coated on porous PS-DVB particles





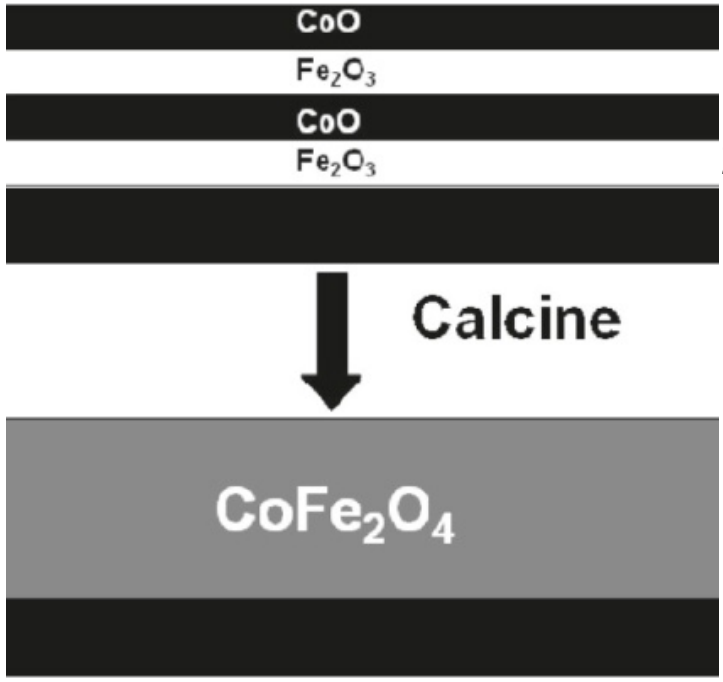
Liang XH, et al., Chemistry of Materials 19: 5388-5394, 2007

Porous Al_2O_3 particles after calcination, then subsequently coated with $CoFe_2O_4$



Skeletal γ-Al_2O_3
(80 m^2/g; 1 cm^3/g pore volume);
inset image shows the size of
the porous γ-Al_2O_3 particles

50 cycles: ~ 20 wt.% $CoFe_2O_4/Al_2O_3$

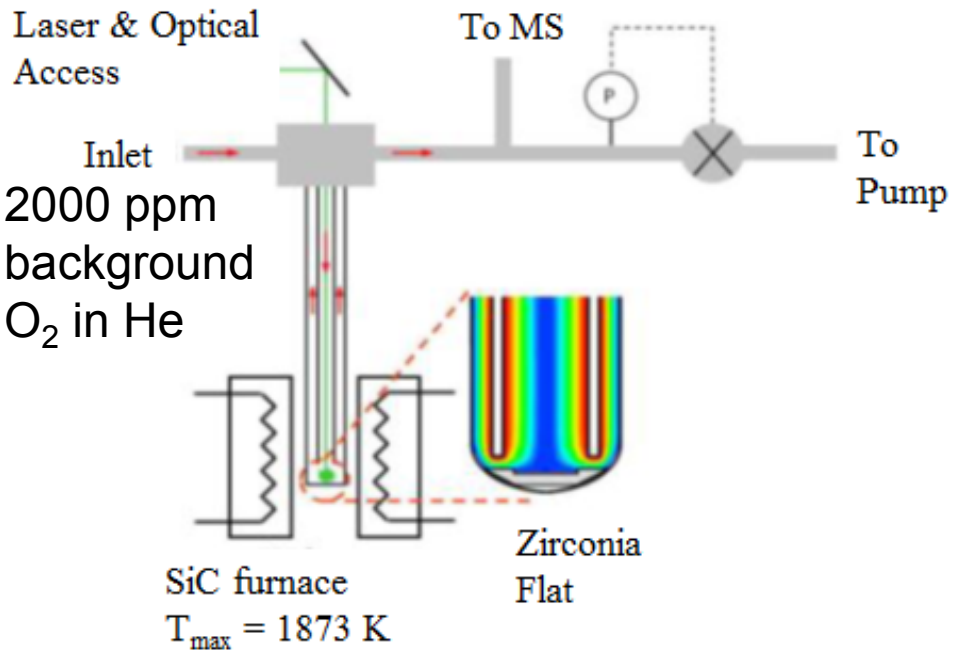


Scheffe, J.R. et al., International Journal of Hydrogen Energy, 35, 3333-3340 (2010)

Experiments

- Laser Assisted Stagnation Flow Reactor
- On-sun Solar Reactor
- Thermogravimetic Analyzer

Laser Assisted Stagnation Flow Reactor



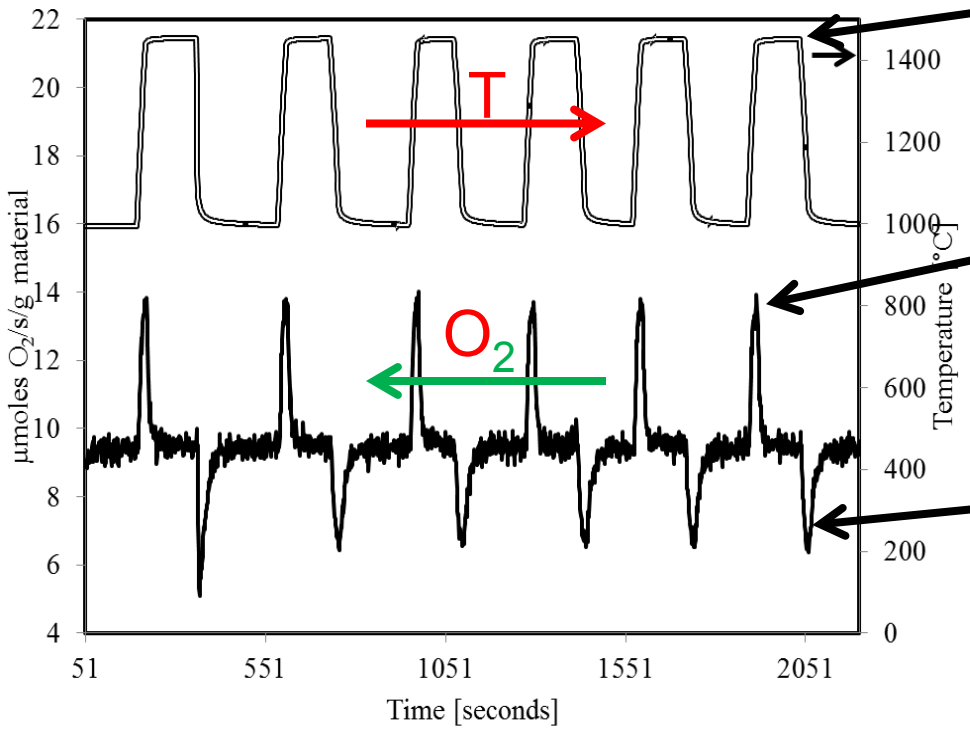
Thermochemical cycles:

1. Thermal Reduction 1300-1450°C; oxidation at 1000 to 1200°C
2. Oxidize Sample with O_2 or CO_2

Apollo Instruments Model F500-NIR600; 500 W NIR diode laser

Samples heat at 15°C/s from baseline 1000°C to reduction temperature; P = 75 torr

Laser-driven Thermal Reduction and O_2 Redox Cycling



Thermal reduction at 1450°C

Rapid O_2 release during reduction

Rapid O_2 reoxidation in 2000 ppm background O_2 at 1000°C

O_2 intake and uptake experiment at 1000°C-1450°C performed at 75 torr.

Fast redox (thermal reduction and O_2 oxidation) with no apparent deactivation

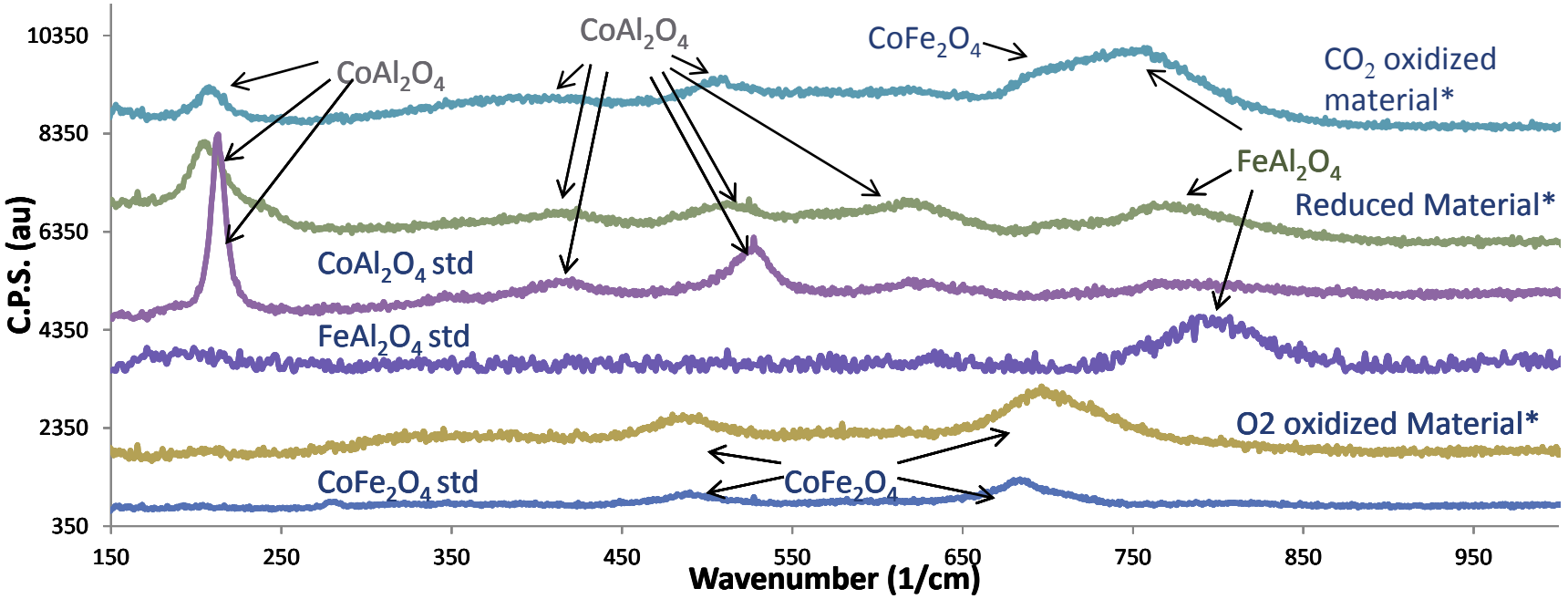
Oxidation with 50% CO_2

- Higher reduction temperature results in higher CO productivity
- Higher CO_2 pressure results in higher CO productivity.

Increasing Thermal Reduction T from 1300 to 1450°C is Equivalent to Increasing CO_2 Pressure from 75 to 600 torr

P [torr]	Thermal Reduction Temperature [ÁC]	CO_2 Oxidation Temperature [ÁC]	Total CO released during oxidation [µmoles CO/g]
600	1300	1000	41.5
600	1450	1000	82.5
75	1450	1000	42.4

Raman Spectroscopy Validates Proposed "Hercynite cycle" Mechanism

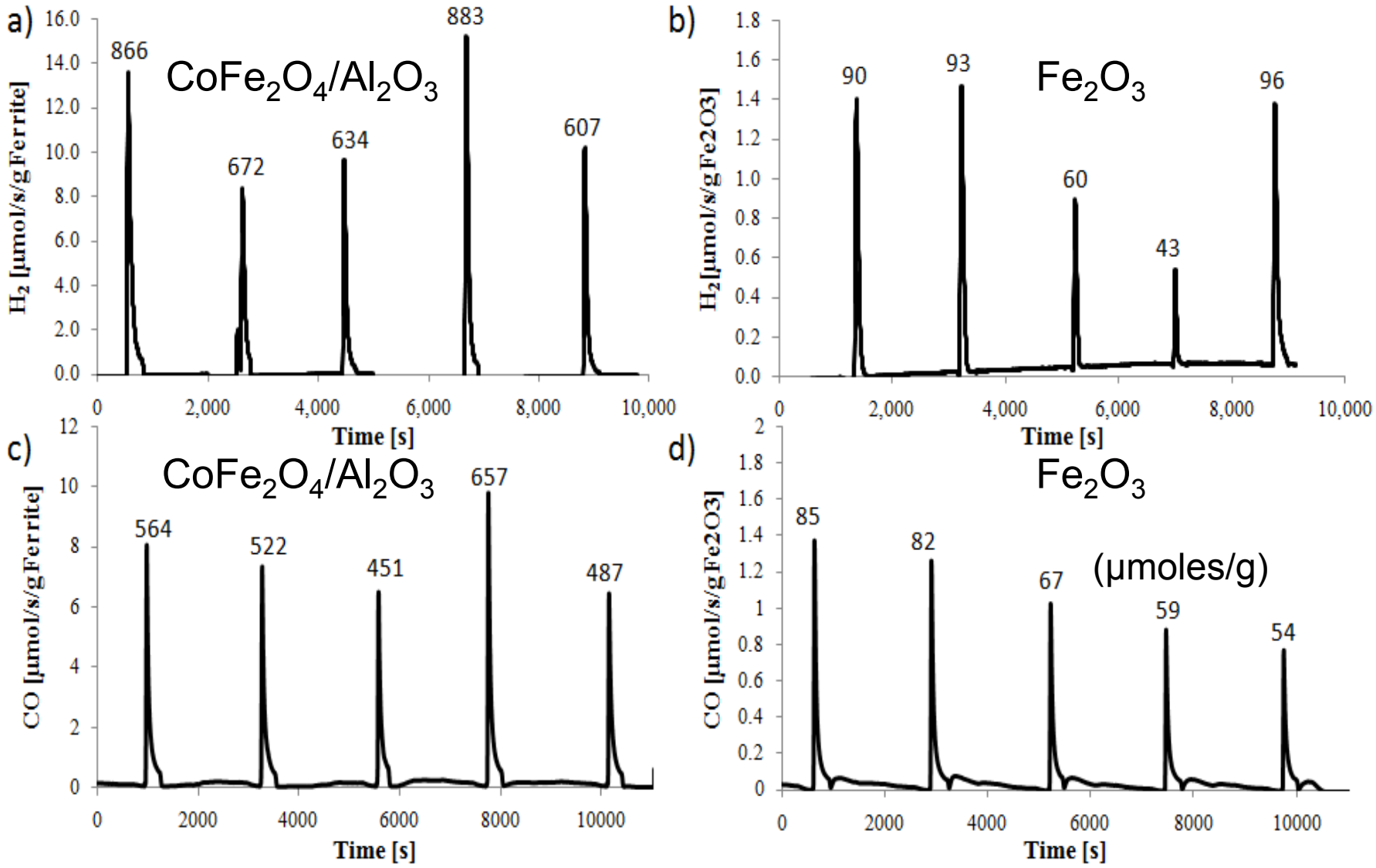


$$CoFe_2O_4 + 3\ Al_2O_3 + \text{thermal energy} \rightarrow CoAl_2O_4 + FeAl_2O_4 + 0.5\ O_2 \qquad \text{Reaction (1)}$$

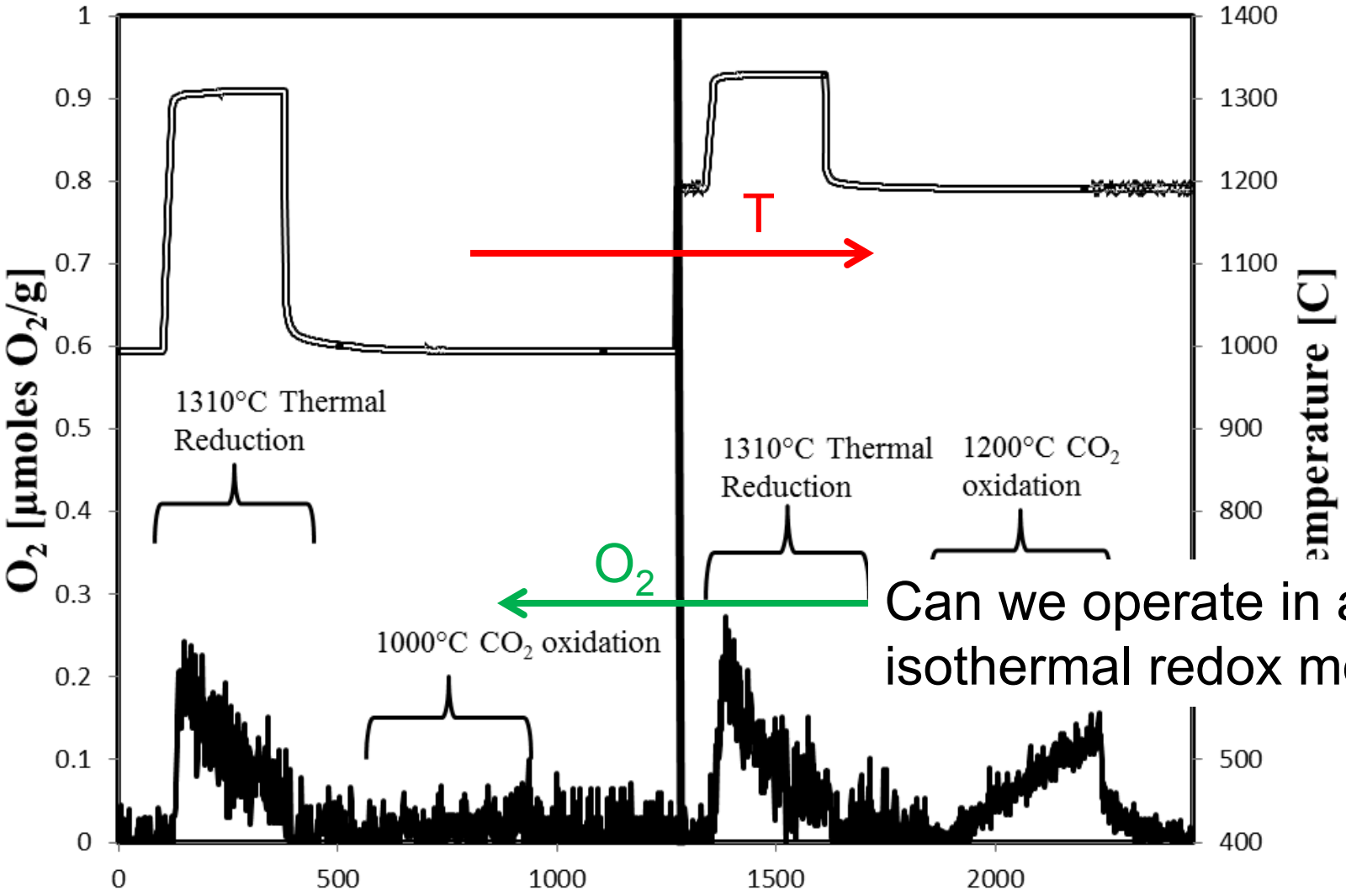
$$CoAl_2O_4 + 2\ FeAl_2O_4 + H_2O \text{ or } CO_2 \rightarrow CoFe_2O_4 + 3\ Al_2O_3 + H_2 \text{ or } CO \qquad \text{Reaction (2)}$$

On-sun Experiments at NREL used to Demonstrate "Hercynite Cycle" Activity

(1350°C reduction/1100°C oxidation; ferrite/alumina ~ 8 to 10X more active than Fe_2O_3)



Slow O_2 Release Occurs During CO_2 Oxidation at Elevated Temperature



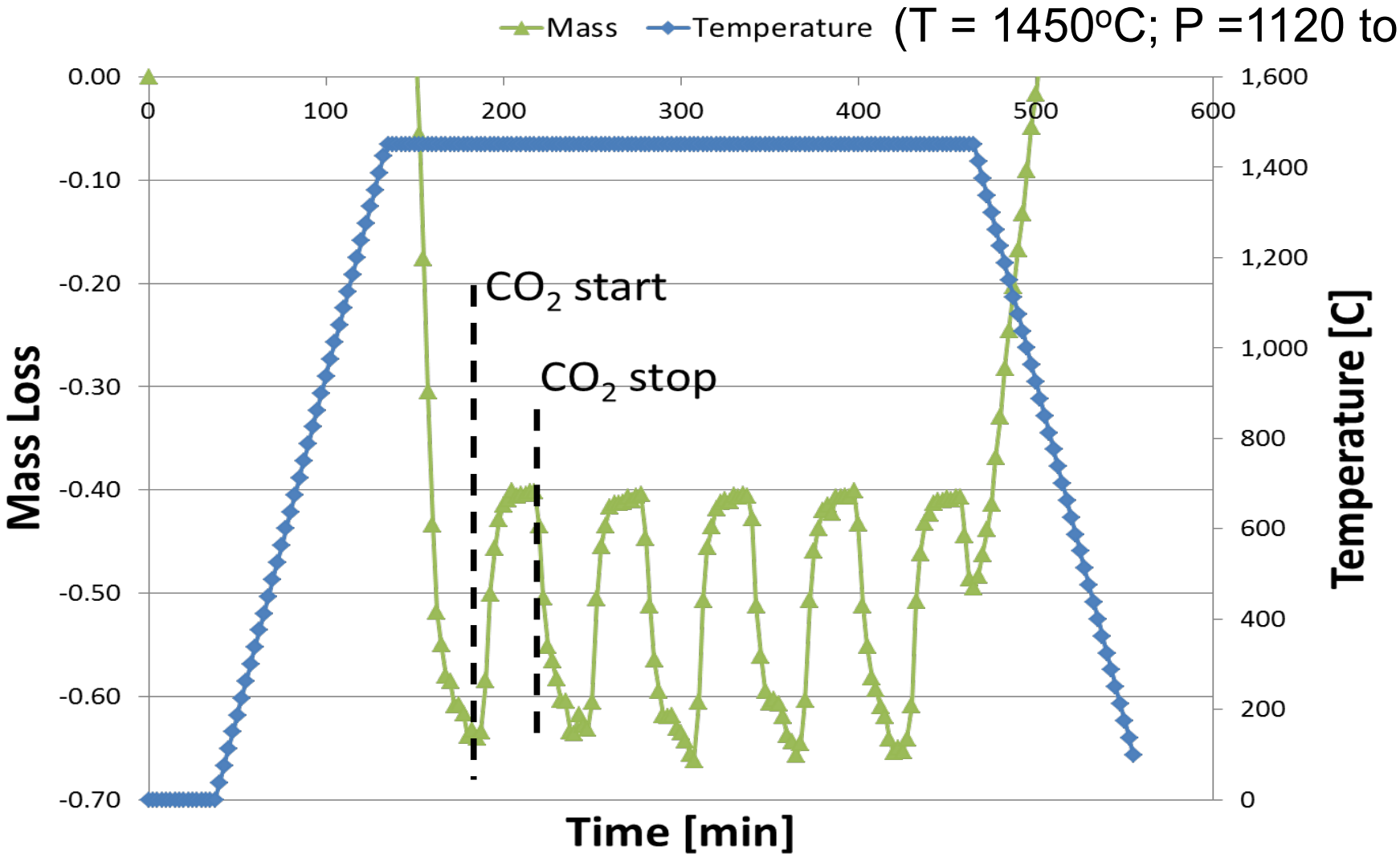
Can we operate in an isothermal redox mode ?

Isothermal Redox

- Preliminary results using TGA/MS
- Solar reactor design strategies
- Effect on economics

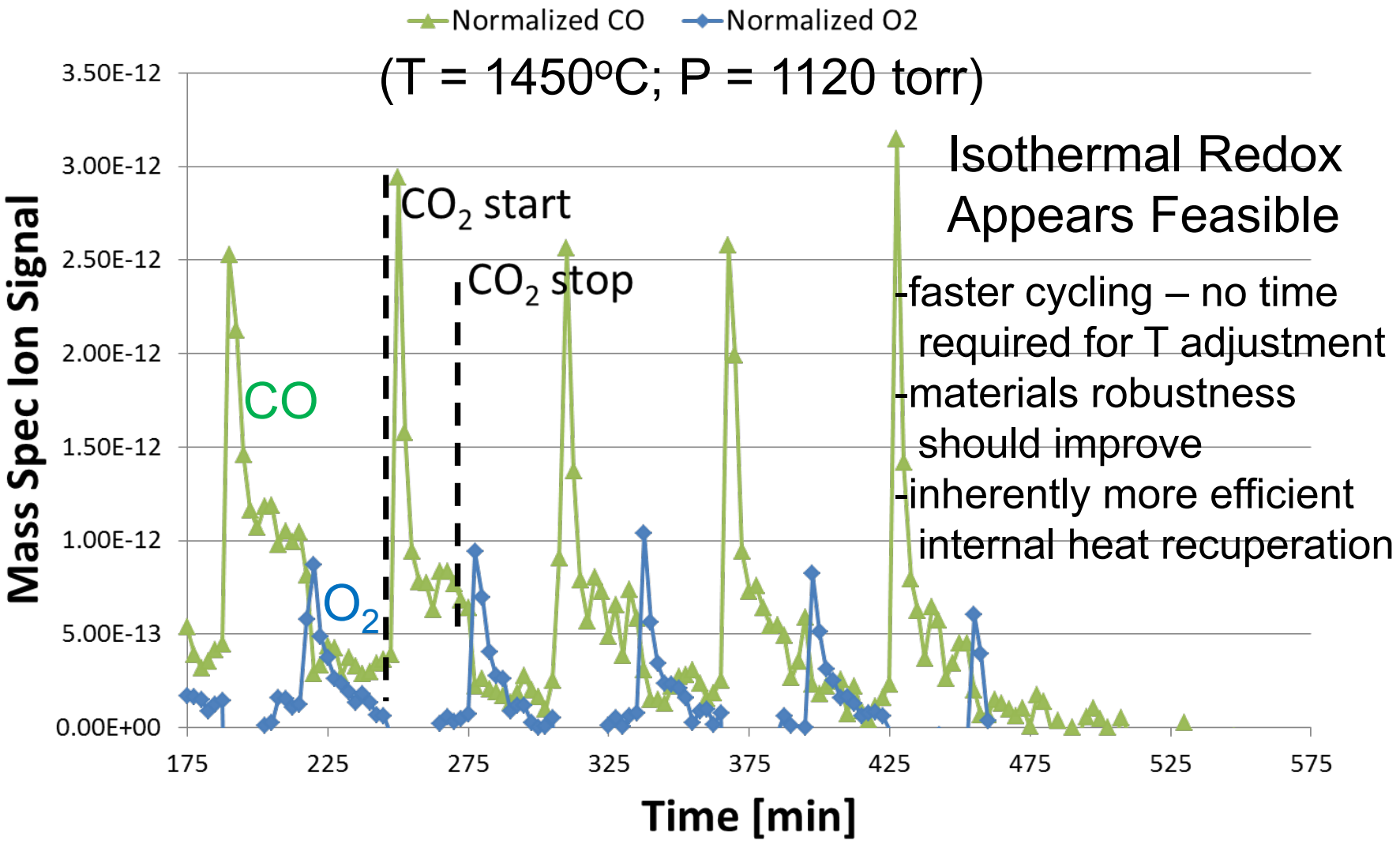
Isothermal Redox Demonstrated in TGA

(Normalized Mass Dynamics Shown vs. CO_2 Flow)



Isothermal Redox Demonstrated in TGA

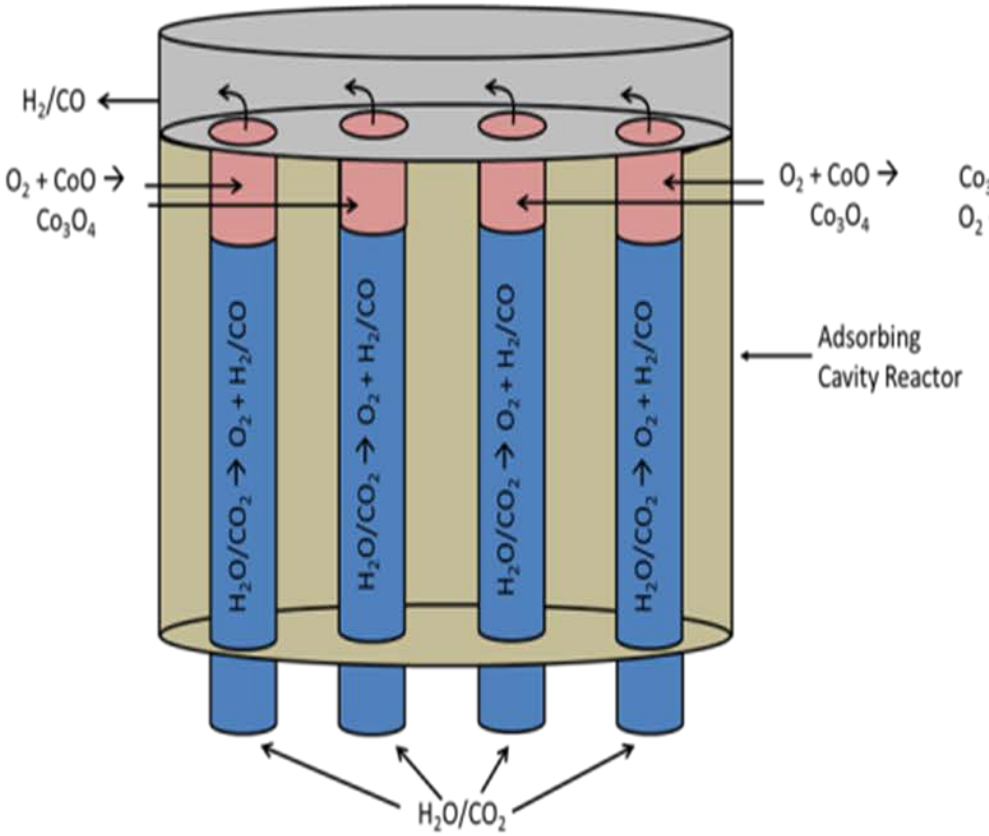
(Normalized Gas Composition Dynamics Shown vs. CO_2 Flow)



Solar Reactor Configuration with in-situ Oxygen Adsorbent for Fugitive O_2 Removal

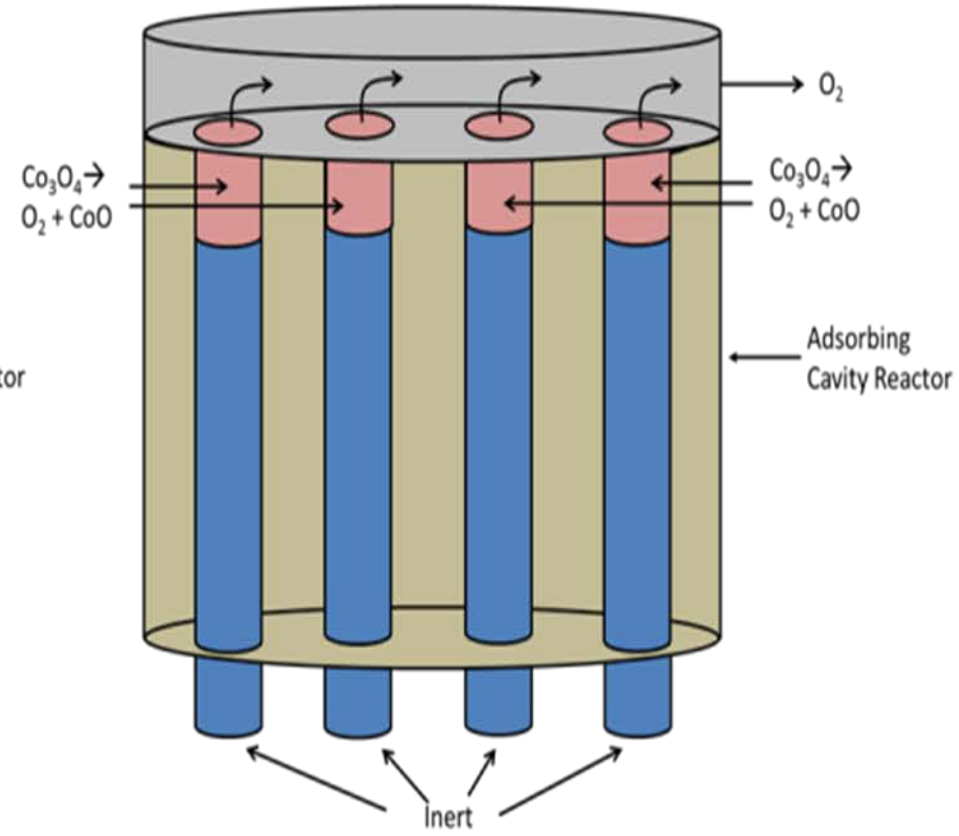
$6CoO + O_2 \rightarrow 2Co_3O_4$

H2/CO Generation



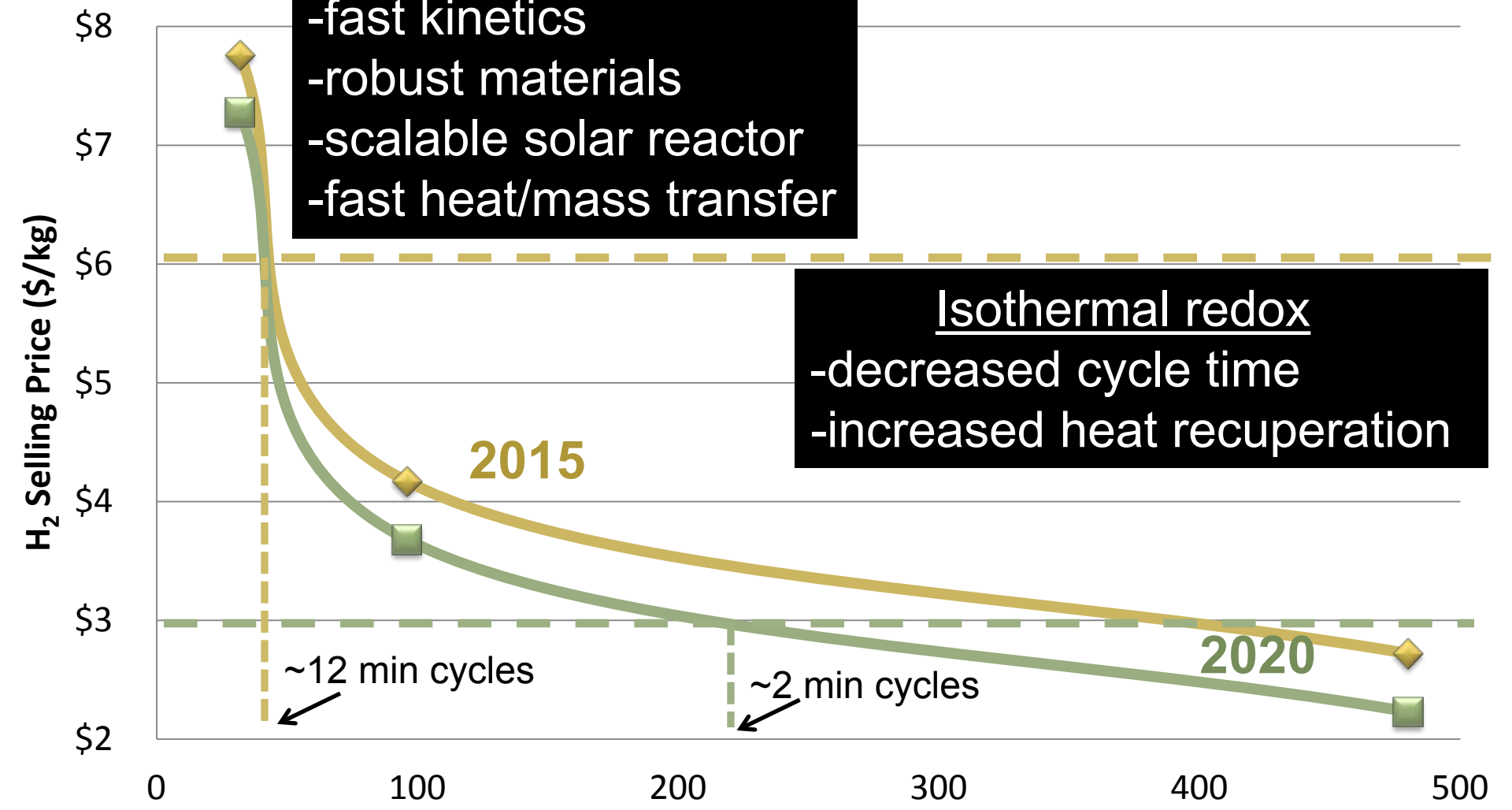
$2Co_3O_4 \rightarrow 6CoO + O_2$

Sorbent Re-generation



Economic Results – 100,000 kg H_2/day (central receiver facility)

Key Requirements
-fast kinetics
-robust materials
-scalable solar reactor
-fast heat/mass transfer



Isothermal redox
-decreased cycle time
-increased heat recuperation

(TIAX, LLC: DE-DT0000951; 2011)

Milestones

- Milestone 1: "Synthesis of cobalt ferrite/alumina "hercynite cycle" active materials formed by ALD using polymer templates; and subsequent demonstration of 1300^{o}C reduction/1000^{o}C oxidation thermochemical redox cycling to split water using a stagnation flow reactor; with H_2 production per gram of total mass of active materials at least twice that of ceria under identical redox conditions (June, 2012); done
- Milestone 2: "On-sun demonstration at NREL HFSF of cobalt ferrite/alumina "hercynite cycle" active materials using polymer templates; demonstration of 1300^{o}C reduction/1000^{o}C oxidation thermochemical redox cycling to split water; with H_2 production per gram of total mass of active materials > 100 μmole/g active material (September, 2012); done

Milestones

- Milestone 3: “Quantify and report the thermochemical performance for the “hercynite cycle” oxide powder and demonstrate both the oxidation and reduction reactions reach 90% of their peak production rates in less than two minutes (September, 2012); done

Future Work

- The "hercynite" cycle is capable of ~150°C lower reduction T than traditional ferrite systems & ~200°C lower than ceria reduction.
  - Investigate temperature/pressure ranges; target lower reduction T and higher H_2O P on redox kinetics.
- It is possible with ALD to tightly control chemical composition of the active material.
  - Investigate $CoFe_2O_4/Al_2O_3$ composition effects on redox performance and physical robustness of the active materials.
- Preliminary studies suggest that isothermal redox can be carried out:
  - Investigate isothermal redox with $CoFe_2O_4$ for water splitting; evaluate in-situ O_2 "sorption" with CoO.

Acknowledgements

9 Peer-reviewed Scientific Papers (2011/2012)
3 PCT/U.S. Patent Filings (2012)

Indemnification

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