Solarthermal Redox-based Water Splitting Cycles

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Overview

Timeline

- **Start: 6-1-2005**
- **End: 9-30-2013**
- **80% completed**

Budget

- **Total Project Funding**
  - **2005-2011: $1,210K DOE**
  - **$347,500 Cost Share**
- **Funds received in FY12**
  - **$217,000 (subcontract from SNL)**
  - **$ 54,250 Cost Share**
- **Planned FY2013 Funding**
  - **$250,000 (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)

Relevance

- 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:

($14.80/kg H_2 in 2015; $3.70/kg H_2 in 2020; ultimately $2/kg H_2)

Milestone – "Synthesize a cobalt ferrite/alumina "hercynite" active material by ALD using polymer templates. Demonstrate isothermal redox water-splitting in a stagnation flow reactor at a temperature of 1350°C yielding a H_2 production per gram of total mass of active material > 100 μmoles/g active material." (> 200 µmoles/g active material achieved in 3/2013)

Approach

- Ceria redox is considered base material for comparative water splitting (WS) performance – fast kinetics & robust
- Evaluate "doped" CeO_2, compared to base
- Evaluate "hercynite cycle" materials, i.e. ferrite/alumina reaction
  - Temperature Swing redox (TS)
  - Isothermal redox (IS)
- Model multi-tube fixed reactor configuration for efficiency estimates & "best" design
- Evaluate effect of increased pressure (P) and temperature (T) on increasing the slower oxidation rates measured at Sandia National Labs in 2012
- Validate high productivity "hercynite cycle" data obtained on-sun at NREL in 2012 (145 μmole H_2/g total)

Stagnation Flow Reactor for Materials Characterization

- CeO$_2$
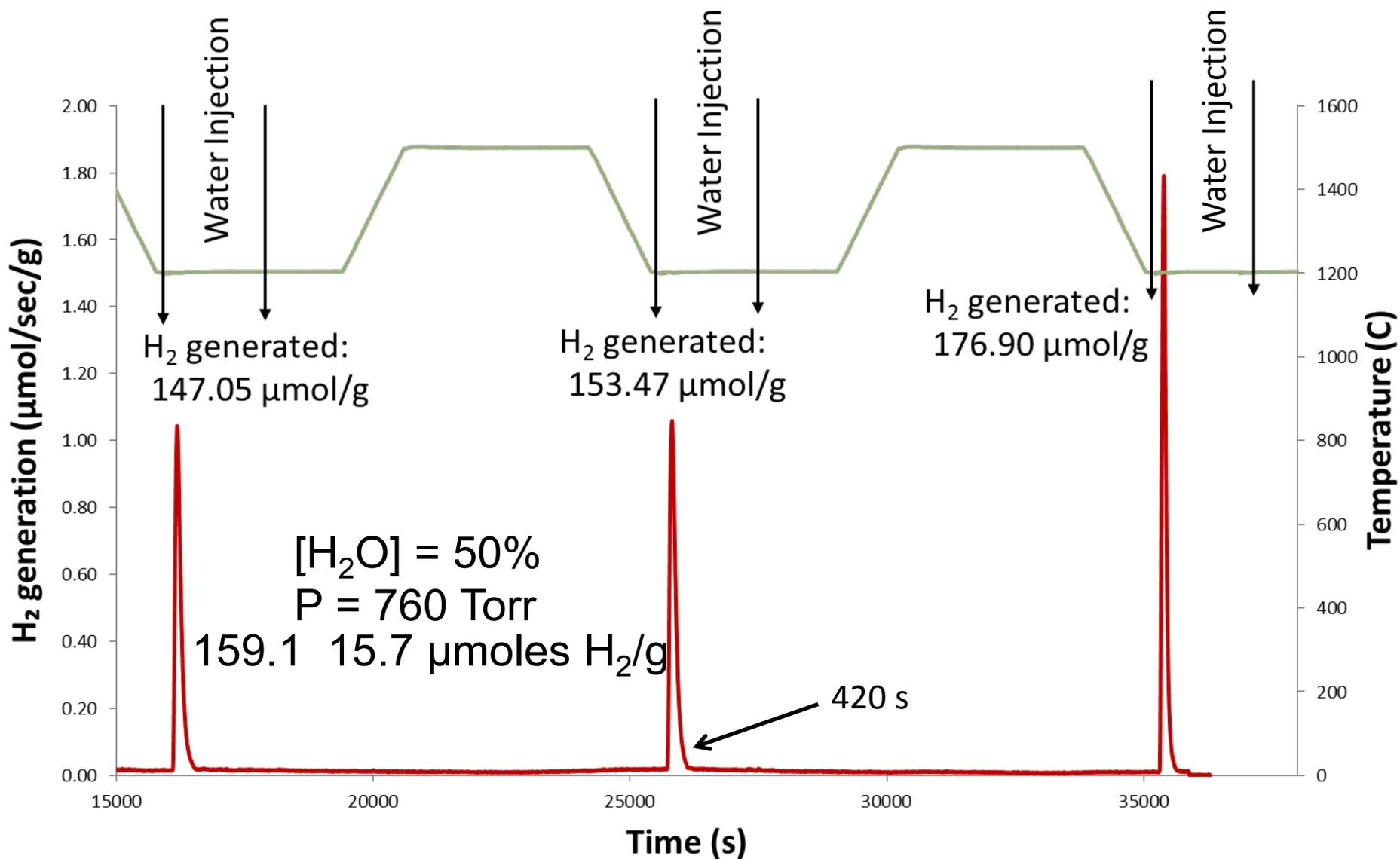- "Hercynite"
- T-Swing redox
- Isothermal redox
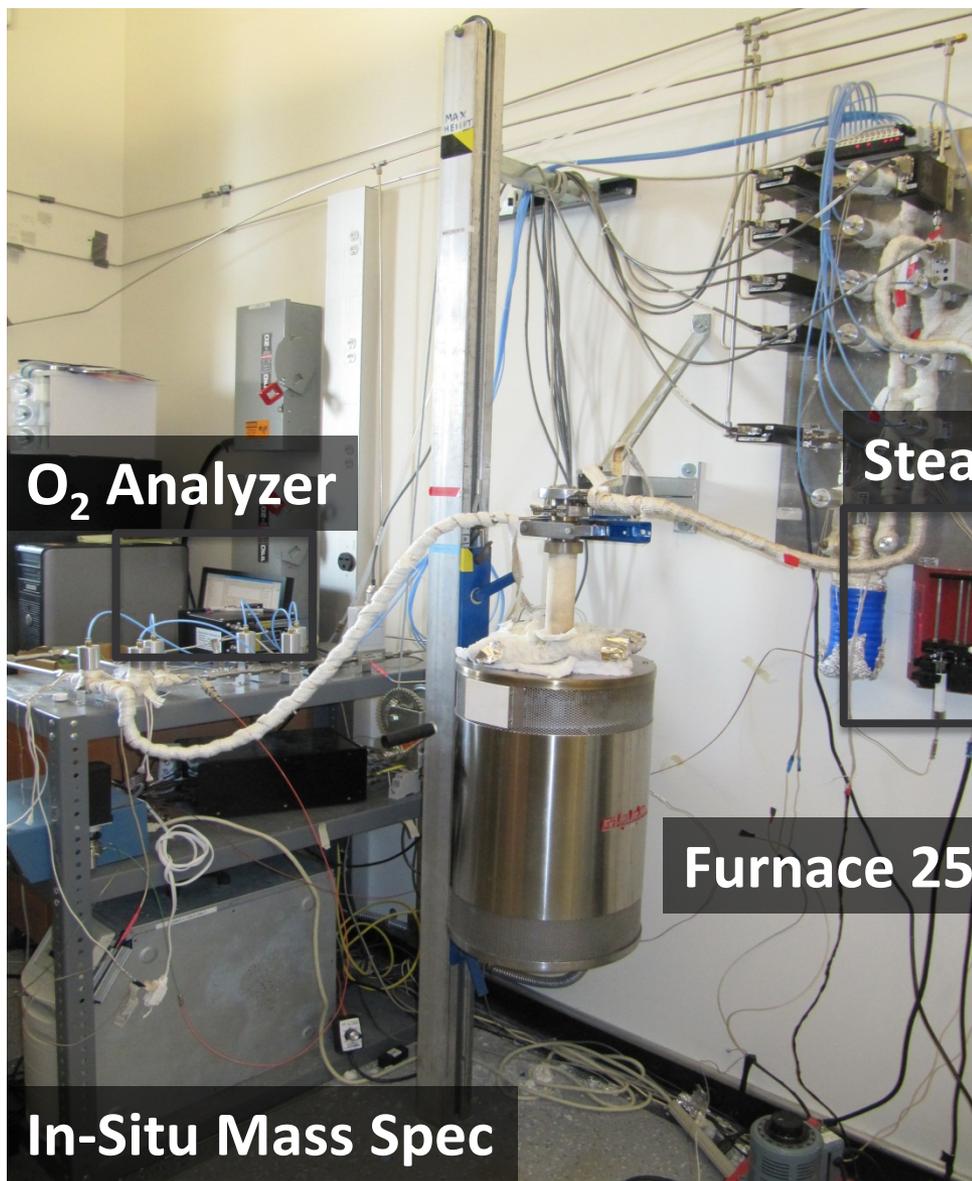
O$_2$ Analyzer

Steam Generator

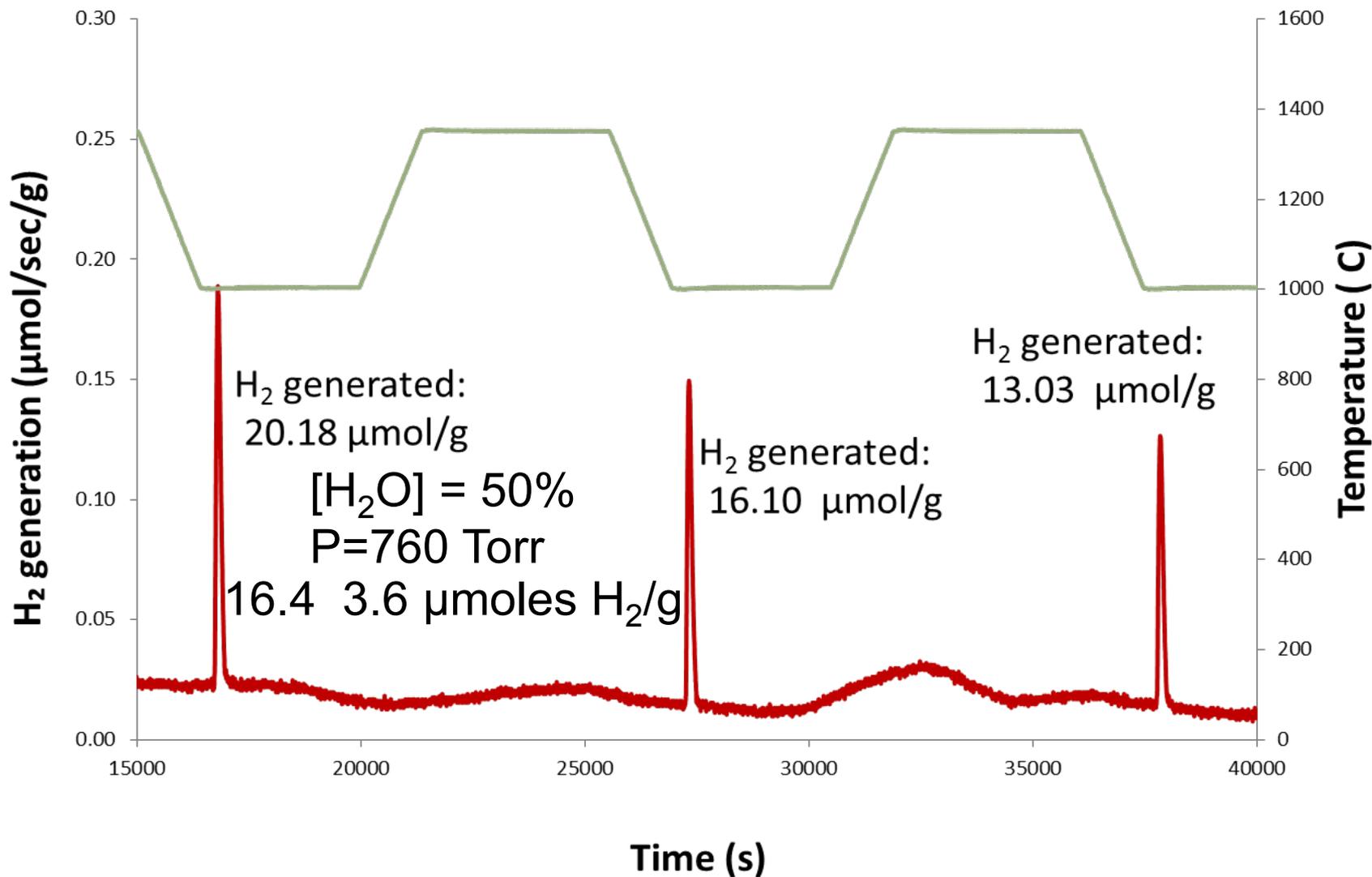Furnace 25 – 1700°C

In-Situ Mass Spec
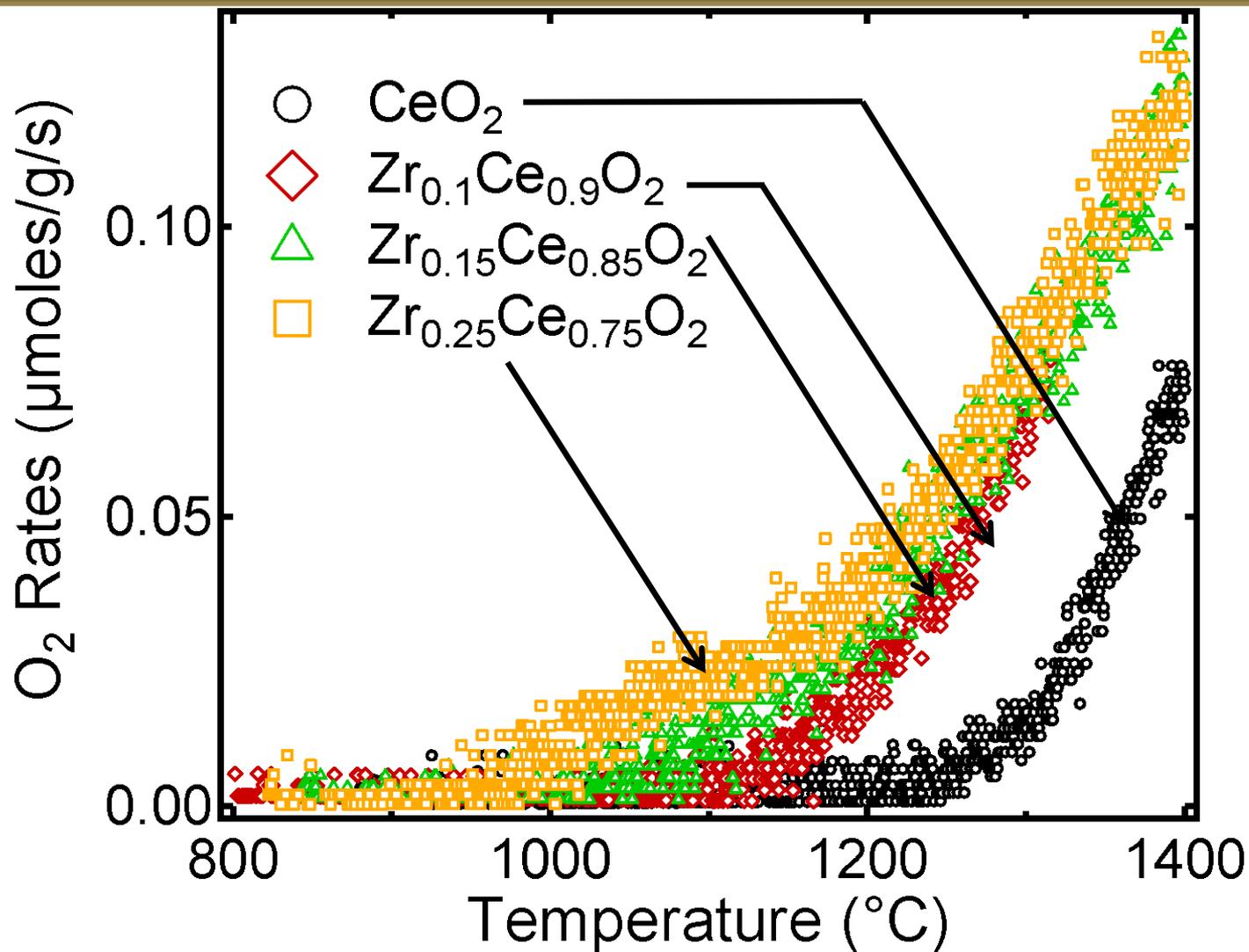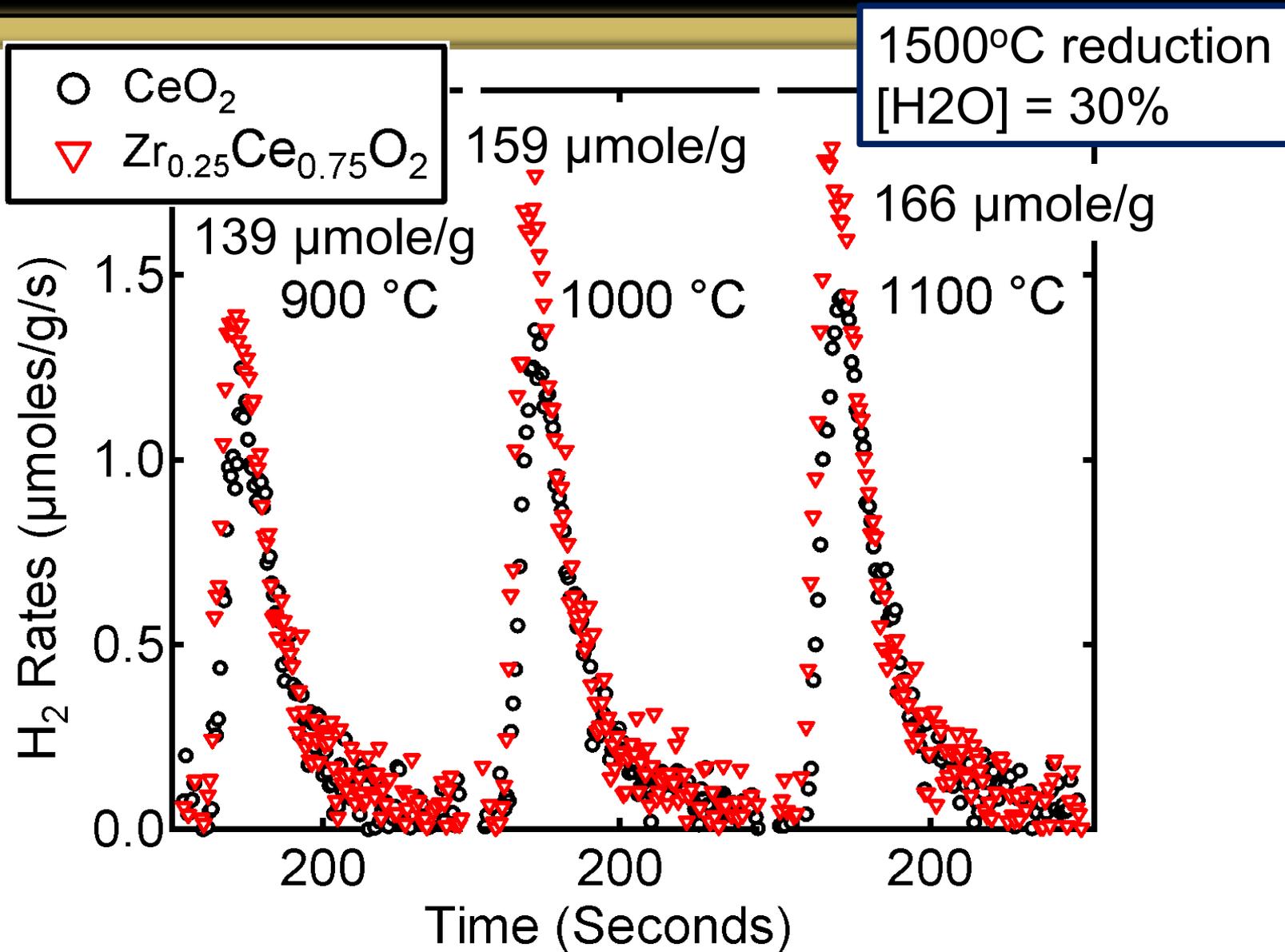
Ceria 1500ºC/1200ºC (redox)

Ceria 1350°C/1000°C (redox)

Zr Substitution Beneficial to Reduction

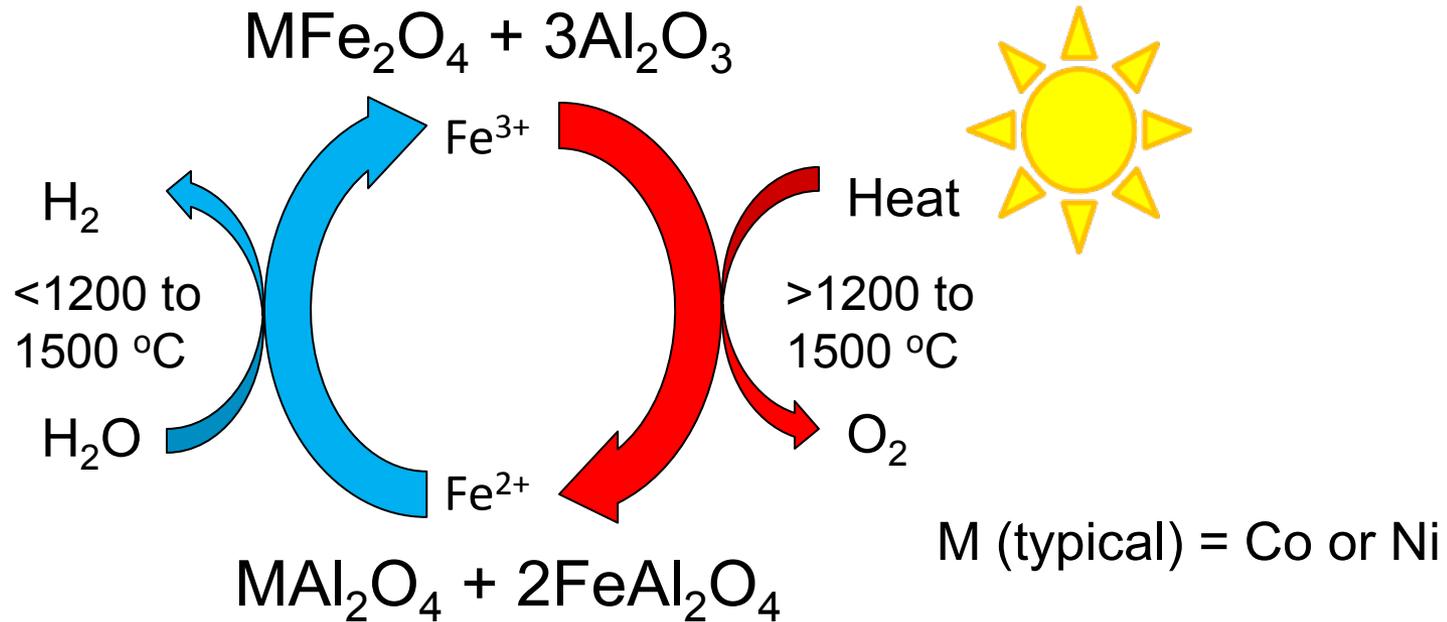Experiments run at Sandia National Laboratories

Zr Substitution Beneficial to Oxidation

1500°C reduction
[H2O] = 30%

CeO$_2$
Zr$_{0.25}$Ce$_{0.75}$O$_2$

139 μmole/g
900 °C

159 μmole/g
1000 °C

166 μmole/g
1100 °C

H$_2$ Rates (μmoles/g/s)

Time (Seconds)

Experiments run at Sandia National Laboratories

"Hercynite Cycle"

$$MFe_2O_4 + 3Al_2O_3$$

Fe^{3+}

H_2

<1200 to 1500 ^oC

H_2O

Fe^{2+}

Heat

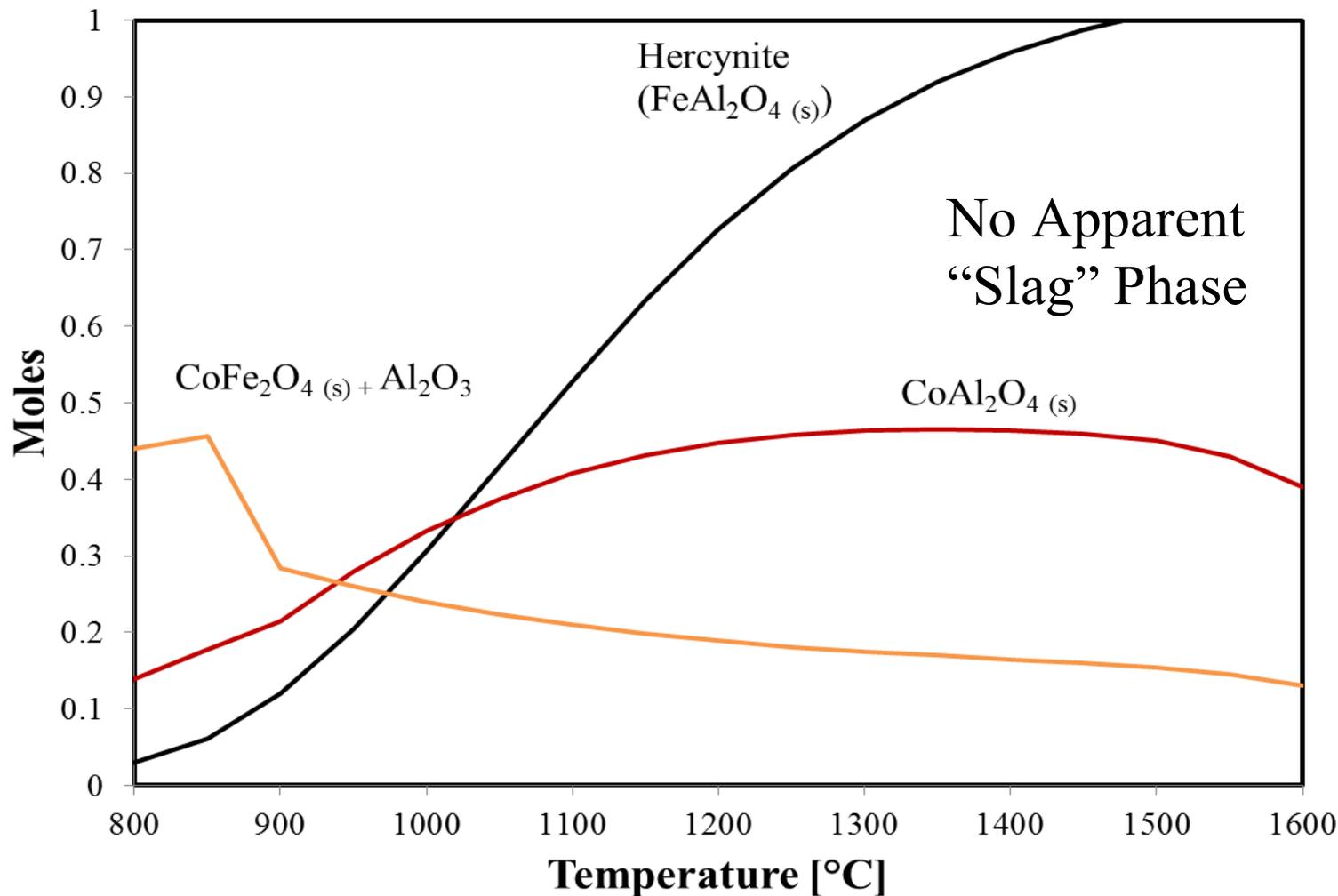>1200 to 1500 ^oC

O_2

$$MAl_2O_4 + 2FeAl_2O_4$$

M (typical) = Co or Ni

- Reduced and oxidized moieties are stabilized in two different compounds;
- Compound formation is more thermodynamically favorable than solid solution formation
- Higher T and P should increase oxidation rate
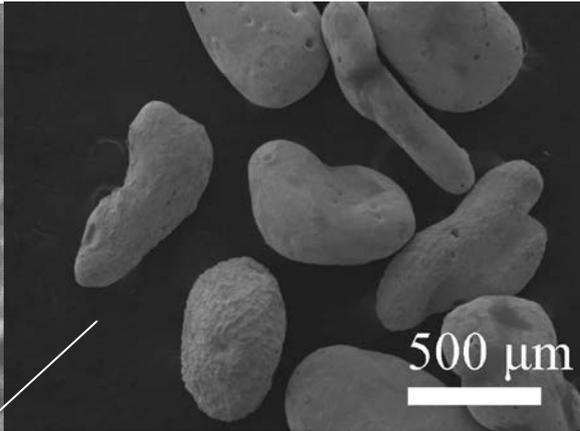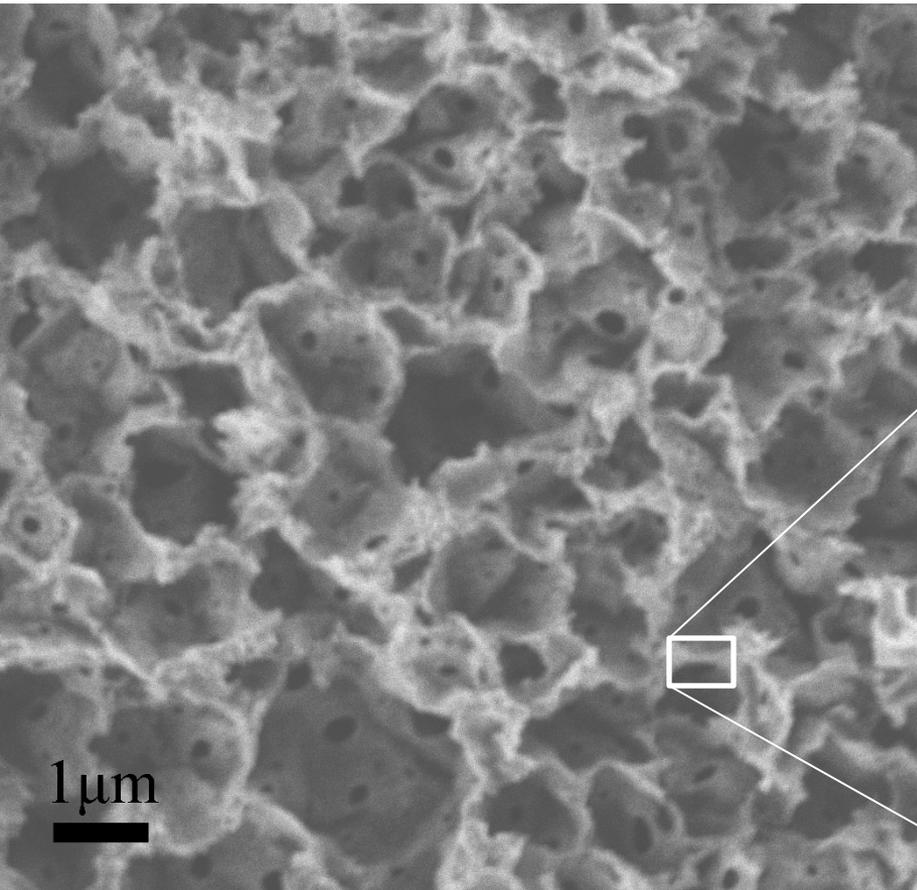
"Hercynite Cycle" Robustness

Chemistry Validated via Raman:
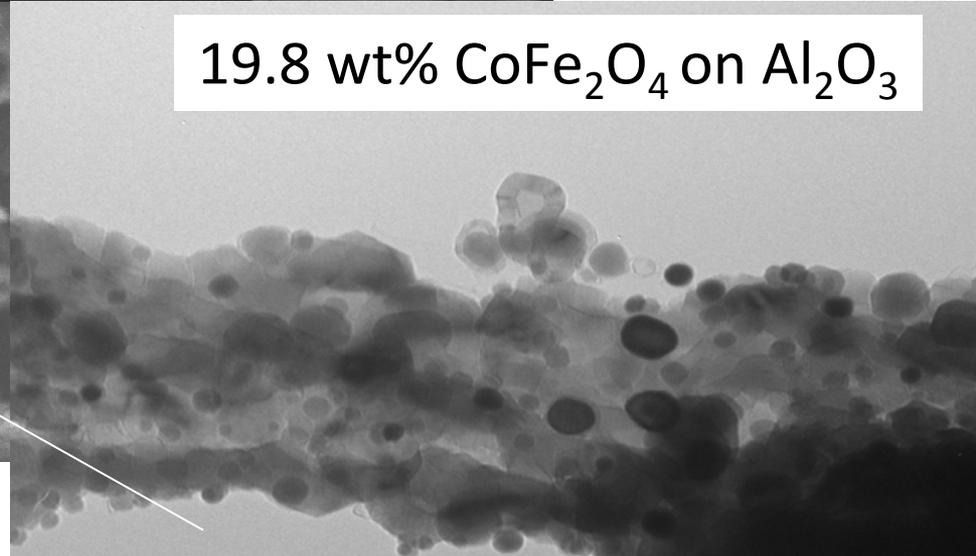Arifin, D. et al. ," Energy & Environmental Science 5, 9438-9443 (2012)

Micrographs of Active Nanostructured "Hercynite" Materials

Liang, X.H. et al., <u>Microporous and Mesoporous Materials</u>, <u>149</u>, 106-110 (2012)

500 μm

1 μm

19.8 wt% $CoFe_2O_4$ on Al_2O_3

<u>Cross-sectioned Particle</u>
Skeletal γ-Al_2O_3
(80 m^2/g; 1 cm^3/g pore volume);

Lichty, P., et al. <u>Int. J. of Hydrogen Energy</u>, <u>37</u>, 16888-16894 (2012)

Reduction temperature is dictated by reduction enthalpy of the active material

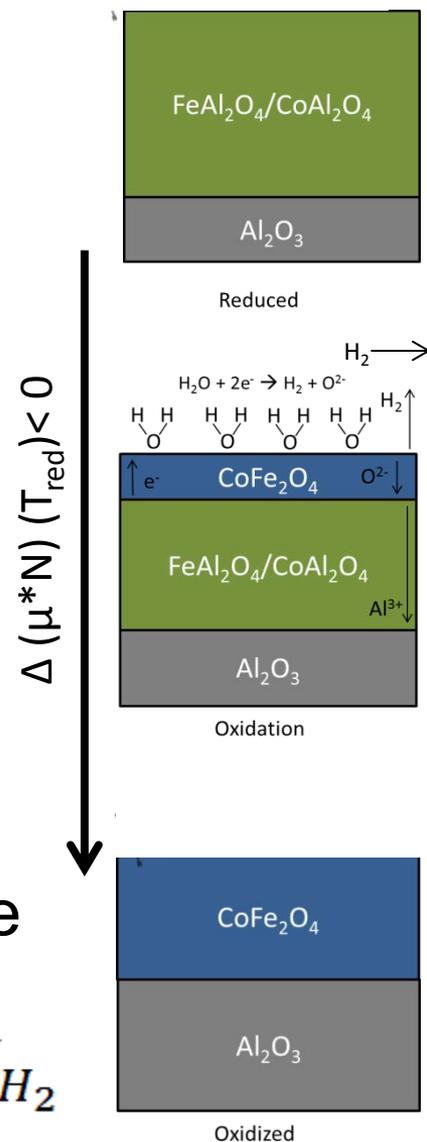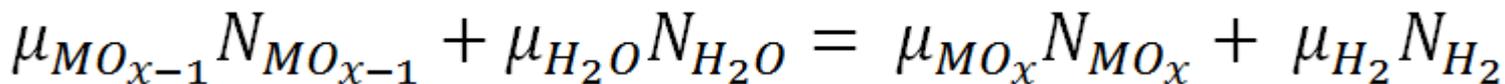However water is not reacting in the gas phase, need to consider three phases:

    -Gas. Surface and Solid

$$\Delta G \;=\; P\Delta V - T\Delta S + \sum_{j=1}^{M} \mu_j \Delta N_j$$
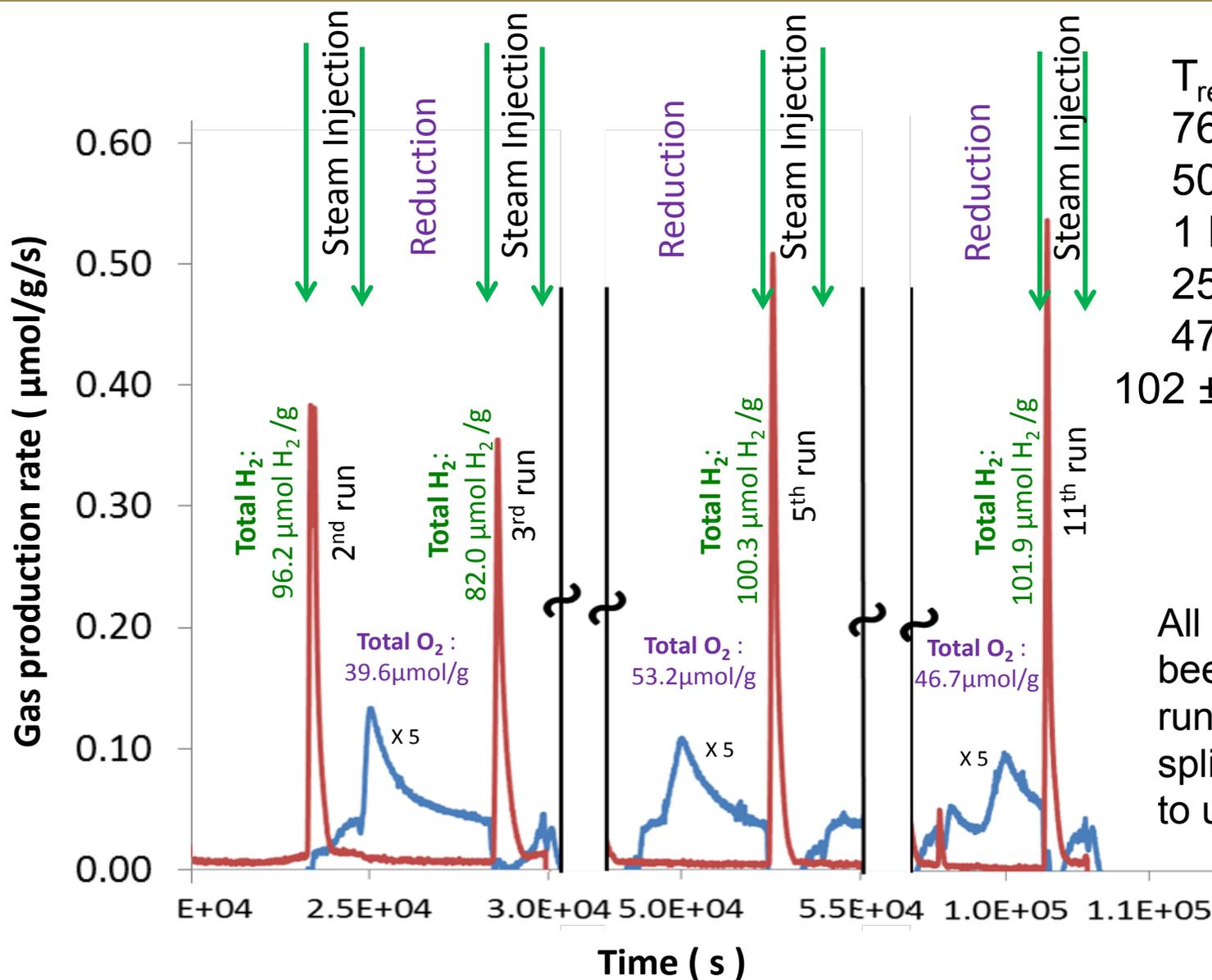
N_x on the surface is related to P_x:

$$N_x = a \,*\, P_x$$

By altering pressure, the free energy can become favorable

$$\mu_{MO_{x-1}} N_{MO_{x-1}} + \mu_{H_2O} N_{H_2O} = \mu_{MO_x} N_{MO_x} + \mu_{H_2} N_{H_2}$$

FeAl$_2$O$_4$/CoAl$_2$O$_4$

Al$_2$O$_3$

Reduced

$\Delta\,(\mu*N)\,(T_{red}) < 0$

H$_2 \longrightarrow$

H$_2$O + 2e$^-$ → H$_2$ + O^{2-}

H H   H H H H H H H$_2$
O   O   O   O

e$^-$ CoFe$_2$O$_4$ O^{2-}

FeAl$_2$O$_4$/CoAl$_2$O$_4$

Al^{3+}

Al$_2$O$_3$

Oxidation

CoFe$_2$O$_4$

Al$_2$O$_3$

Oxidized

"Hercynite Cycle" Isothermal Water Splitting

$T_{red}=T_{ox}=1350 \,^{\circ}C$
760 Torr
50% $[H_2O]$
1 hour reduction
25 min oxidation
47% Active
102 ± 18 μmoles H_2/g

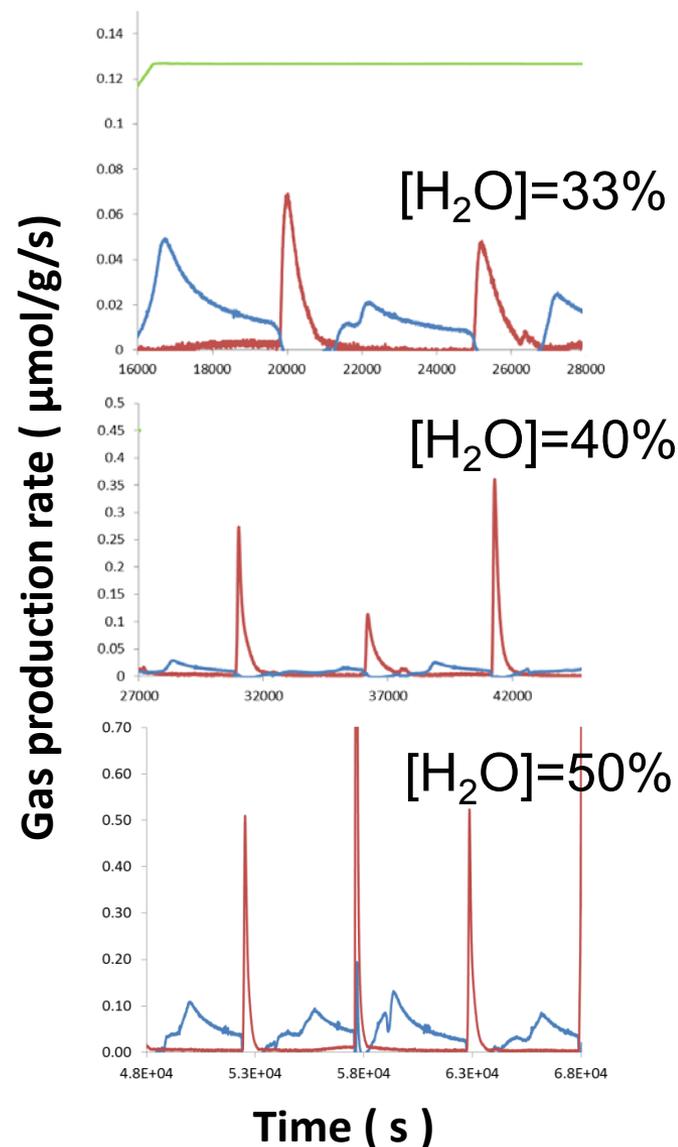All material has been aged by running > 150 water splitting cycles prior to use.

% [H_2O]	P_{H2O} (Torr)	H_2 production[a] ($\mu mol/g$)[b]	Peak rate[b] ($\mu mol/g/s$)
33	253.3	40 ± 9	0.06 ± 0.02
40	325.7	72 ± 8	0.15 ± 0.07
50	380	102 ± 18	0.35 ± .18

[a] Error was calculated at 95% confidence level.
[b] Rates represent μmol H_2/g of total material. Multiply by 2.13 to get μmol H_2/g active material.
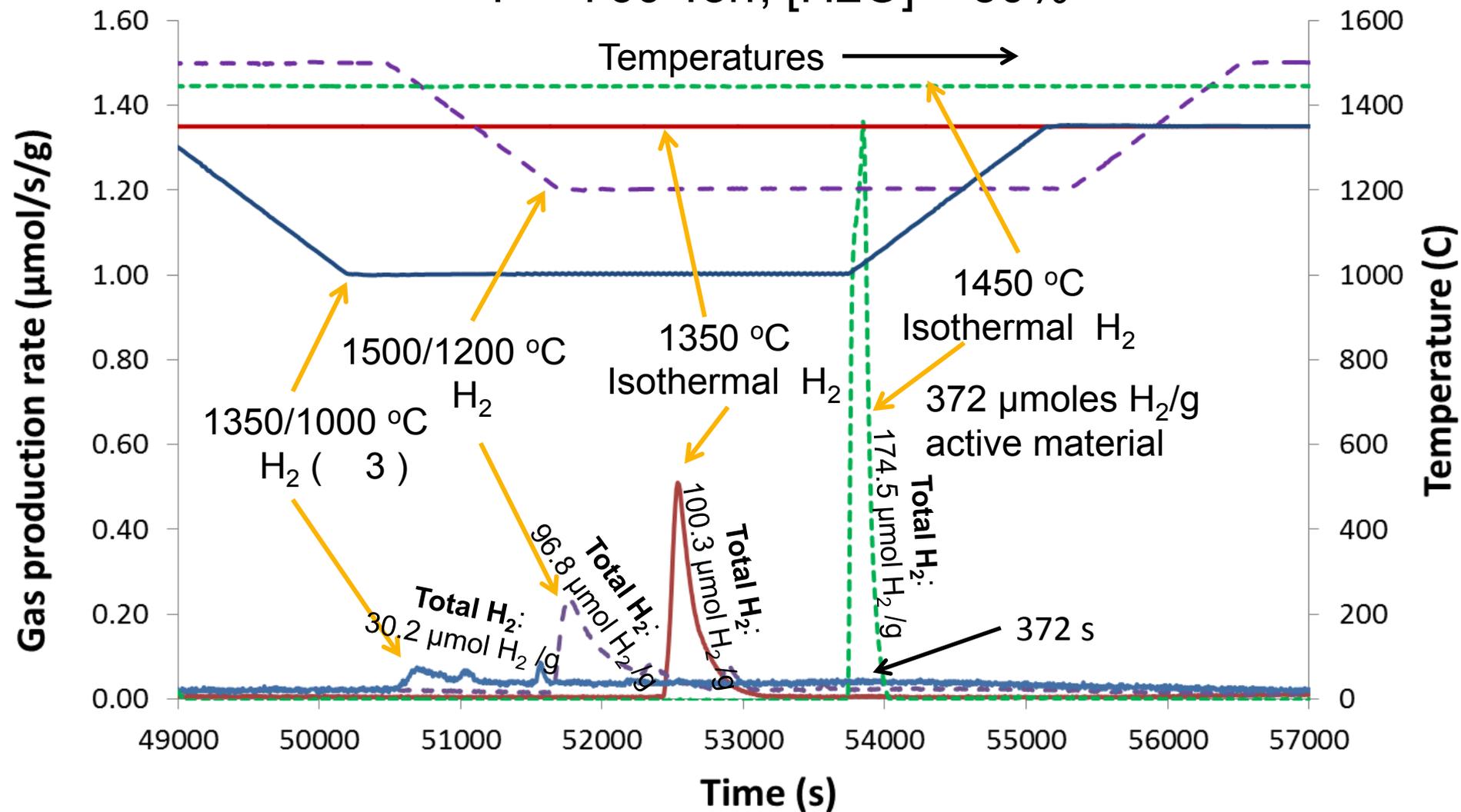
- Increased H_2O pressure increases total H_2 produced
- Increased H_2O pressure increases peak rates of H_2 production
- Increased H_2O pressure decreases time for complete re-oxidation.

[H_2O]=33%

[H_2O]=40%

[H_2O]=50%

Gas production rate ($\mu mol/g/s$)

Time (s)

P = 760 Torr, [H2O] = 50%

Water Splitting Comparisons

| Temp Swing (TS) & Isothermal (IT) (Red/Ox); Temperature (^{o}C)	CeO_2 (μmole/g)	Nanostructured "Hercynite" (μmole/g); x 2.13 / g active	CeO_2 Peak Rate (μmole/g/s)	Nanostructured "Hercynite" Peak Rate (μmole/g/s); x 2.13 / g active
1500/1200	159.1 ± 15.7	93.7 ± 19.2	1.28 (avg)	0.32 (avg)
1350/1000	16.4 ± 3.6	31.4 ± 2.3	0.15 (avg)	0.03 (avg)
1350/1350		102 ± 18		0.55 ± 0.16
1450/1450		167.4 (avg)		1.34 (avg)

P = 760 Torr; [H_2O] = 50%

- At high reduction T, TS CeO_2 produces ~ equal H_2 as IT "hercynite cycle" per total g of material ("hercynite cycle" produces about 2X more on active material basis).

- At low reduction T, IT "hercynite cycle" produces ~ 5X more H_2 compared to CeO_2 and ~10X more on basis of active material

- IT "hercynite cycle" produces substantially more H_2 than TS "hercynite cycle".
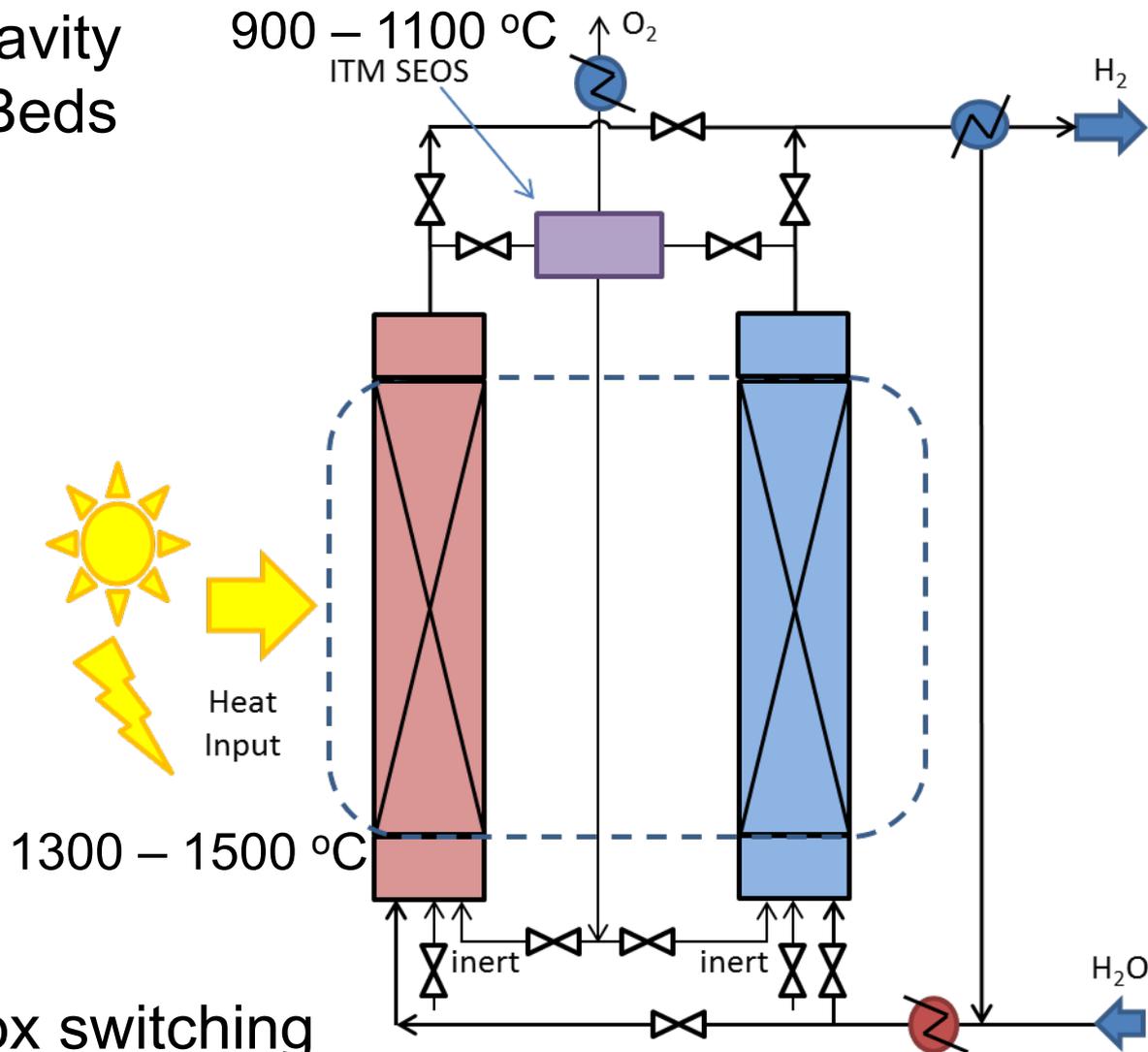
Isothermal Redox Similar to PSA

Insulated, Absorbing Cavity
w/ Multi-tubular Fixed Beds

900 – 1100 °C
ITM SEOS

O_2

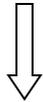H_2

Heat
Input

1300 – 1500 °C

inert   inert

H_2O
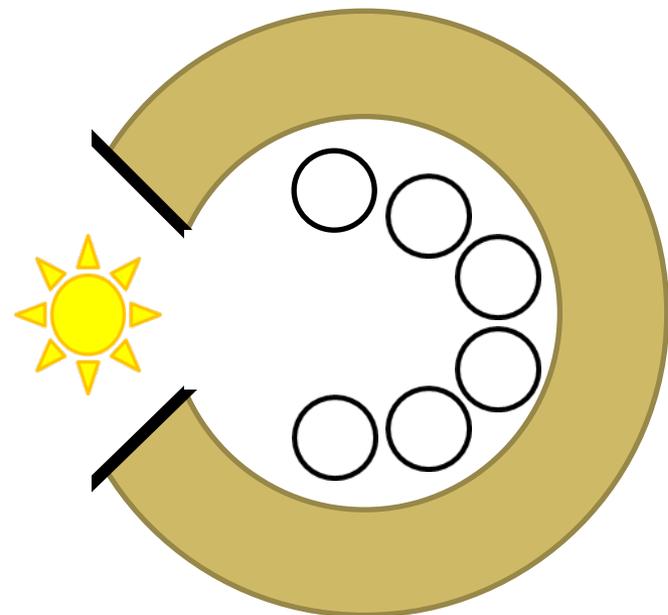
Top-Down View

Pseudo-Side View

- Potentially faster redox switching
- Fewer concerns with thermal shock
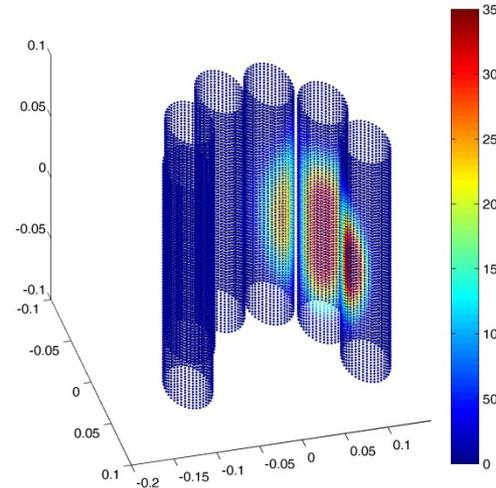
3D Monte Carlo ray-tracing model:

- Provides profiles of absorbed solar energy on all surfaces from defined solar profile at aperture

Solar energy flux absorbed on tube array

Time – dependent receiver temperature profiles

3D transient CFD model:

- Fluid flow through packed bed

- Convective / conductive / radiative heat transfer in packed bed and cavity

- Natural convection in cavity space

- Kinetic reaction rates = f (T, local fluid composition, reaction extent)

- Equilibrium limitations via kinetic rates of reverse reactions

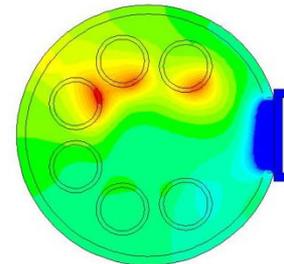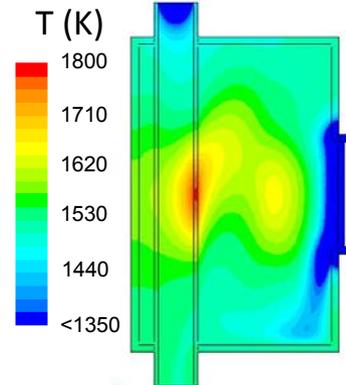## Objectives

- Develop steady state & dynamic models of a multi-tube solar receiver
- Identify parameters controlling receiver efficiency
- Identify optimal tube/cavity configurations & solar flux input
- Quantify impacts of isothermal operation on receiver efficiency

Time-averaged receiver efficiency based on transient H_2 production

Battery Limits

- 4 kW solar input
- Adiabatic external boundaries
- 6 cm square aperture
- 6 min cycle time
- Flux - Solar beam width / direction optimized independently for each design

"Hercynite Cycle"

$$\overline{\eta} = \frac{\int_{cycle} \dot{n}_{H_2} LHV_{H_2} dt}{\int_{cycle} P_{solar} dt + \int_{cycle} E_{O_2} \dot{n}_{O_2} dt} = \frac{\text{Heating value of } H_2 \text{ produced}}{\text{Solar energy} + \text{Energy to separate } O_2 \text{ from inert}} = \frac{LHV_{H_2} \overline{n}_{H_2,i}}{P_{solar} + E_{O_2} \overline{n}_{O_2}}$$

r cavity (cm)	h cavity (cm)	r tube (cm)	mol $CoFe_2O_4$ per tube	sccm H_2O per tube	Maximum T (^{o}C)	Average T (^{o}C)	$\eta_{LHV} H_2$
14.6	18	2.3	2.6	1	1620	1532	5.5
20.1	22	3.3	6.3	6	1427	1257	16.7

$\eta_{LHV} H_2$ increases with a decreased surface/volume ratio for solar reactor

Collaborations

- High-flux Solar Furnace On-sun Operations at NREL

- Laser-assisted Stagnation Flow Reactor Operations at Sandia – Livermore (one Ph.D. student in-place at all times)

Proposed Future Work

- Evaluate isothermal redox at T > 1450°C; P > 760 Torr; and [H$_2$O] = 100%

- Evaluate improved compositions approaching stoichiometric CoFe$_2$O$_4$/Al$_2$O$_3$ = 3

- Develop reaction kinetics rate expressions for "hercynite cycle" active materials

- Incorporate improved reduction and oxidation reaction kinetics into the multi-tubular receiver model; update model

- Demonstrate isothermal redox on-sun

- Evaluate a high-T oxygen transport membrane for O$_2$ removal during redox cycling (ITM-SEOS)

- Carry out H2A Analysis for Isothermal Redox Processing

- Synthesize Micro-containers of Nano-sized Active Materials & test in a Particle Flow Reactor

- Particle ALD can be used to produce nano-coated nano-particles that are then spray dried/calcined to 60 microns
  $CoFe_2O_4/Al_2O_3 = 1/3$ (molar)

Al_2O_3 (3.95 g/cc)

$CoFe_2O_4$ (5.15 g/cc)
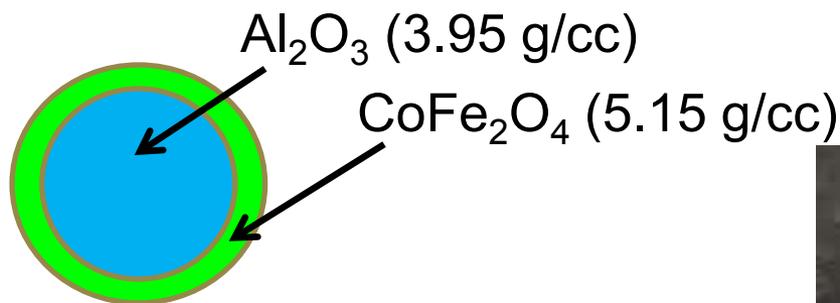
dp Al_2O_3 (nm)	$CoFe_2O_4$ Film Thickness (nm)
20	1.7
40	3.3
150	12.5

Spray Dried

15.0kV x750 20μm
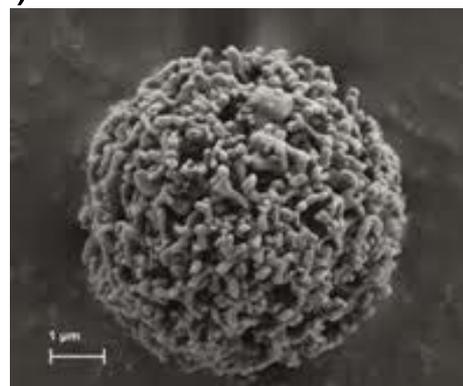
Calcined

(Typical d_{50} = 60-80 μm)

Or, directly spray dry nano Al_2O_3, Fe_2O_3 and CoO

Summary

- Zr-doped CeO_2 increases H_2 productivity by ~ 20% over un-doped CeO_2;

- Hercynite cycle nanostructured active materials operating isothermally at 1450°C have comparable peak reaction rates and H_2 production rates/g compared to Zr-doped CeO_2 reduced at 1500°C and oxidized at 1200°C. On the basis of g active materials only, hercynite cycle materials are 2X performance - demonstrated 372 µmoles H_2/g active material.

- Hercynite cycle nanostructured active materials operating isothermally at 1350°C have 5X peak reaction rates and H_2 production rates/g compared to CeO_2 reduced at 1350°C and oxidized at 1000°C. On the basis of g active materials only, hercynite cycle materials are 10X H_2 production performance.

Summary Continued

- Active "hercynite cycle" nanostructures maintained their redox activity for over 150 cycles, after 1st cycle;

- Increased [H_2O], operating P and operating T increase total H_2 produced, increase the peak rate of H_2 production, and decrease the time for complete re-oxidation for isothermal "hercynite cycle" materials; and

- A small adiabatic 4-kW$_{thermal}$ solarthermal multi-tube fixed bed reactor operating isothermally with "hercynite cycle" materials is predicted to have a η_{LHV} H_2 > 15%.

- 16 Peer-reviewed scientific papers published in 2012;
- 7 already published in 2013 (+ 3 in press)
- 4 U.S. Patents issued in 2012; 1 Issued thus far in 2013
- Three Ph.D. students won 1st, 2nd, and 3rd Place Posters and an U/G student took 1st Place at 2012 Annual AIChE Meeting (Pittsburgh)
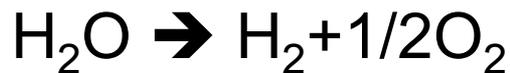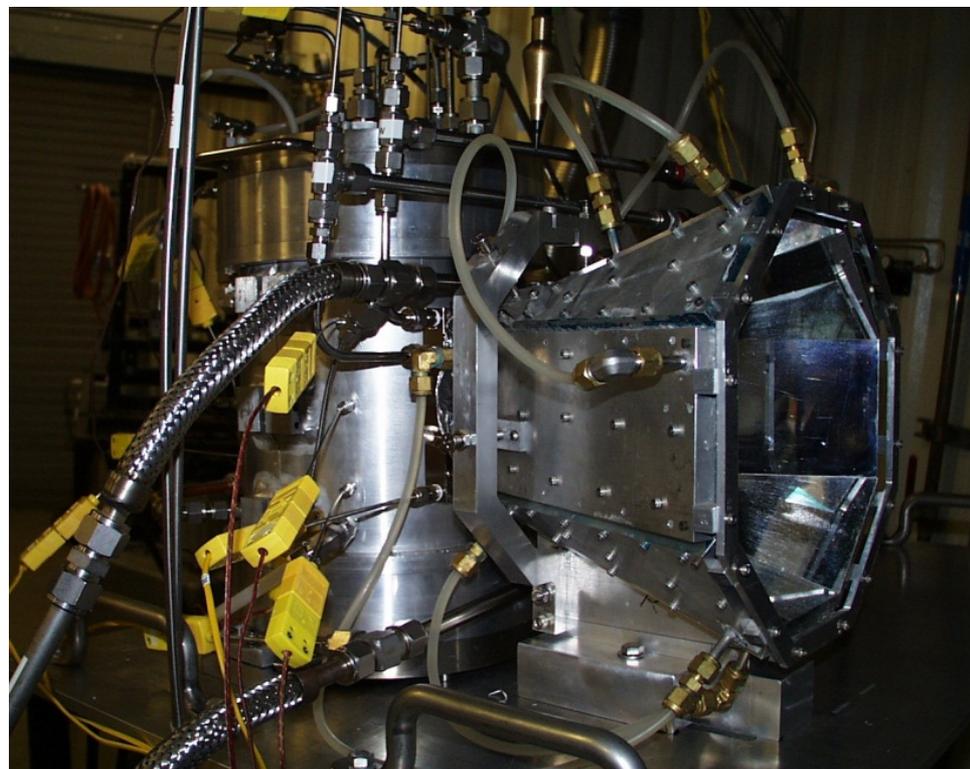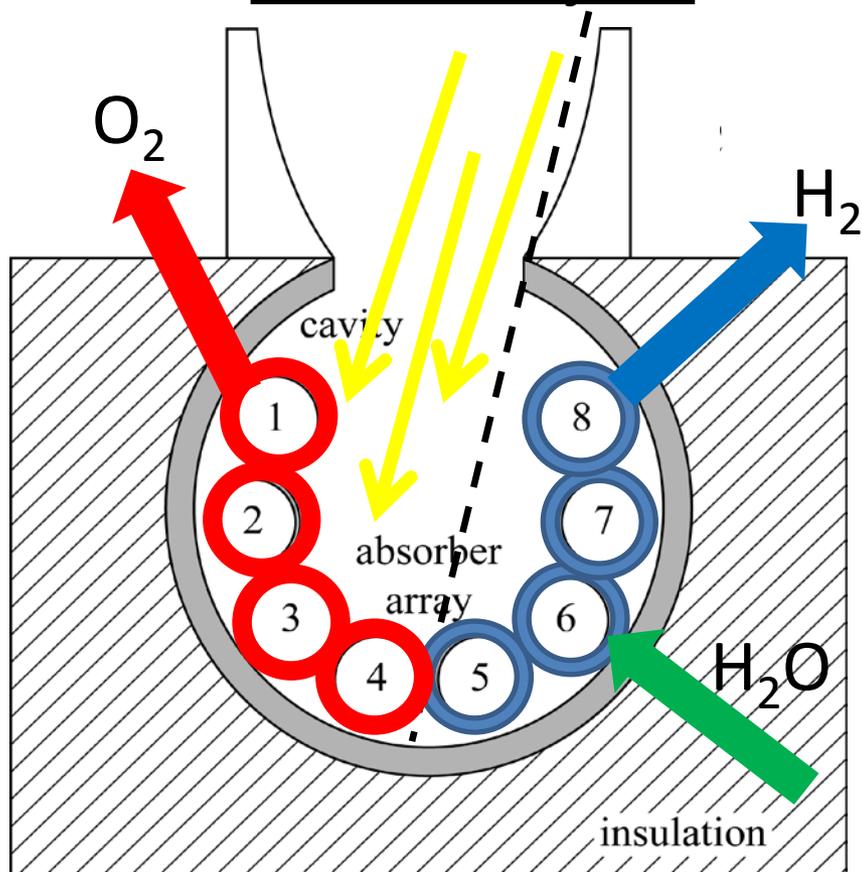
Technical Backup Slides

$$CoFe_2O_4 + 3\,Al_2O_3 \rightarrow CoAl_2O_4 + 2Fe_2AlO_4 + 1/2O_2$$
$$CoAl_2O_4 + 2Fe_2AlO_4 + H_2O \rightarrow CoFe_2O_4 + 3\,Al_2O_3 + H_2$$

$$H_2O \rightarrow H_2 + 1/2O_2$$

1st Half Cycle

University of Colorado
Multi-tube Solar Receiver/Reactor

$1350^oC/1000^oC$ Redox (P=1120 Torr; 50% [H_2O])

Nanostructured ALD "Hercynite" Materials

Integrated H_2 production in µmole/g ferrite
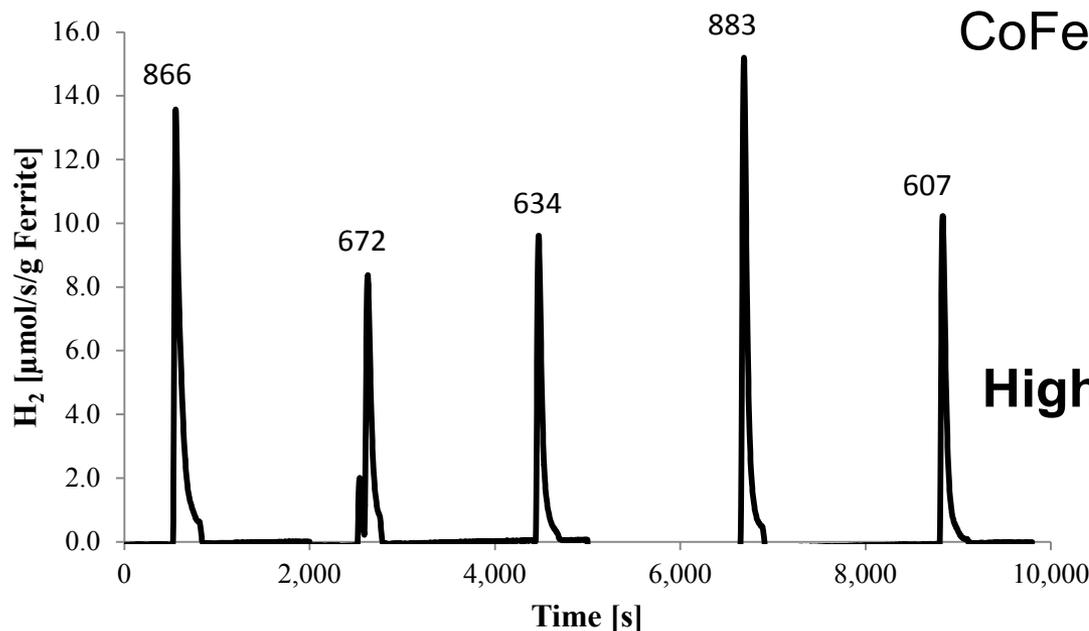
Averaged H_2 Production Rate
$CoFe_2O_4$ + 3 Al_2O_3 + excess Al_2O_3 →
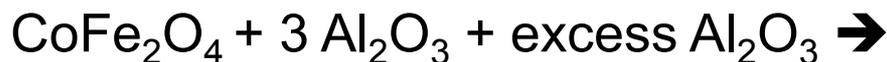
145 µmole/g total
309 µmole/g active material
732 µmole/g ferrite
47 % active material

Higher P favors higher productivity (need to validate)

Lichty, P., et al., International Journal of Hydrogen Energy, 37, 16888-16894 (2012)

Nanostructured "hercynite cycle" active materials

Slow CO_2 oxidation @ 1000^oC & 600 Torr
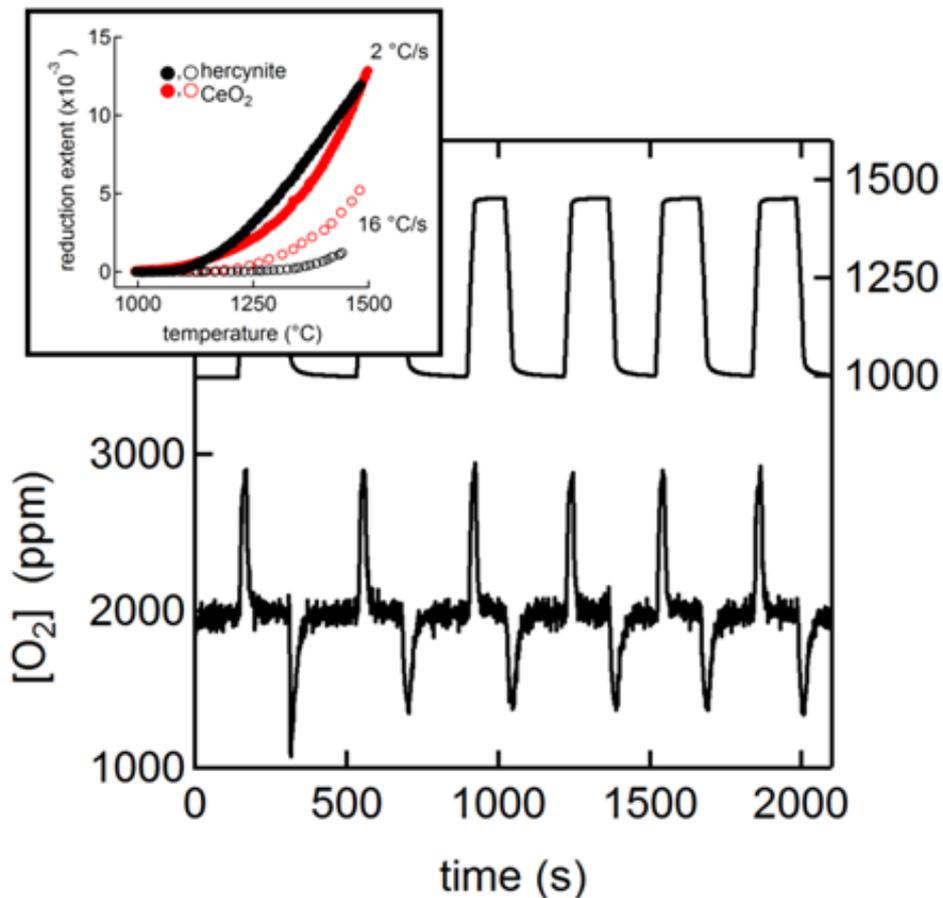
Fast Reduction Kinetics & Oxygen Exchange
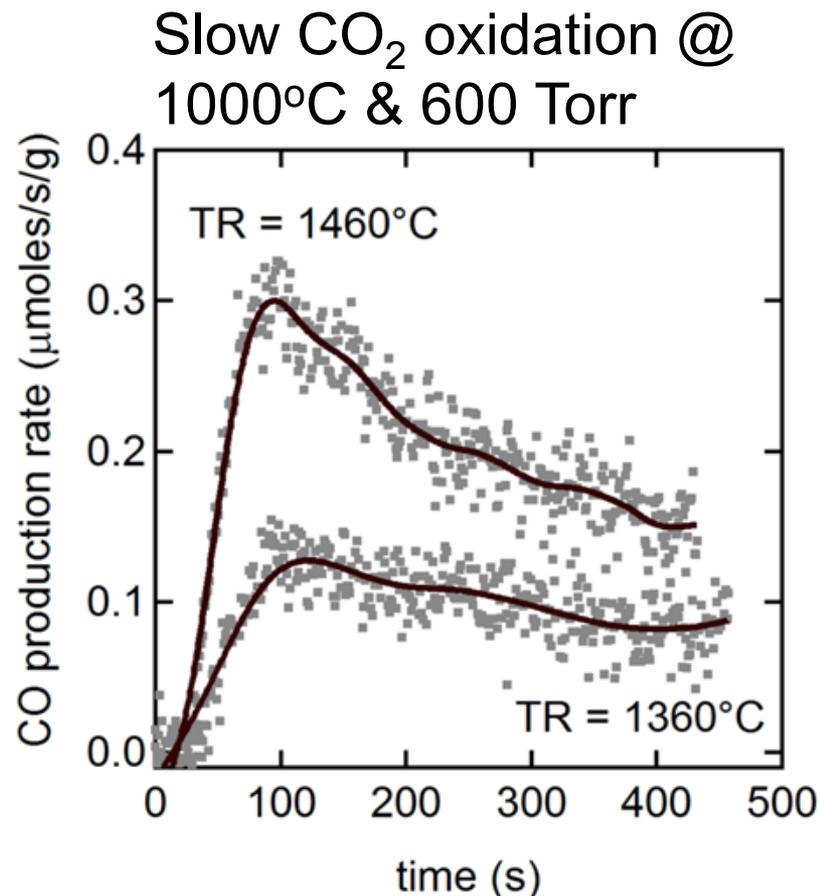
Need to determine impact of higher T & P on oxidation rate
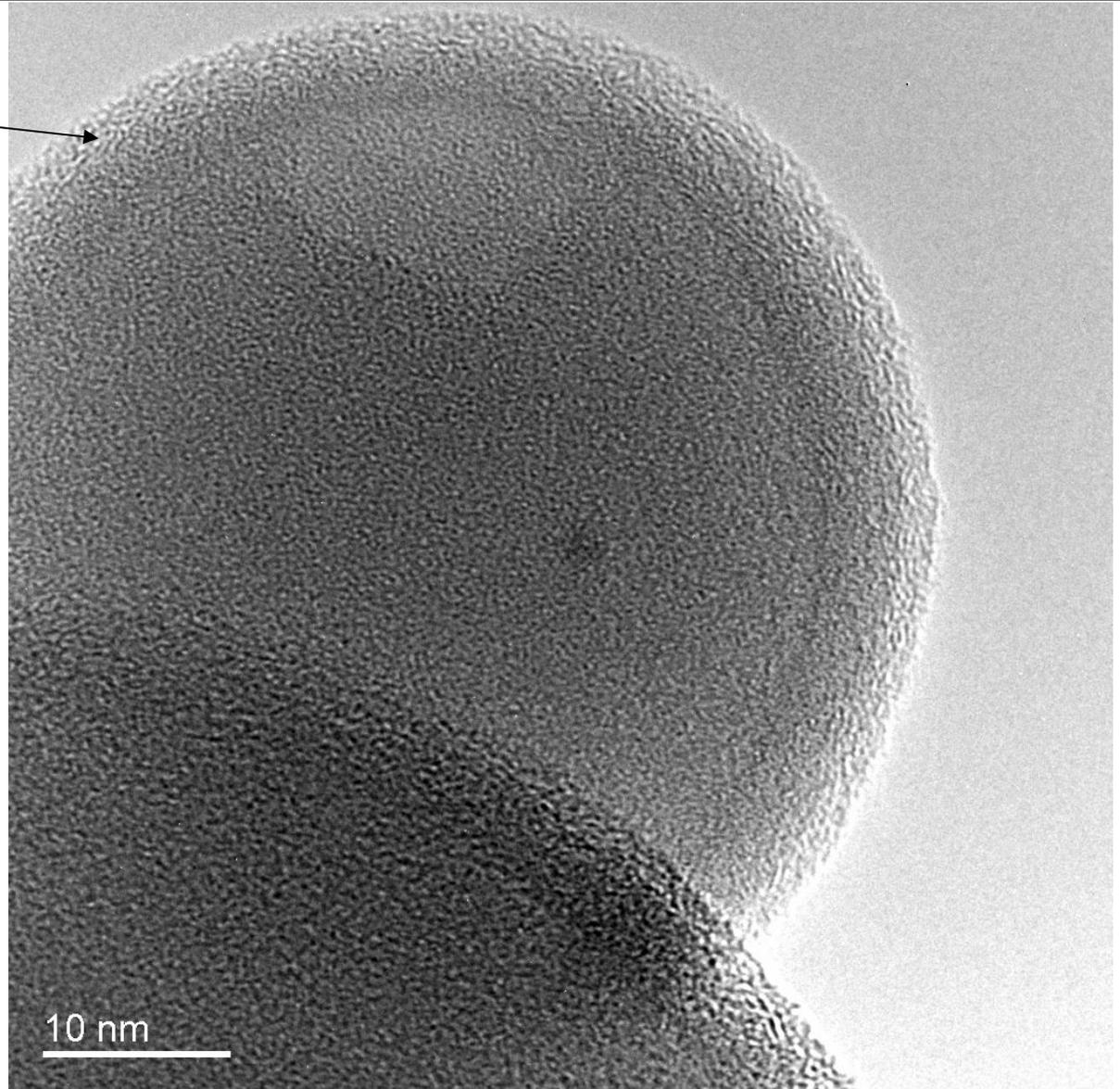
Arifin, D. et al., Energy & Environmental Science 5, 9438-9443 (2012)

5.2 nm film
(1.2 Å/cycle)

Film thickness is
uniform throughout
the entire sample

10 nm

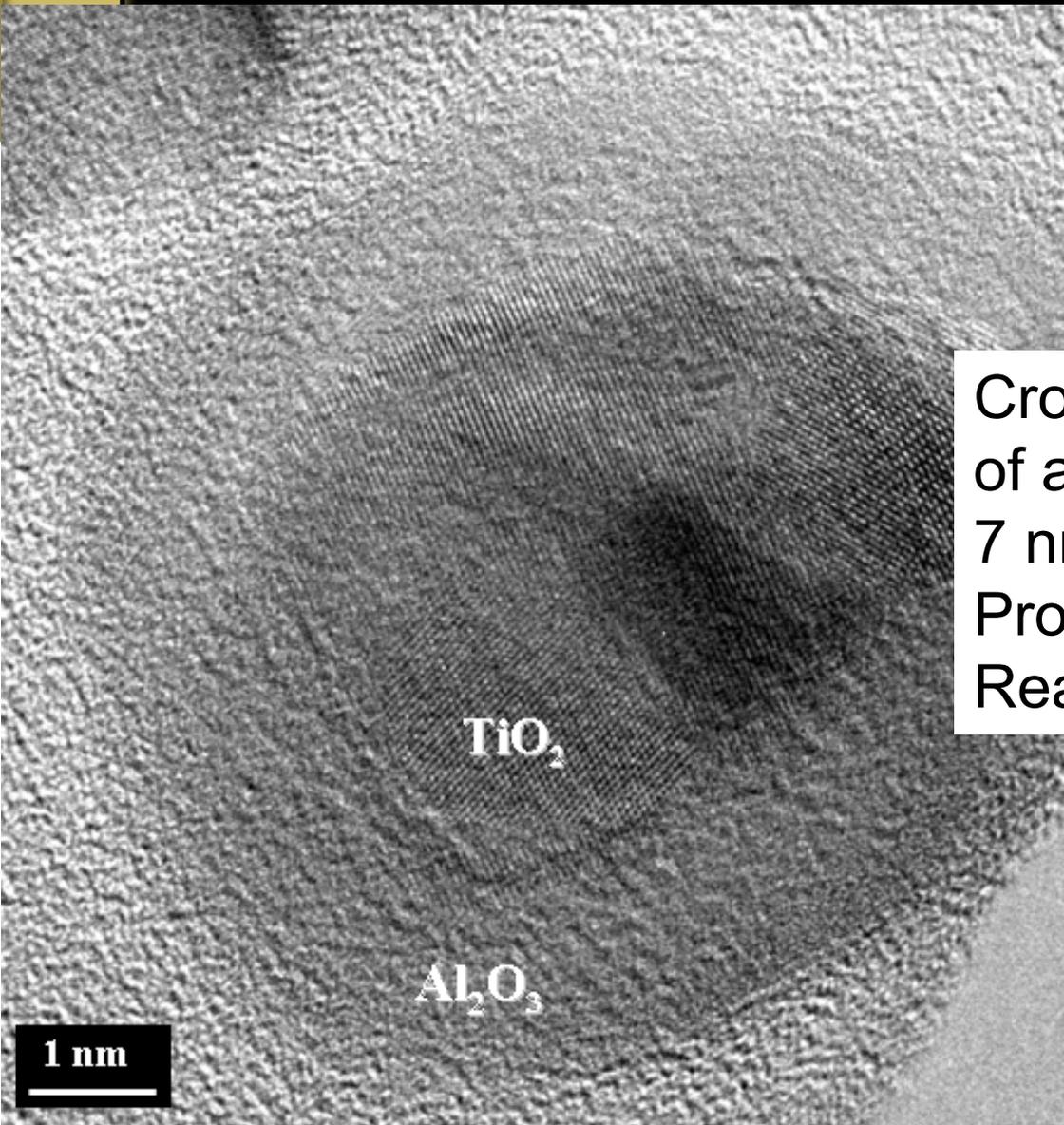L.F. Hakim, S.M. George, and A.W. Weimer, <u>CVD,</u> <u>11</u>, 420 (2005)

5.2 nm film
(1.2 Å/cycle)
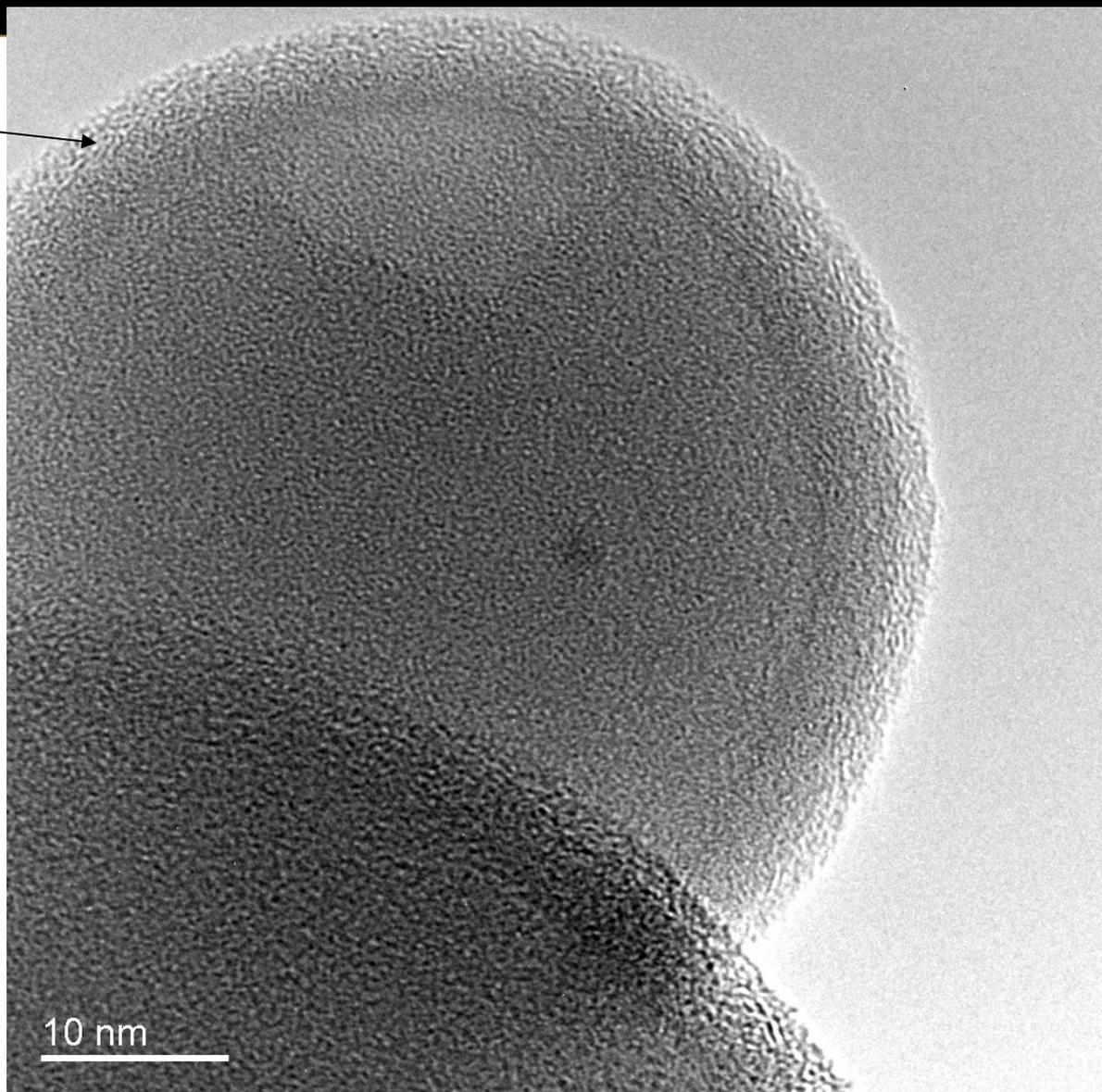
Film thickness is
uniform throughout
the entire sample
of primary particles;
coated in a
fluidized bed

10 nm

L.F. Hakim, S.M. George, and A.W. Weimer, <u>CVD,</u> <u>11</u>, 420 (2005)

Cross-section HRTEM Image of an Al_2O_3 (15 Å) ALD Coated 7 nm TiO_2 Nanoparticle Processed in a Fluidized Bed Reactor

L. F. Hakim et al., Advanced Functional Materials, 17, 3175 (2007)