Solar-thermal ALD Ferrite-Based Water Splitting Cycles

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Project ID No. PD028

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

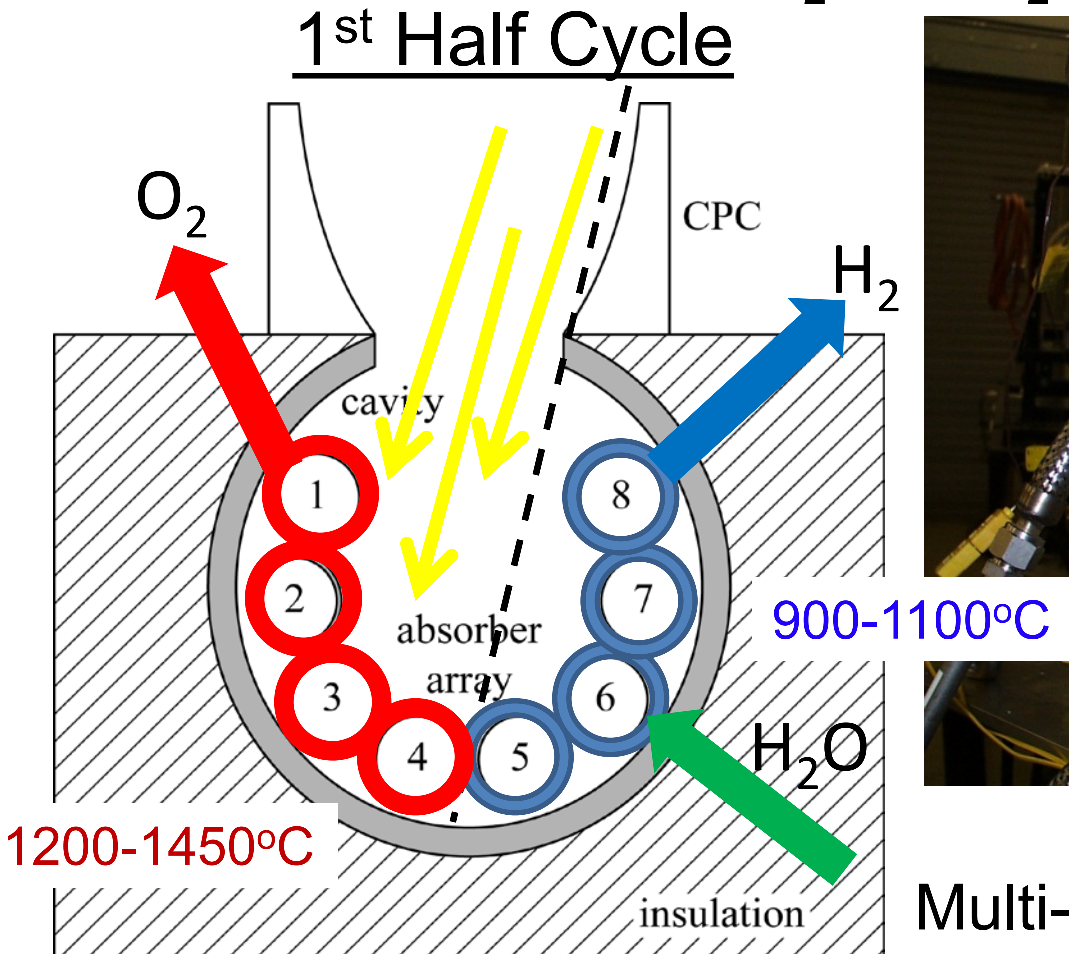
- Chemistry & Reactor Configuration
- Materials Requirements
- Thermodynamics Predicted Robustness

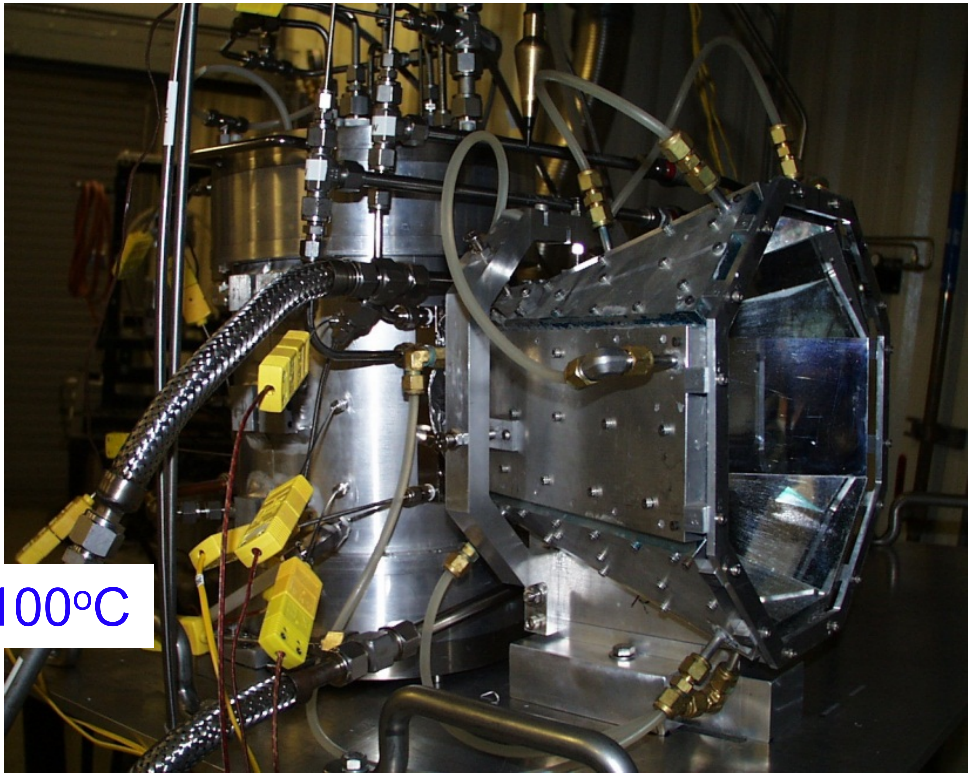
SurroundSun™ Multi-tubular Switching Redox Reactor/Receiver

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

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

$H_2O \rightarrow H_2 + 1/2O_2$

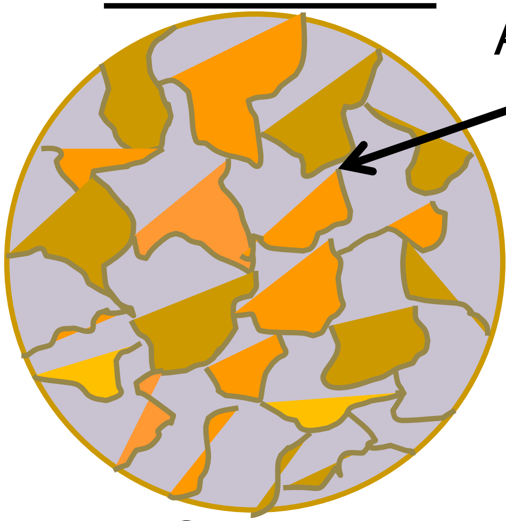




University of Colorado
Multi-tube Solar Receiver/Reactor

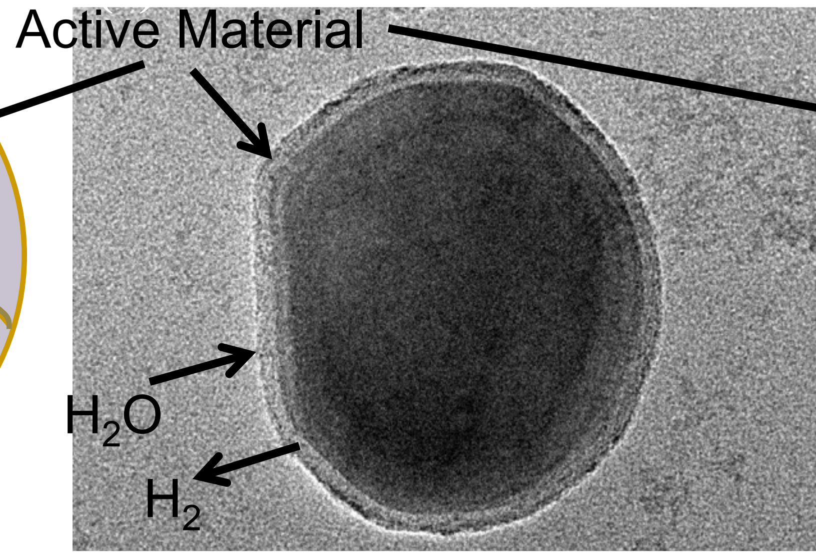
Active Material Types

Bulk/Solid



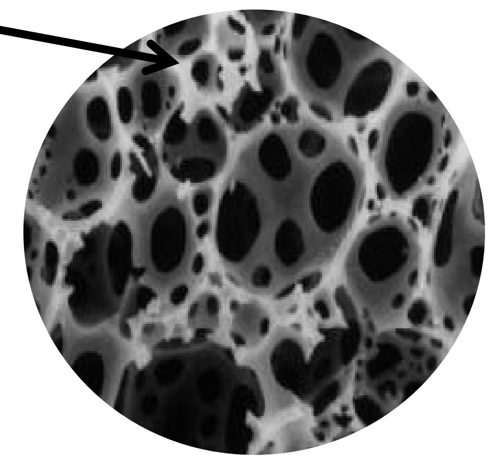
Active Sites Scattered, but Near Surface; Rates Limited by Heat Conduction & Diffusion; Sensible Heat Losses

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

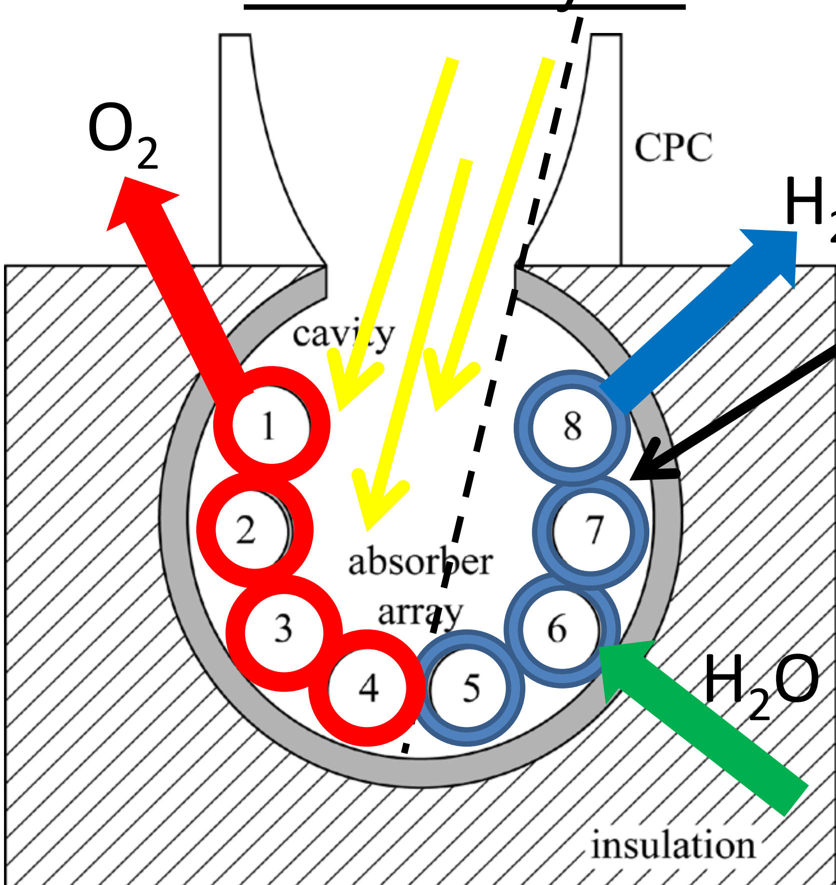
Nanostructured Materials Design is Key for Optimal Performance

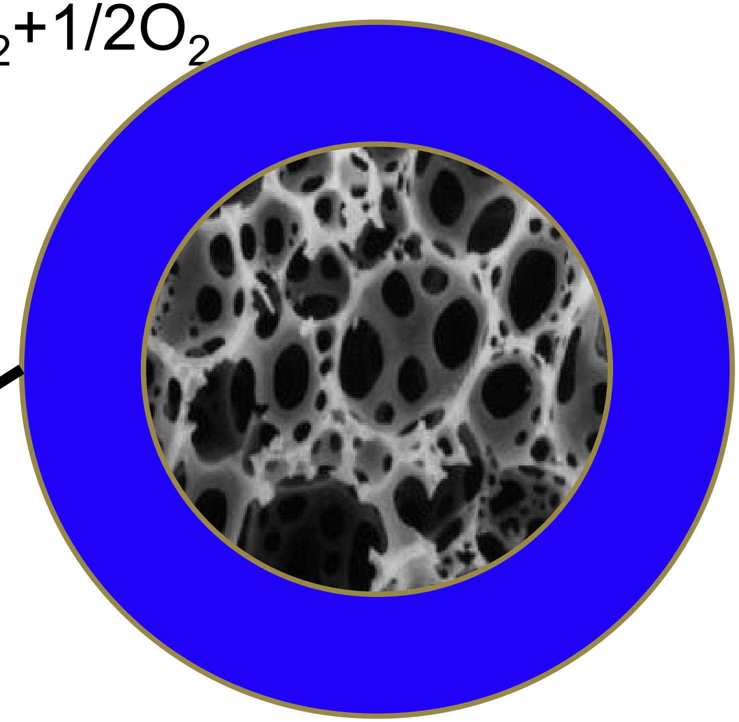
(R): $CoFe_2O_4 + 3\ Al_2O_3 \rightarrow [CoAl2O4{:}2Fe2AlO4] + 1/2O_2$

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

$H_2O \rightarrow H_2 + 1/2O_2$

1st Half Cycle



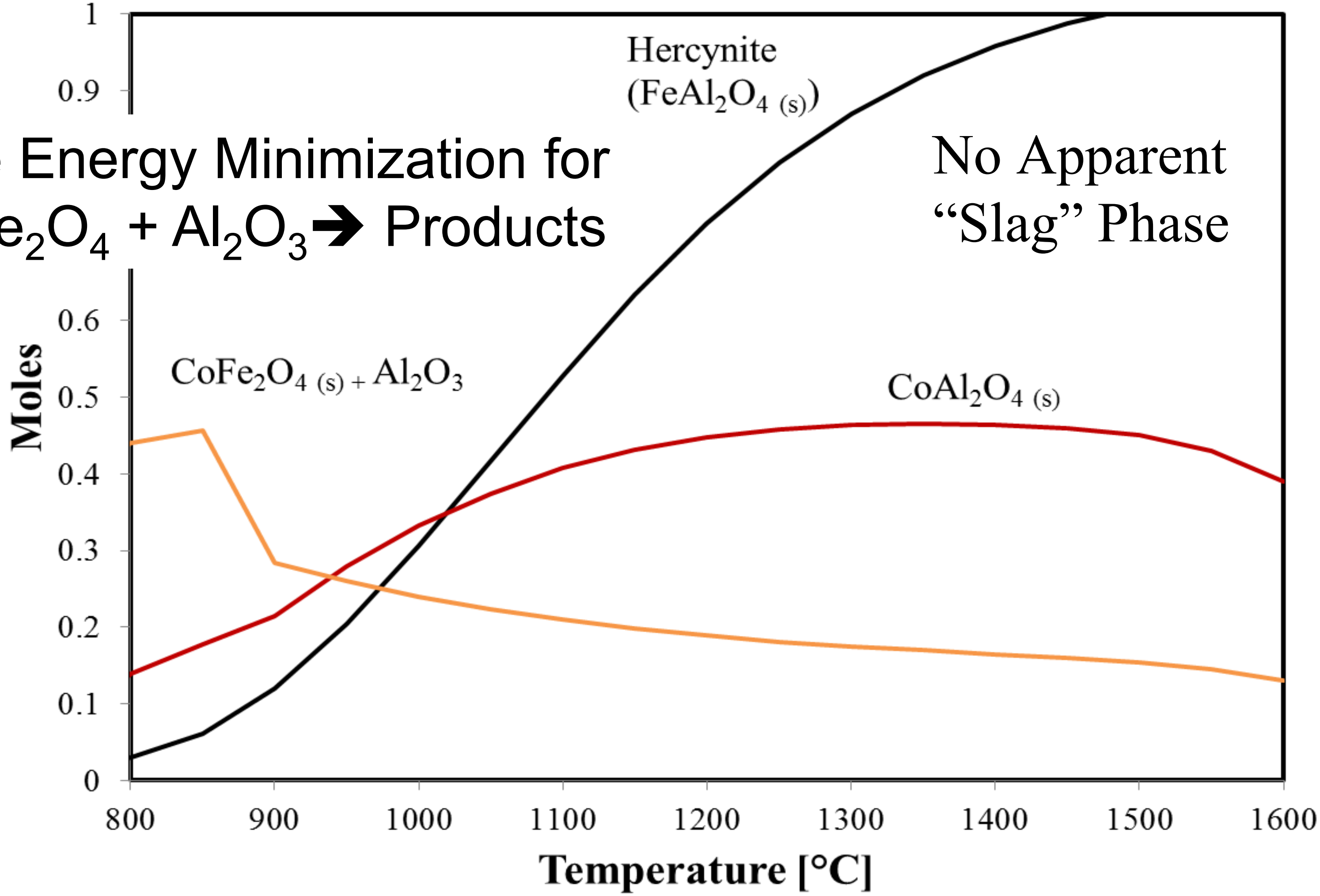


- Fast radiative heat transport
- Fast mass flow (large pores & porosity)
- Ultrathin walls to limit sensible heat loss
- Ultrathin active films to eliminate diffusional resistances (i.e. fast kinetics)

"Hercynite Cycle" is Predicted Thermodynamically to be Robust

Free Energy Minimization for $CoFe_2O_4 + Al_2O_3 \rightarrow$ Products

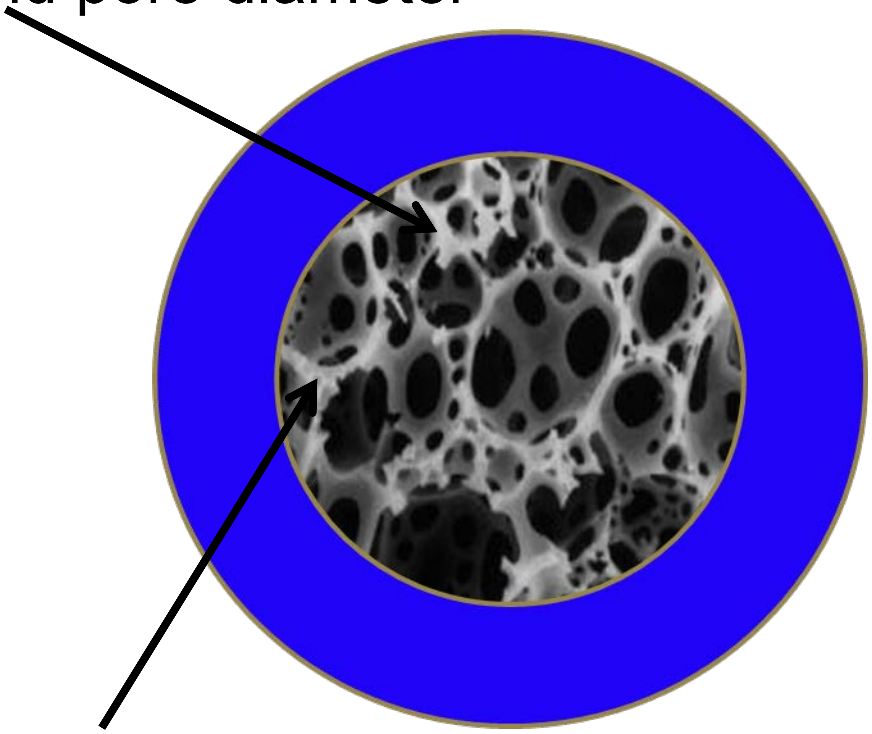
No Apparent "Slag" Phase



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

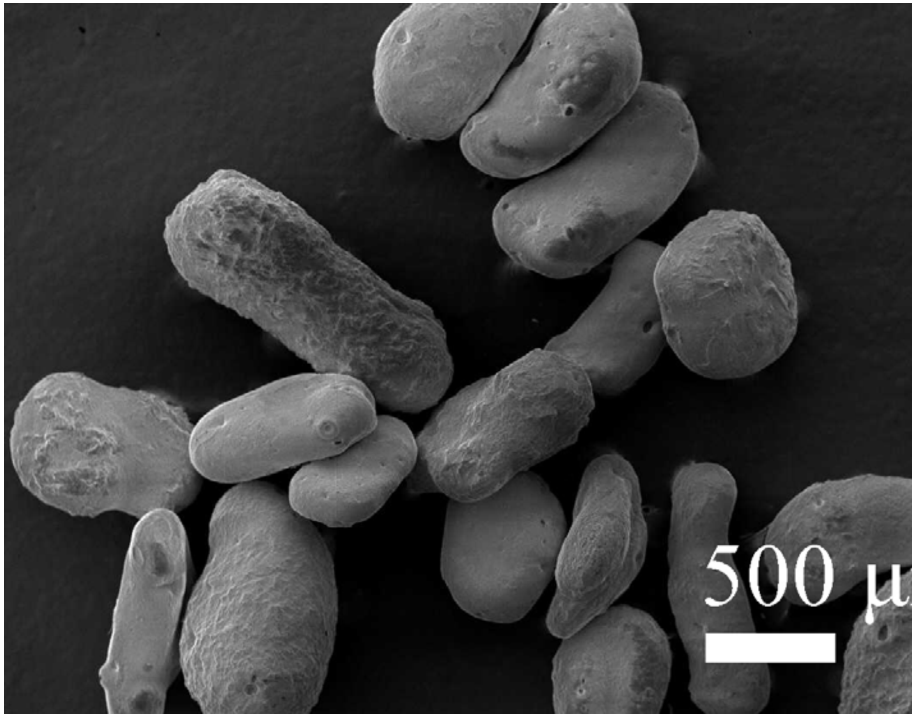
Designed Active Materials Fabrication

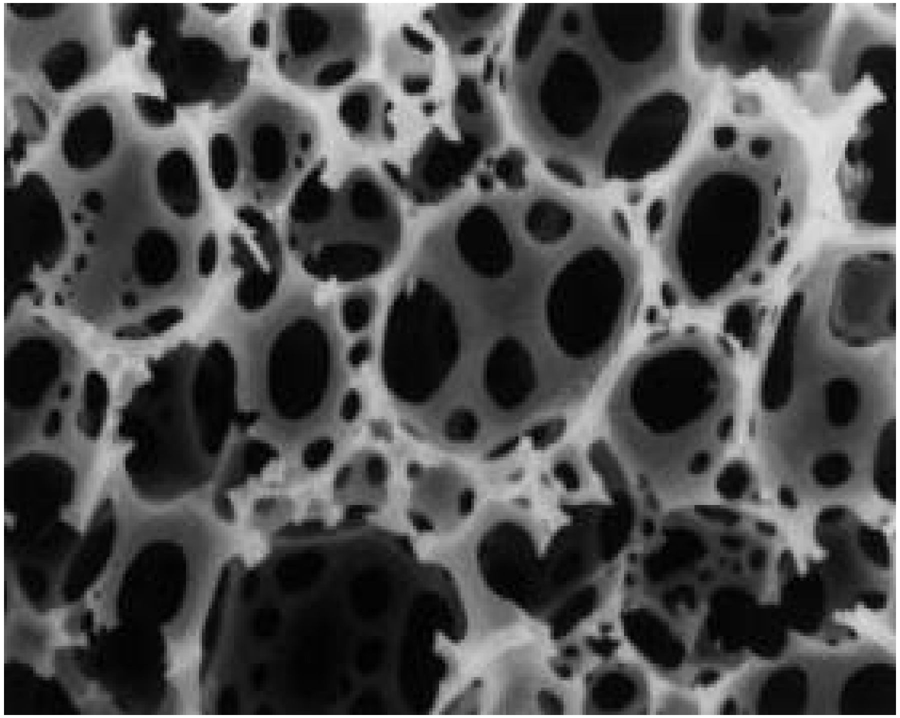
- Sacrificial Polymer Template is used for achieving desired porosity and pore diameter



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

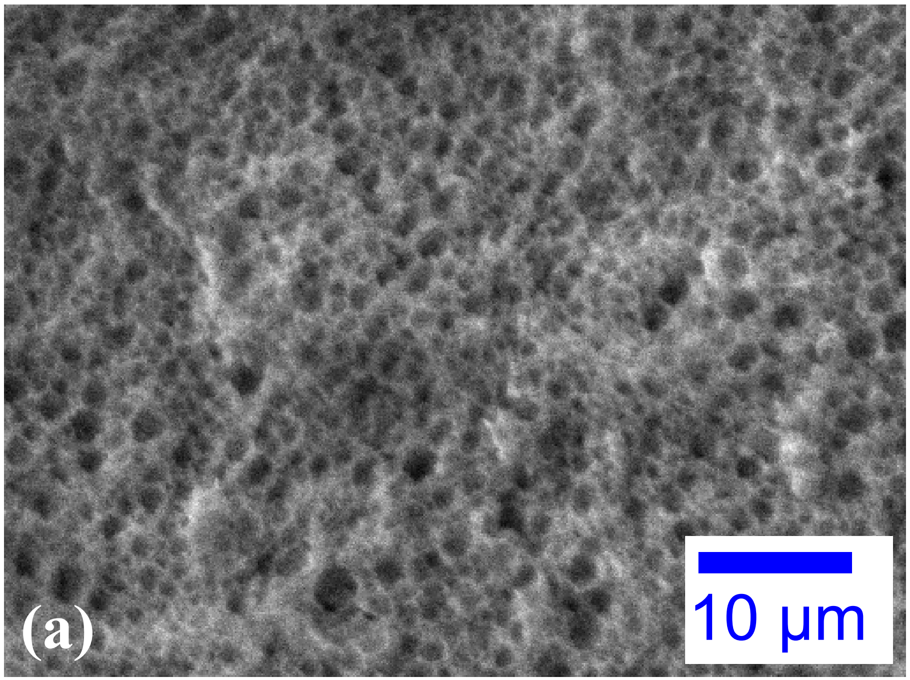
Uncoated poly(styrene-divinylbenzene) particles (Dowex™ or Cavilink™)

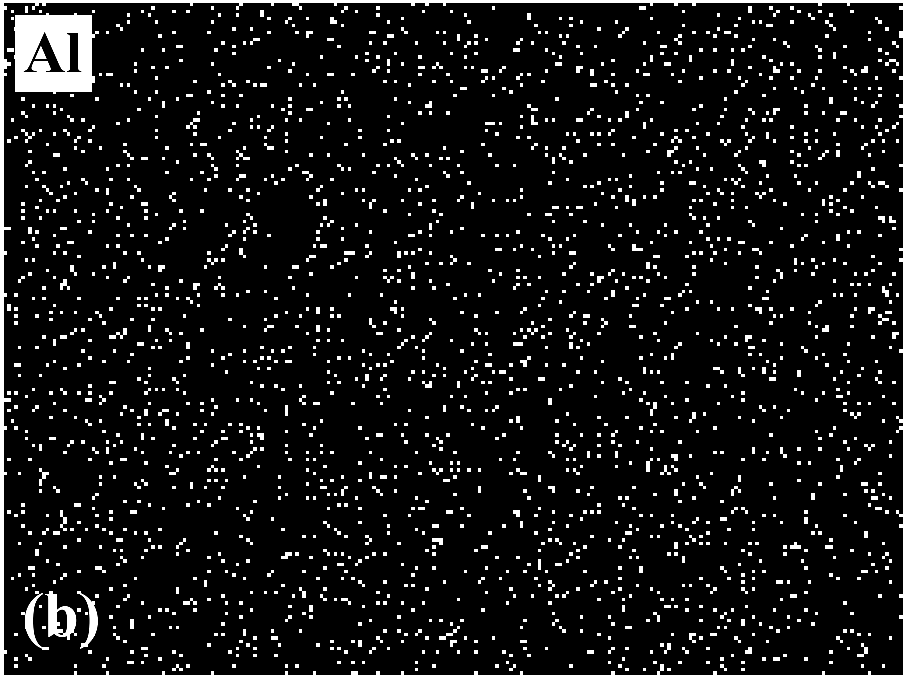




Particle size of ~600 µm, a porosity of 85%, a pore volume of 8-10 cm^3/g, a surface area of 43.5 m^2/g, and a density of 70 kg/m^3

Alumina films were coated throughout the inner surface of the particles

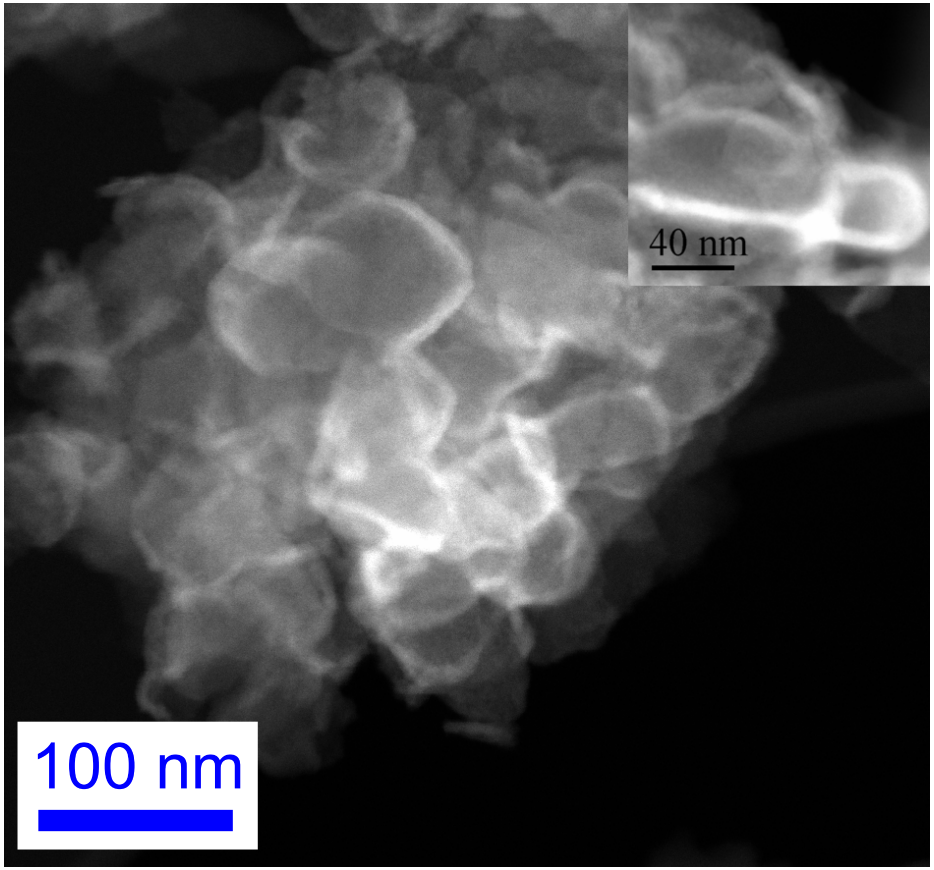


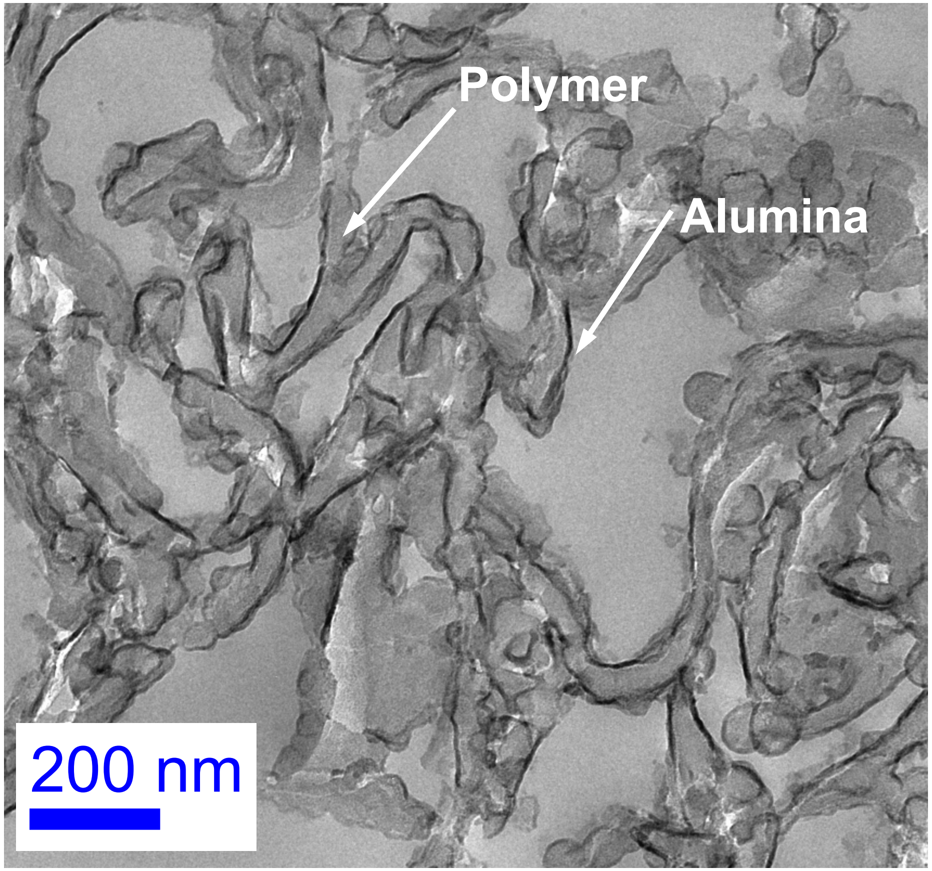


FESEM of cross sectional surface after 25 cycles of Al_2O_3 coating

Al EDS mapping

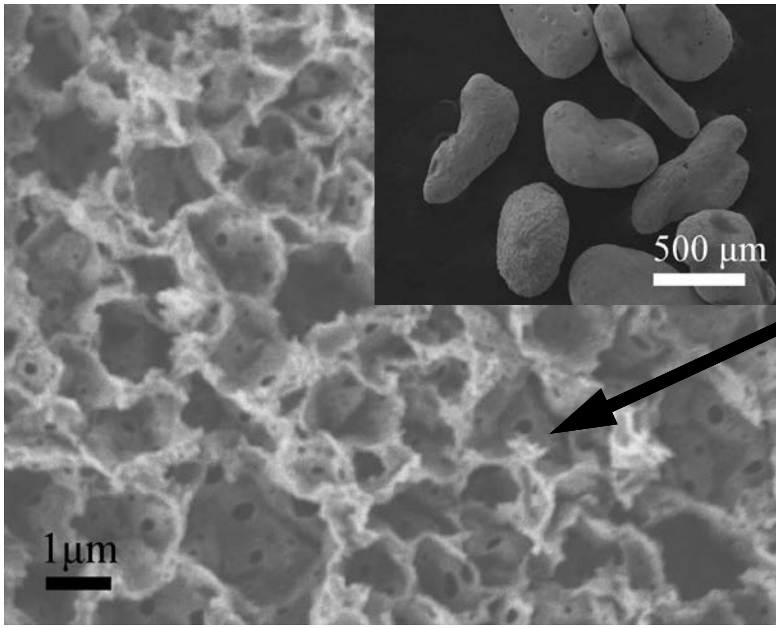
Conformal Al_2O_3 films coated on porous PS-DVB particles





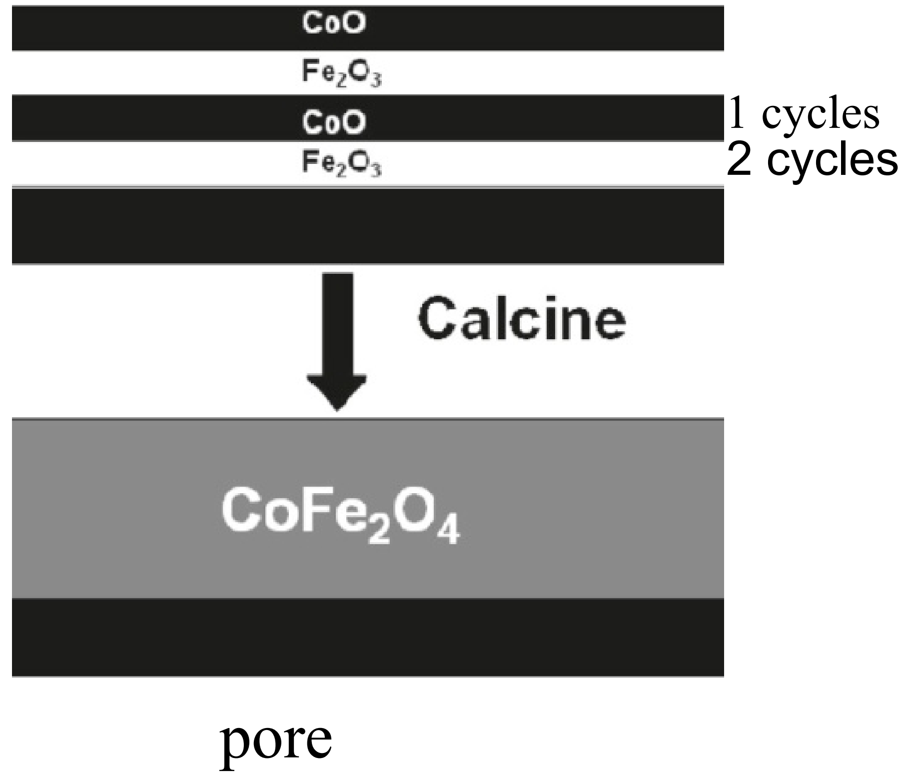
Liang XH, et al., Chemistry of Materials 19: 5388-5394, 2007

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.% $CoFe_2O_4/Al_2O_3$

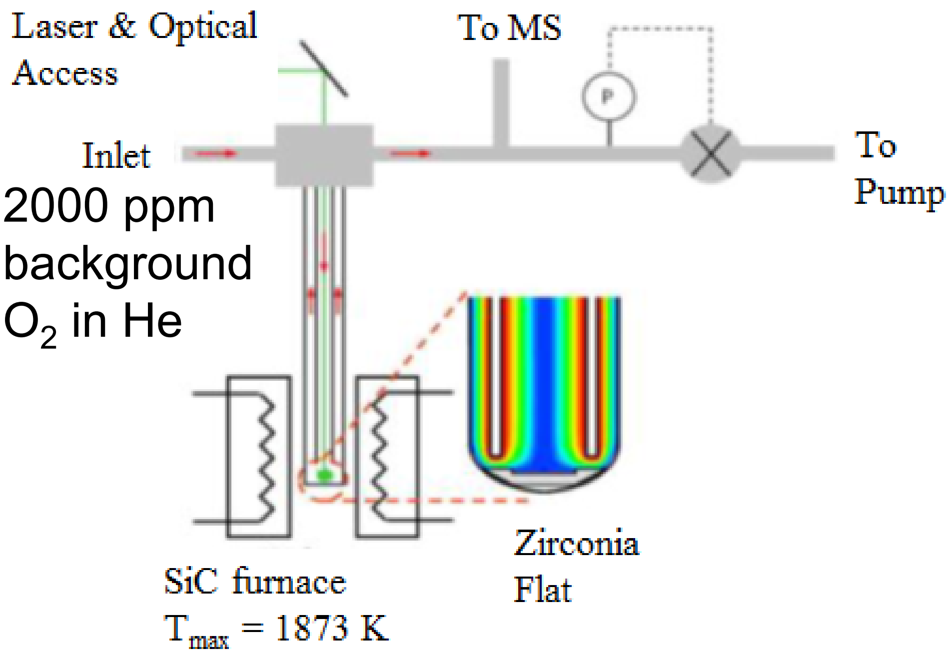


Scheffe, J.R. et al., International Journal of Hydrogen Energy, 35, 3333-3340 (2010)

Experiments

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

Laser Assisted Stagnation Flow Reactor



2000 ppm background O_2 in He

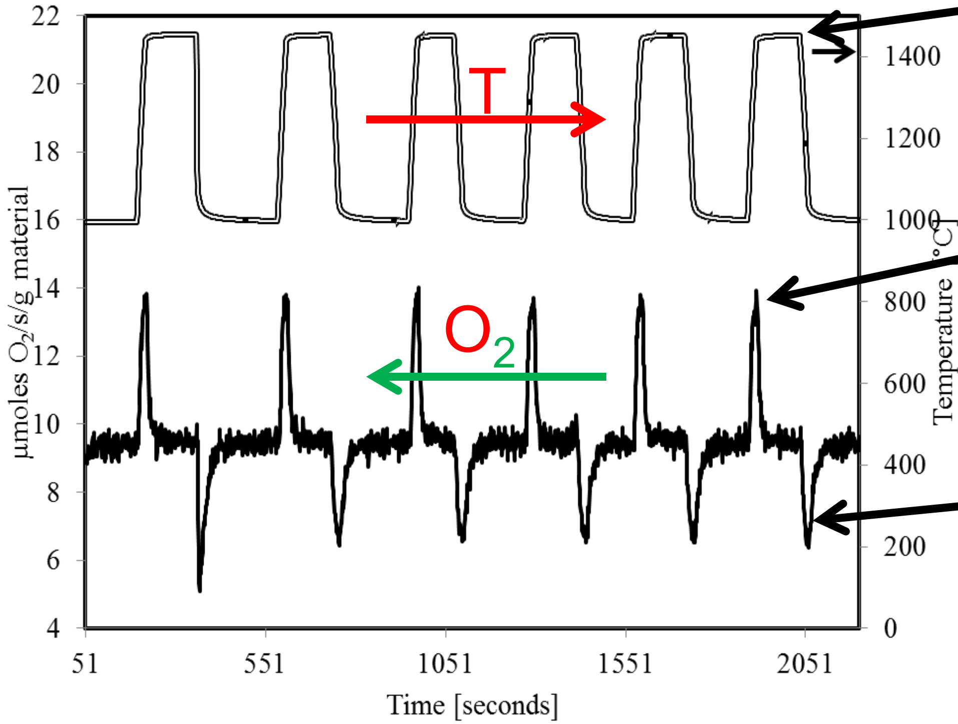
Apollo Instruments Model F500-NIR600; 500 W NIR diode laser

<u>Thermochemical cycles:</u>

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

Samples heat at 15ºC/s from baseline 1000ºC 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

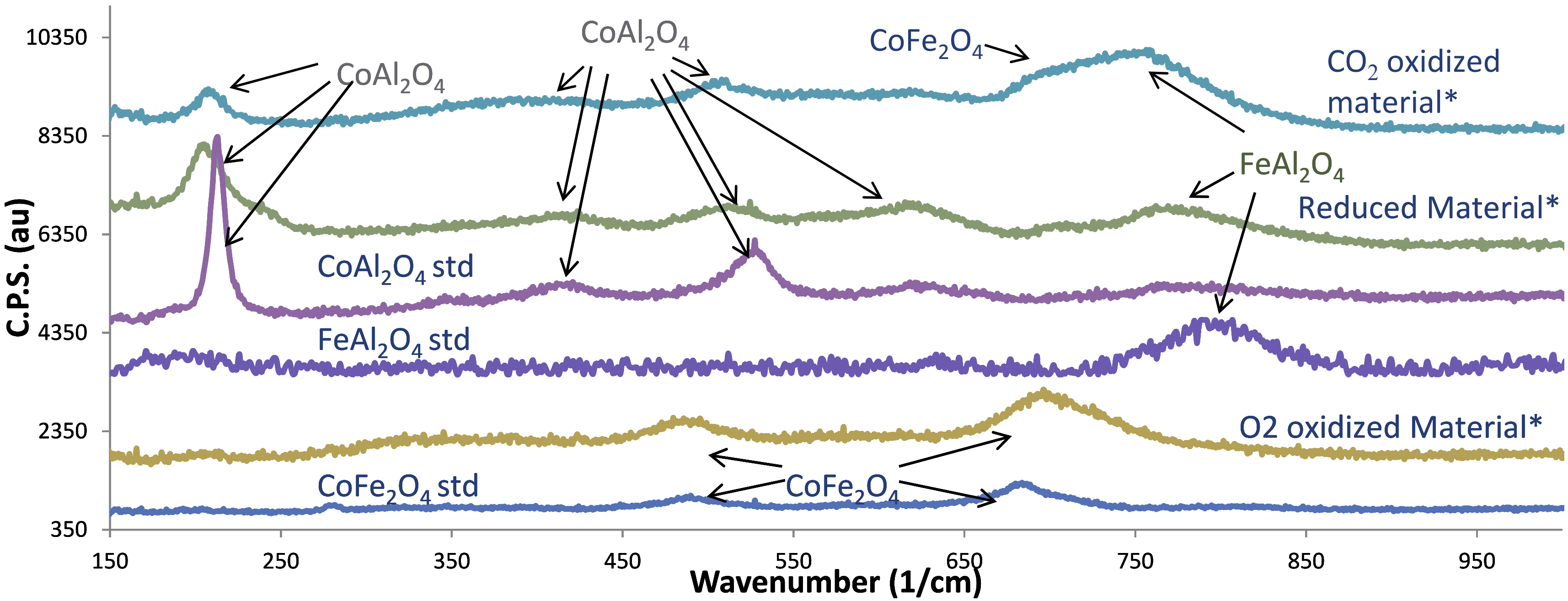
Oxidation with 50% CO_2

- 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

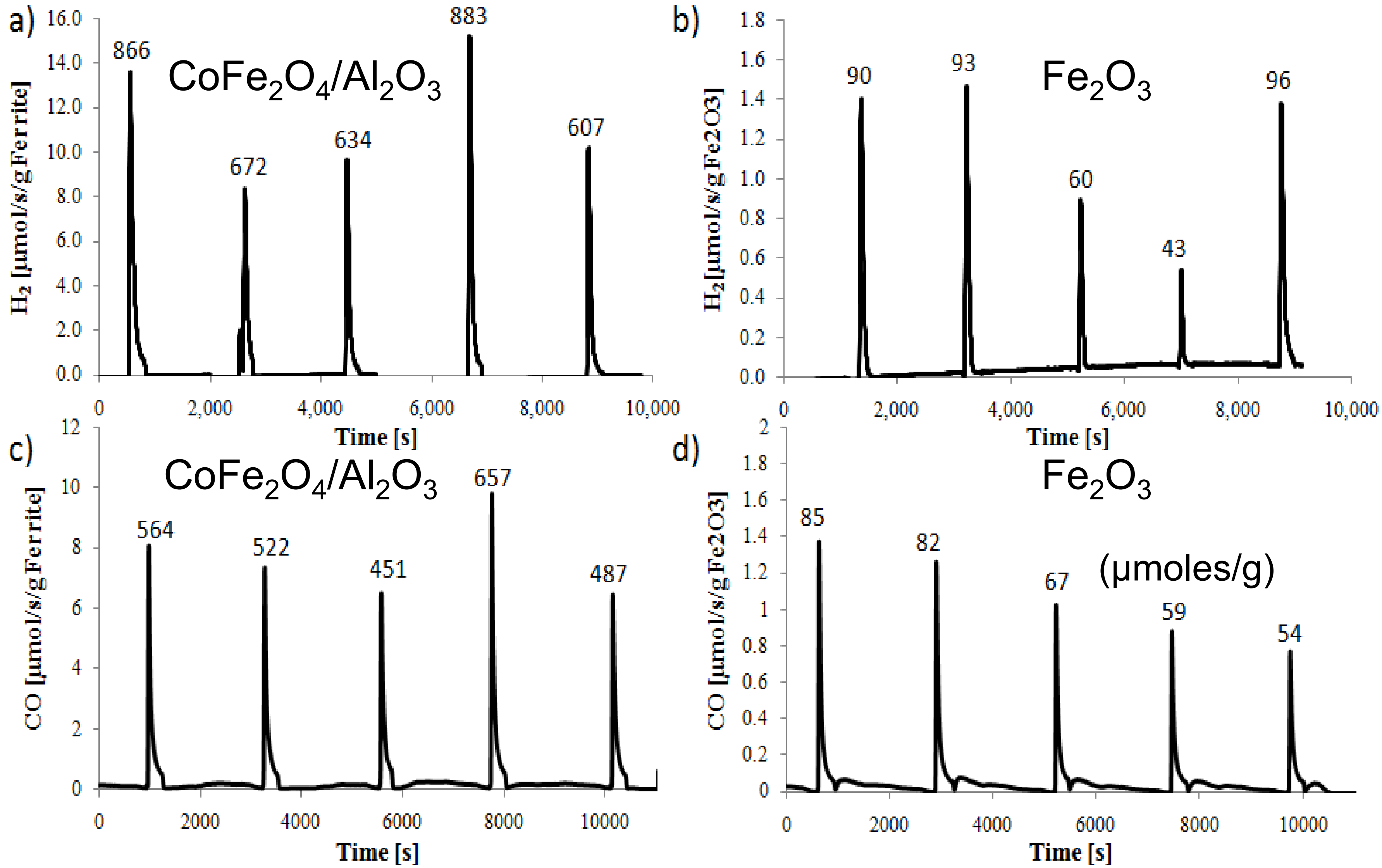


$CoFe_2O_4 + 3\,Al_2O_3$ + thermal energy $\rightarrow CoAl_2O_4 + FeAl_2O_4 + 0.5\,O_2$ Reaction (1)

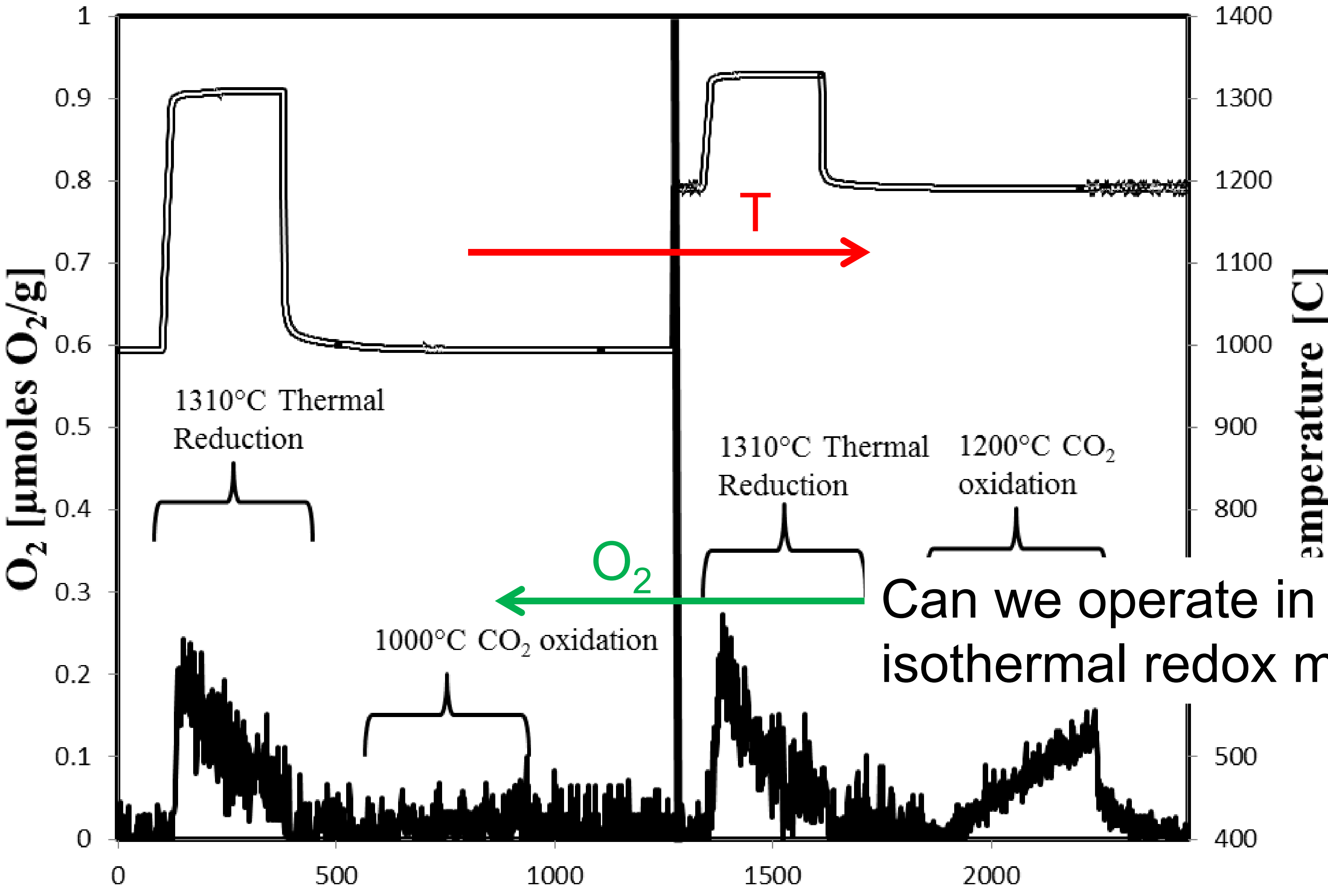
$CoAl_2O_4 + 2\,FeAl_2O_4 + H_2O$ or $CO_2 \rightarrow CoFe_2O_4 + 3\,Al_2O_3 + H_2$ or CO Reaction (2)

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



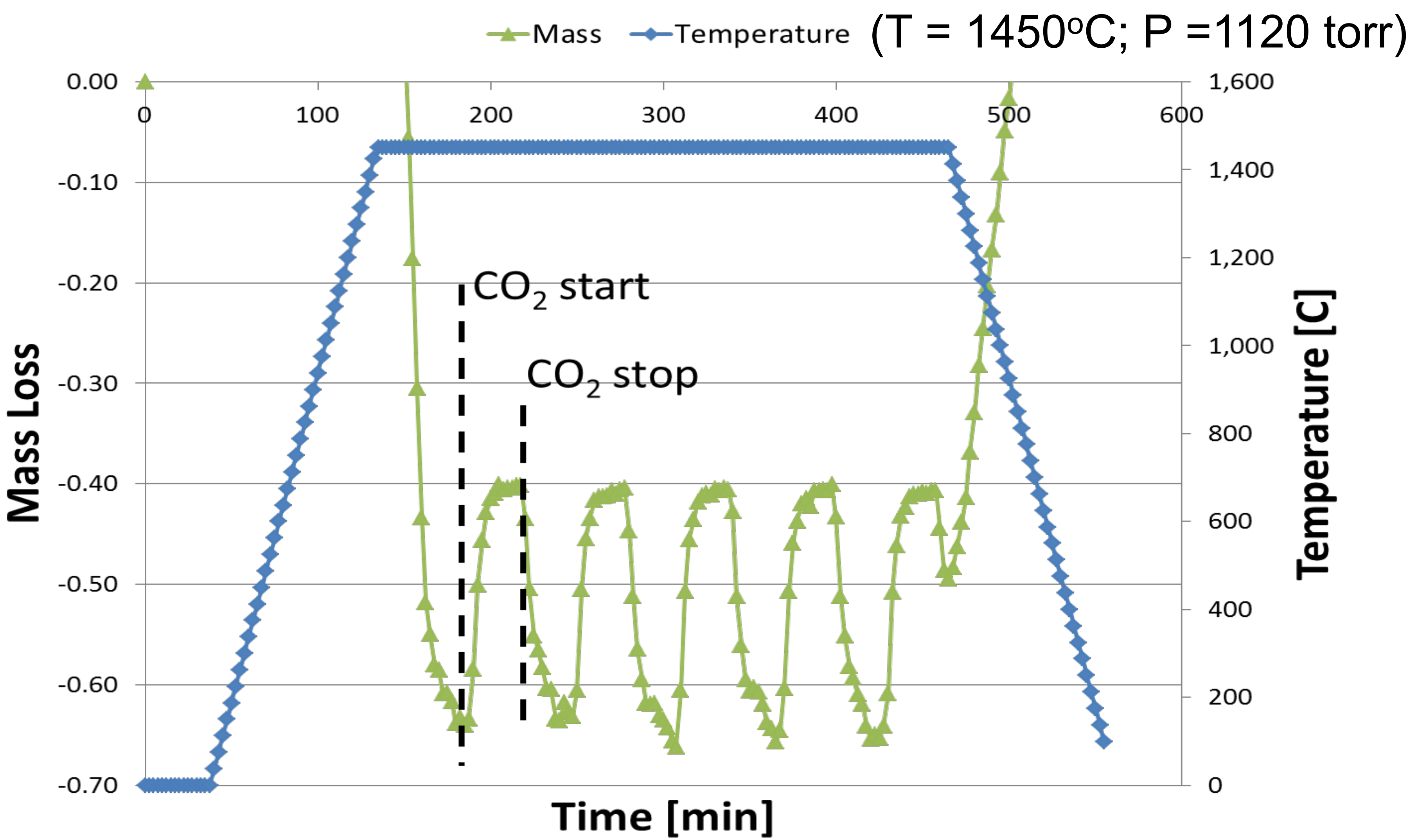
Can we operate in an isothermal redox mode ?

Isothermal Redox

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

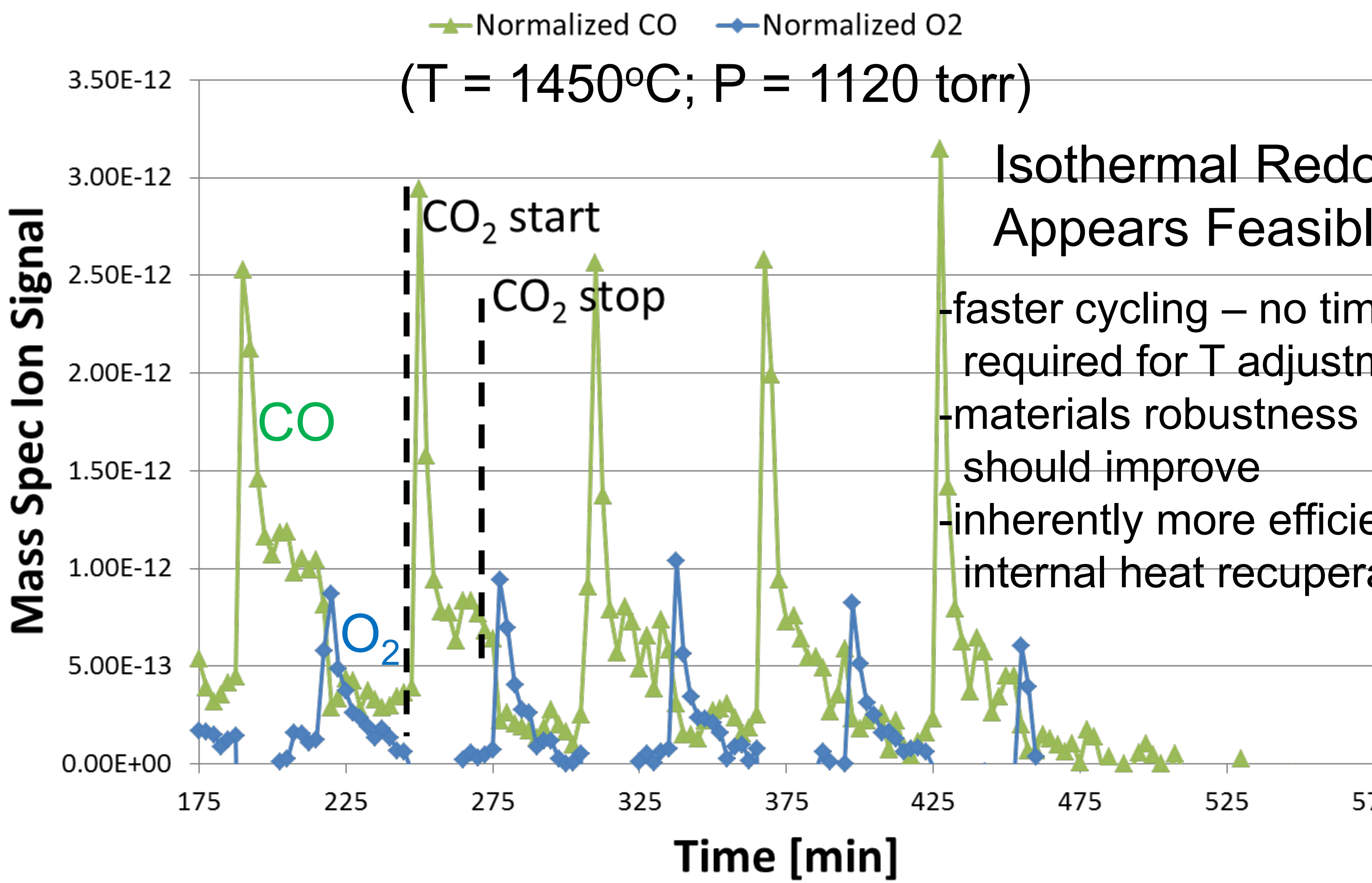
Isothermal Redox Demonstrated in TGA

(Normalized Mass Dynamics Shown vs. CO_2 Flow)



Isothermal Redox Demonstrated in TGA

(Normalized Gas Composition Dynamics Shown vs. CO_2 Flow)



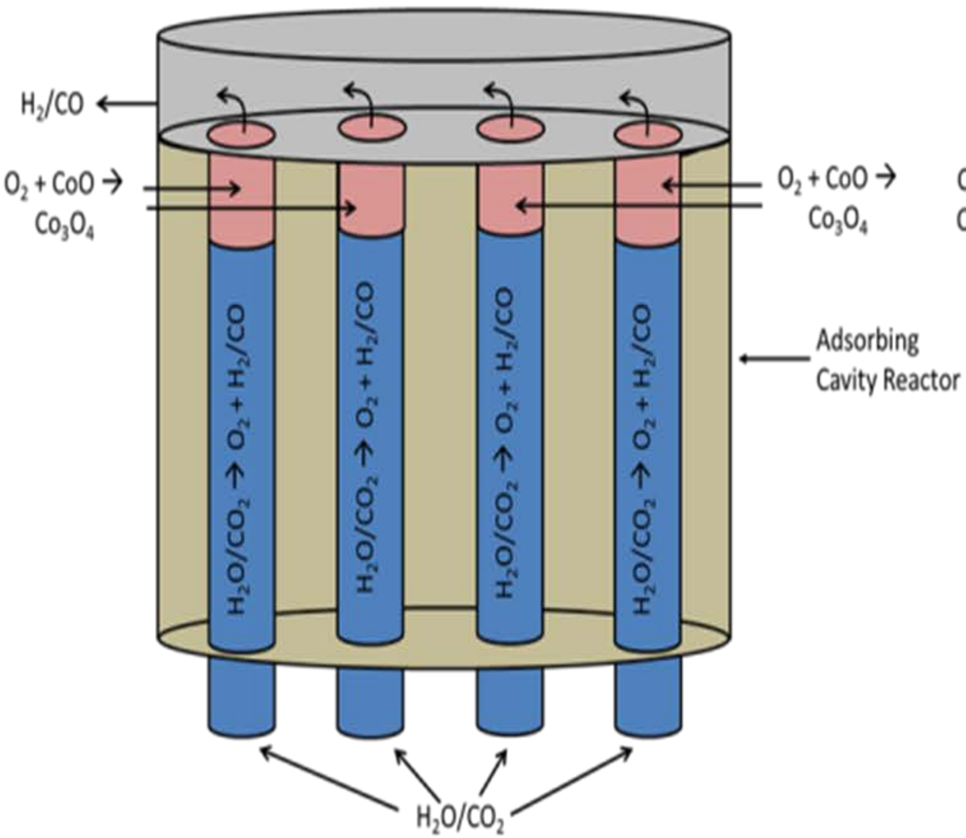
Isothermal Redox Appears Feasible

- faster cycling – no time required for T adjustment
- materials robustness should improve
- inherently more efficient internal heat recuperation

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

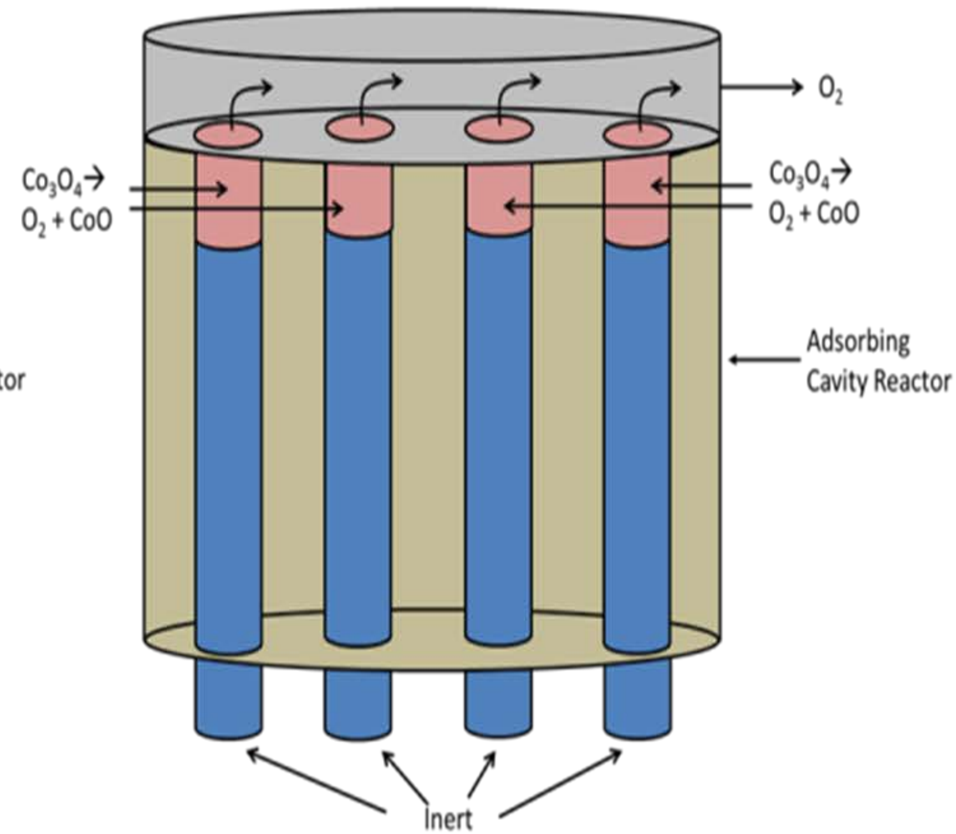
$6CoO + O_2 \rightarrow 2Co_3O_4$

H2/CO Generation

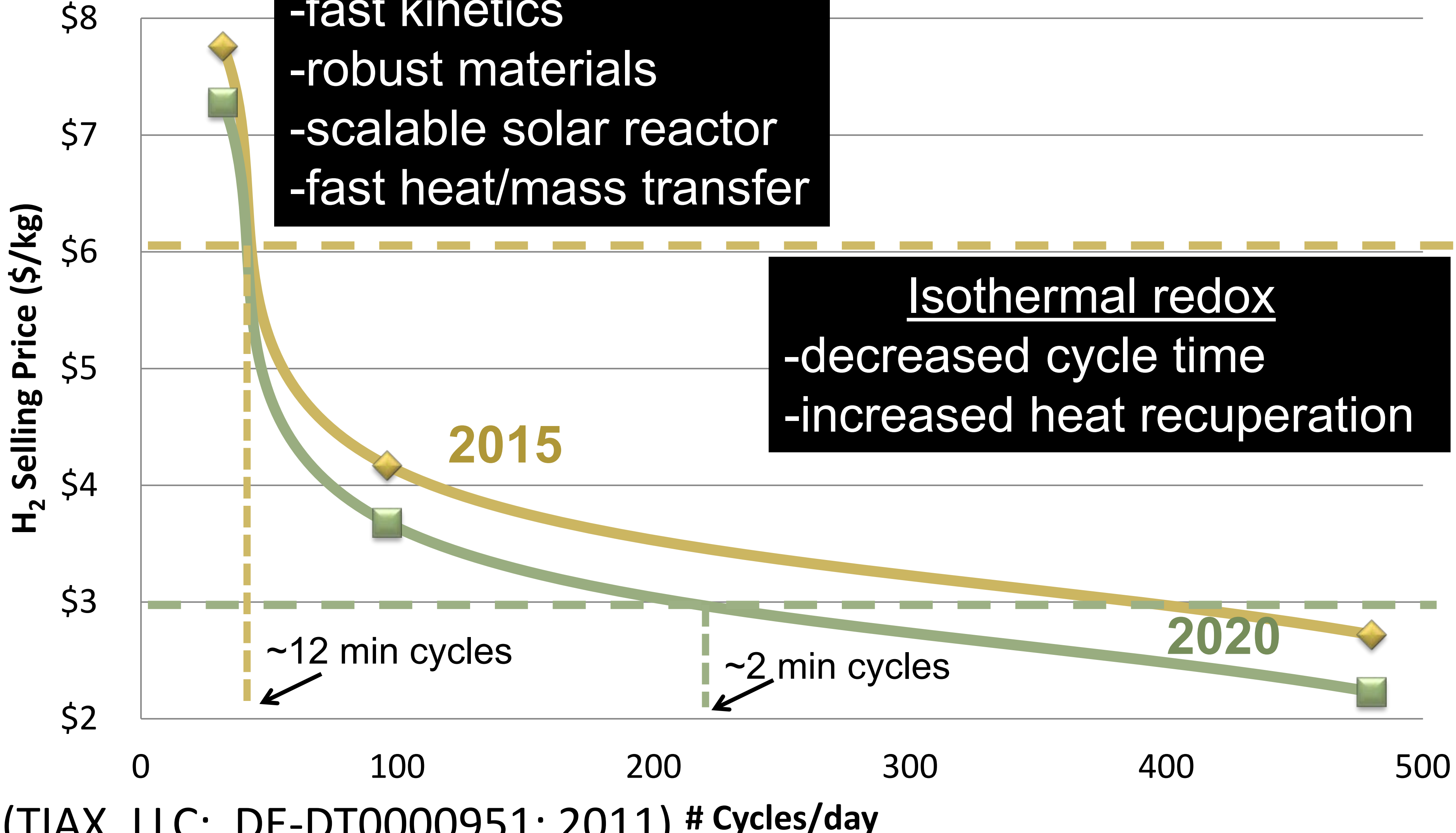


$2Co_3O_4 \rightarrow 6CoO + O_2$

Sorbent Re-generation



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



(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 & ~200ºC 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

By submitting a presentation file to Alliance Technical Services, Inc. for use at the U.S. Department of Energy's Hydrogen and Fuel Cells Program and Vehicle Technologies Program Annual Merit Review Meeting, and to be provided as hand-out materials, and posting on the DOE's website, the presentation authors and the organizations they represent agree to defend, indemnify and hold harmless Alliance Technical Services, Inc., its officers, employees, consultants and subcontractors; the National Renewable Energy Laboratory; the Alliance for Sustainable Energy, LLC, Managing and Operating Contractor of the U.S. Department of Energy's National Renewable Energy Laboratory; and the U.S. Department of Energy from and against any and all claims, losses, liabilities or expenses which may arise, in whole or in part, from the improper use, misuse, unauthorized use or disclosure, or misrepresentation of any intellectual property claimed by others. Such intellectual property includes copyrighted material, including documents, logos, photos, scripts, software, and videos or animations of any type; trademarks; service marks; and proprietary, or confidential information.