Solar-thermal ALD Ferrite-Based Water Splitting Cycles

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Project ID No. PD028

This presentation does not contain any proprietary, confidential or otherwise restricted information

Overview

Timeline

- 6-1-2005
- 9-30-2010
- 95% completed

Budget

•Total Project Funding

$900,000 DOE

$225,000 Cost share

•Funds received in FY10

$ 0

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

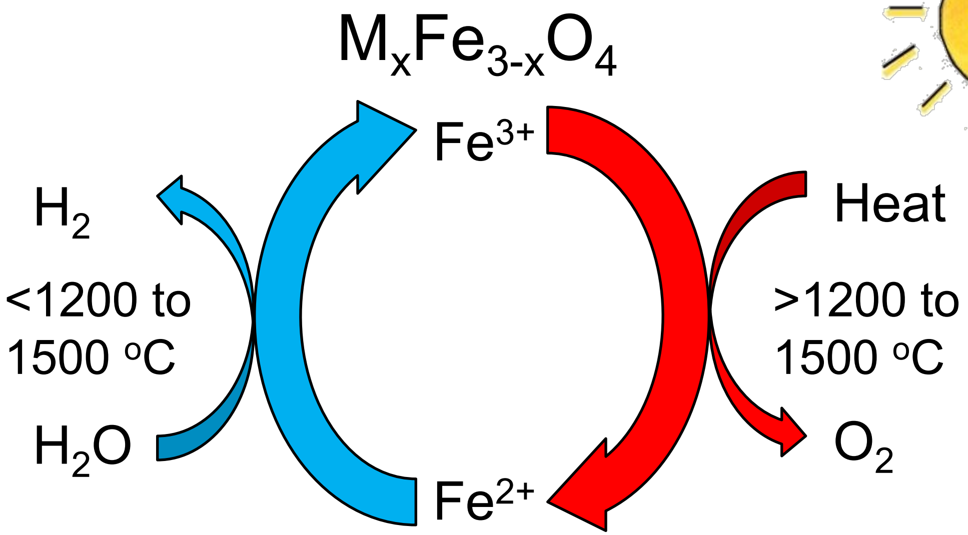
Partners

Swiss Federal Research Institute (ETH Zurich)

Objectives

- Use H2A analysis to provide guidance for conceptual process design that is cost effective; determine feasibility;
- Conceptualize a scalable central solar reactor/receiver per H2A guidance on economics;
- Develop and demonstrate suitable materials for robust thermochemical redox cycling that will integrate easily into the solar reactor design; and
- Develop an overall plan (and start pursuing it) to take the technology to the point of demonstration in 5 years, providing that market conditions warrant this

Solar-thermal Water Splitting Ferrite Cycles



Reduction: $M_xFe_{3-x}O_4$ + solar energy → $MO(Fe^{2+}+Fe^{3+}+M^{+}) + 0.5O_2$

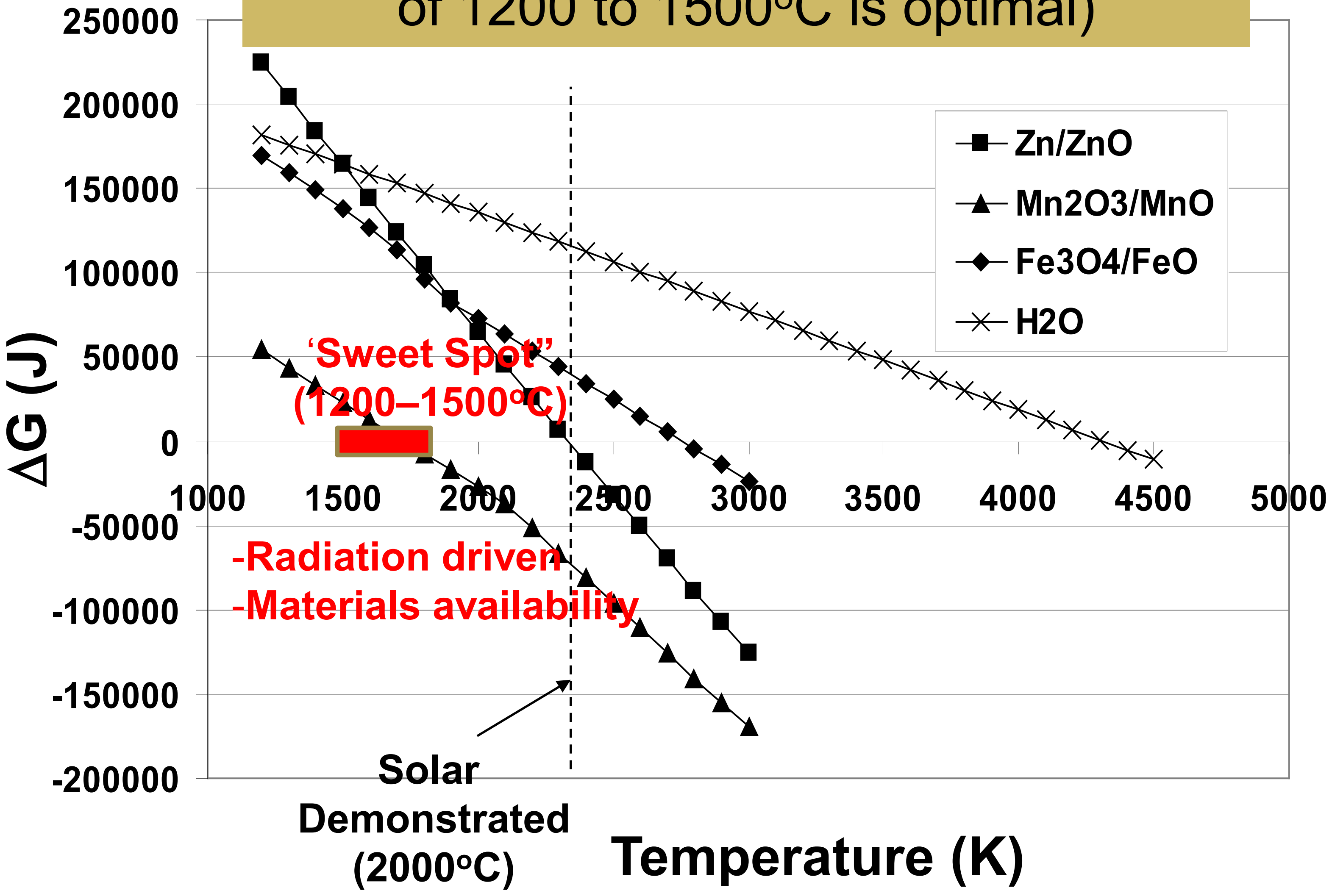
Oxidation: $MO(Fe^{2+}+Fe^{3+}+M^{+}) + H_2O$ → $M_xFe_{3-x}O_4 + H_2$

Overall: H_2O + solar energy → $H_2 + 0.5O_2$

M = Co, Mn, Ni, Zn, or other transition metals

Free Energy Change for Single Metal Decomposition Reactions (P = 1 atm)

(A 2-step process operating in the range of 1200 to 1500°C is optimal)

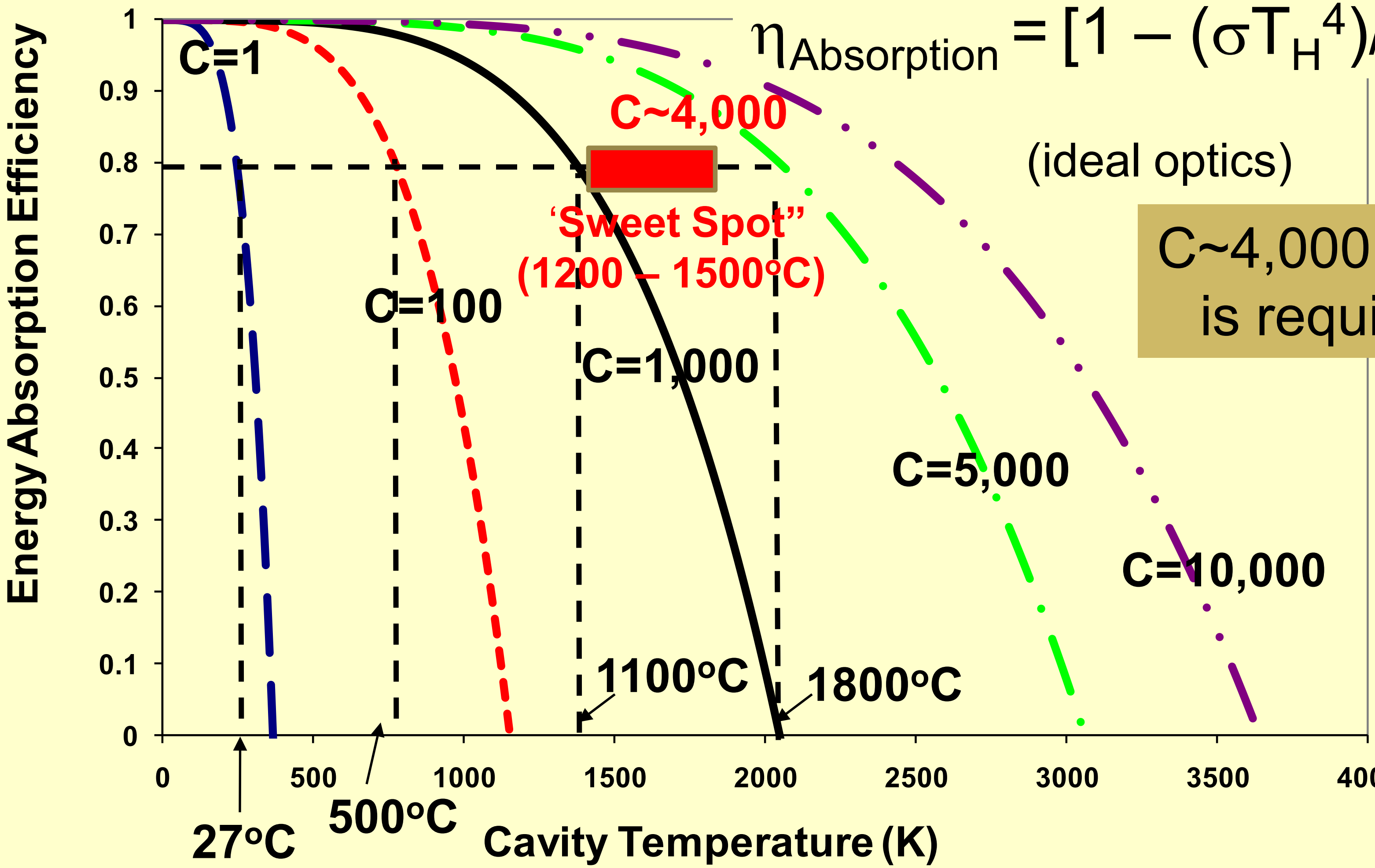


'Sweet Spot' (1200–1500°C)

-Radiation driven
-Materials availability

Solar Demonstrated (2000°C)

Energy Absorption Efficiency of a Black Body Cavity with its T at Various Solar Concentration Ratios



$$\eta_{Absorption} = [1 - (\sigma T_H^4)/IC]$$

(ideal optics)

C~4,000 suns is required

The team ha

Address Identified Weakness

Weakness –

“The assumption that ALD can be economical at the scale of production that is required needs to be validated by the team.”

“High utilization of solar flux is critical for this project because the heliostat field is very expensive. The use of solar flux to heat carrier must be included in the economics. Proposing high-carrier solids while doing economics on zero-carrier solids is not unacceptable for this project.”

“The team has not included enough studies on 24/7” operation. “

H2A used to Address Weakness

- Use AspenPLUS^{TM} simulation and H2A to calculate allowable ALD ferrite costs to hit central receiver targets (\$6/kg H_2 in 2015 and \$3/kg H_2 in 2025)

  - vary # redox cycles/day (1 cycle/day to ~1 cycle/minute)

  - incorporate 100 m^2/g inert support for sensible heat

  - incorporate heat integration

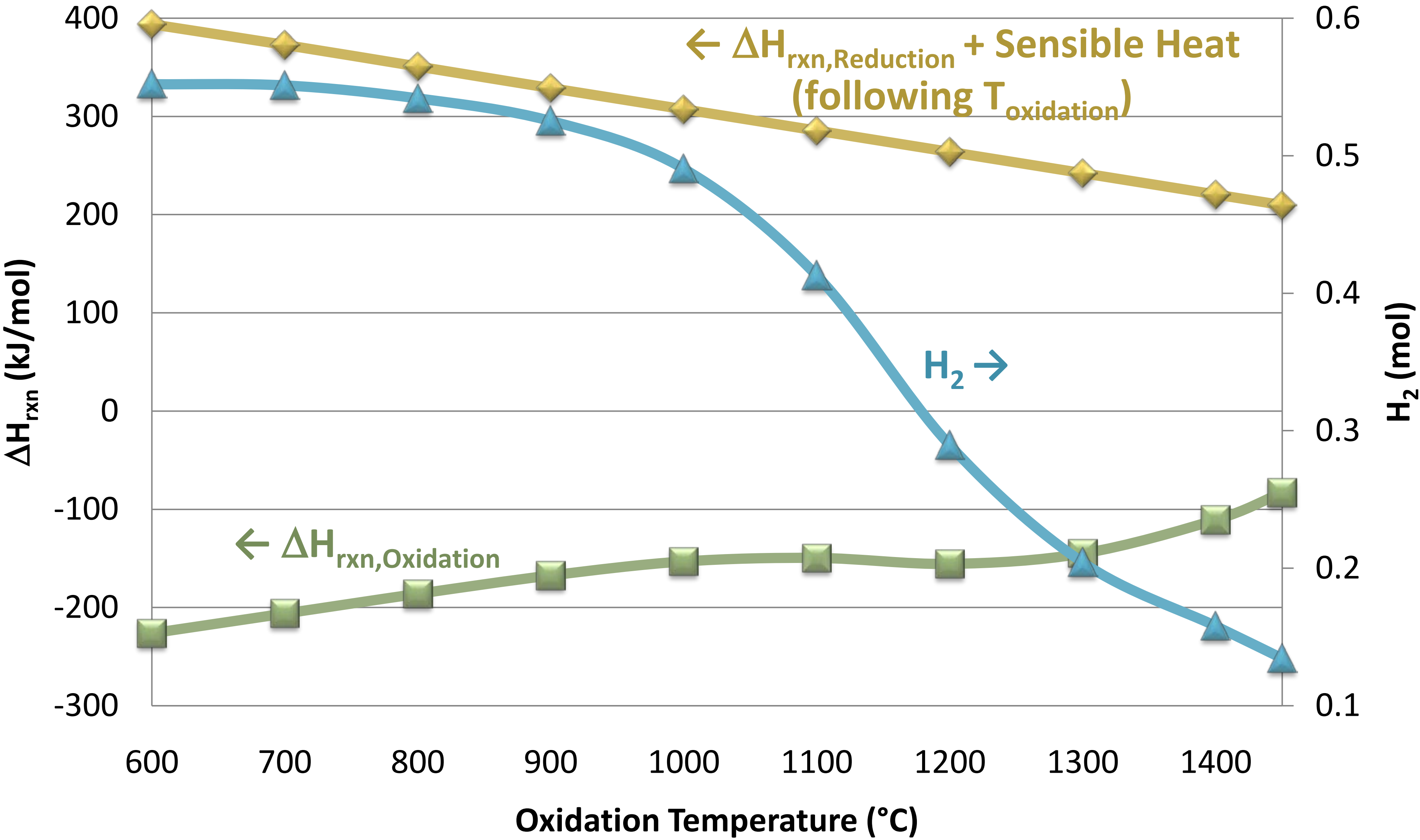
  - base calcs on predicted free energy minimization products (i.e. conversions) from FACTSage^{TM} for $NiFe_2O_4$ decomposition

Base Case H2A Operating Assumptions

- 2015 Case
  - $126.50/m^2 heliostat installed
  - $6/kg H_2 (plant gate)
- 2025 Case
  - $90/m^2 heliostat installed
  - $3/kg H_2 (plant gate)
- Solar Tower Cost
  - Sargent and Lundy
- Land ($2,024/acre)
- Solar parasitic e^- = 0.2 W/m^2

- Solar Reactor
  - 1450 C reduction
  - Optimized oxidation temperature
  - Mohave Desert Location
  - O_2 removed mechanically
  - High surface area ferrite/ZrO_2 support by ALD within SiC tubes
  - 5 minute redox cycles
  - Internal heat recuperation
  - $\Delta H_{solar} = \Delta H_{red} + \Delta H_{sens} - \Delta H_{oxid}$

FactSage™ – Gibbs Free Energy Minimization ($NiFe_2O_4$ Reduced at 1,450°C)



Results - Annual Reduction Energy Requirements (total solar heat input required without heat integration)

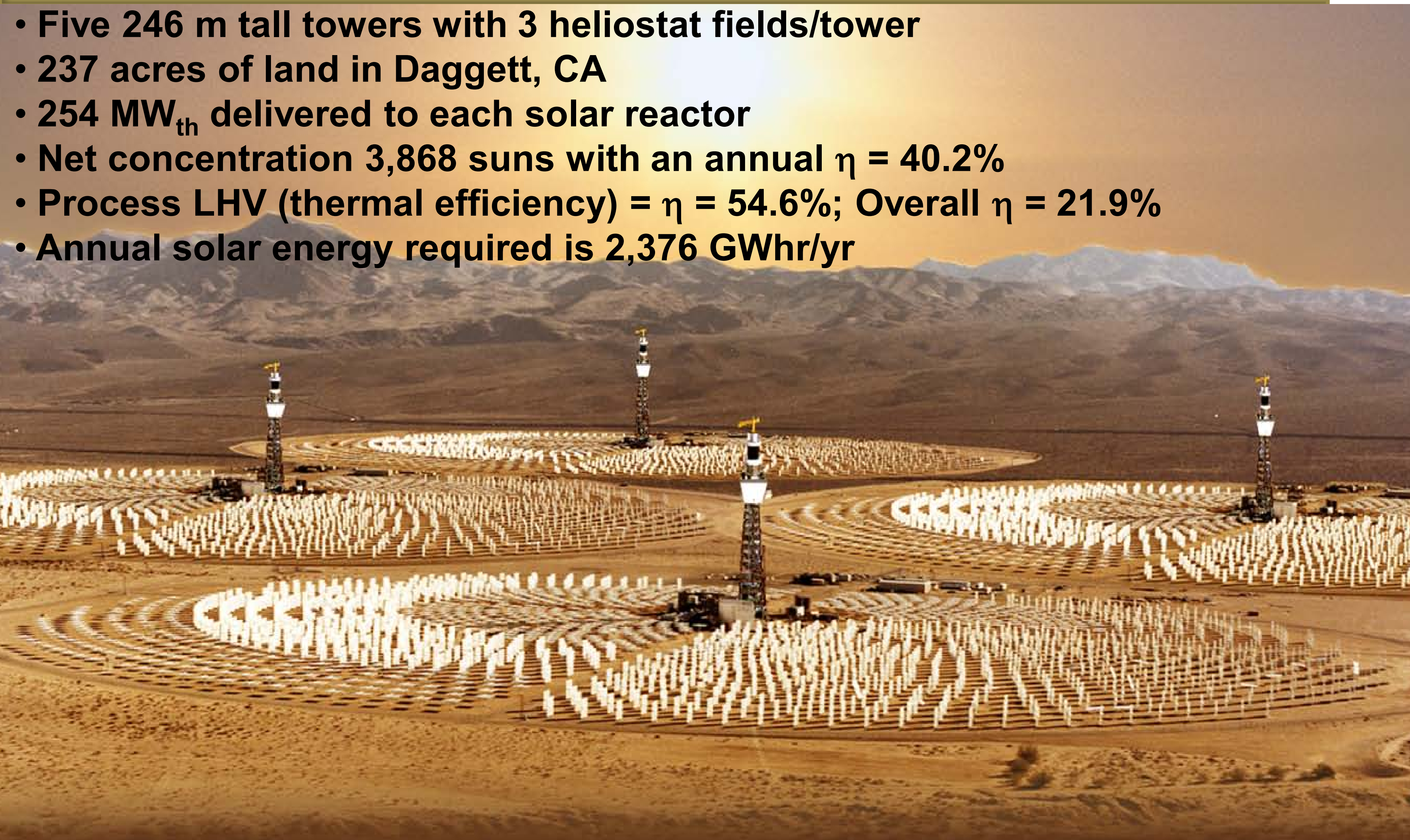
$$NiFe_2O_4 \rightarrow MeO\ (Fe^{2+}+Fe^{3+}+Ni^{2+}) + \tfrac{1}{2}x\ O_2$$

$$MeO\ (Fe^{2+}+Fe^{3+}+Ni^{2+}) + x\ H_2O \rightarrow NiFe_2O_4 + x\ H_2$$

Oxidation Temperature	**800°C**	**900°**	**1,000°C**	**1,100°C**
Moles H_2 Produced	0.54	0.53	0.49	0.41
Solar Energy Required (GWhr/yr); ΔH_{rxn} = 209.8 kJ/mol				
Overall Heat of Reaction	1,947	2,008	2,151	2,555
Sensible Heat Required	1,646	1,436	1,258	1,163
Total Solar Energy Required	3,593	3,444	3,409	3,719

Solar Field Design

(Mr. Allan Lewandowski, NREL)



- Five 246 m tall towers with 3 heliostat fields/tower
- 237 acres of land in Daggett, CA
- 254 MW_{th} delivered to each solar reactor
- Net concentration 3,868 suns with an annual η = 40.2%
- Process LHV (thermal efficiency) = η = 54.6%; Overall η = 21.9%
- Annual solar energy required is 2,376 GWhr/yr

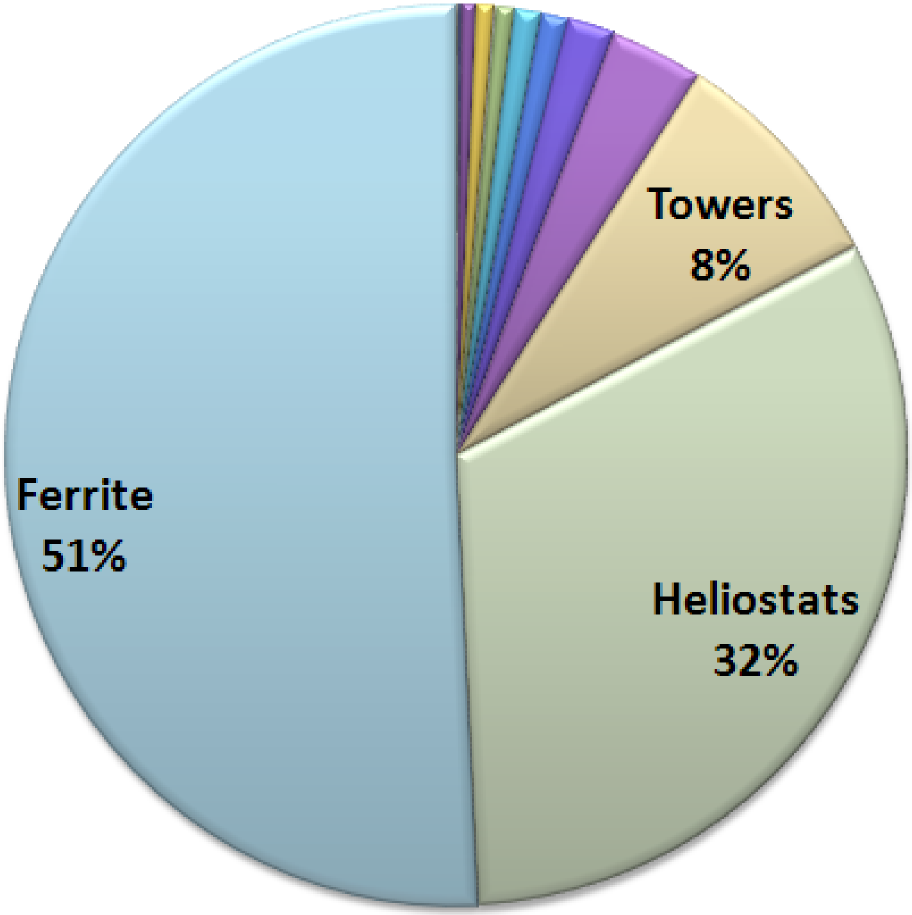
Capital Cost Breakdown

(5 minute cycles; 100,000 kg H_2/day)

2015 H_2 \$6/kg

Allowed Ferrite Cost: \$2,600/kg

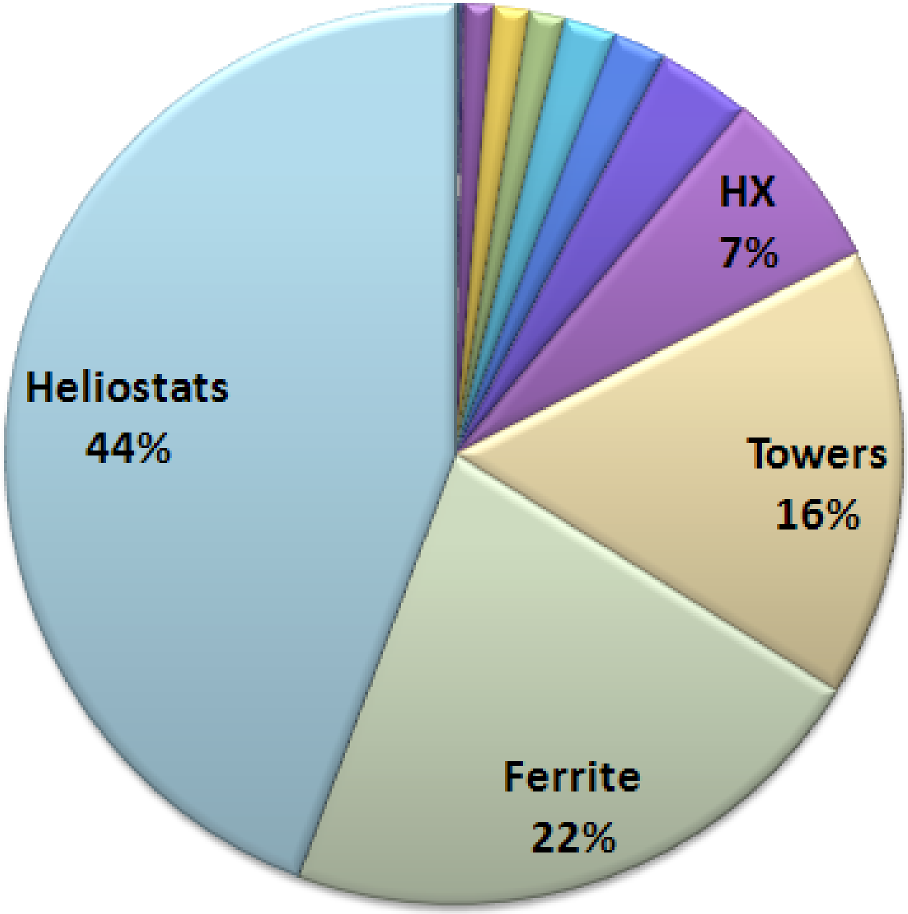
TCI \$841M



2025 H_2 \$3/kg

Allowed Ferrite Cost: \$571/kg

TCI \$430M



Ferrocene Cost

Combined cost of precursor ferrocene and nickelocene today is ~$240/kg Ni-ferrite;

If allowable cost in 2015 is $2600 and in 2025 is $571, the allowable cost of ALD appears to be reasonable

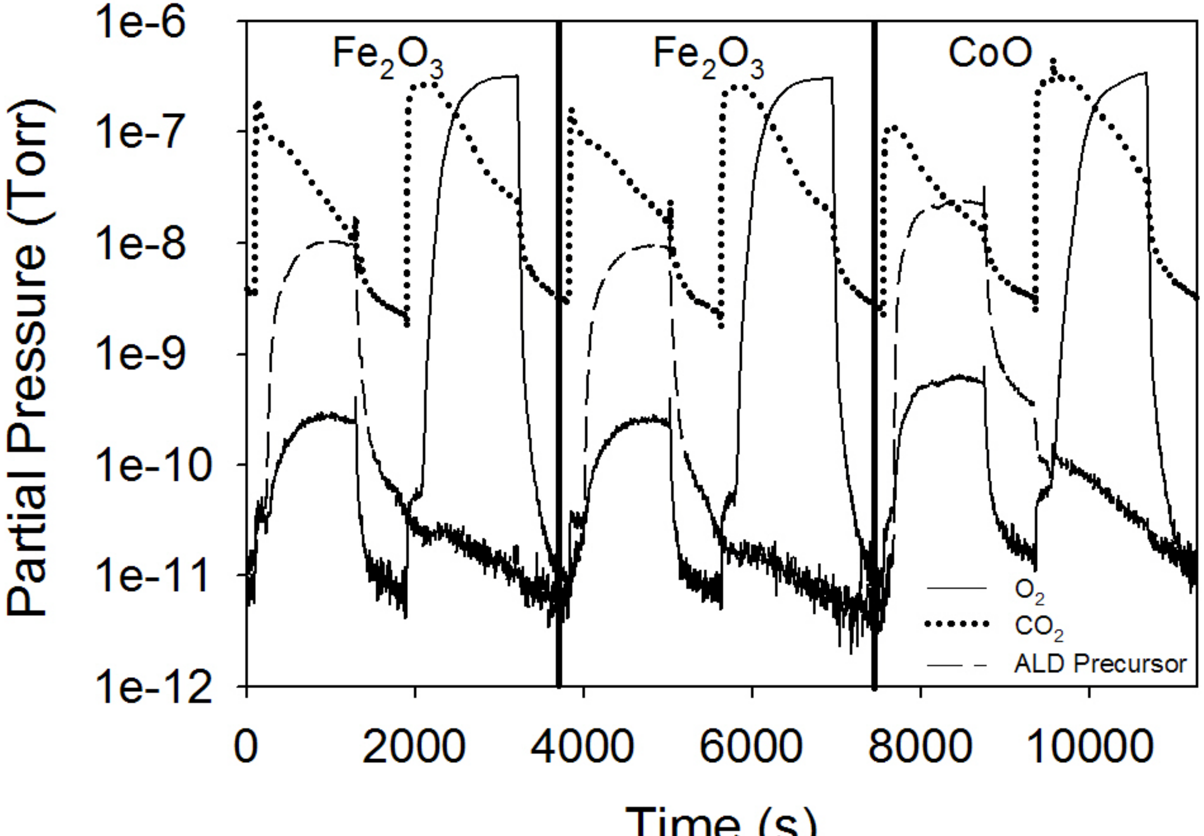
Direction from H2A

- Lowest cost process is one with rapid & robust thermochemical redox cycling (limits quantity of active material required); preferably ≤ 5 minutes/cycle;
- Reactor design needs to provide for as near a complete heat recuperation/integration as possible to limit sensible heat losses/cost
- Above two considerations dictate that solar reactor/receiver operates as fixed bed of active solids instead of a moving bed

Evaluate Thin Films for Fast Cycling

- Reduce Diffusional Resistances
- Promote Radiation-driven Heat Transfer
- Design and synthesize spinel ferrite materials at the atomic/molecular level using atomic layer deposition (ALD)
- Investigate effect of surface area on redox reaction rates

Synthesis of Nanoscale Ferrites by ALD, e.g. $Co_xFe_{3-x}O_4$



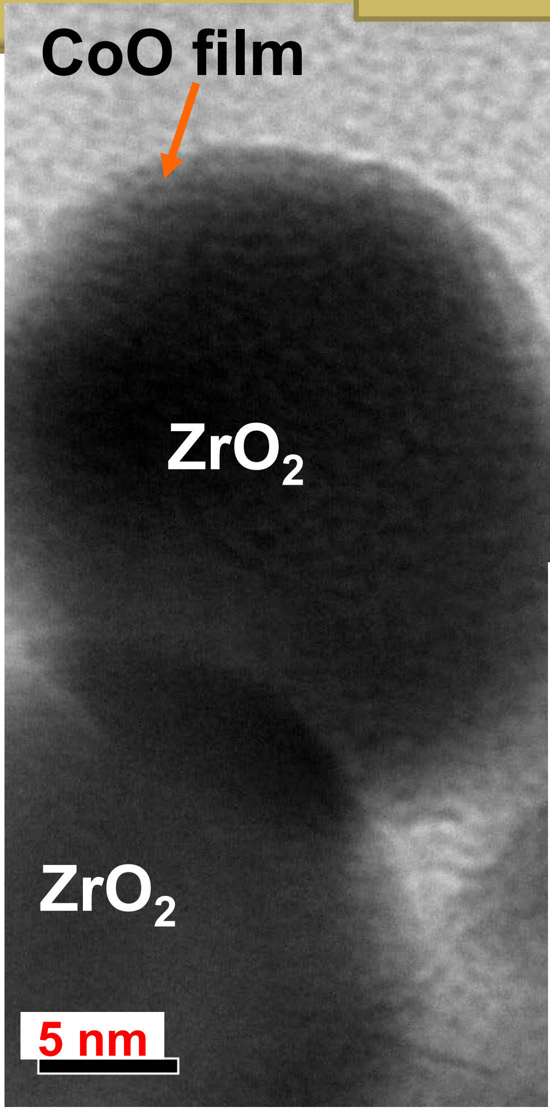
Monitor ALD chemistry in situ via mass spectrometry

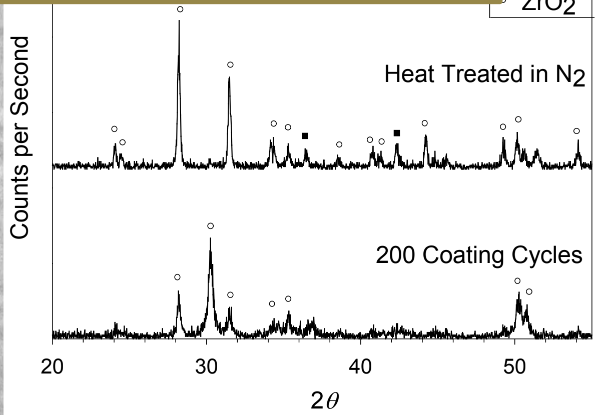
T = 450 °C

Results - Self Limiting Surface Chemistry

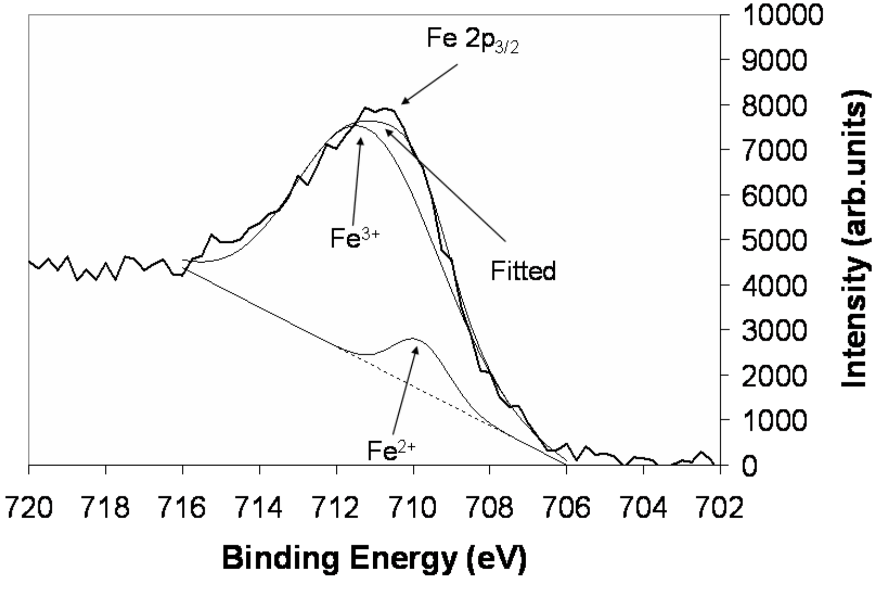
CoO confirmed by XRD

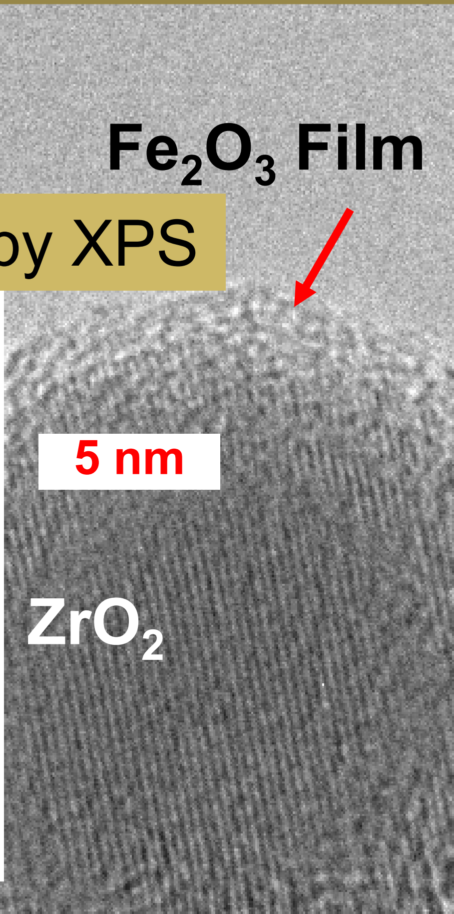
Multi-layer Ultra-thin Film Deposition by ALD is Achievable





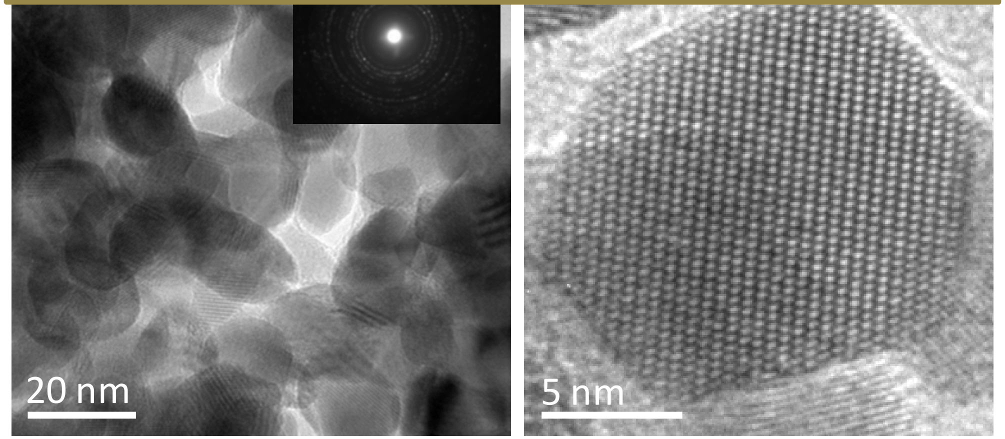
Fe_2O_3 confirmed by XPS



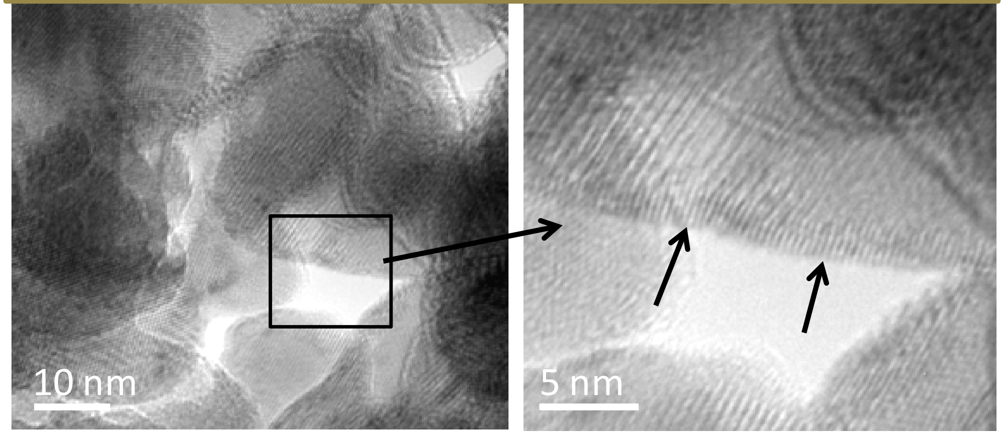


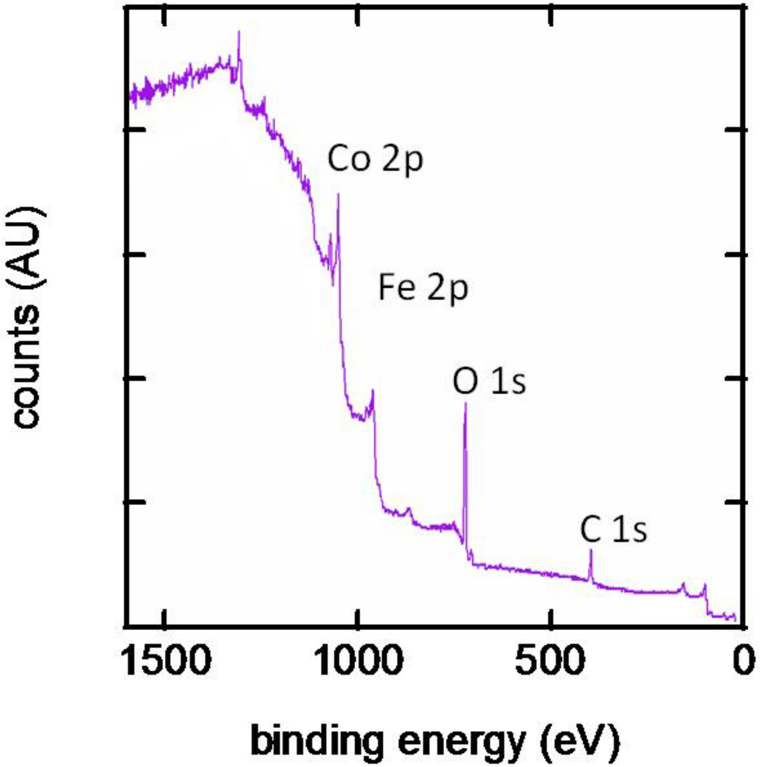
HRTEM and XPS Confirm Film Uniformity

As Received (50 m²/g catalyst support)



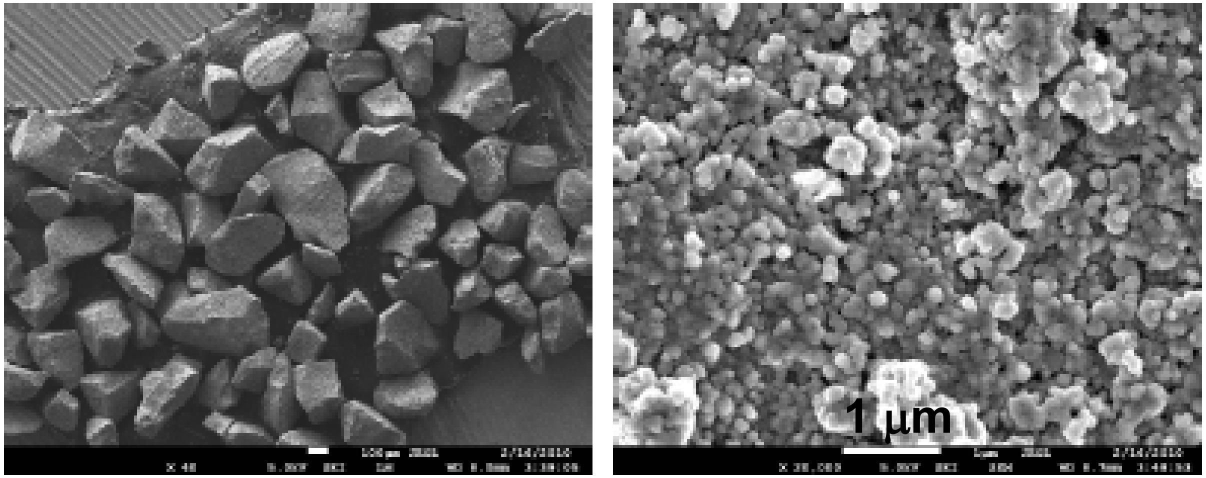
2 nm $CoFe_2O_4$ deposited film after ALD



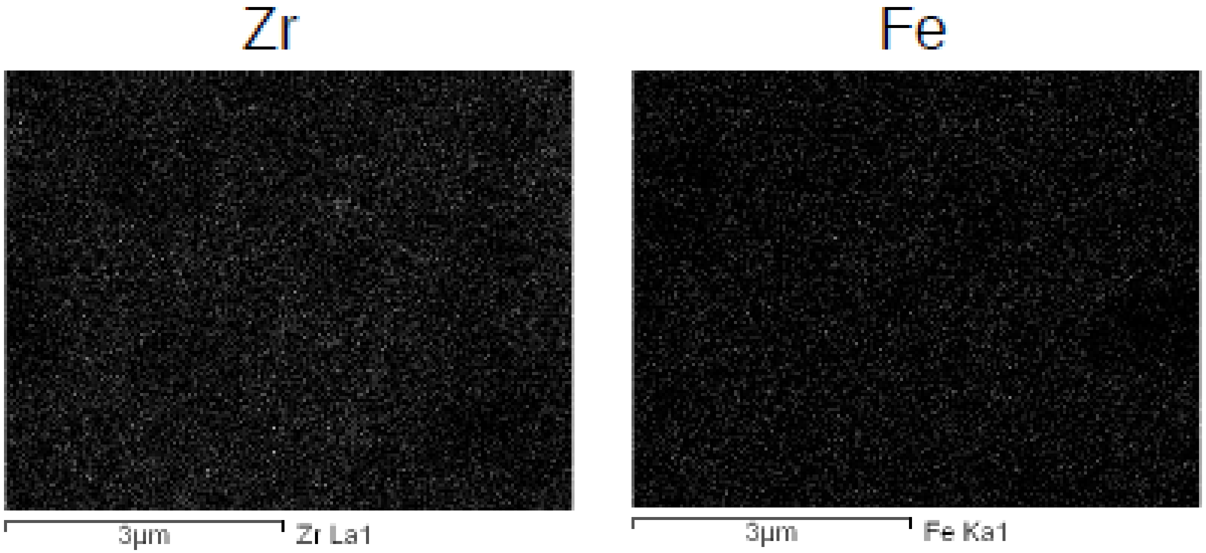


- Co, Fe and O peaks clearly observed
- No Zr peaks observed – indicates conformal coverage

Deposition on Porous ZrO_2 Supports

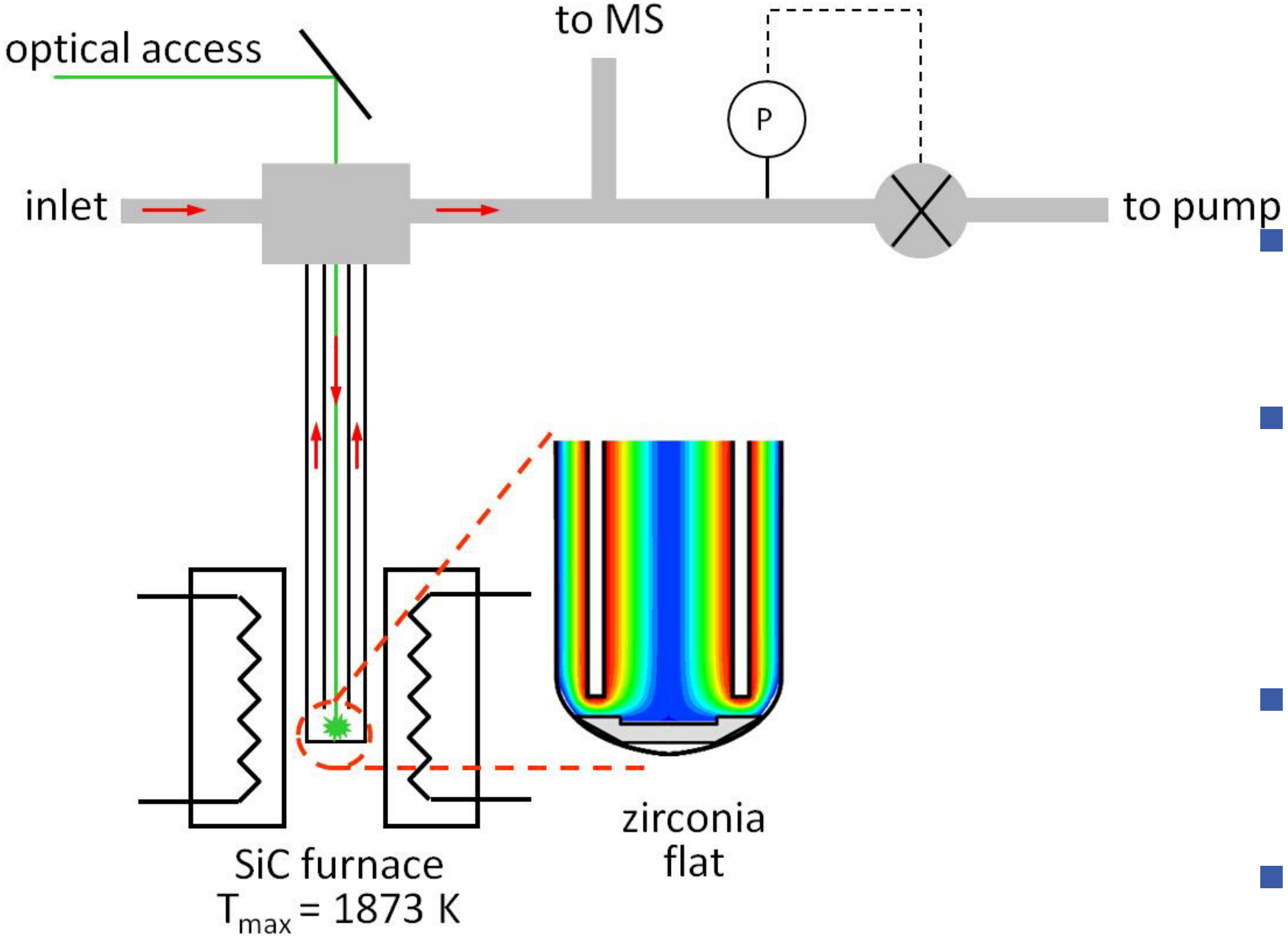


- FESEM image of porous ZrO_2 support -sintered nanoparticles (≈50 nm, SA = 50m^2/g)



- EDX mapping confirms that Zr and Fe are distributed homogeneously

Stagnation Flow H_2O Splitting Reactor



- Uniform flux across the sample
- Products measured with modulated beam mass spectrometer
- Operational between 1 and 760 Torr
- Max Temperature 1550 °C

Chemical Redox Water Splitting Studies to Evaluate Impact of Surface Area

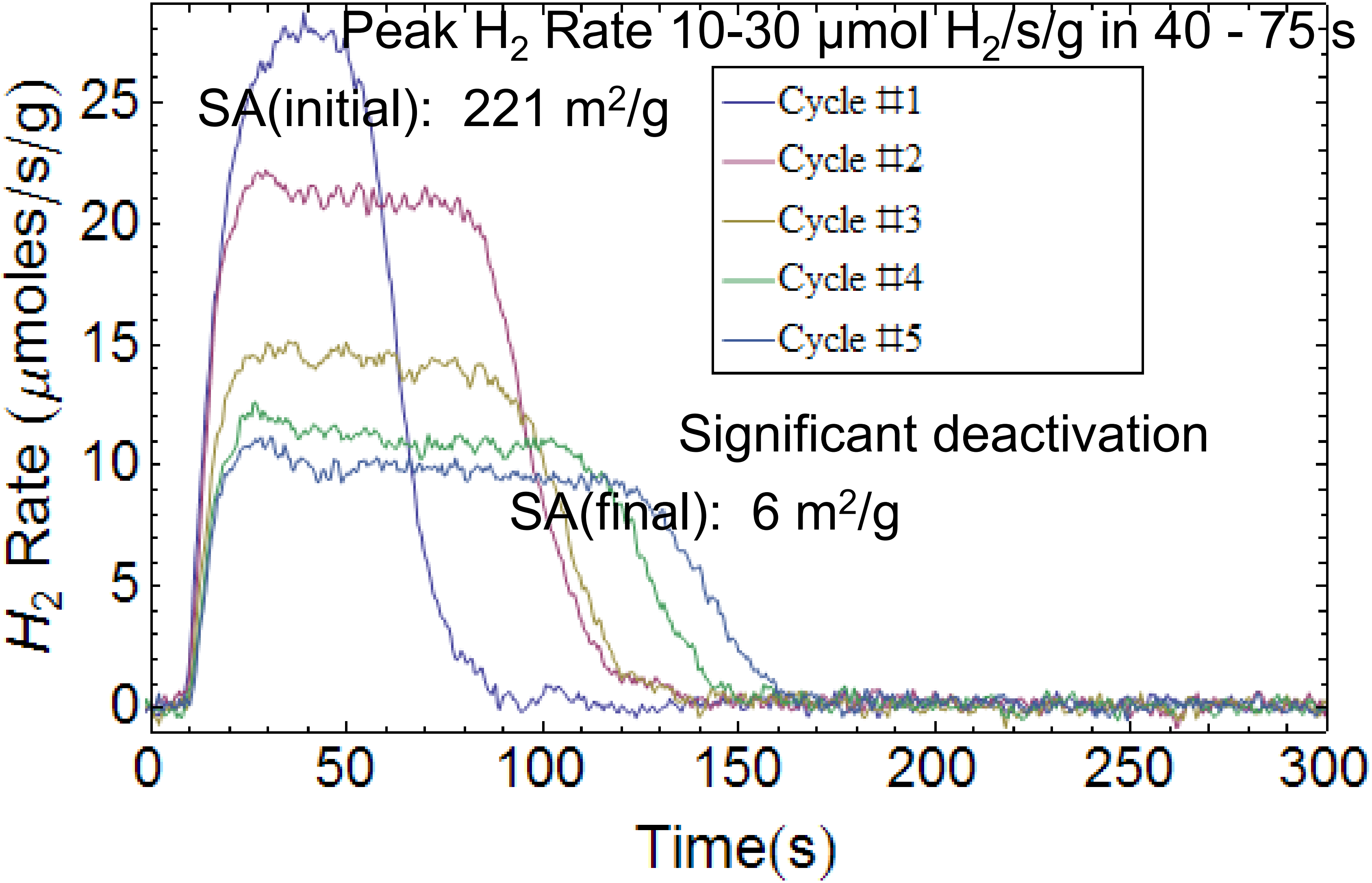
Bulk Fe_3O_4/ZrO_2 powder (blended)

vs. ALD Fe_3O_4 films/ZrO_2 porous support

vs. ALD $CoFe_2O_4$ films/ZrO_2 porous support

Chemical reduction: 600°C (1% H_2 / 1%CO / 2%CO_2 in He)
Oxidation: 600°C (mole fraction H_2O = 0.125, in He)
P = 75 torr

Chemical redox (bulk Fe_3O_4/ZrO_2)



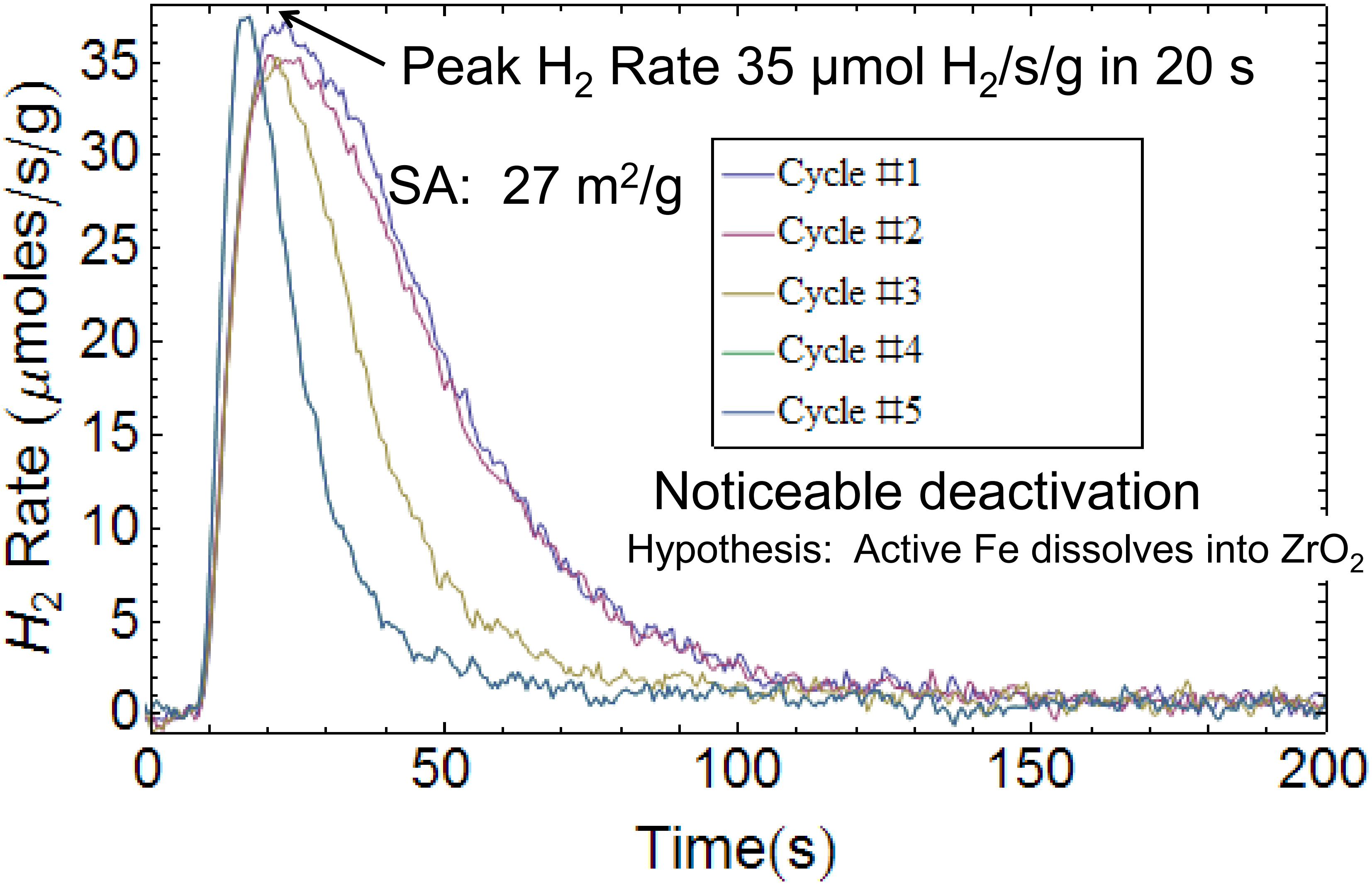
Peak H_2 Rate 10-30 µmol H_2/s/g in 40 - 75 s

SA(initial): 221 m^2/g

Significant deactivation

SA(final): 6 m^2/g

ALD Fe_3O_4 films/ZrO_2 porous support



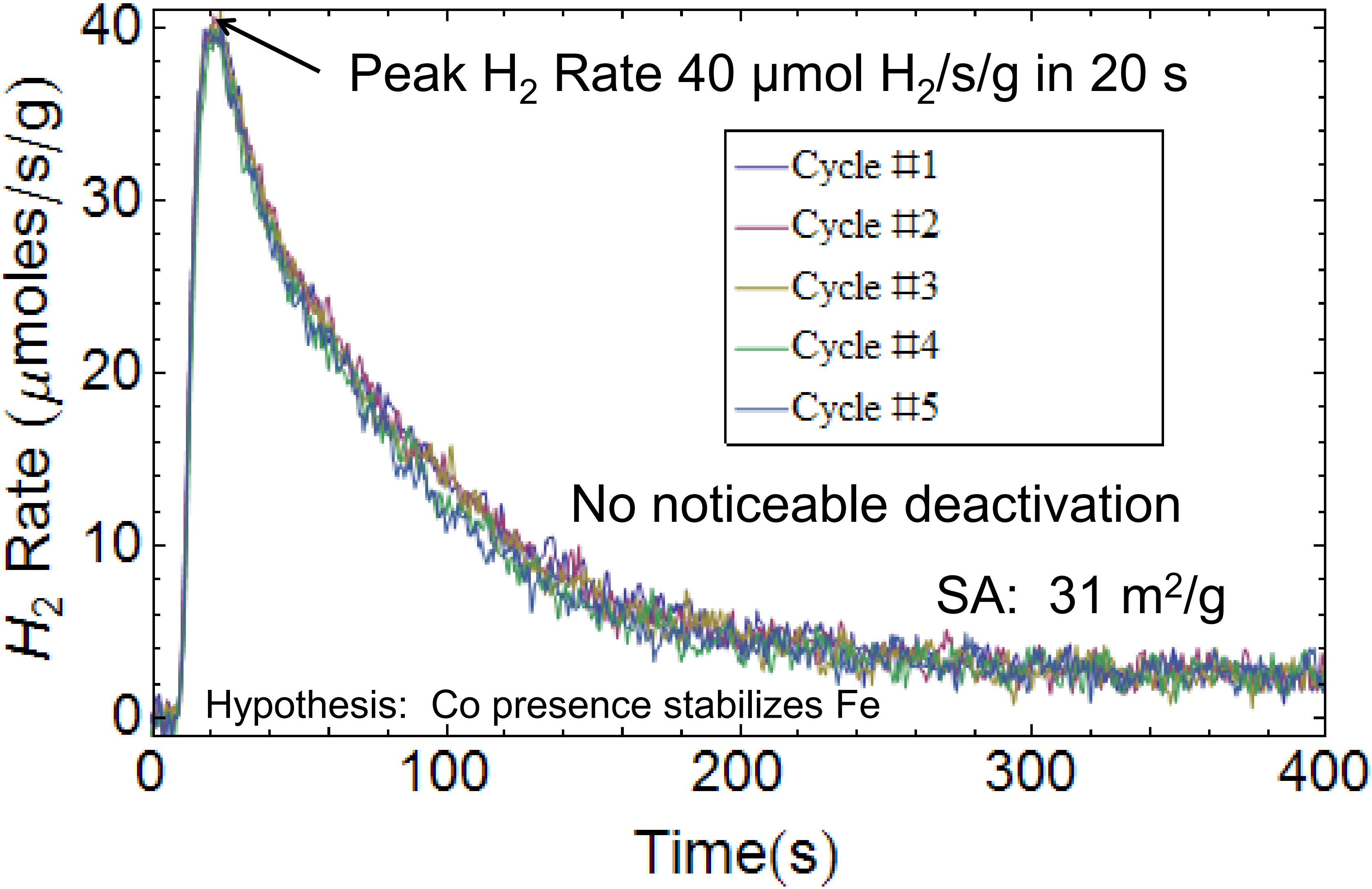
Peak H_2 Rate 35 µmol H_2/s/g in 20 s

SA: 27 m^2/g

Noticeable deactivation

Hypothesis: Active Fe dissolves into ZrO_2

ALD $CoFe_2O_4$ films/ZrO_2 powder



Peak H_2 Rate 40 μmol H_2/s/g in 20 s

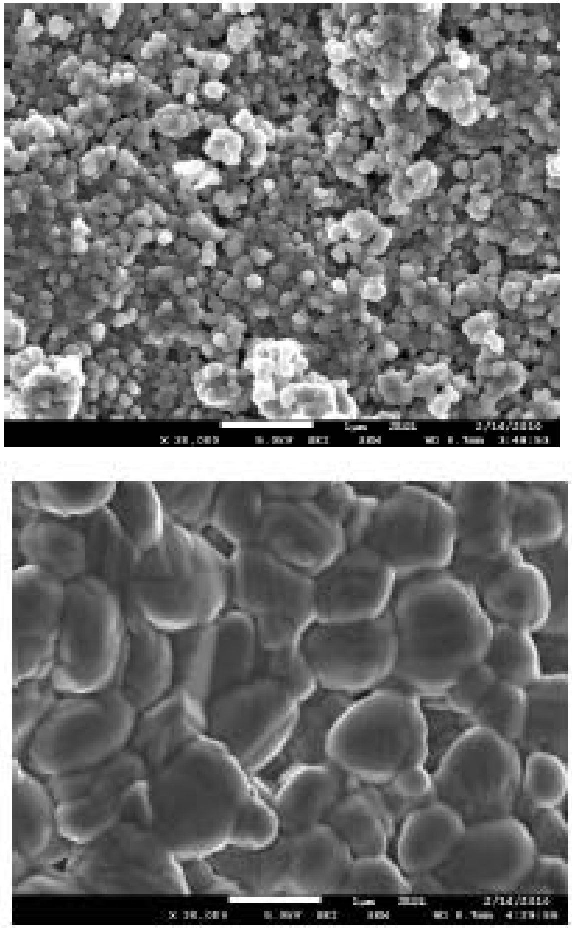
No noticeable deactivation

SA: 31 m^2/g

Hypothesis: Co presence stabilizes Fe

Sintering and Phase Segregation During Thermal Cycling to 1450°C

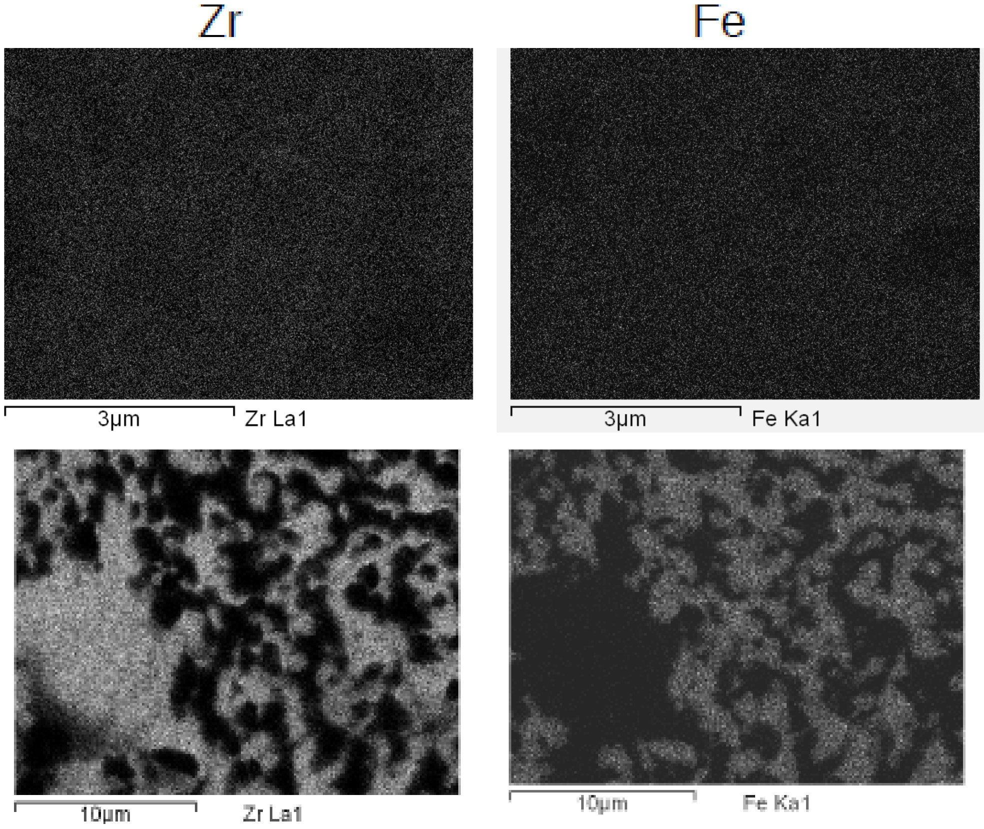
Grain Growth and Sintering



Pre-Processing

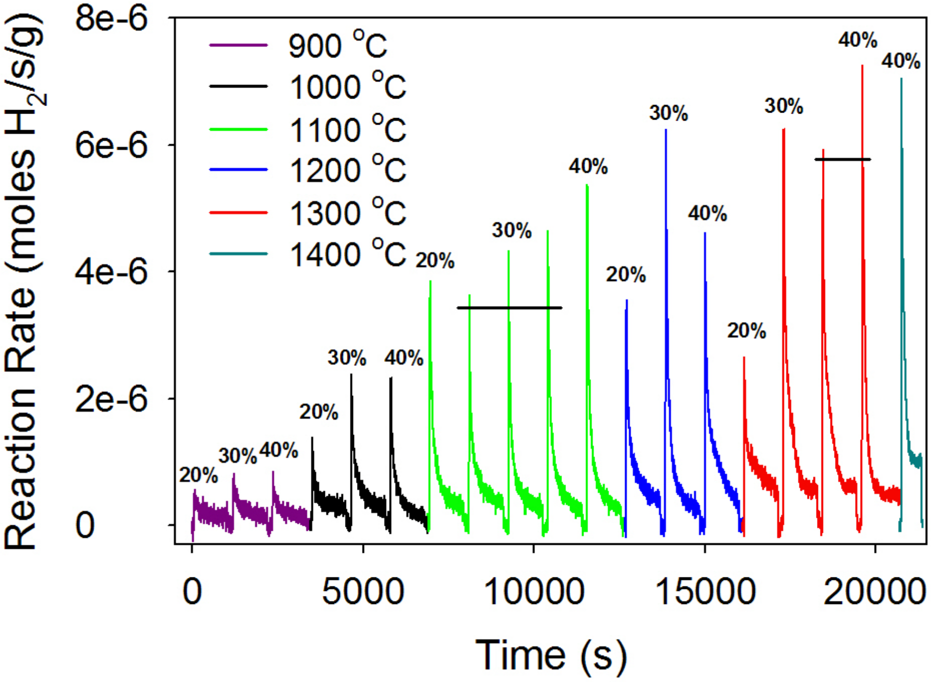
Post-Processing

Phase Segregation

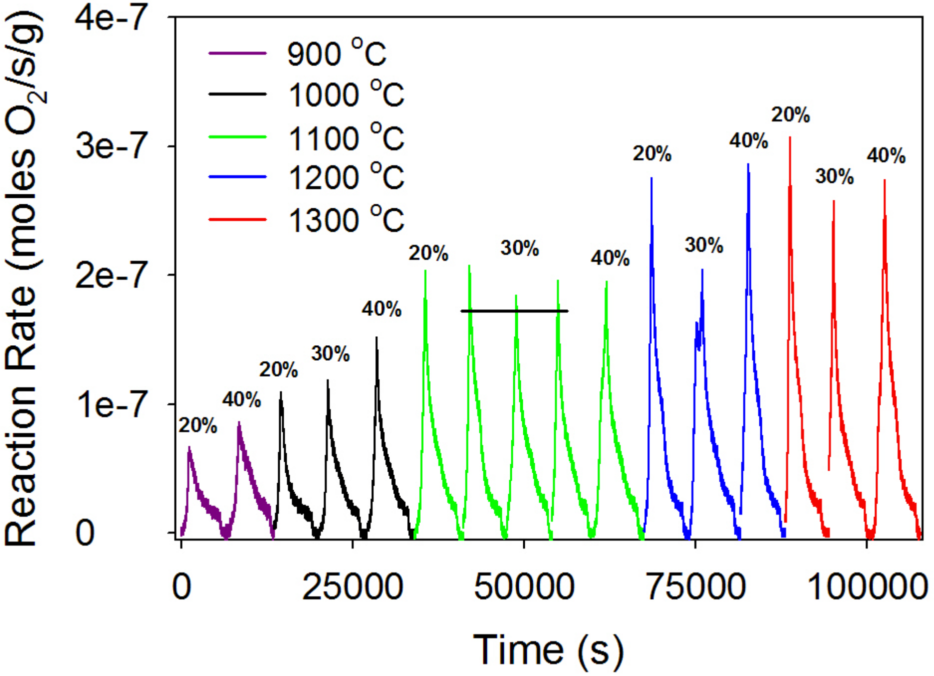


(Nonetheless, material remains active after 25 cycles with no observed deactivation)

Cyclical Repeatability: ALD $CoFe_2O_4$



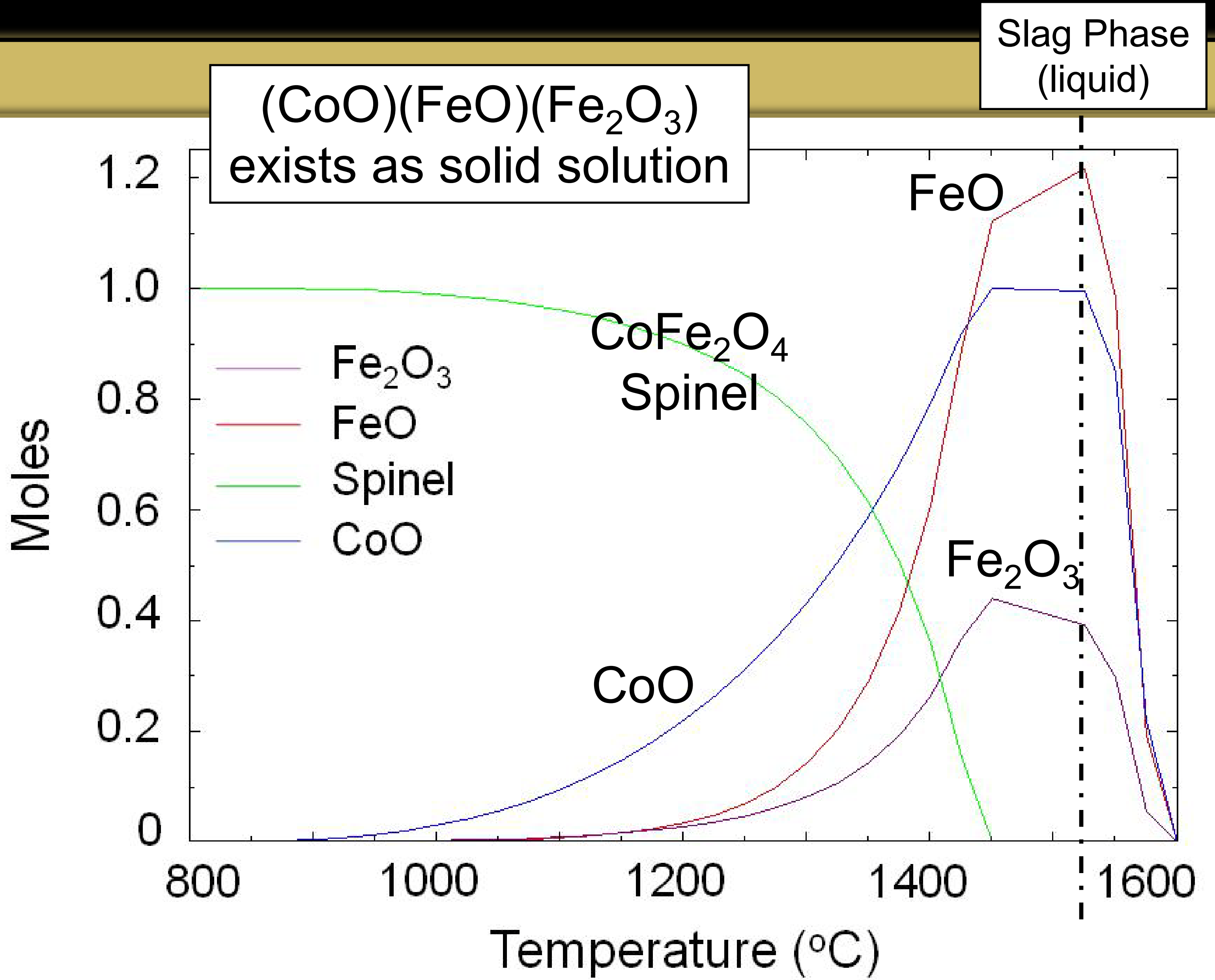
H_2O Oxidation



Thermal Reduction @ 1450 °C

- Material capable of being cycled repeatedly
- Redox rates increase with increasing oxidation temperature
- Oxidation even achievable at 1400°C
- Experiments indicate a 50°C ΔT redox cycle is possible!

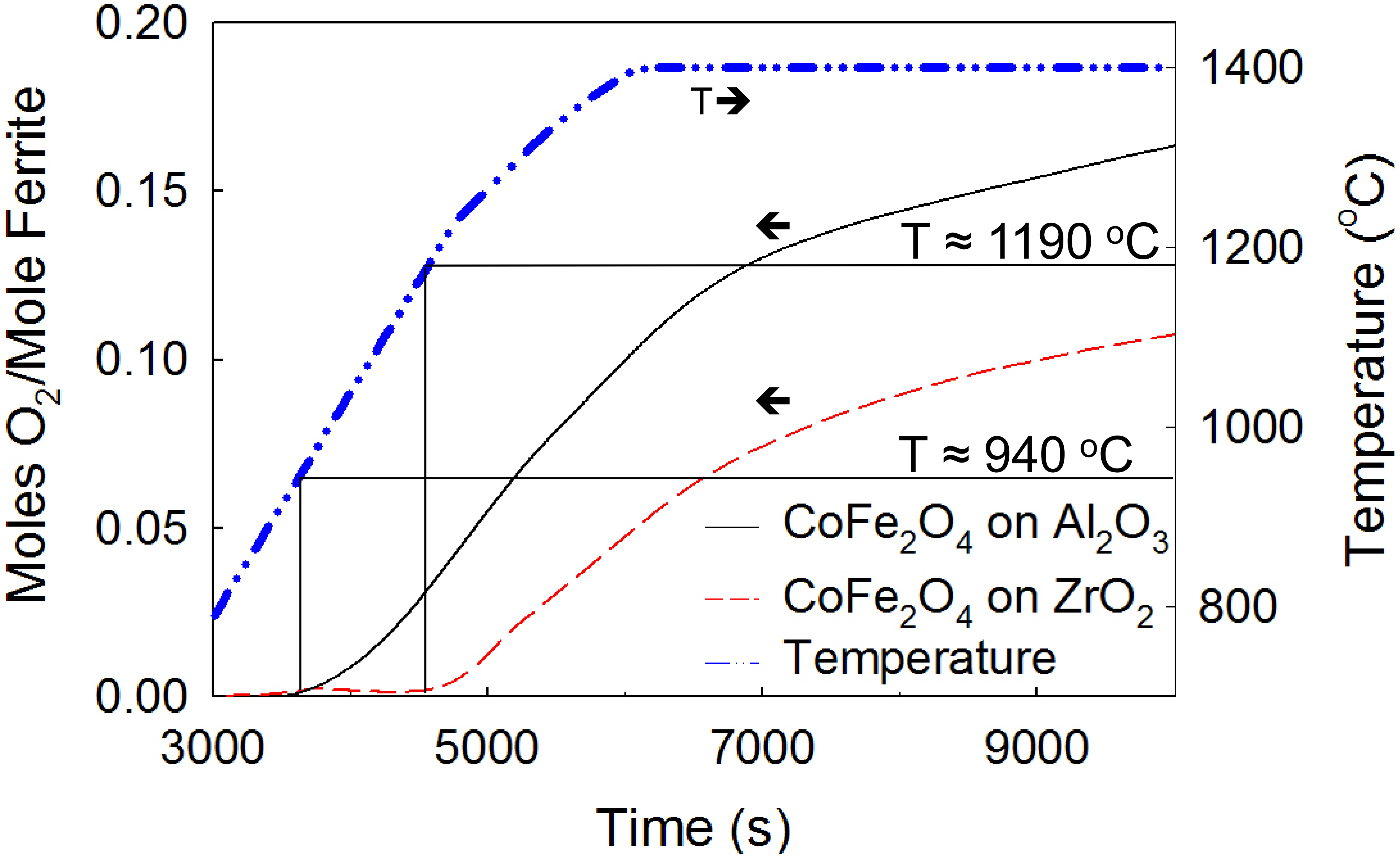
$CoFe_2O_4$ Decomposition Occurs at T>1200°C



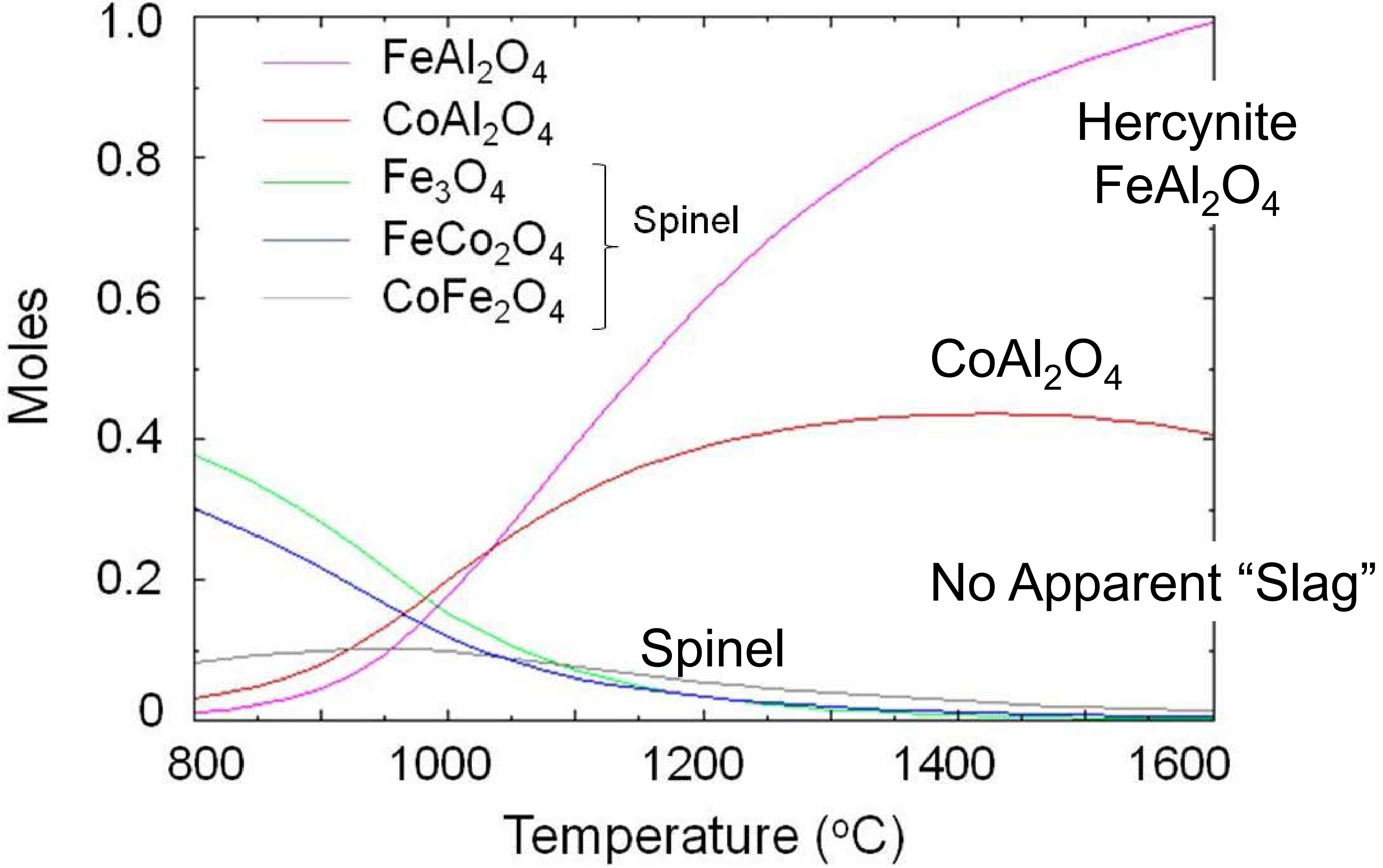
$(CoO)(FeO)(Fe_2O_3)$ exists as solid solution

Slag Phase (liquid)

$CoFe_2O_4$ Deposited on Al_2O_3 reduces at Lower Temperatures than on ZrO_2



$CoFe_2O_4/Al_2O_3$ Decomposition Occurs at T>900 °C

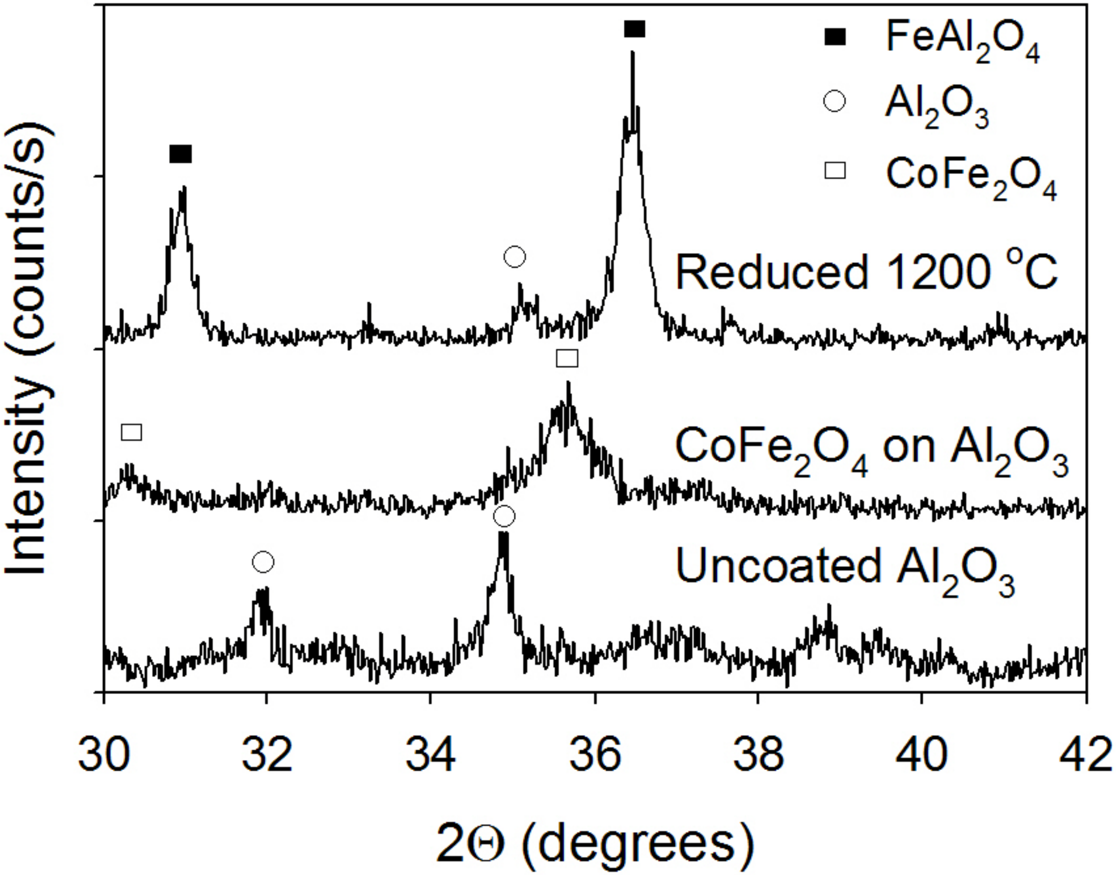


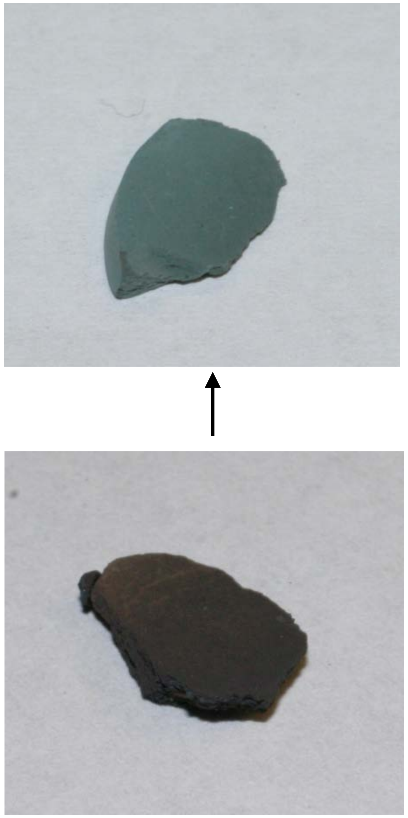
Hercynite ($FeAl_2O_4$) is Formed after Thermal Reduction

Reduction: $CoFe_2O_4 + 3Al_2O_3 + \text{solar-thermal energy} \rightarrow CoAl_2O_4 + 2Fe_2AlO_4 + 0.5O_2$

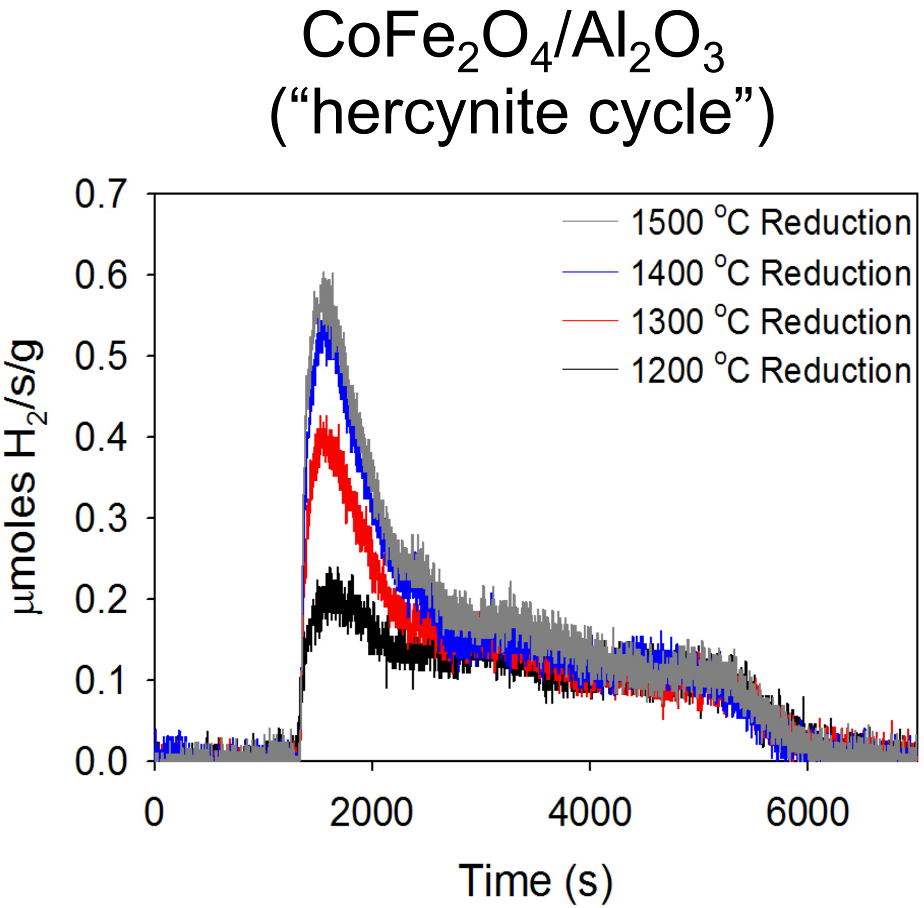
Oxidation: $CoAl_2O_4 + 2Fe_2AlO_4 + H_2O \rightarrow CoFe_2O_4 + 3Al_2O_3 + H_2$

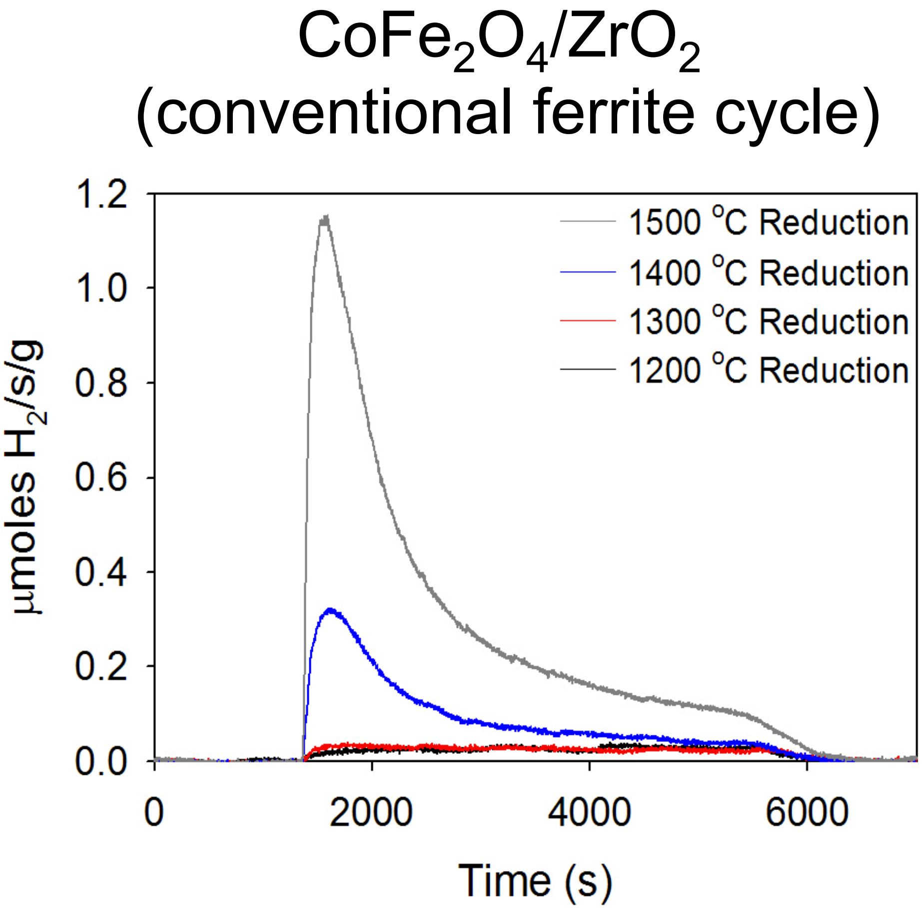
$H_2O + \text{solar-thermal energy} \rightarrow H_2 + 0.5O_2$





Hercynite and Ferrite Cycle Performance





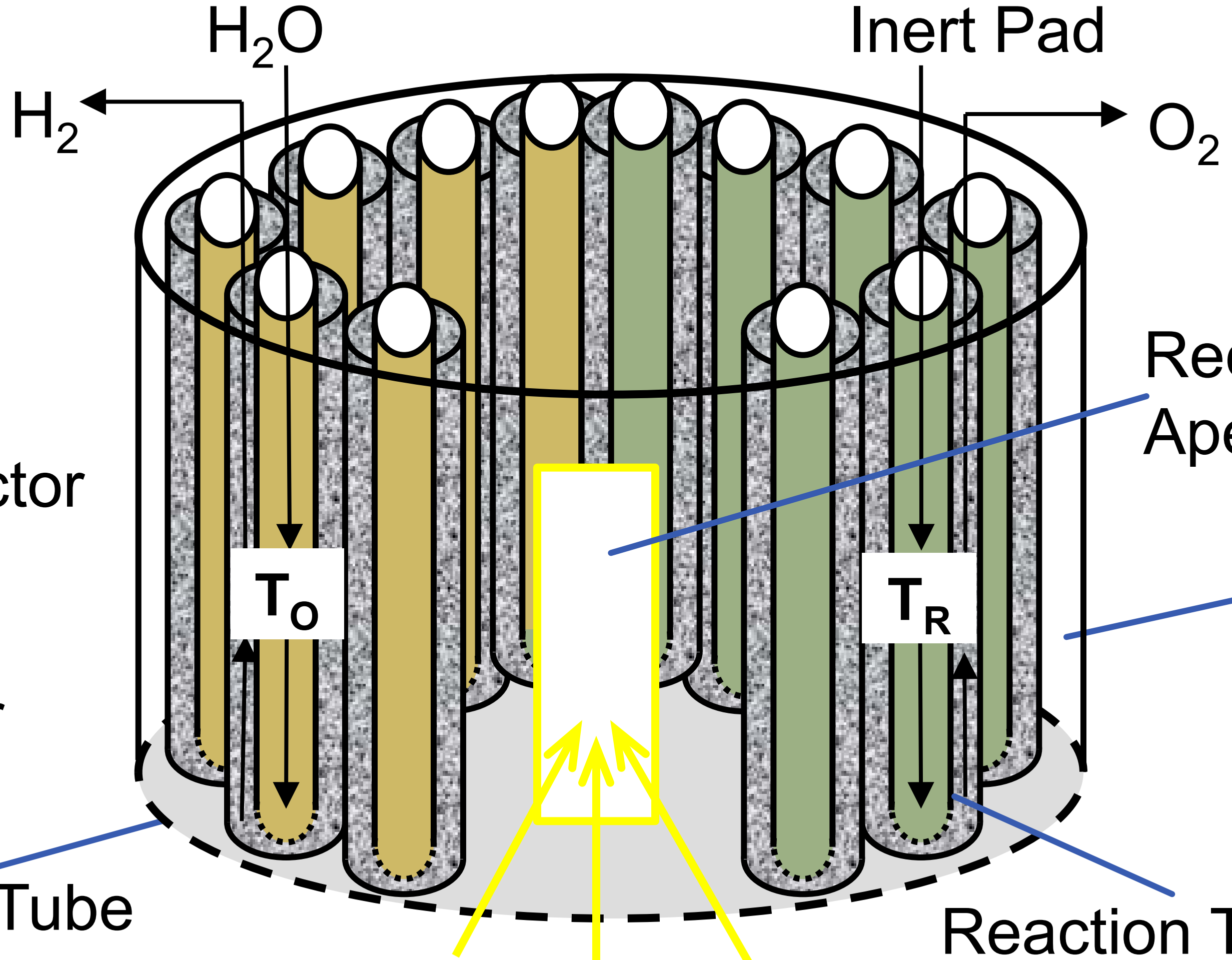
Scheffe, J.R., J. Li and A.W. Weimer, Int. J. of H_2 Energy, 33, 3330-3340 (2010))

Address Identified Weakness

Weakness –

“Further work on this project is recommended to address how the proposed reaction can be accomplished in a high throughput reactor.”

Stationary Multi-tube Cavity Solar Reactor



Insulated Multi-tube Cavity Solar Reactor for Redox Cycling to Split Water

Rectangular Aperture

Insulated Cavity

Reaction Tube (oxidation mode)

Concentrated Solar Radiation

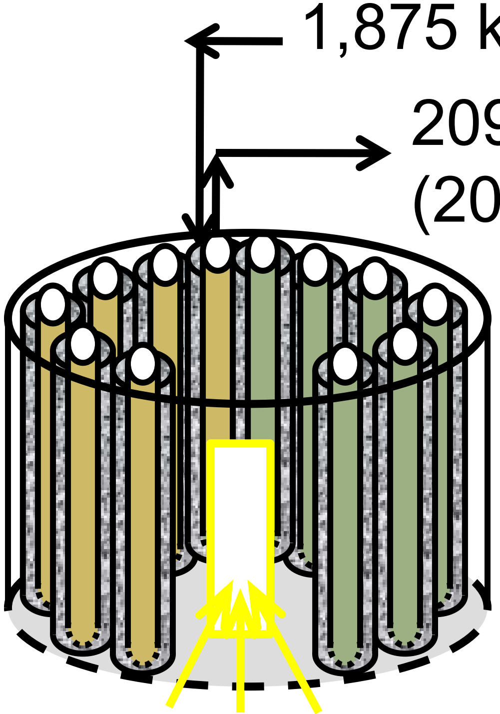
Reaction Tube (reduction mode)

Receiver Concept Advantages

- Outstanding internal heat recuperation since all redox tubes are within an absorbing cavity
- No moving solids – mitigates erosion and complications of moving solids around
- Provides an opportunity to drive redox quickly via radiation heat transfer
- Simplified valving arranged at top; operates semi-continuously like a PSA
- Control oxidation T with steam flow (challenging, but do-able)

5 min Cycle Process Design Perspective

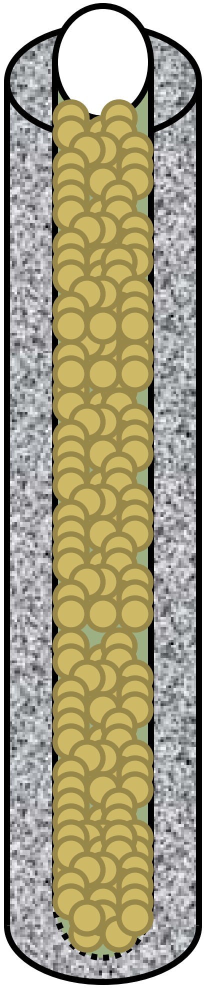
Receiver



1,875 kg H_2O/cycle

209 kg H_2/cycle
(20,000 kg H_2/day)

24,416 kg $NiFe_2O_4$ (4.71 m^3)
(5 nm film via ALD)
9,425 kg ZrO_2 support (1.74 m^3)
(100 m^2/g)



72 tubes
14"/16" tubes
x 20' long
assuming 1" gap

or

26 tubes
12"/16" tubes
x 20' long
assuming 3" gap

Single Tube

Address Identified Weakness

Weakness –

“The team has not presented a critical path which leads to achieve the technical and economic DOE targets.”

Proposed Future Work

- Evaluate robustness of “hercynite cycle” thin films
  - High SA substrate (reticulate ceramics, “honeycomb” catalyst support, aerogels, substrates formed in-situ with SiC tubes, etc.)
  - Deposit alumina by ALD, i.e. high SA substrate / Al_2O_3 / ferrite / Al_2O_3 / ferrite…
  - Evaluate $(1 - y)CeO_2 \bullet yM_xFe_{3-x}O_4 / Al_2O_3$

- Evaluate annular SiC tube reactor concept, especially in-situ synthesis of porous support and films

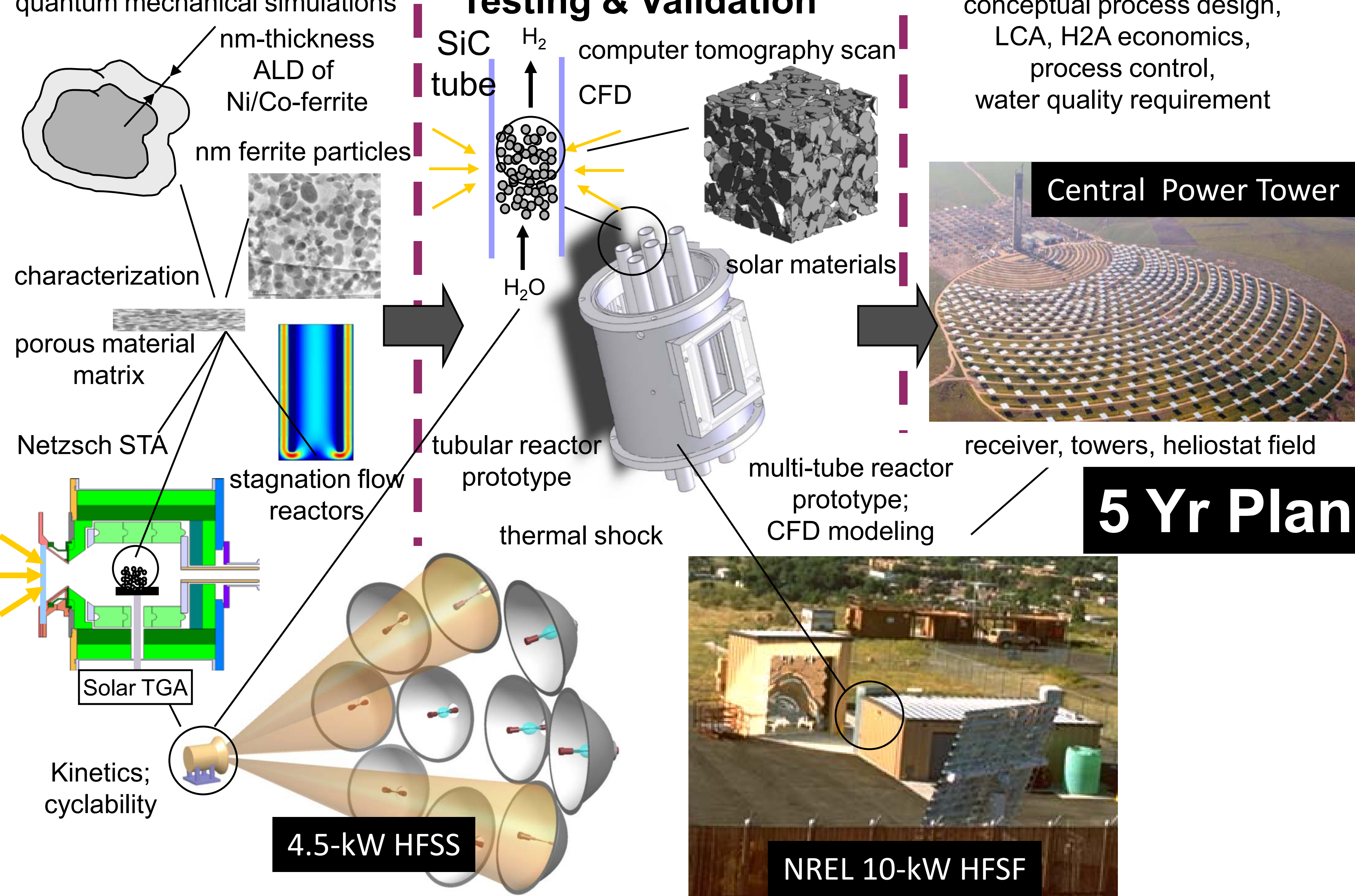
- Test small prototype multi-tube reactor/receiver on-sun

- Continue to update process design and H2A

Designed Solids

Device Fabrication, Characterization, Testing & Validation

Architecture, Solar Delivery, & Systems Analysis



thermodynamics
quantum mechanical simulations

nm-thickness
ALD of
Ni/Co-ferrite

nm ferrite particles

characterization

porous material
matrix

Netzsch STA

stagnation flow
reactors

Solar TGA

Kinetics;
cyclability

4.5-kW HFSS

SiC
tube

H_2

H_2O

computer tomography scan

CFD

solar materials

tubular reactor
prototype

thermal shock

multi-tube reactor
prototype;
CFD modeling

NREL 10-kW HFSF

conceptual process design,
LCA, H2A economics,
process control,
water quality requirement

Central Power Tower

receiver, towers, heliostat field

5 Yr Plan

Sundrop Fuels RDF Construction (June, 2009)

Sundrop Fuels, Inc. ~1 $\mathrm{MW}_{\mathrm{thermal}}$ Pilot Facility (Broomfield, CO)

“Sunlight in Your Tank,” Science, Vol. 326 , 1471-1475 (Dec 11, 2009)

First Sun, September, 2009

Conclusions

- ALD thin films advantageous in terms of fast redox cycling
- Conventional ferrite cycles have an operating window < 100^{o}C (~ 1425 to < 1525^{o}C) due to avoiding a liquid “slag” phase
- “Hercynite cycle” operates in the solar thermal “sweet spot” of 1200 to 1450^{o}C
  - radiation driven
  - SiC containment materials suitable
  - forgiving chemistry (no apparent liquid “slag” phase < 1600^{o}C)
- 2015 DOE price target (\$6/kg) for solar-thermal H_2 production is achievable; 2025 price target of \$3/kg is a stretch
- Allowable ferrite purchase price depends heavily on the ability to carry out redox cycles quickly (preferably < 5 minutes)

Collaborations/Tech Transfer

- ETH-Zurich (Swiss Federal Research Institute)

  - Prof. Steinfeld, ETH students & facilities involved
- Sandia (Tony McDaniel & Mark Allendorf) / NSF

  - PhD student spent ~1 yr working in their lab ($25M Grand Challenge – interested in ALD ferrites)
- NREL HFSF on-sun experiments (Carl Bingham)
- ALD NanoSolutions, Inc. (Broomfield, CO)

  - agreed to produce larger quantities of ALD ferrite materials for the project (licensed ferrite ALD patent)
- Sundrop Fuels (Louisville, CO)

  - interested in on-sun demonstration at their solar pilot facility (current focus is green gasoline; redox next)

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LET YOUR LIGHT SHINE
1876

Acknowledgments

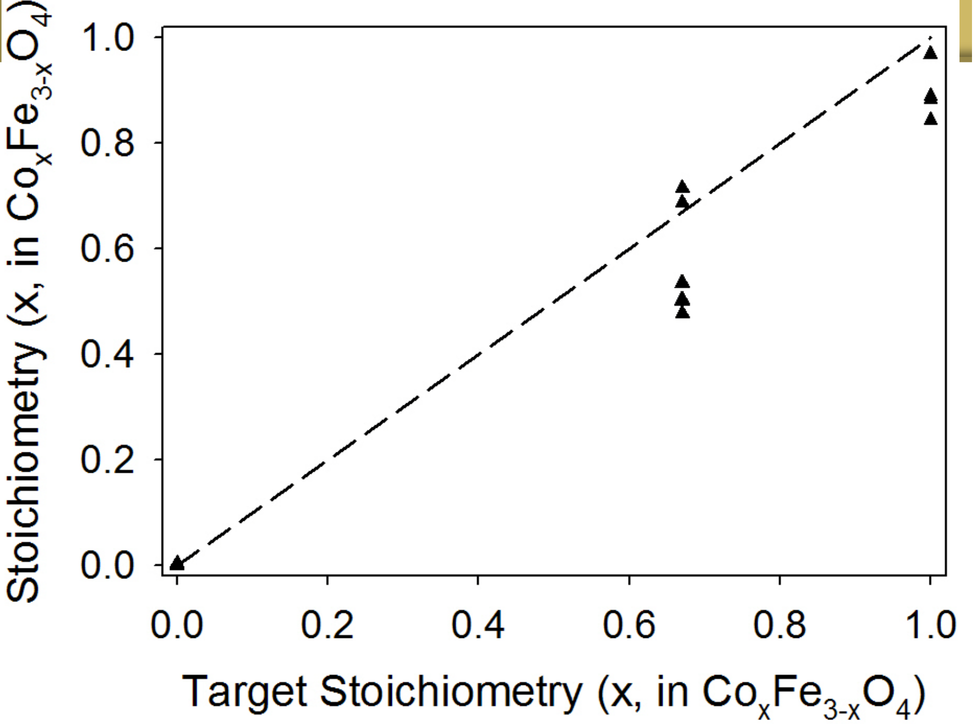
DEPARTMENT OF ENERGY
UNITED STATES OF AMERICA

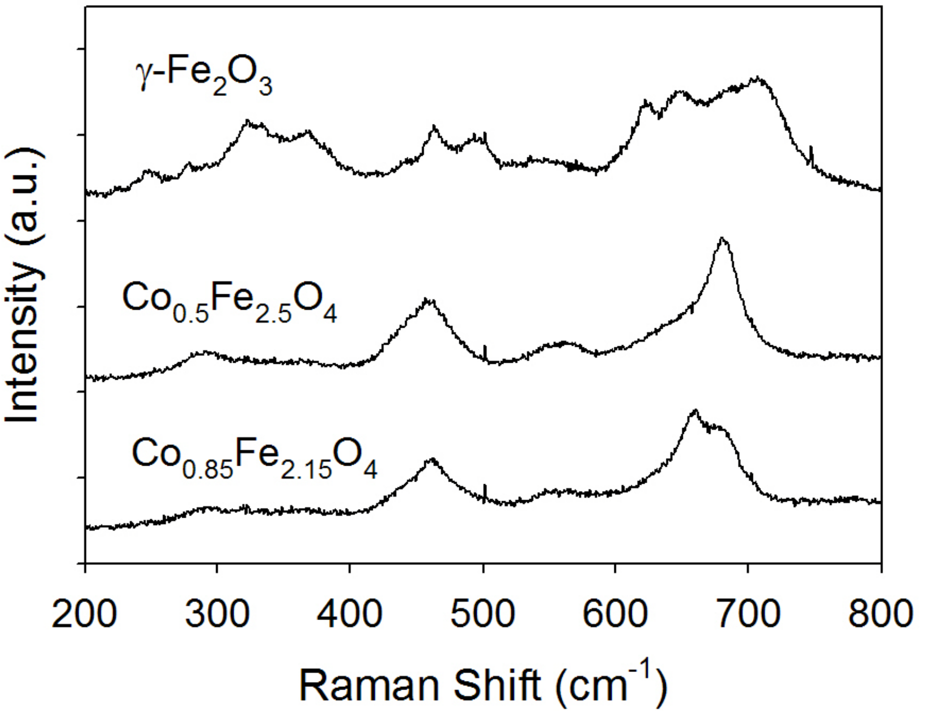
S2P
SUNSHINE 2 PETROL

Questions

Supplementary Slides

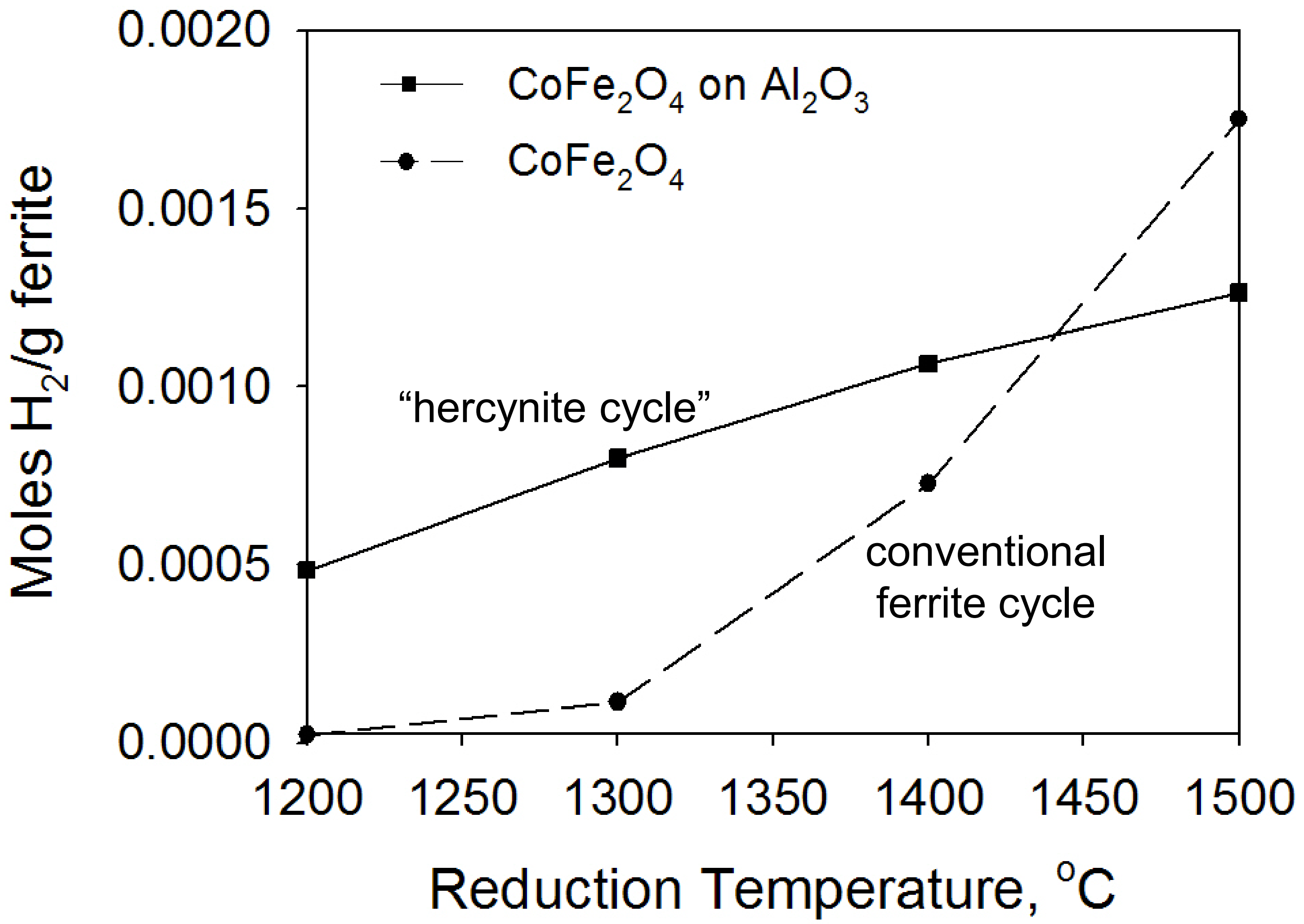
ICP-AES and Raman Verify Stoichiometry and Phases



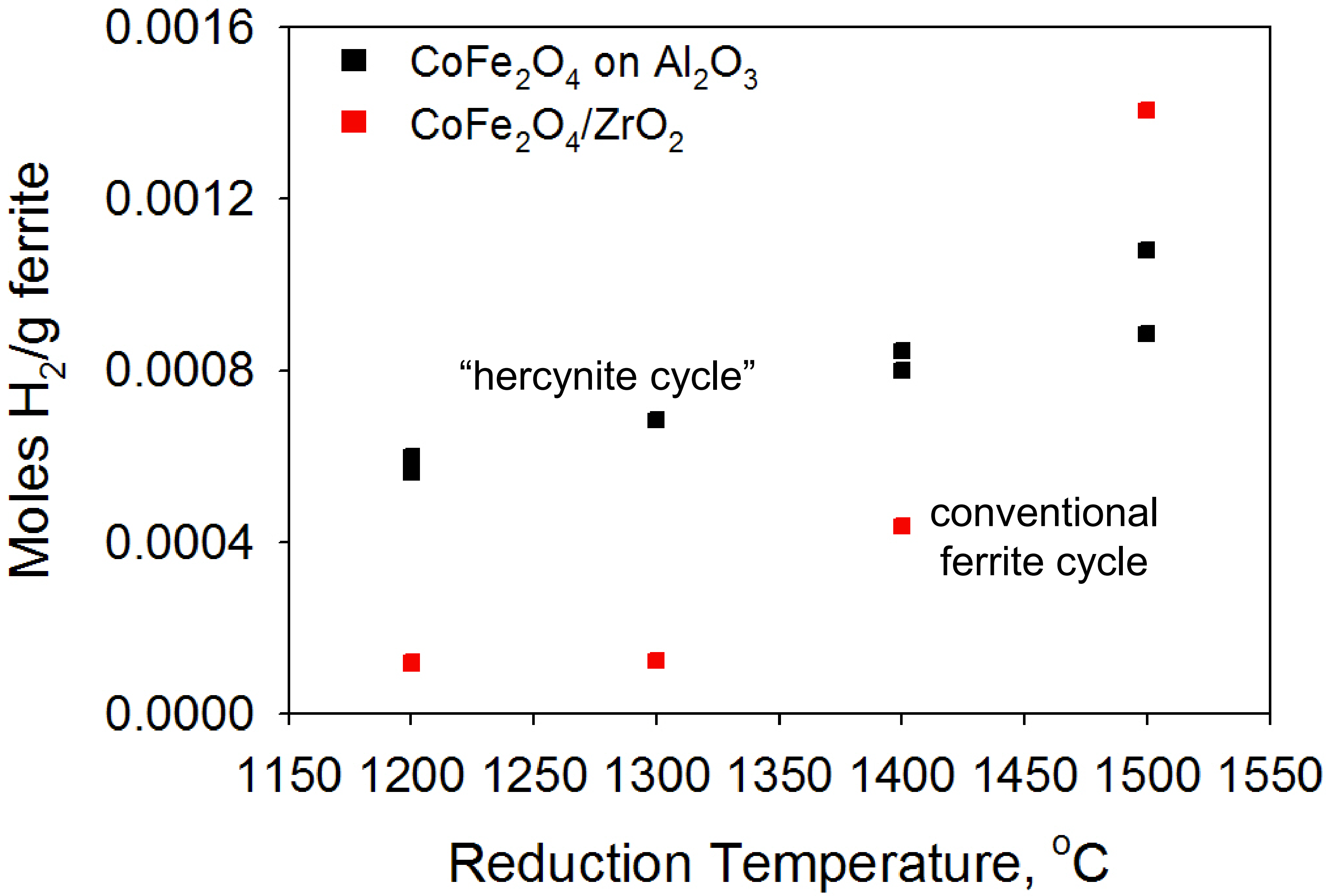


- Film is deposited conformally on ZrO_2 supports – no ZrO_2 observed
- Maghemtite (γ-Fe_2O_3) forms without the presence of Co – verification of nano-sized film (<10nm)
- Substitution of Co results in spinel phase

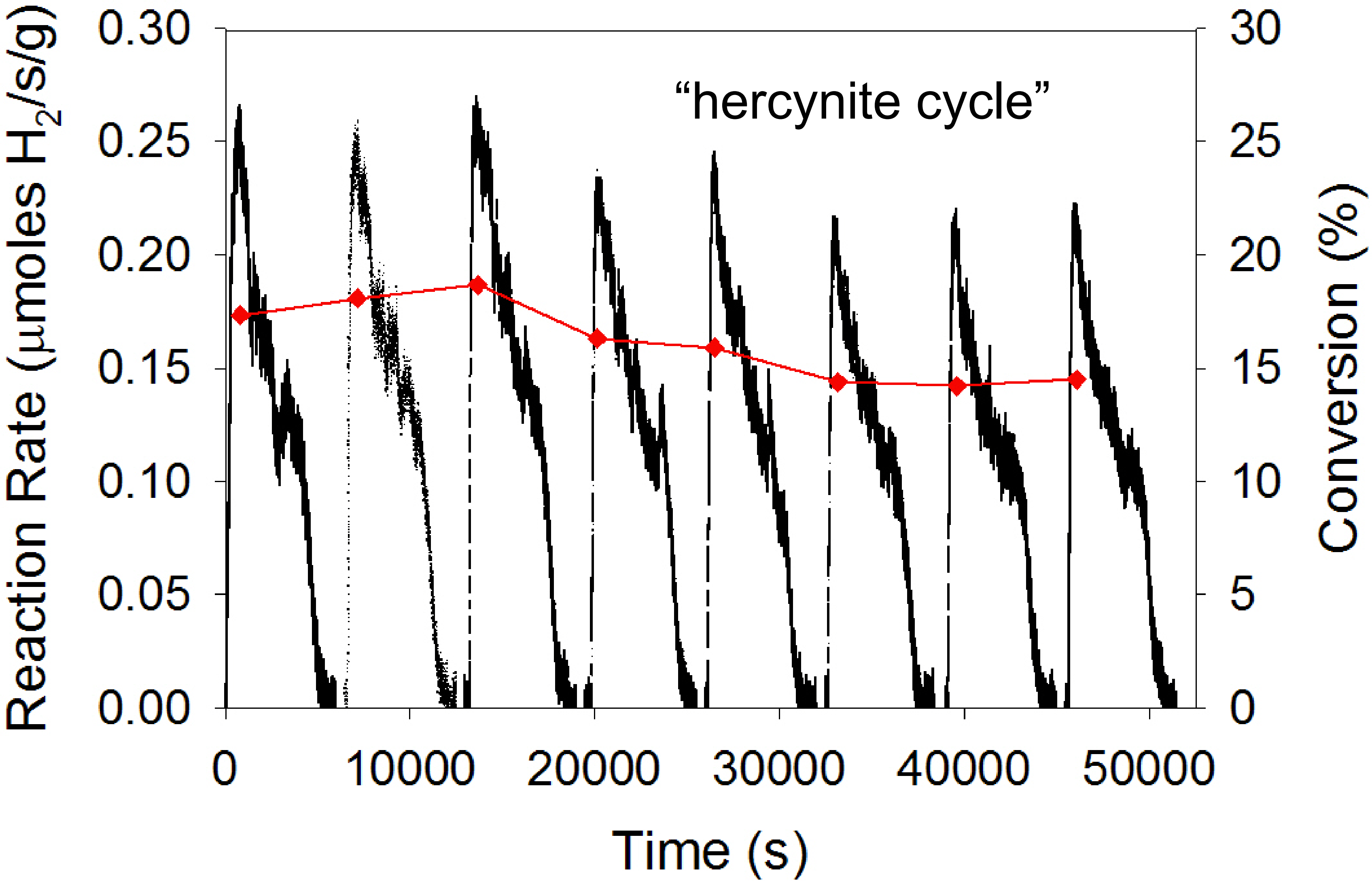
Thermodynamics Predicts More H_2 Generation on Al_2O_3 at Low Temperatures



Experimental Validation

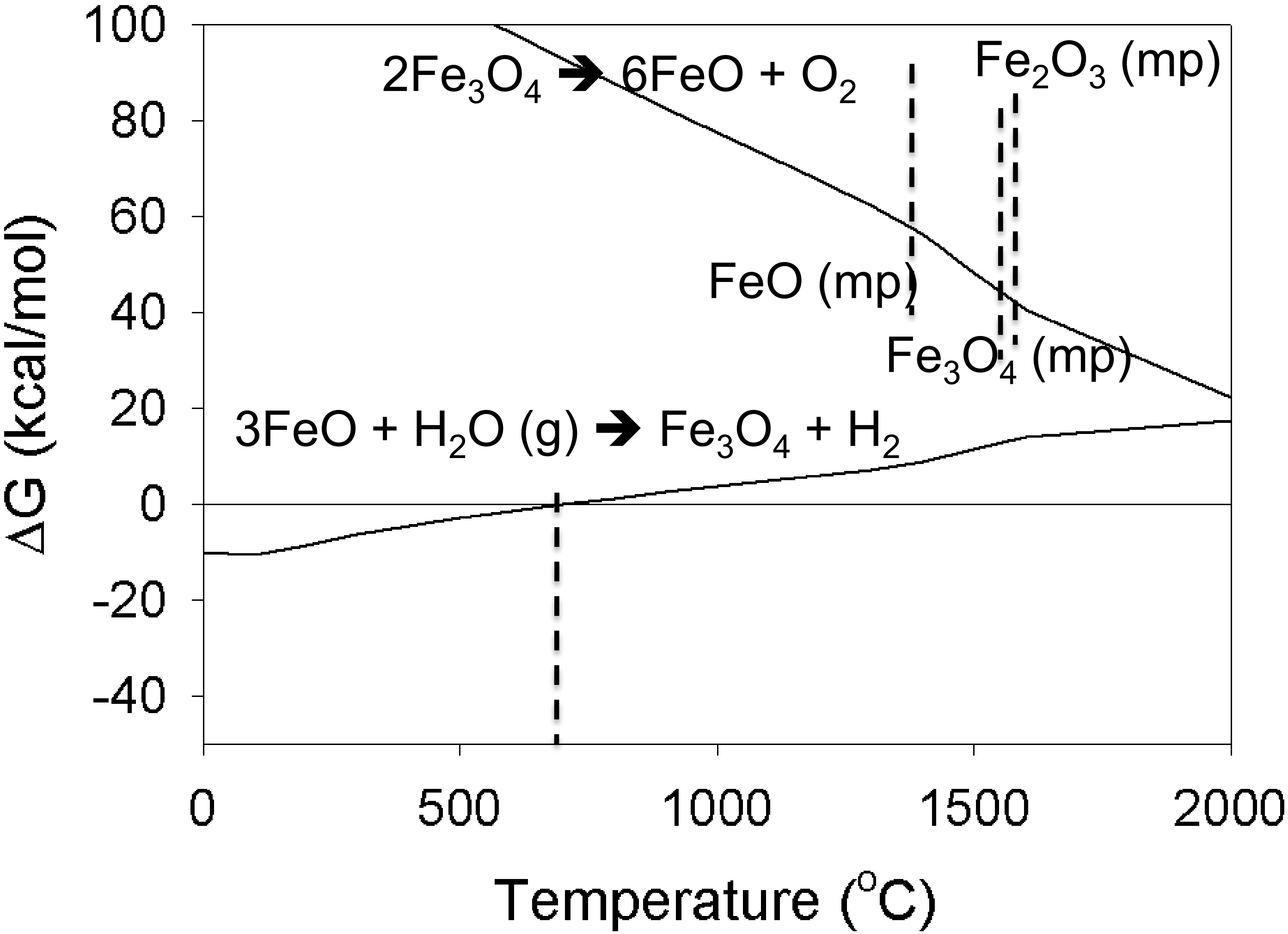


Redox Cycling Demonstrated (1200 °C /1000 °C)

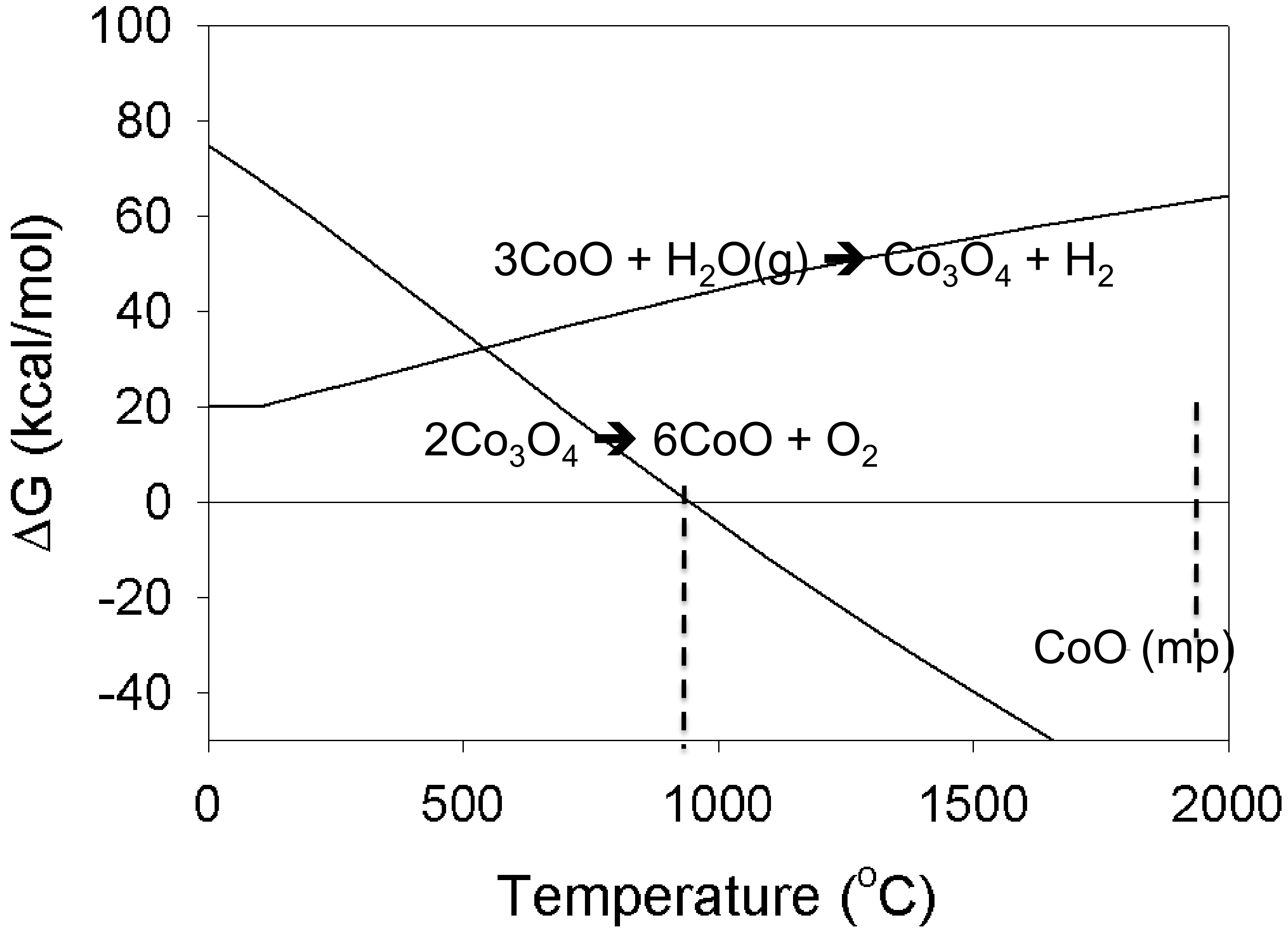


Fe_3O_4 Redox Thermodynamics

1st proposed as a solar H_2O splitting cycle by Nakamura (1977)



Co_3O_4 Redox Thermodynamics



Research Direction

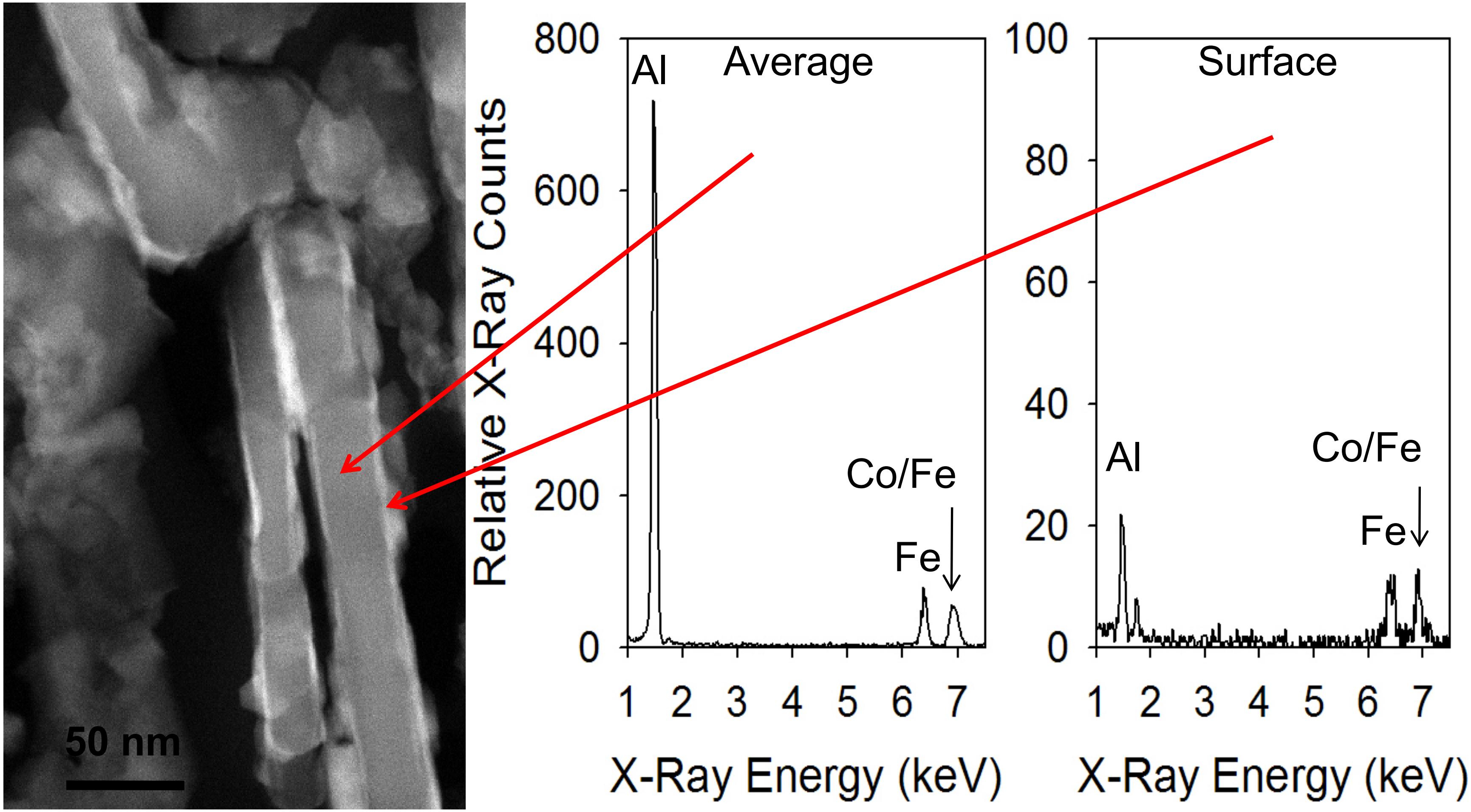
Mixed metal oxides investigated for driving water splitting thermochemical cycles, i.e.

$M_xFe_{3-x}O_4$; M = **Co**, Mn, **Ni**, Zn

$CoFe_2O_4$ ALD on Al_2O_3 Supports

STEM

EDX



Research Direction

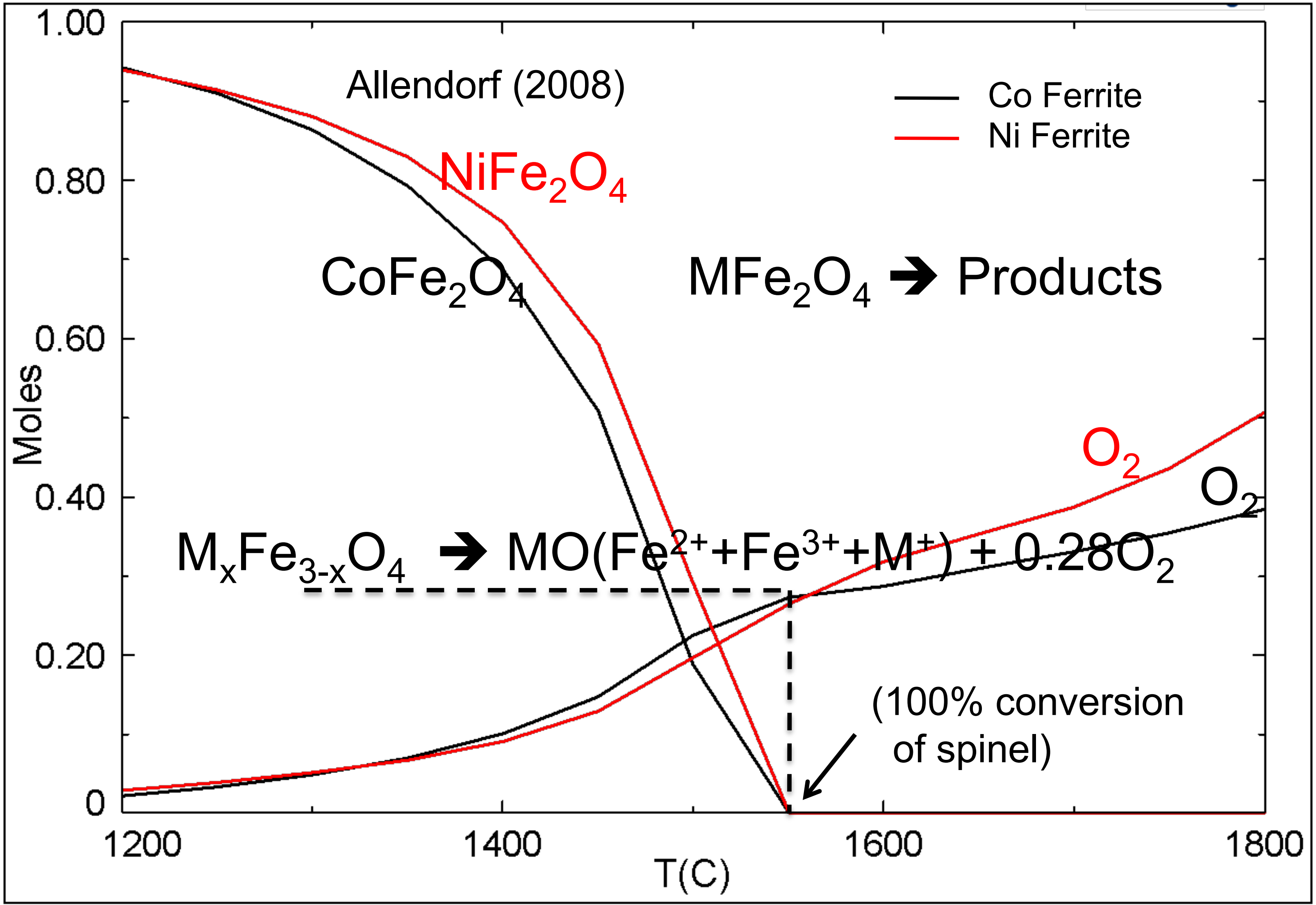
Kodama (2003) suggested using mixed metal oxides supported on inert substrates, i.e. ZrO_2, to avoid sintering/deactivation via “slag” liquid phase

$$M_xFe_{3-x}O_4/ZrO_2$$

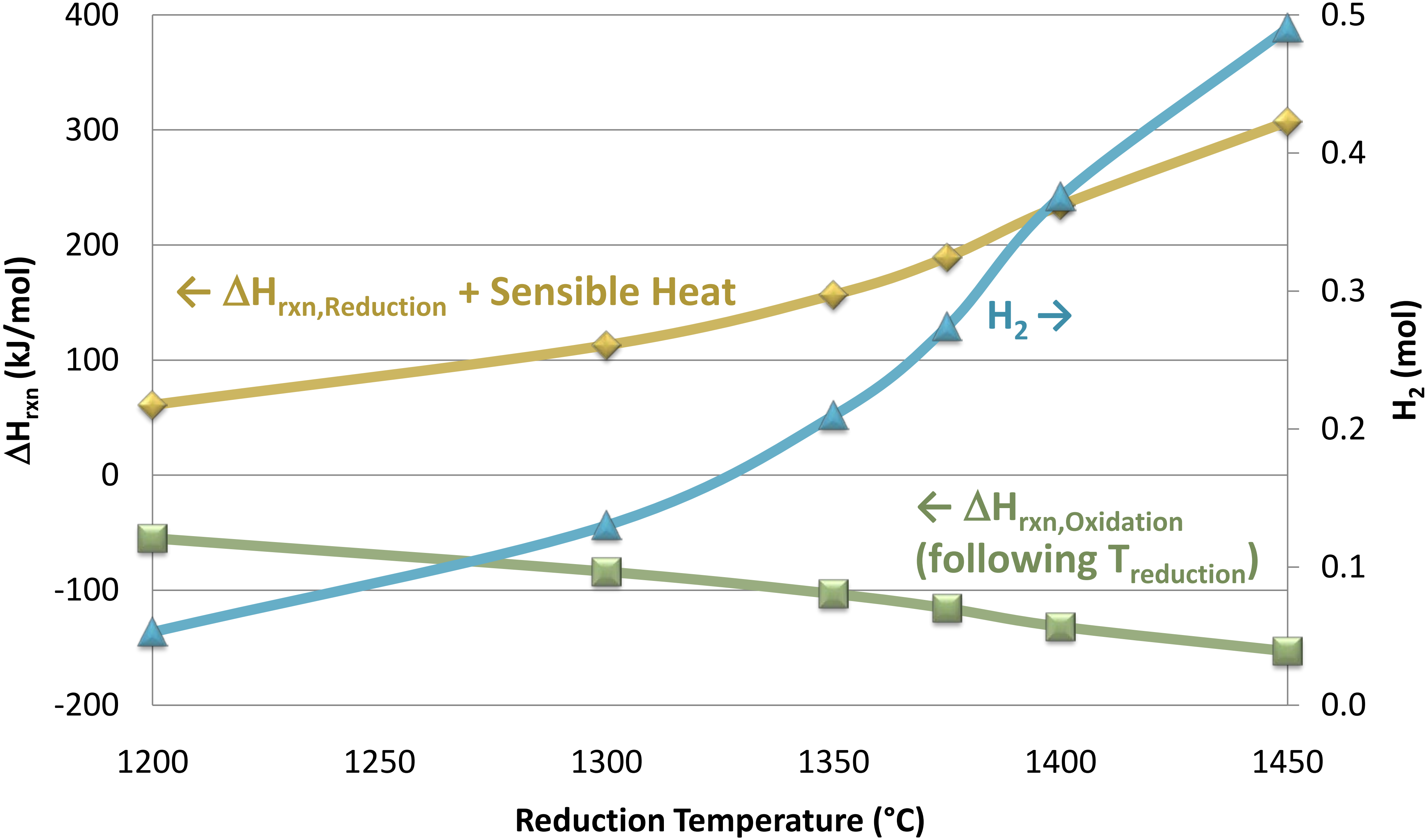
$$M_xFe_{3-x}O_4 + \text{solar energy} \rightarrow MO(Fe^{2+}+Fe^{3+}+M^{+}) + 0.5O_2$$

(no conversions ever reported to be close to this)

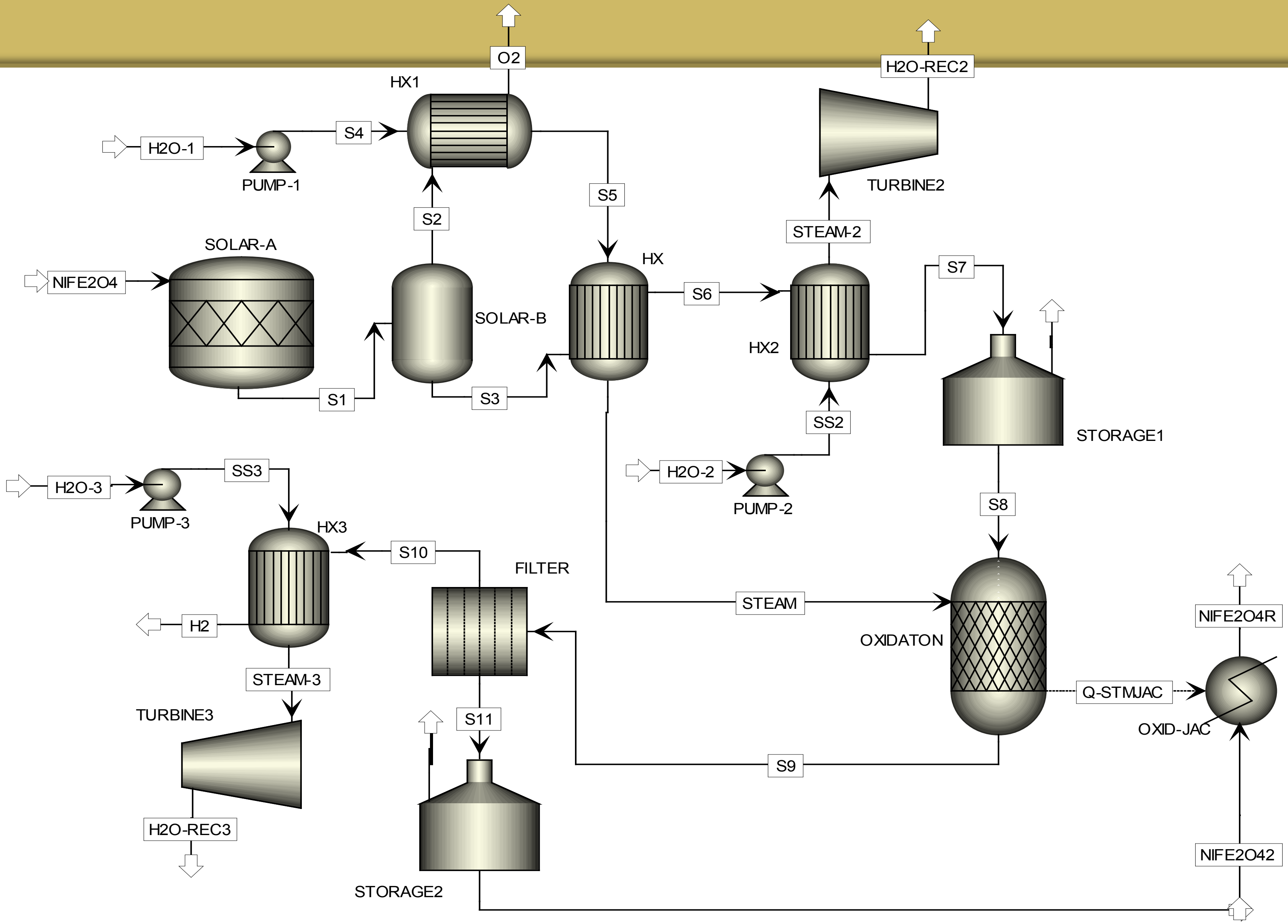
Approach - Free Energy Minimization Theoretical Limit (P = 0.001 MPa)



FactSage™ – Gibbs Free Energy Minimization ($NiFe_2O_4$ Oxidized at 1,000°C)



AspenPlus™ PFD



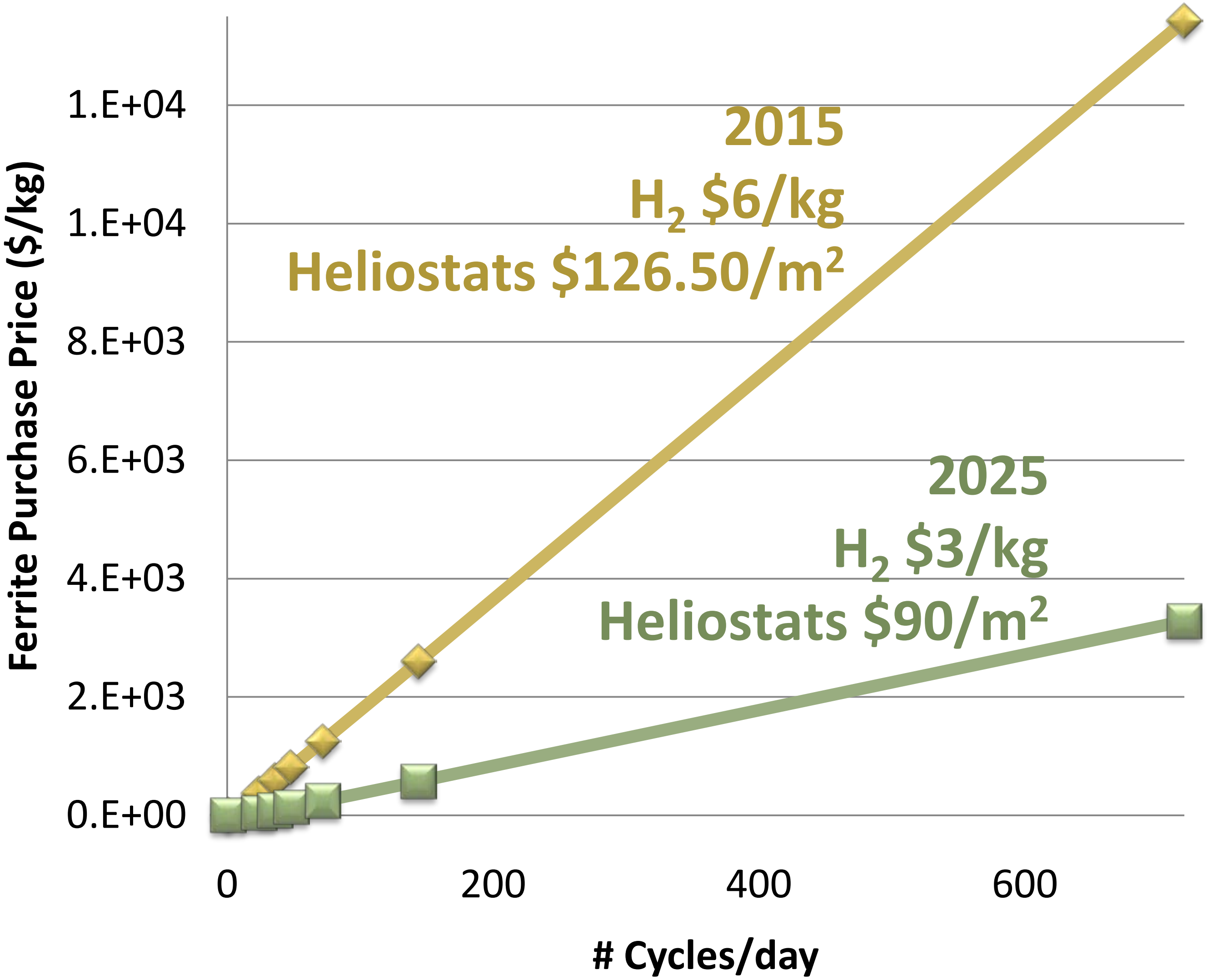
Cost Analysis Results

Allowable Ferrite Purchase Price		
# Cycles day	2012 H_2 \$6/kg (\$/kg)	2017 H_2 \$3/kg (\$/kg)
1	\$6.54	---
24	\$375	\$37
36	\$589	\$84
48	\$810	\$136
72	\$1,255	\$240
144	\$2,594	\$571
720	\$13,427	\$3,271

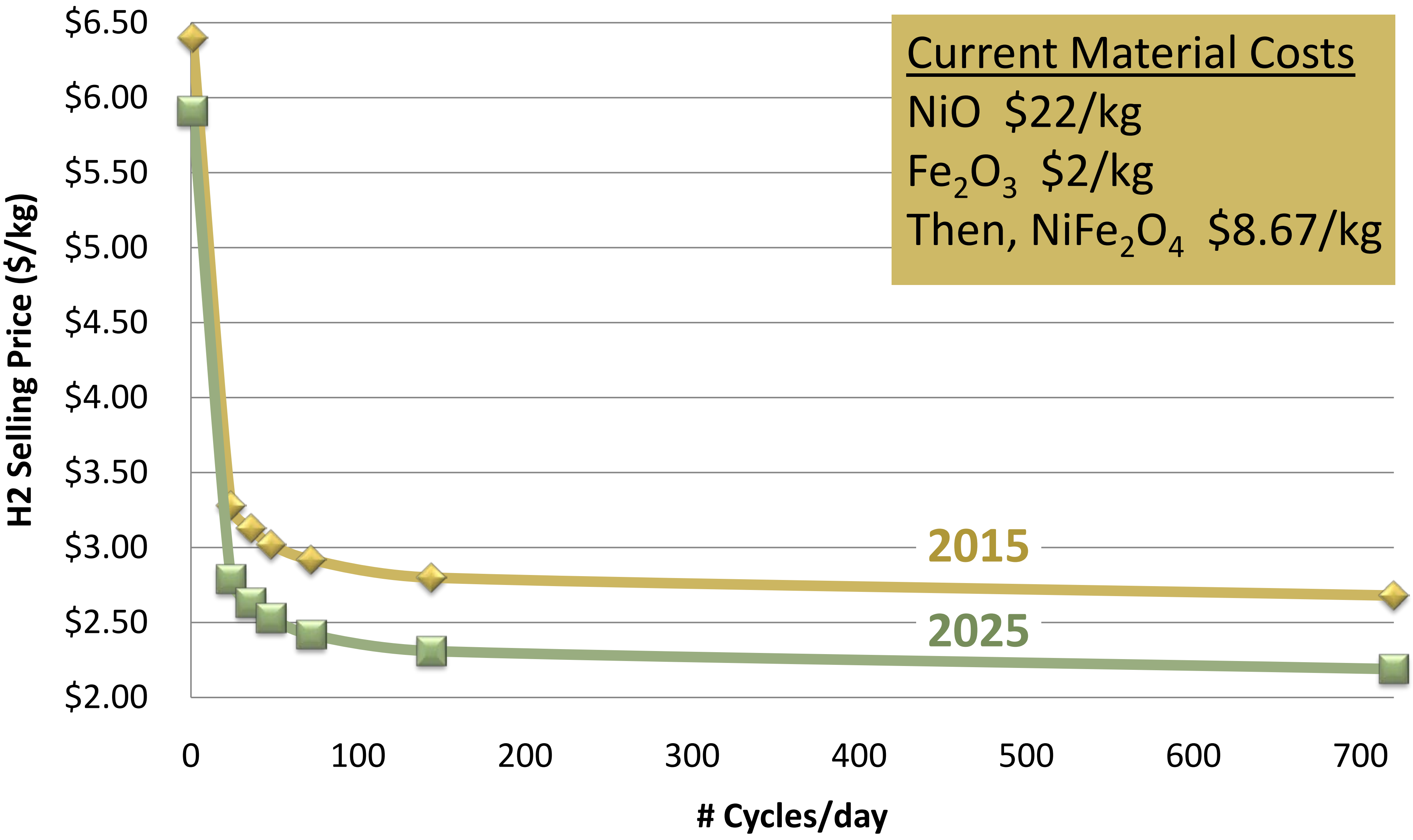
H_2 Selling Price \$8.67 Ferrite		
# Cycles day	2015 (\$/kg)	2025 (\$/kg)
1	\$6.40	\$5.91
24	\$3.28	\$2.79
36	\$3.13	\$2.63
48	\$3.02	\$2.53
72	\$2.92	\$2.42
144	\$2.80	\$2.31
720	\$2.68	\$2.19

Results – Ferrite Purchase Price vs Number of Cycles per Day

#Cycles day	Minutes Cycle
1	24hr
24	30
36	20
48	15
72	10
144	5
720	1



Results – H_2 Selling Price for \$8.67/kg Ferrite Material Cost



<u>Current Material Costs</u>

NiO \$22/kg

Fe_2O_3 \$2/kg

Then, $NiFe_2O_4$ \$8.67/kg

Results – Process Efficiencies

Source	**Efficiency, η**	**Equation**
Heliostat Field (Solar to Receiver)	40.2%	Soltrace
Thermal (LHV)	54.6%	$\eta_{thermal} = \frac{(H_2\,LHV + e^-_{produced})}{(Solar + e^-_{consumed})}$
Overall	**21.9%**	$\eta_{Overall} = \eta_{Solar} * \eta_{Thermal}$
STCH	**21.9%**	$\eta_{STCH} = \frac{(H_2\,LHV + e^-_{produced})}{(Solar/\eta_{Field} + e^-_{consumed}/\eta_{offsite\,e-})}$

Required Heat of Reduction

$$\left(100{,}000\frac{kgH2}{day}\right)\left(\frac{molH2}{2.01588g}\right)\left(\frac{1\ molNiFe2O4}{0.4901\ molH2}\right)\left(\frac{1000\ g}{kg}\right)=1.01E8\frac{molNiFe2O4}{day}$$

$$\left(1.01E8\frac{mol\ NiFe2O4}{day}\right)\left(209{,}751\frac{J}{mol}\right)=2.12E13\frac{J}{day}$$

$$\left(2.12E13\frac{J}{day}\right)\left(\frac{hr}{3{,}600s}\right)\left(\frac{GW}{10^9*\frac{J}{s}}\right)=5.9\frac{GW\,hr}{day}$$

$$\left(5.9\frac{GW\,hr}{day}\right)\left(365\frac{day}{yr}\right)=\mathbf{2,151}\frac{\mathbf{GW\,hr}}{\mathbf{yr}}$$

$NiFe_2O_4$ Sensible Heat Input

$$\left(1.01E8\,\frac{mol\ NiFe2O4}{day}\right)\left(213.384\,\frac{J}{mol*K}\right)(1{,}723-1{,}273)K = 9.71E12\,\frac{J}{day}$$

$$\left(9.71E12\,\frac{J}{day}\right)\left(\frac{hr}{3600s}\right)\left(\frac{GW}{10^9*\frac{J}{s}}\right) = 2.70\,\frac{GWhr}{day}$$

$$\left(2.70\,\frac{GWhr}{day}\right)\left(365\,\frac{day}{yr}\right) = \mathbf{984}\,\frac{\mathbf{GWhr}}{\mathbf{yr}}$$

ZrO_2 Sensible Heat Input

$$\left(7.42E7\,\frac{mol\,ZrO2}{day}\right)\left(123.228\,\frac{J}{mol*K}\right)(1{,}723-1{,}273)K = 2.70E12\,\frac{J}{day}$$

$$\left(2.70E12\,\frac{J}{day}\right)\left(\frac{hr}{3600s}\right)\left(\frac{GW}{10^9*\frac{J}{s}}\right) = 0.75\,\frac{GW\,hr}{day}$$

$$\left(0.75\,\frac{GW\,hr}{day}\right)\left(365\,\frac{day}{yr}\right) = \mathbf{274\,\frac{GW\,hr}{yr}}$$

Total Sensible Heat Input

$$(984 + 274)\frac{GWhr}{yr} = 1{,}258\frac{GWhr}{yr}$$

Total Solar Heat Input

$$(1{,}258 + 2{,}151)\frac{GWhr}{yr} = 3{,}409\frac{GWhr}{yr}$$

Oxidation Heat Integration

(FACTSage: -83 kJ/mol)

$$\left(100{,}000\,\frac{kgH2}{day}\right)\left(\frac{molH2}{2.01588g}\right)\left(\frac{1molNiFe2O4}{0.4901molH2}\right)\left(\frac{1000\,g}{kg}\right)\left(-83{,}090\,\frac{J}{mol\,NiFe2O4}\right)$$
$$= -8.40E12\,\frac{J}{day}$$

$$\left(-8.40E12\,\frac{J}{day}\right)\left(\frac{hr}{3{,}600\text{ sec}}\right)\left(\frac{GW}{10^{9}*\frac{J}{s}}\right) = -2.33\,\frac{GWhr}{day}$$

$$\left(-2.33\,\frac{GWhr}{day}\right)\left(365\,\frac{day}{yr}\right) = \mathbf{-852\,\frac{GWhr}{yr}}$$

$$\left(100{,}000\,\frac{kgH2}{day}\right)\left(\frac{molH2}{2.01588g}\right)\left(\frac{1molNiFe2O4}{0.4901molH2}\right)\left(\frac{1000\,g}{kg}\right) = 1.01E8\,\frac{mol\,NiFe2O4}{day}$$

$$\left(-852\,\frac{GWhr}{yr}\right)\left(\frac{yr}{365\,day}\right)\left(\frac{10^{9}\,J/_{s}}{GW}\right)\left(3{,}600\,\frac{sec}{hr}\right)\left(\frac{mol*K}{213.384\,J}\right)\left(\frac{day}{1.01E8\,molNiFe2O4}\right)$$
$$= -389\,K$$

$$T_{NiFE2O4,feed} = (1253-(-389))K = 1{,}642\,K = \mathbf{1{,}369\,{}^{\circ}C}$$

$NiFe_2O_4$ Sensible Heat

$$\left(1.01E8\frac{mol\ NiFe2O4}{day}\right)\left(213.384\frac{J}{mol*K}\right)(1{,}723-1{,}642)K=1.74E12\frac{J}{day}$$

$$\left(1.74E12\frac{J}{day}\right)\left(\frac{hr}{3600s}\right)\left(\frac{GW}{10^9*\frac{J}{s}}\right)=0.48\frac{GW\,hr}{day}$$

$$\left(0.48\frac{GW\,hr}{day}\right)\left(365\frac{day}{yr}\right)=\mathbf{176}\frac{\mathbf{GW\,hr}}{\mathbf{yr}}$$

ZrO_2 support Sensible Heat

$$\left(7.42E7\frac{mol\,ZrO2}{day}\right)\left(123.228\frac{J}{mol*K}\right)(1{,}723-1{,}642)K=4.84E11\frac{J}{day}$$

$$\left(4.84E11\frac{J}{day}\right)\left(\frac{hr}{3600s}\right)\left(\frac{GW}{10^9*\frac{J}{s}}\right)=0.13\frac{GW\,hr}{day}$$

$$\left(0.13\frac{GW\,hr}{day}\right)\left(365\frac{day}{yr}\right)=\mathbf{49\frac{GW\,hr}{yr}}$$

$NiFe_2O_4 + ZrO_2$ Sensible Heat

$$(176 + 49)\frac{GWhr}{yr} = \mathbf{225}\frac{\mathbf{GWhr}}{\mathbf{yr}}$$

Total Solar Heat Input

$$(225 + 2{,}151)\,\frac{GWhr}{yr} = \mathbf{2{,}376}\,\frac{\boldsymbol{GWhr}}{\boldsymbol{yr}}$$

Process Design Perspectives

Assuming ~20,000 kg H_2/day/tower (~ 250 MWth)

If 5 redox cycles/min. can be achieved via thin films, then:

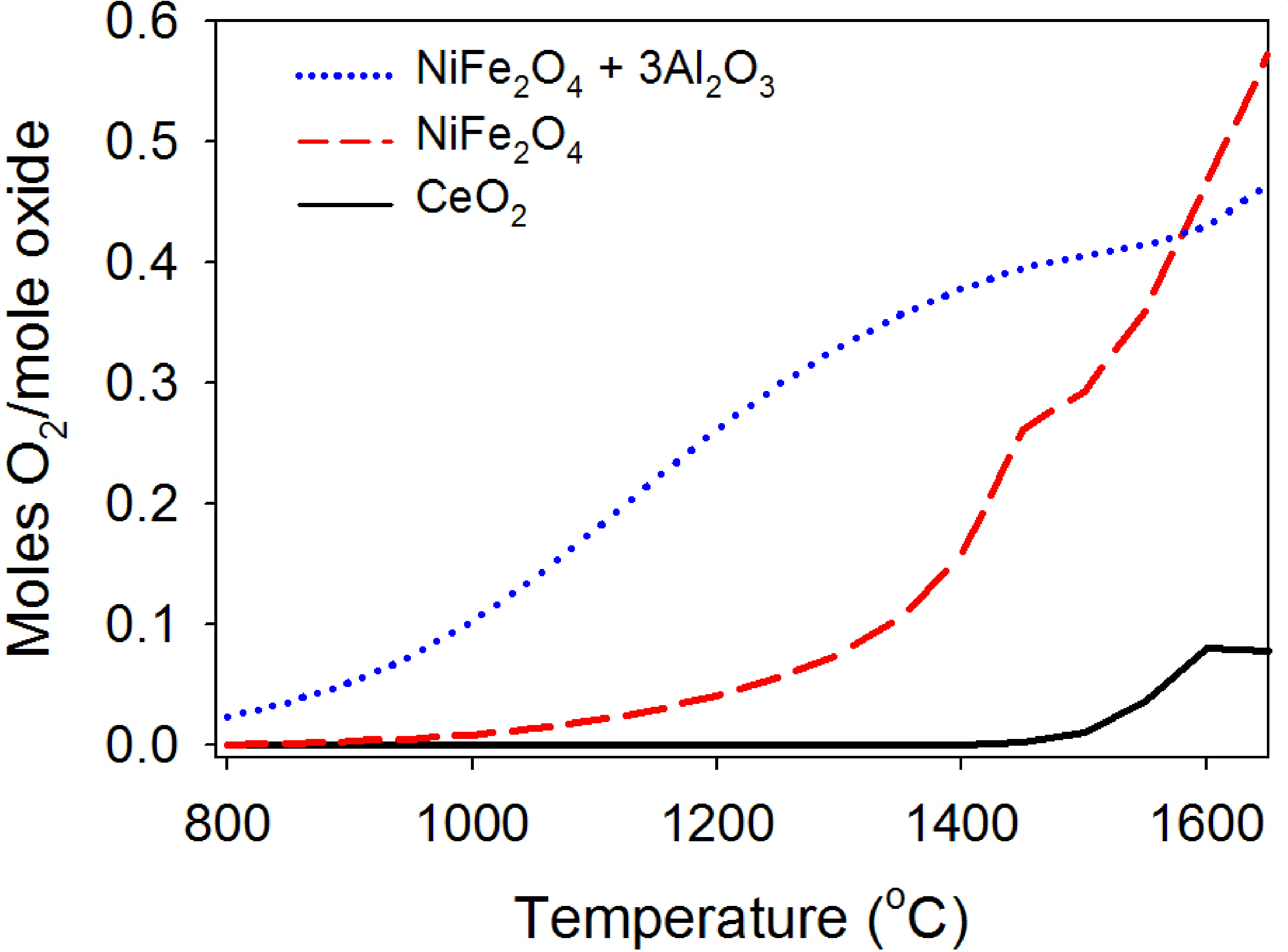
- 209 kg H_2/cycle/tower
- 1,875 kg H_2O/cycle/tower
- 24,416 kg $NiFe_2O_4$/cycle/tower

(for 5.18 g/cc $NiFe_2O_4$ density, this is ~ 4.71 m^3 of active material)

- depositing a 5 nm thick film of active material by ALD on a 100 m^2/g ZrO_2 support, this is a need for 9,425 of substrate ZrO2

(For comparison, a 100 MWth CSP salt storage system holds 1600 t of salt; the tank is 18 m in diameter and 9 m tall)

O_2 Evolution for CeO_2, $NiFe_2O_4$ and $NiFe_2O_4/3Al_2O_3$ Reduction



Ferrocene Cost

Ferrocene: $Fe(C_2H_5)_2$; M_w = 113.85 g/mol

2 mol $Fe(C_2H_5)_2$/ 1 mol $NiFe_2O_4$

Current bulk price of ferrocene is $16/kg for 24,000 kg/yr (quote from SAFC-Hitech)

0.97 kg ferrocene/kg Ni-ferrite; therefore, cost of ferrocene is ~ $15/kg Ni-ferrite

Nickelocene: $Ni(C_2H_5)_2$; Mw = 116.7 g/mol

1 mol $Ni(C_2H_5)_2$/ 1 mol $NiFe_2O_4$

Assuming cost of nickelocene is 30 X ferrocene based on semi-conductor organometallic pricing; then $450/kg

0.5 kg nickelocene /kg Ni-ferrite; therefore, cost of nickelocene is ~$225/kg Ni-ferrite

Combined cost of precursor “ocenes” is ~$240/kg Ni-ferrite