Solar-thermal ALD Ferrite-Based Water Splitting Cycles

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May 12, 2011

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

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)

Swiss Federal Research Institute (ETH Zurich)

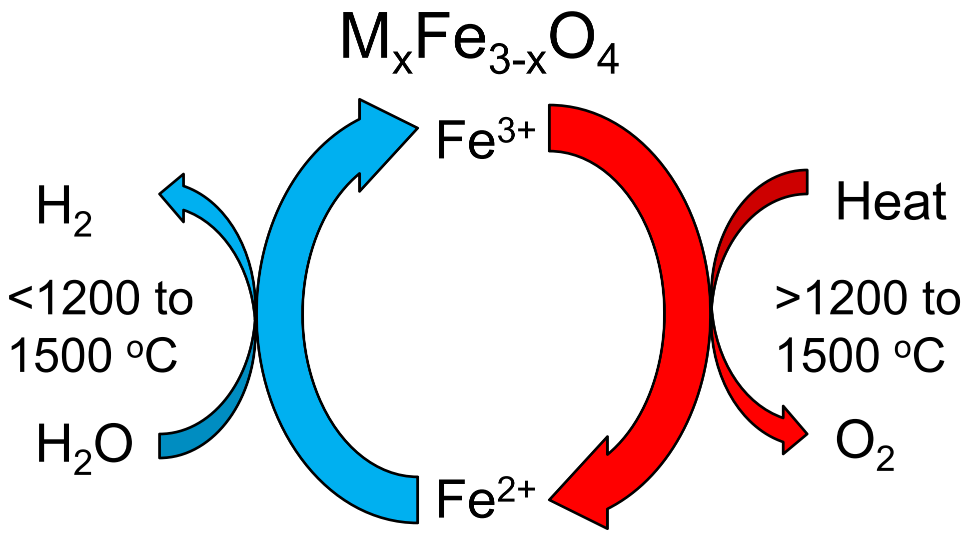
Sandia National Laboratories (SNL)

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/kg H_2 in 2015; \$3/kg H_2 in 2020)
- Milestone – On-sun demonstration of the hercynite cycle for a single reactor tube with monitoring of product gases using mass spectrometry

Solar-thermal Water Splitting Ferrite Cycles



<u>Idealized redox</u>

Reduction: $M_xFe_{3-x}O_4$ (Fe^{3+}) + solar heat $\rightarrow$ [xMO + (3-x)FeO](Fe^{2+}) + $0.5O_2$

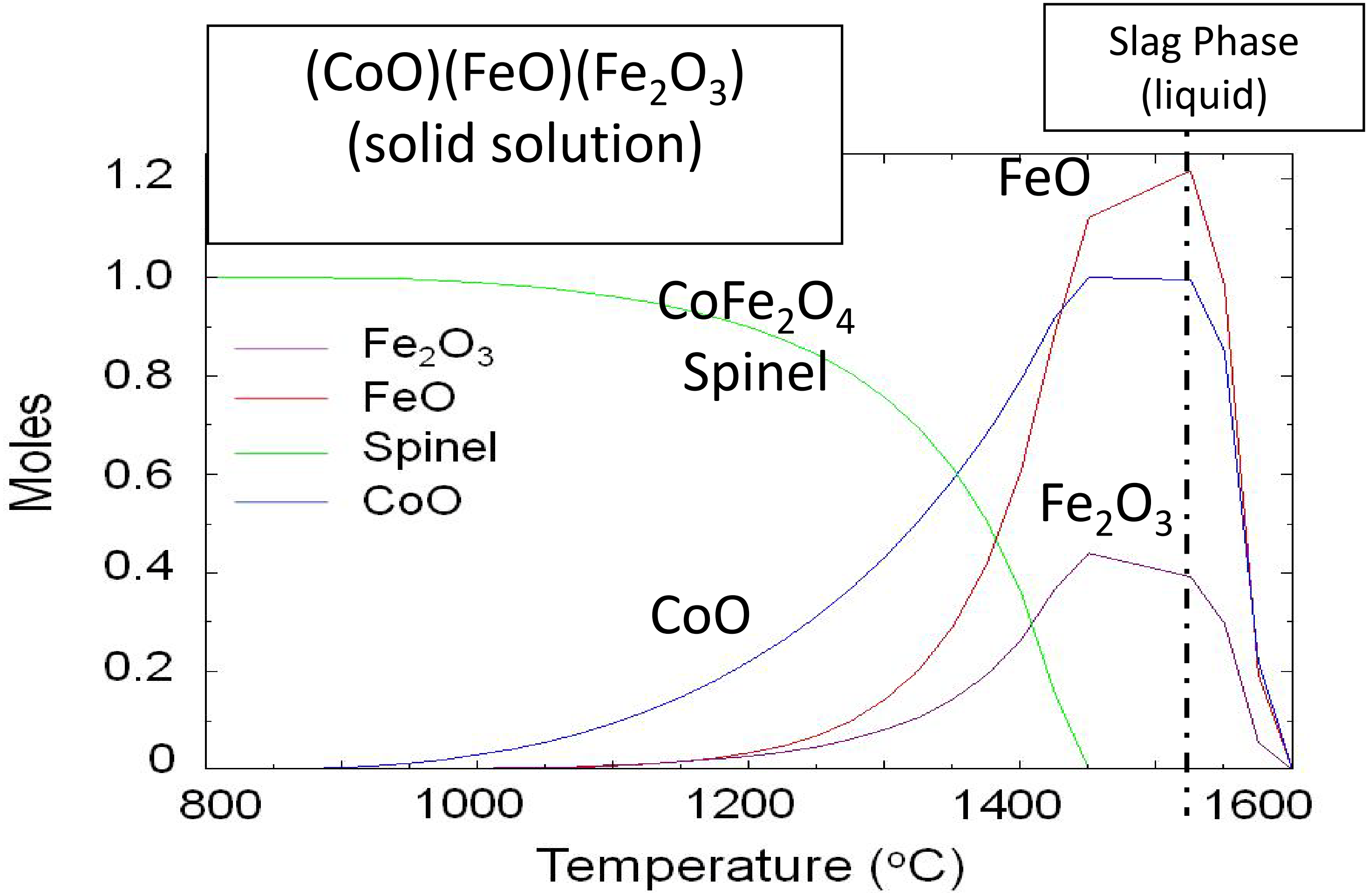
Oxidation: [xMO + (3-x) FeO](Fe^{2+}) + H_2O $\rightarrow$ $M_xFe_{3-x}O_4$(Fe^{3+}) + H_2

Overall: H_2O + solar energy $\rightarrow$ H_2 + $0.5O_2$

M = <u>Co</u>, Mn, <u>Ni</u>, Zn, or other transition metals

Ferrite Cycle Challenges

•Transport Limitations; • Small Operating T Window; • Sintering/Deactivation



The team ha

Address Identified Weakness

<u>Weakness Identified (H2A related)</u> –

"…include processing cost to make the films…"

"…account for inert substrate sensible heat loss – i.e. high-carrier solids…"

"…operation and maintenance costs are underestimated…"

"…all key H2A assumptions and corresponding bases need identified..“

<u>Weakness Addressed</u>

Team worked with independent H2A contractor TIAX and H2A economics presented here have been reviewed by TIAX and compared with other solarthermal processes

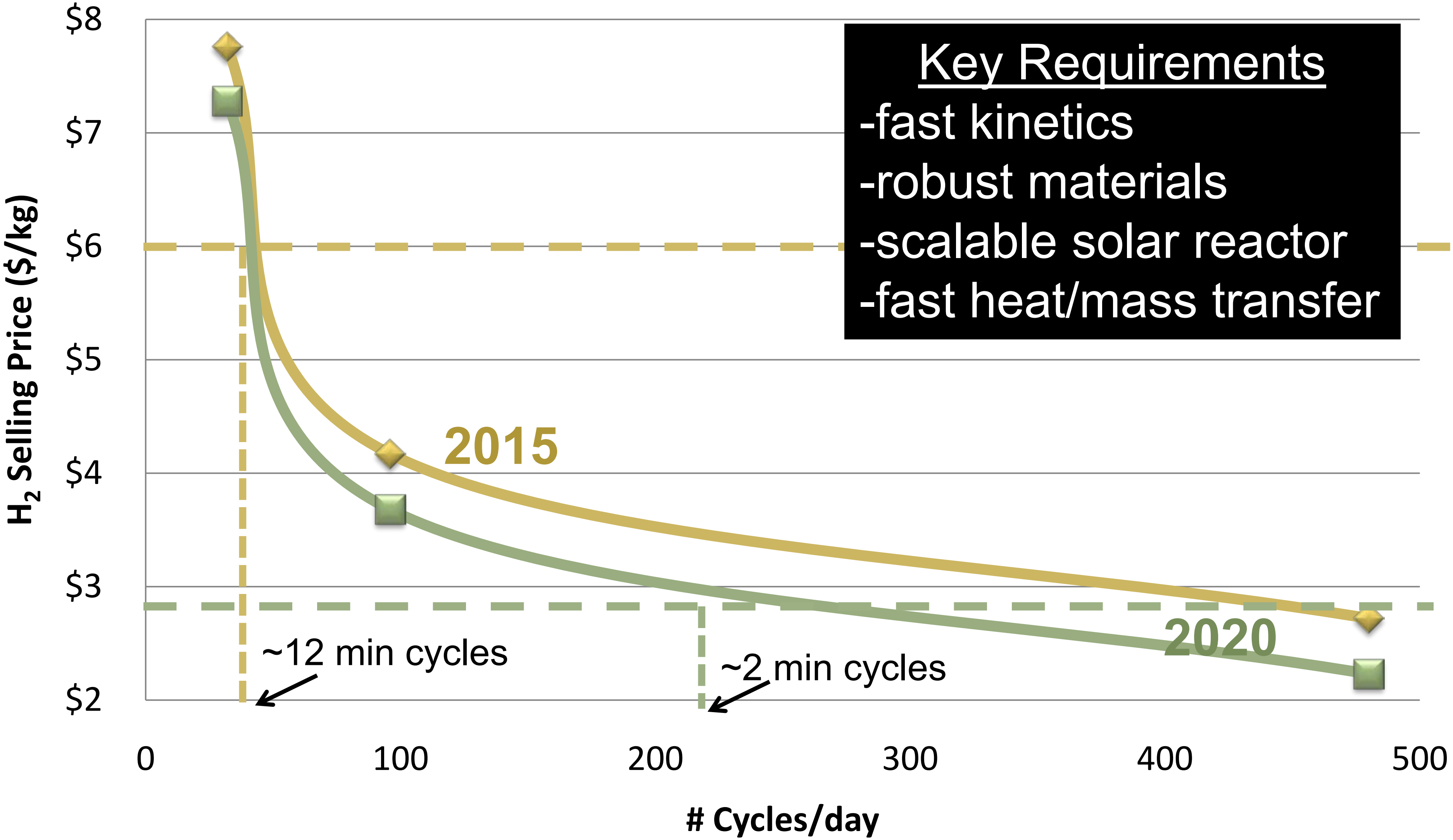
100,000 kg H_2/day Field Design

- Six 223 m tall towers with 3 heliostat fields/tower (2,332 GWhr/yr)
- 1,168 acres of land in Daggett, CA
- 209 MW_{th} delivered to each solar reactor
- Net concentration 3,868 suns with an annual η = 40.2%

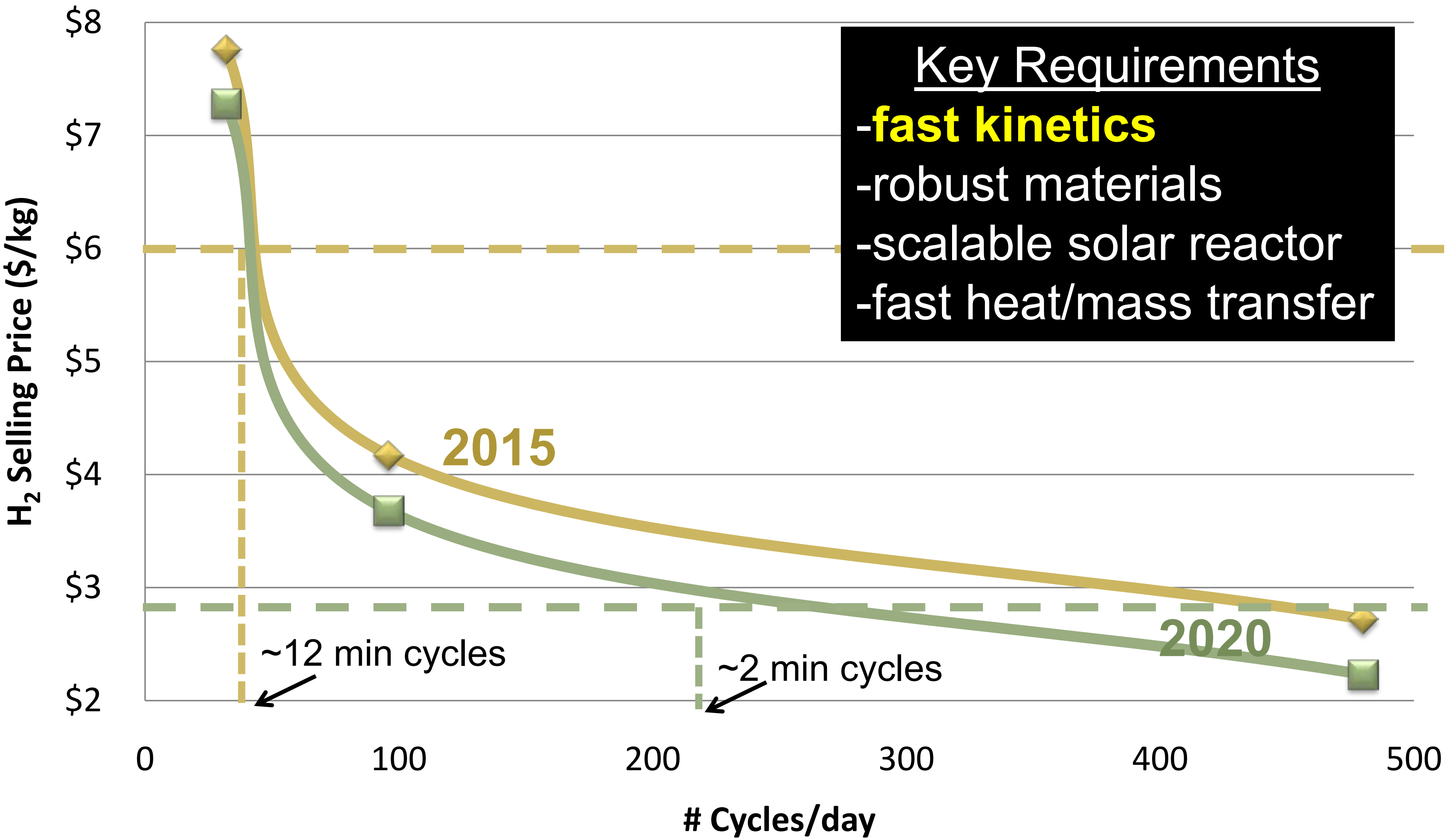
Results – Process Efficiencies

Source	Efficiency, η	Equation
Heliostat Field (Solar to Receiver)	40.2%	Soltrace
Thermal	51.7%	$\eta_{Thermal} = \frac{H_2 LHV}{Solar + e^-_{Consumed}}$
STCH	**20.8%**	$\eta_{STCH} = \frac{H_2 LHV}{Solar/\eta_{Field} + e^-_{Consumed}/\eta_{Offsite\ e-}}$

H2A Results – 100,000 kg H_2/day (central)



H2A Results – 100,000 kg H_2/day (central)

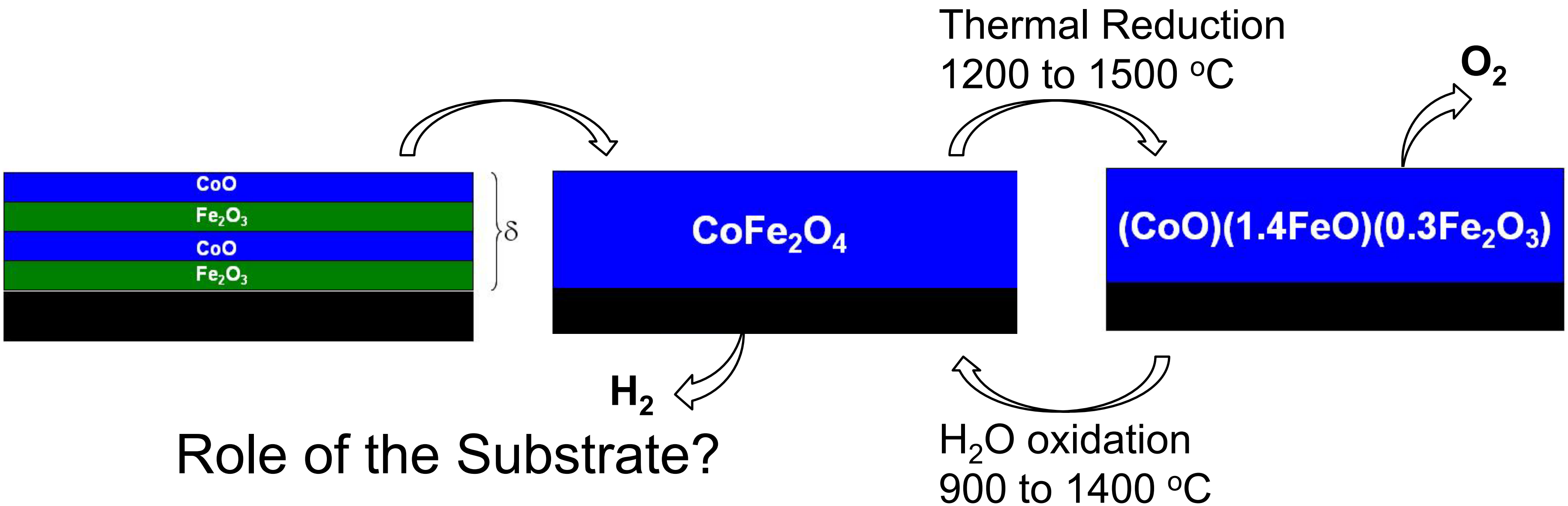


Key Requirements
- **fast kinetics**
- robust materials
- scalable solar reactor
- fast heat/mass transfer

Materials Design is Key

(reduce/eliminate diffusional resistances)

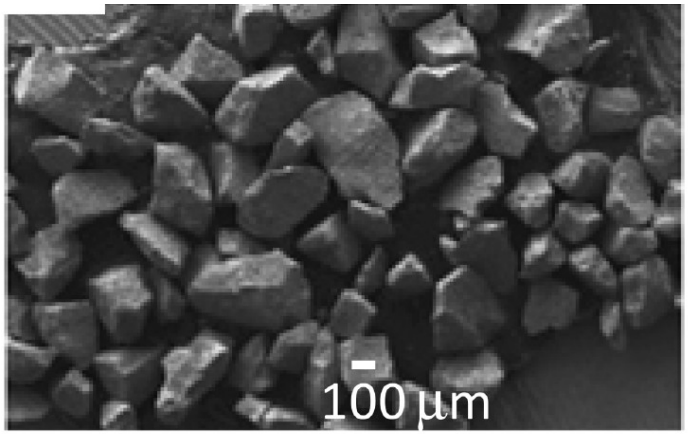
- Atomic layer deposition (ALD) provides an ideal platform to study this chemistry
- Deposition on high surface area supports
  - increase reactive surface area
  - vary surface area in a controlled manner
  - Vary substrate chemistry/morphology
- Control of film/layer thickness and stoichiometry



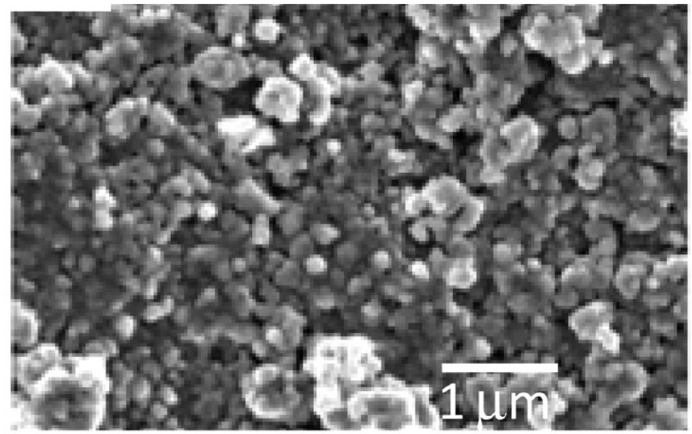
Role of the Substrate?

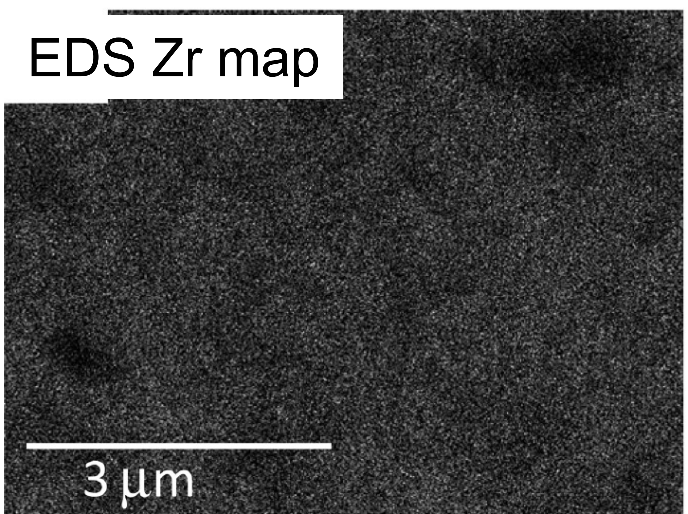
Support and EDS Mapping
($CoFe_2O_4$ thin ALD films)

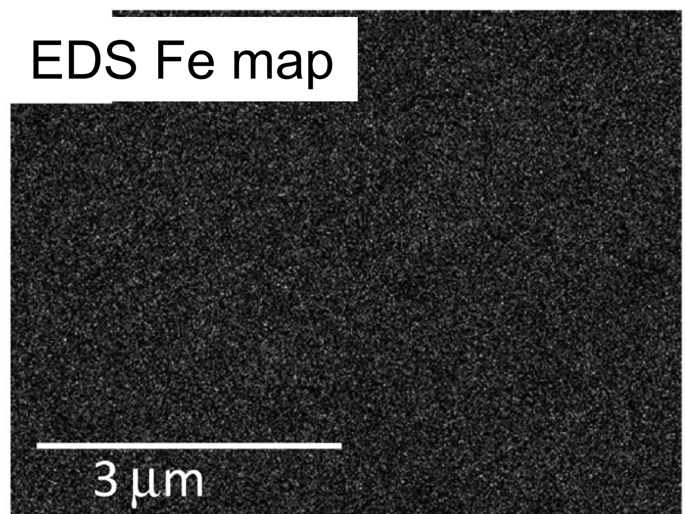
Low X bulk m-ZrO_2 Support



High X bulk m-ZrO_2 Support

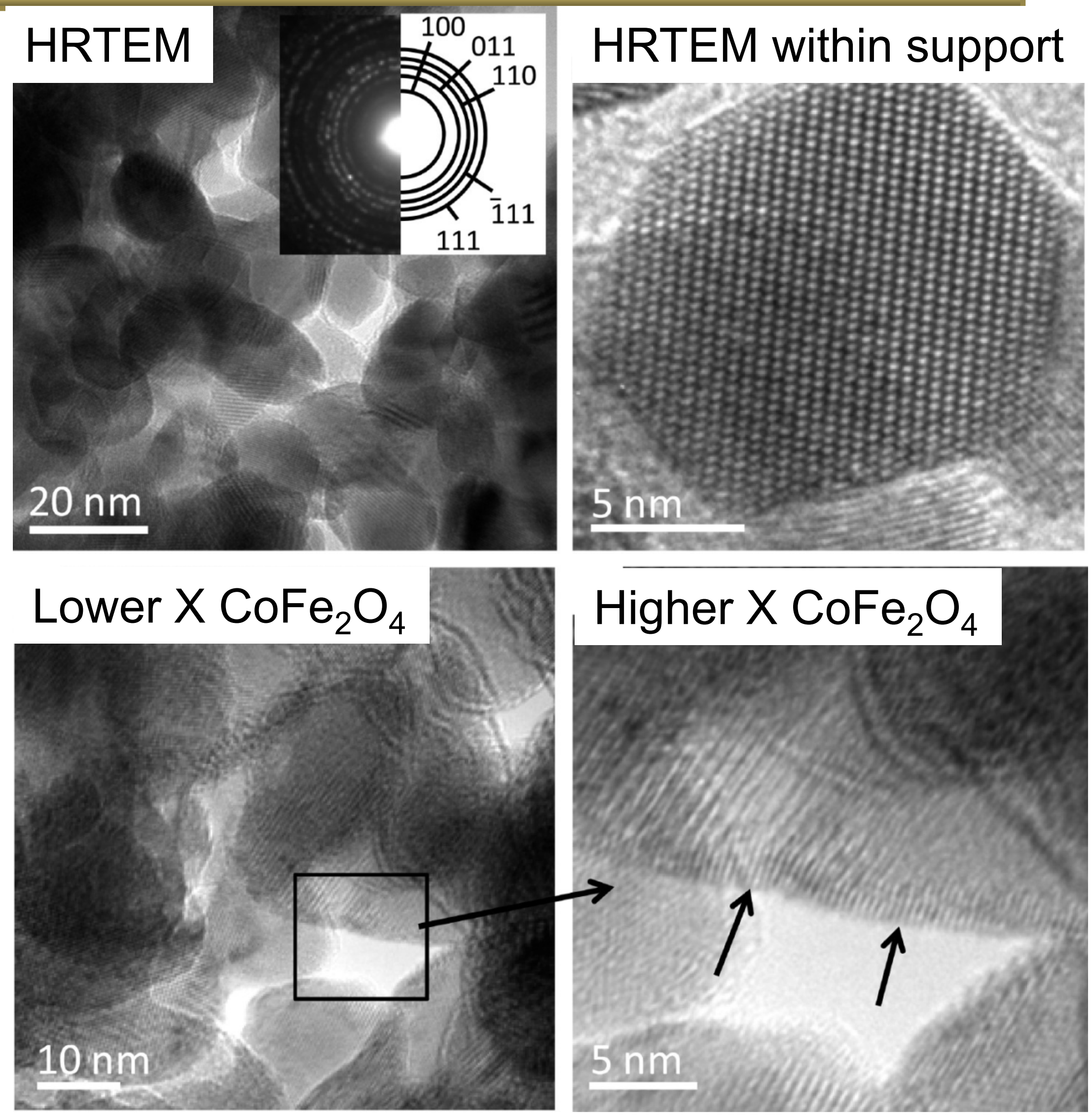






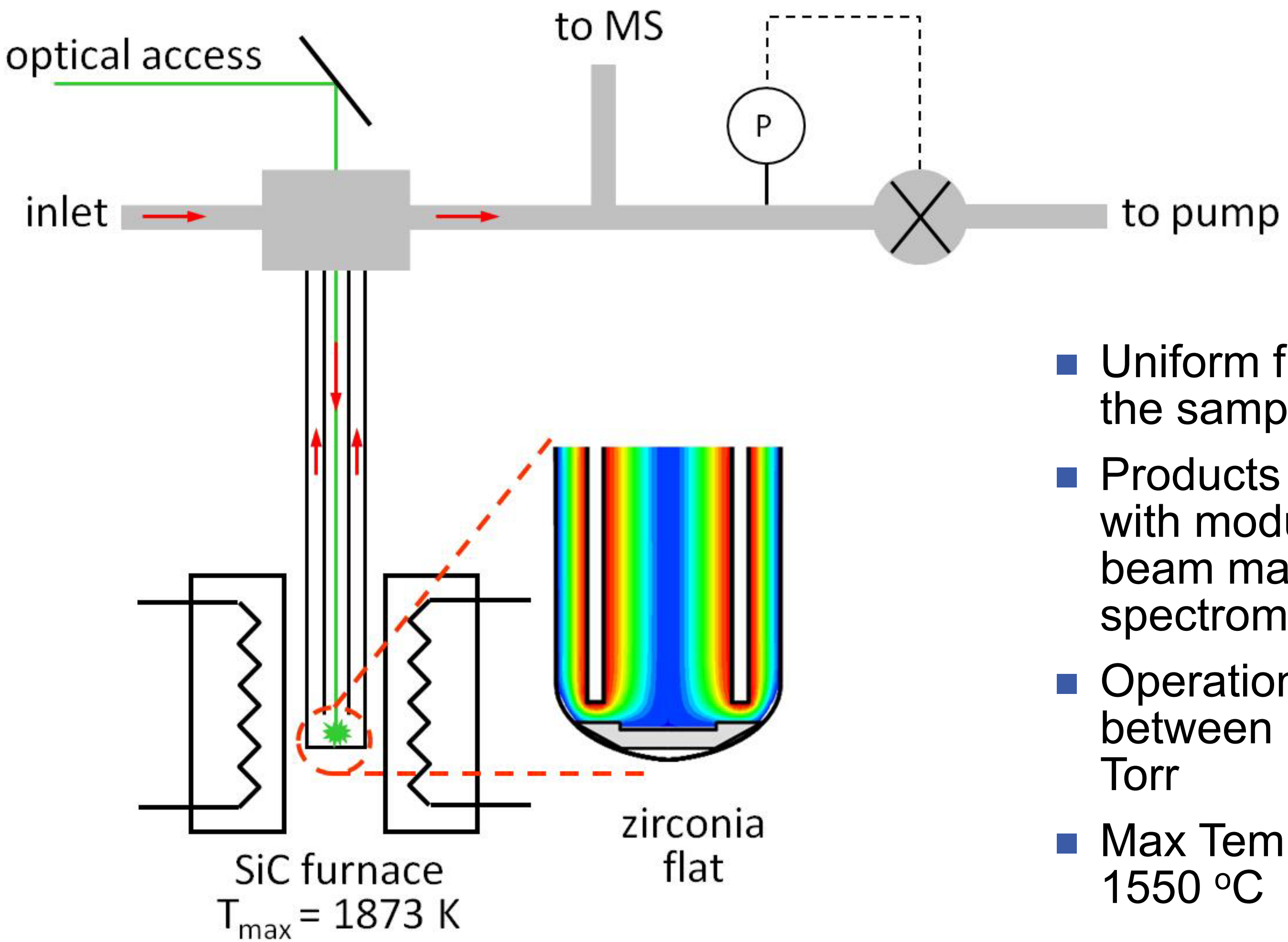
ALD $CoFe_2O_4$ on ZrO_2 Supports

- ZrO_2 support; 50 m^2/g as received
- 2 nm $CoFe_2O_4$ film via ALD
- Raman Spectra confirm $CoFe_2O_4$



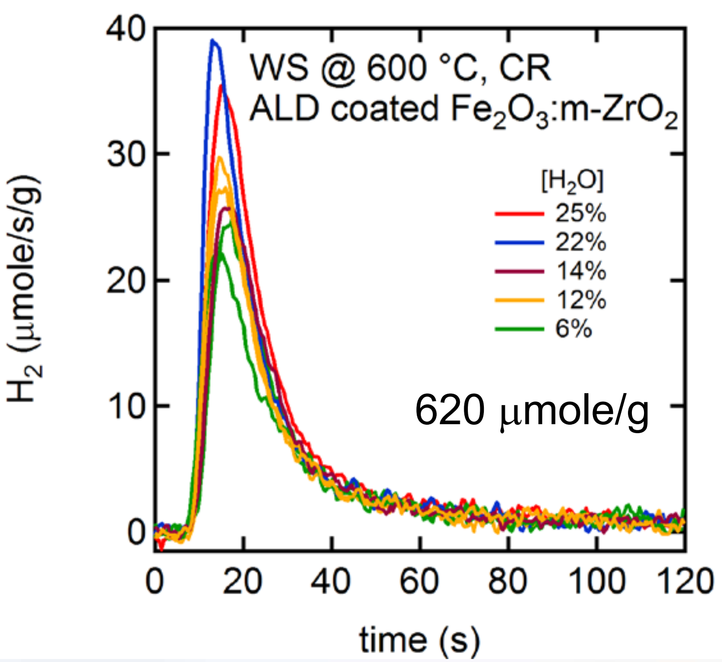
Scheffe, J.R. et al., in press, Chemistry of Materials (2011)

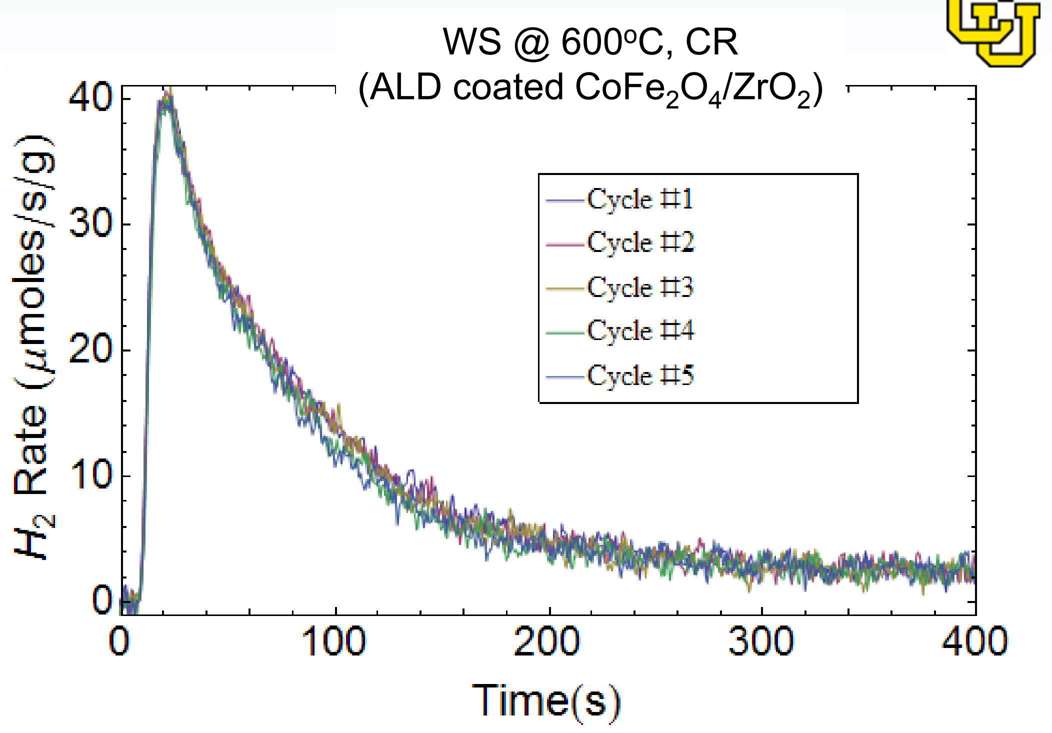
CO_2/H_2O Splitting in High Temperature Stagnation Flow Reactor



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

Thin Films Provide for Rapid Kinetics



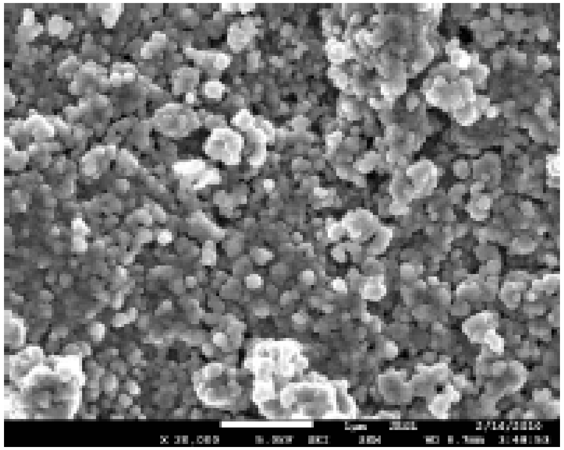


Peak H_2 Rate 40 μmol H_2/s/g in 20 s

- **50% conversion achieved in < 23 s for thin film**
  - High surface area, likely no oxide film diffusion limitation
  - No noticeable deactivation for ALD $CoFe_2O_4$ films/ZrO_2

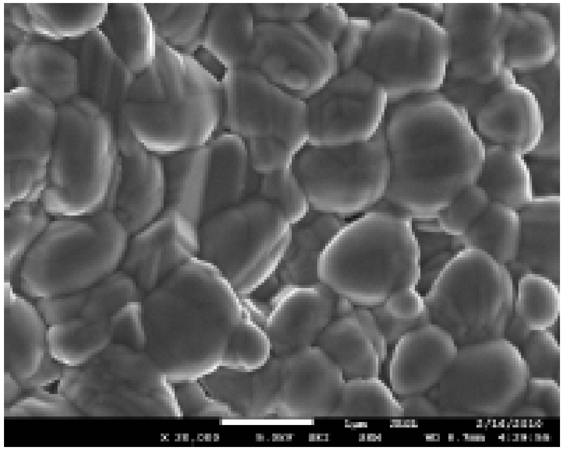
Sintering and Phase Segregation During High Temperature Cycling (1450°C reduction)

Grain Growth and Sintering



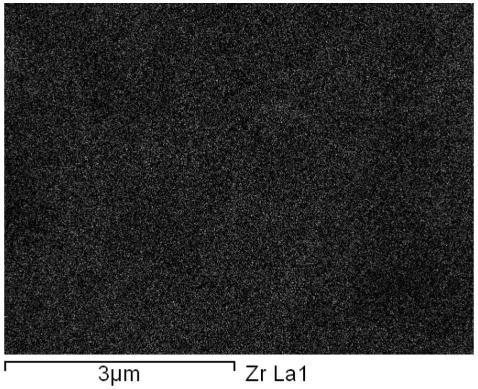
Pre-Processing

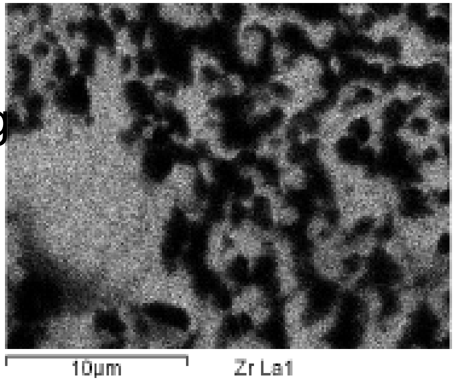
Post-Processing



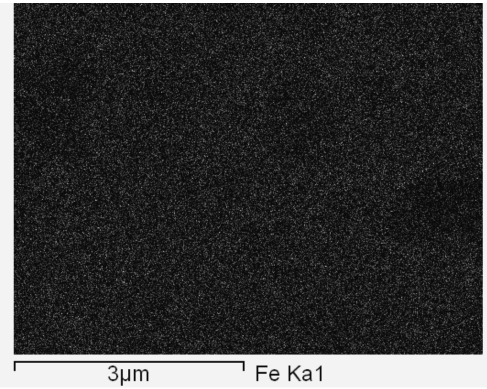
Phase Segregation

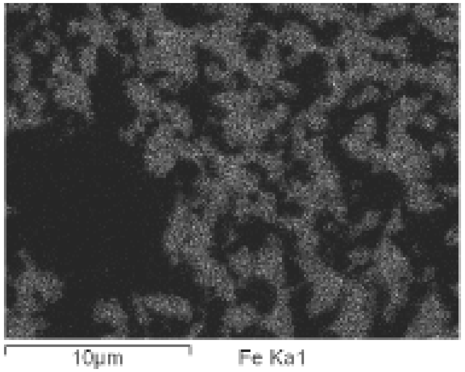
Zr





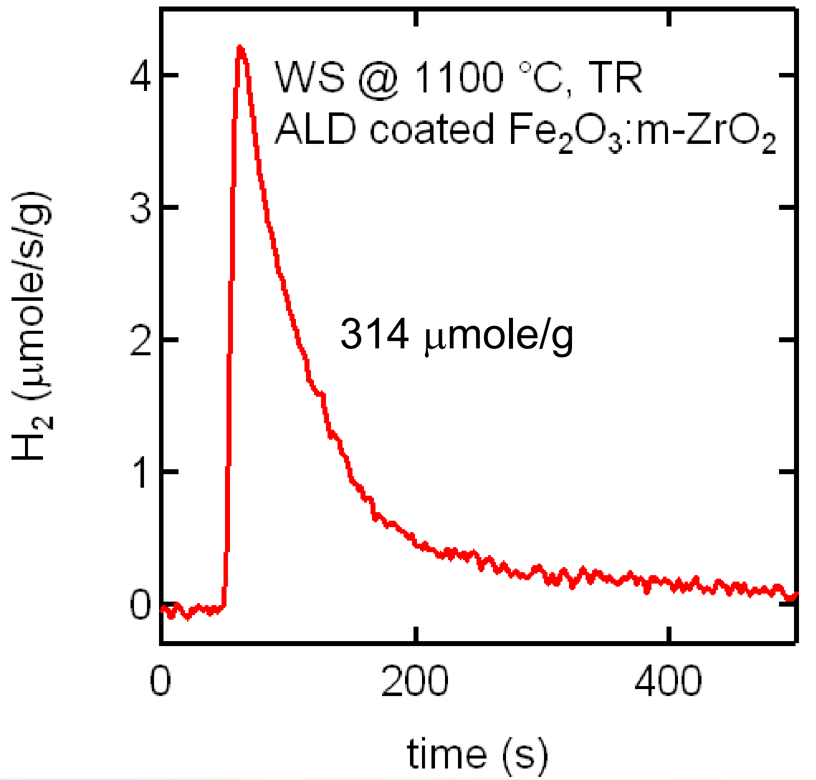
Fe



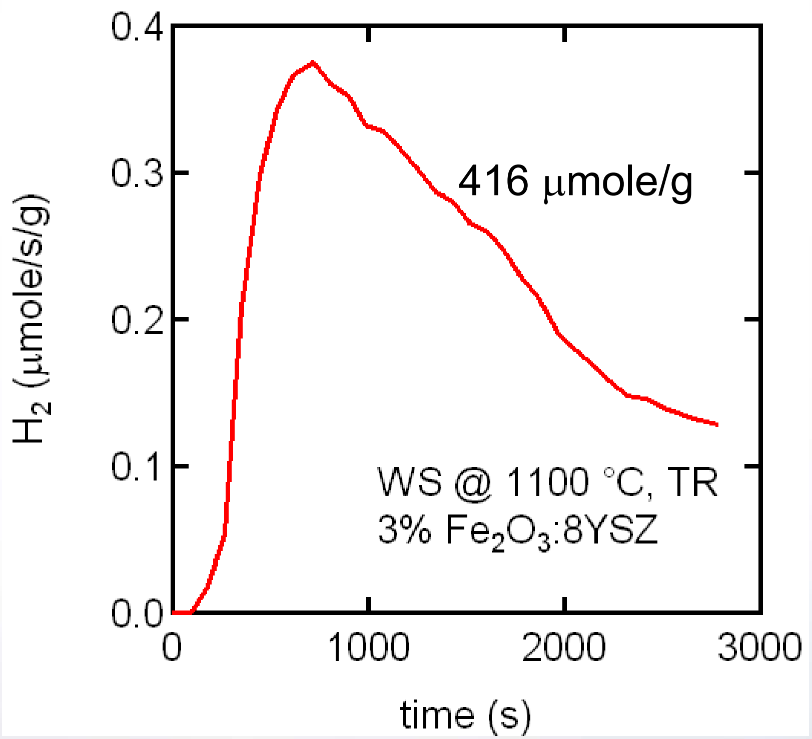


H_2O Oxidation Behavior Comparison

ALD Prepared Film



Co-precipitated
Bulk Prepared



- **Similar amount of H_2 produced by both structures/cycle.**
- **Peak rate analysis indicates differences between sintered ALD and co-precipitate composite structures.**
  - Greater peak H_2 production rate (~ 10 X) for sintered ALD film

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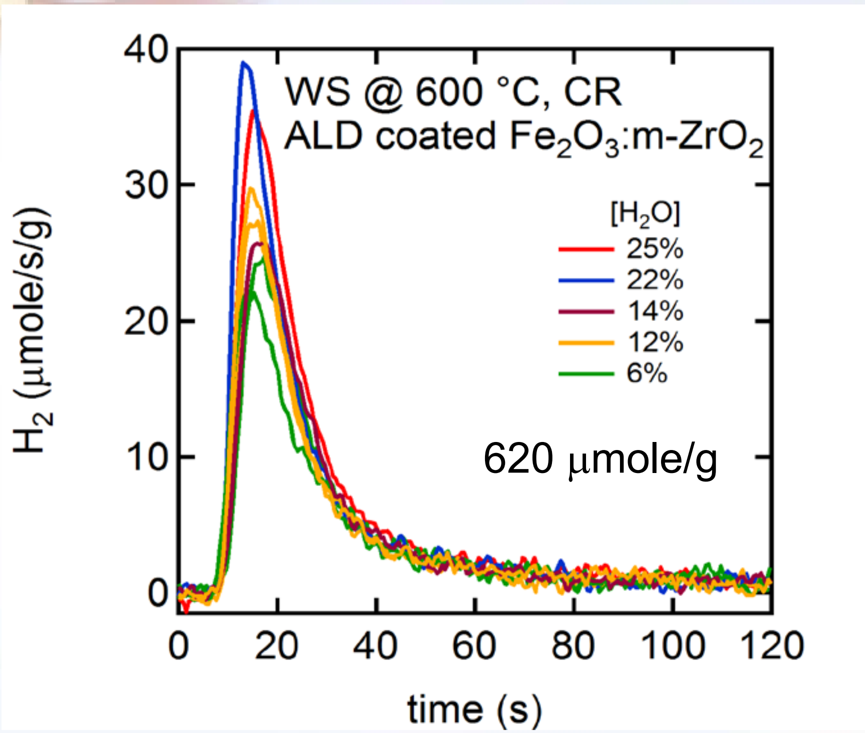
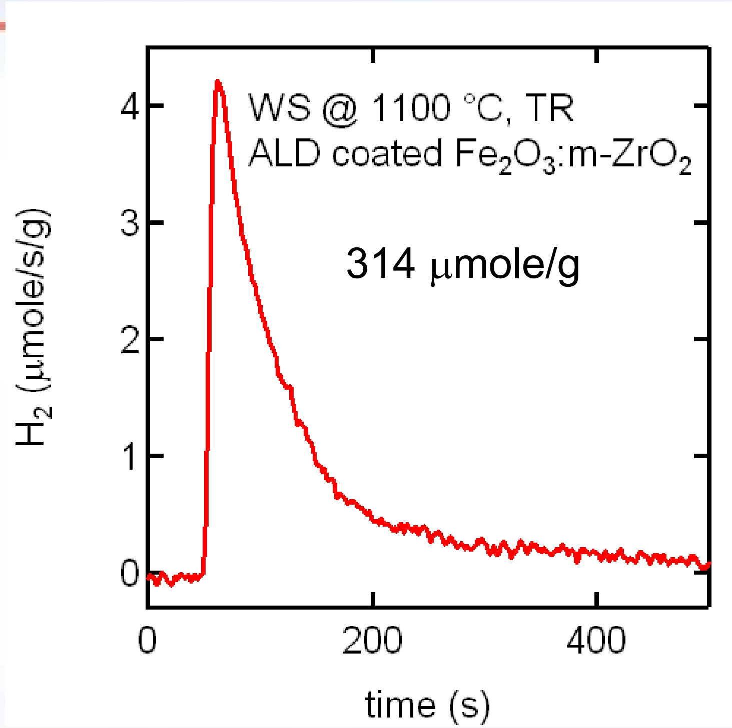
ALD Rate comparison – thin film vs. aggregates



Chemical Reduction
(thin films)



Thermal Reduction
(aggregates)

- **More H_2 produced using thin films/cycle (~ 2X)**
- **Peak rate analysis indicates differences between intact thin films and sintered ALD structures.**
  - Greater peak H_2 production rate (~ 10 X) for ALD thin film

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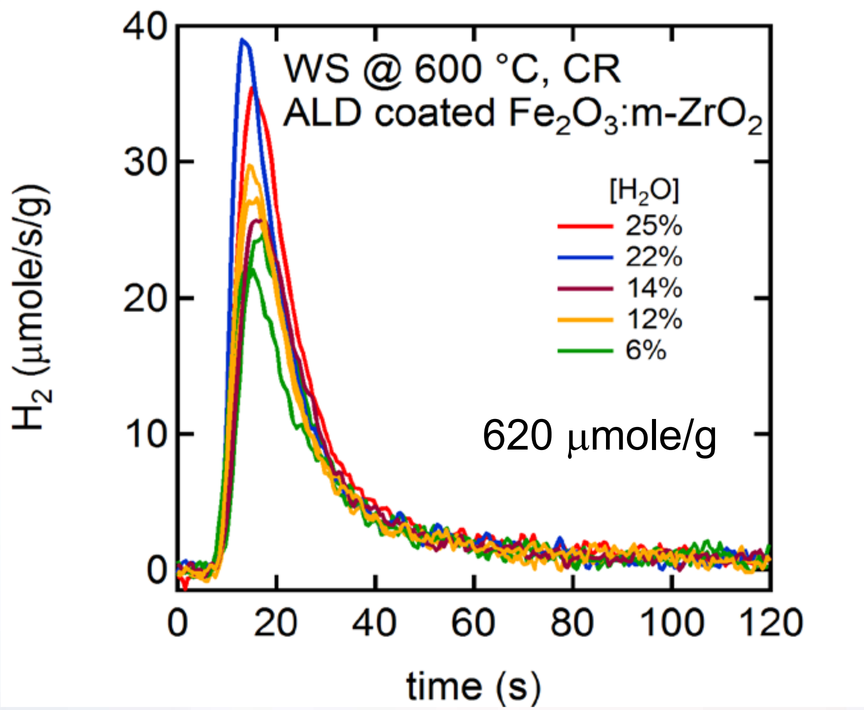
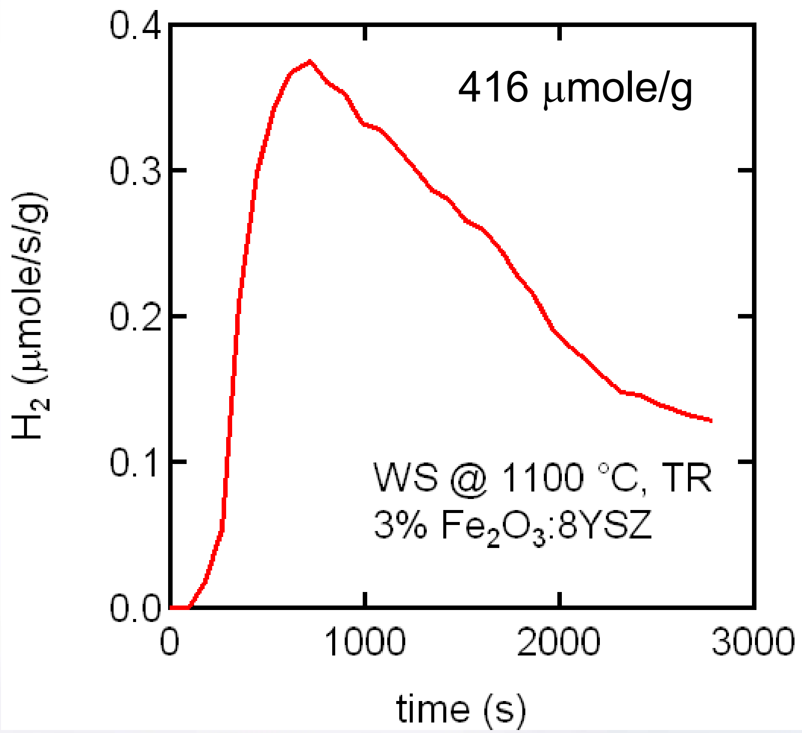
ALD Rate comparison – thin film vs. bulk prepared



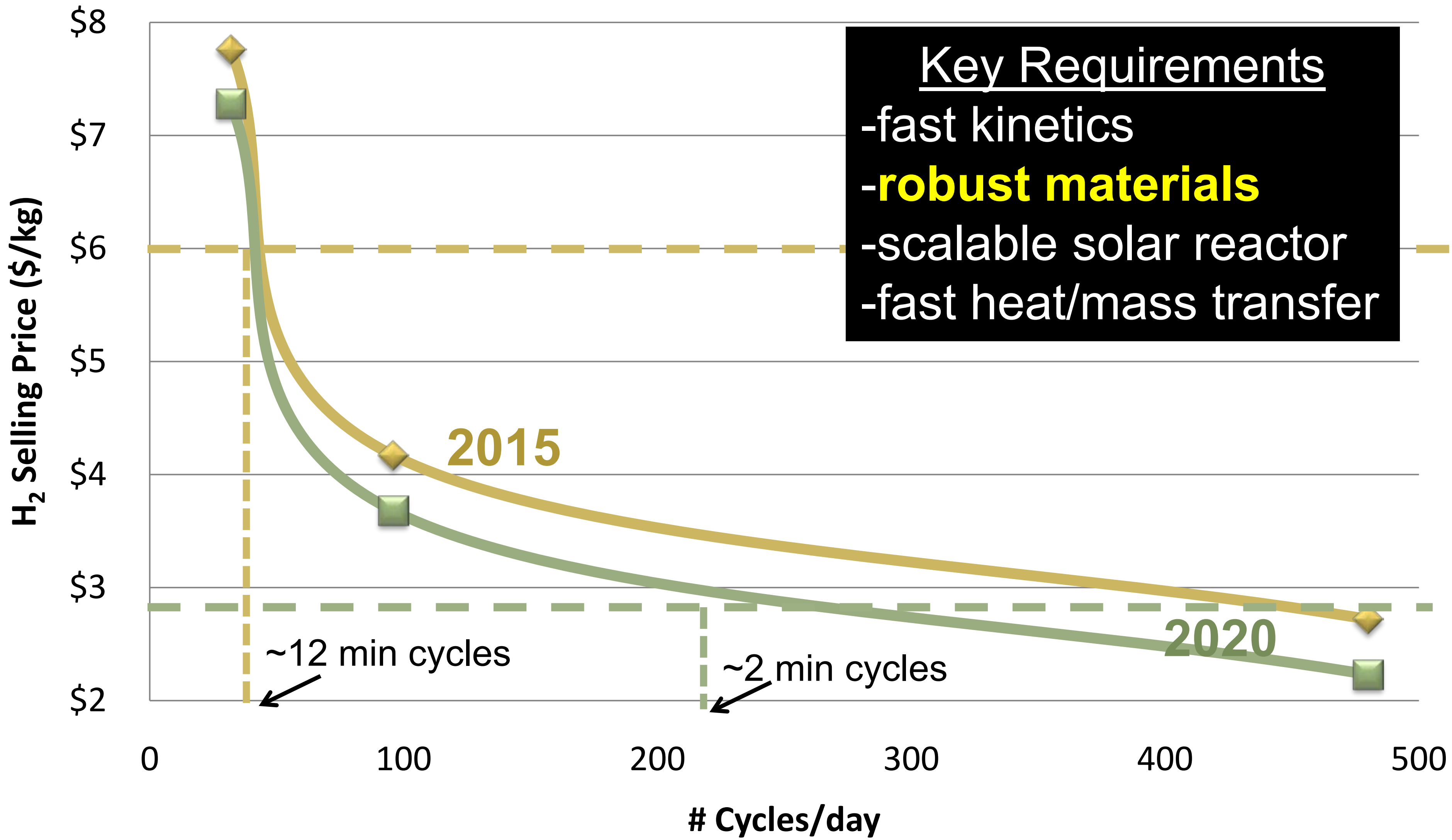


Chemical Reduction
(ALD thin film)

Thermal Reduction
(co-precipitated; bulk prepared)

- **ALD thin film peak production rate ~ 100X faster than bulk**

H2A Results – 100,000 kg H_2/day (central)

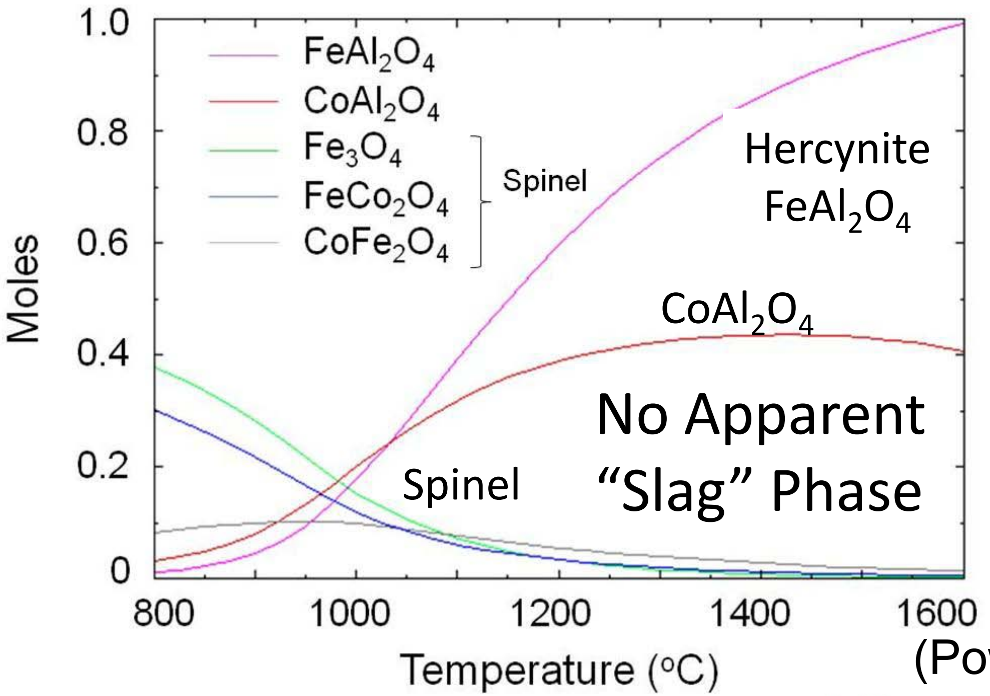


"Hercynite Cycle" Advantages

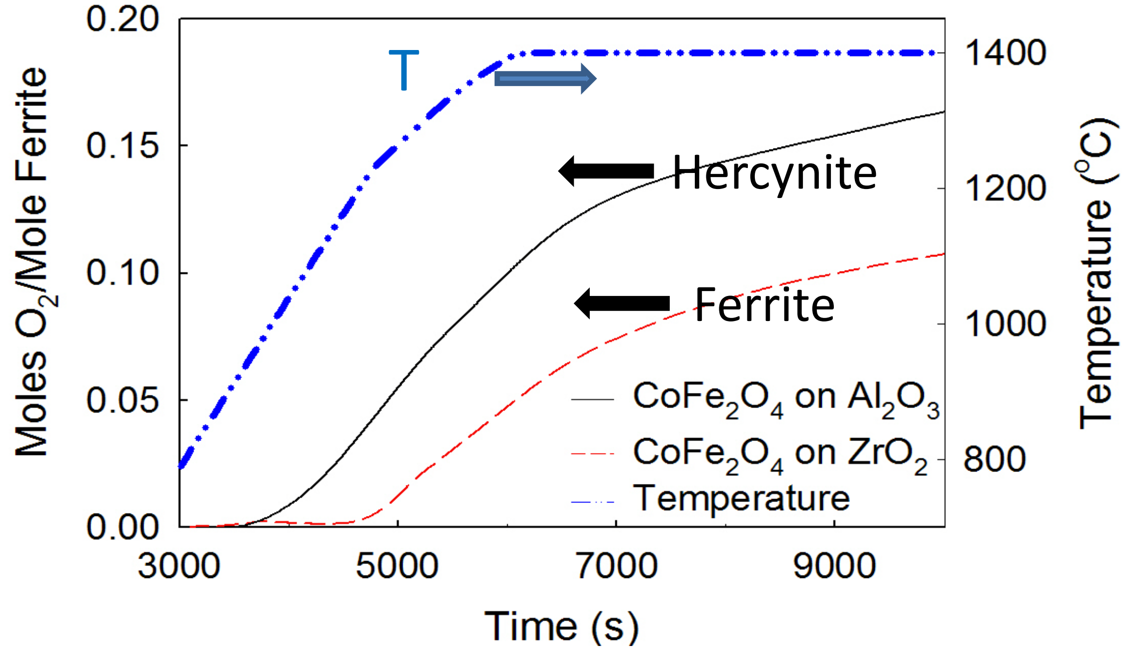
$$MFe_2O_4 + 3Al_2O_3 \rightarrow MAl_2O_4 + 2Fe_2AlO_4 + 1/2O_2$$

$$MAl_2O_4 + 2Fe_2AlO_4 + H_2O \rightarrow MFe_2O_4 + 3Al_2O_3 + H_2$$

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



(Powder XRD Confirms "Hercynite")



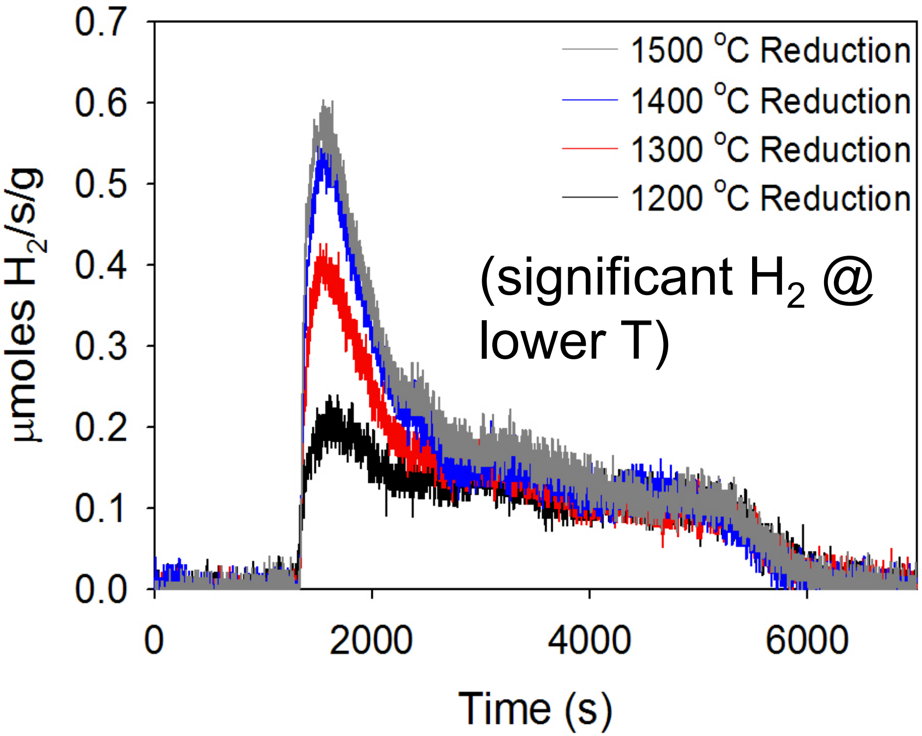
<u>~ 250°C Lower T Reduction</u>

Hercynite: 940°C

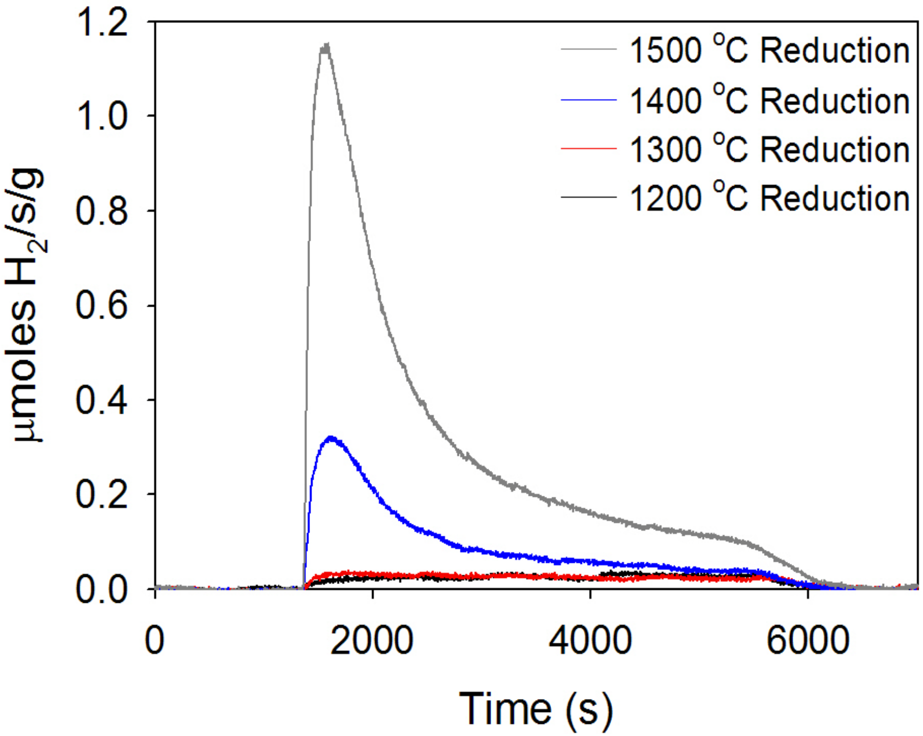
Ferrite: 1190°C

“Hercynite” vs. Ferrite Cycle H_2 Production (oxidation @1000ºC)

$CoFe_2O_4/Al_2O_3$ (“hercynite cycle”)

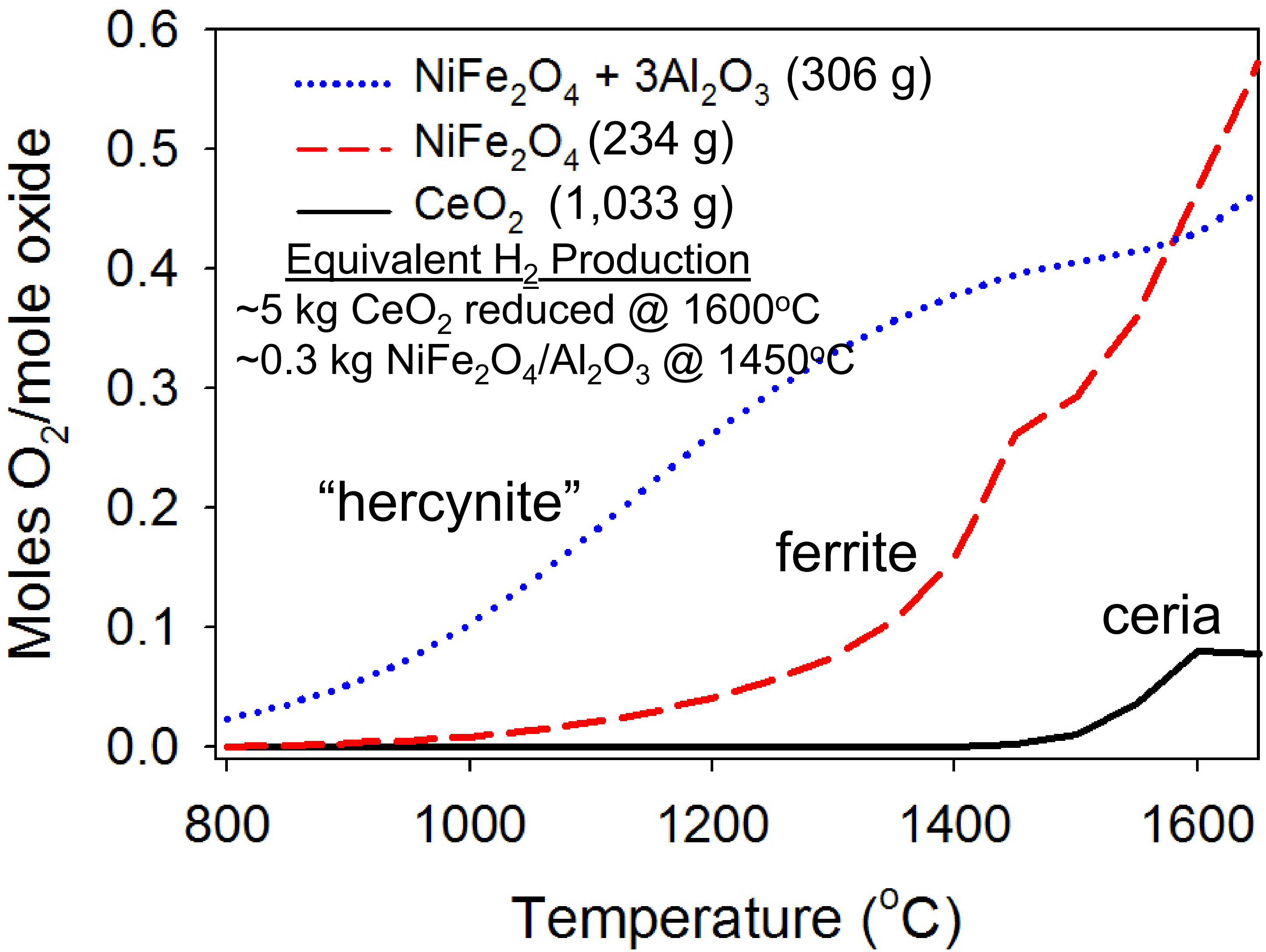


$CoFe_2O_4/ZrO_2$ (conventional ferrite cycle)

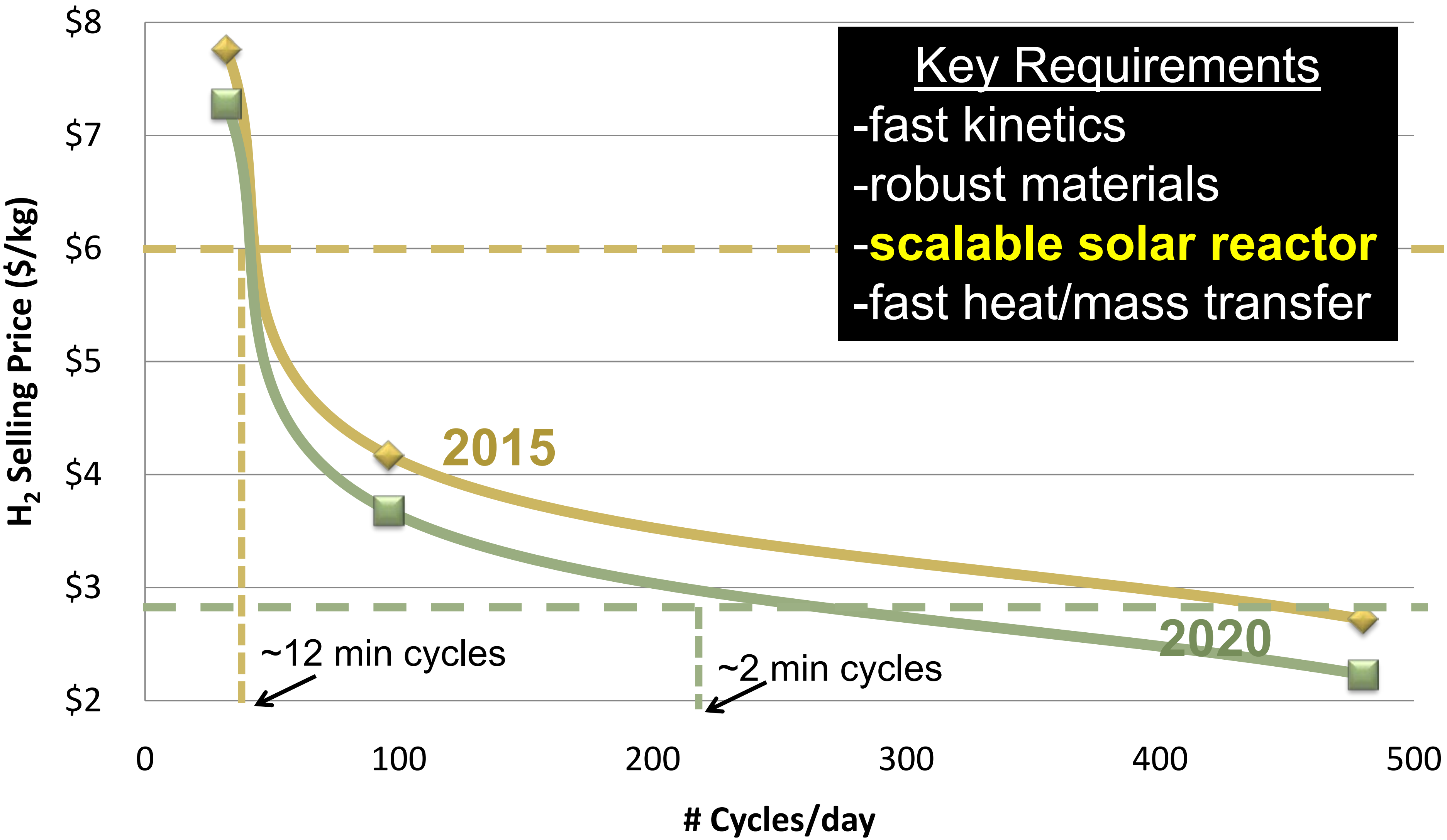


Scheffe, J.R. et al., Int. J. of H_2 Energy, 33, 3330-3340 (2010)

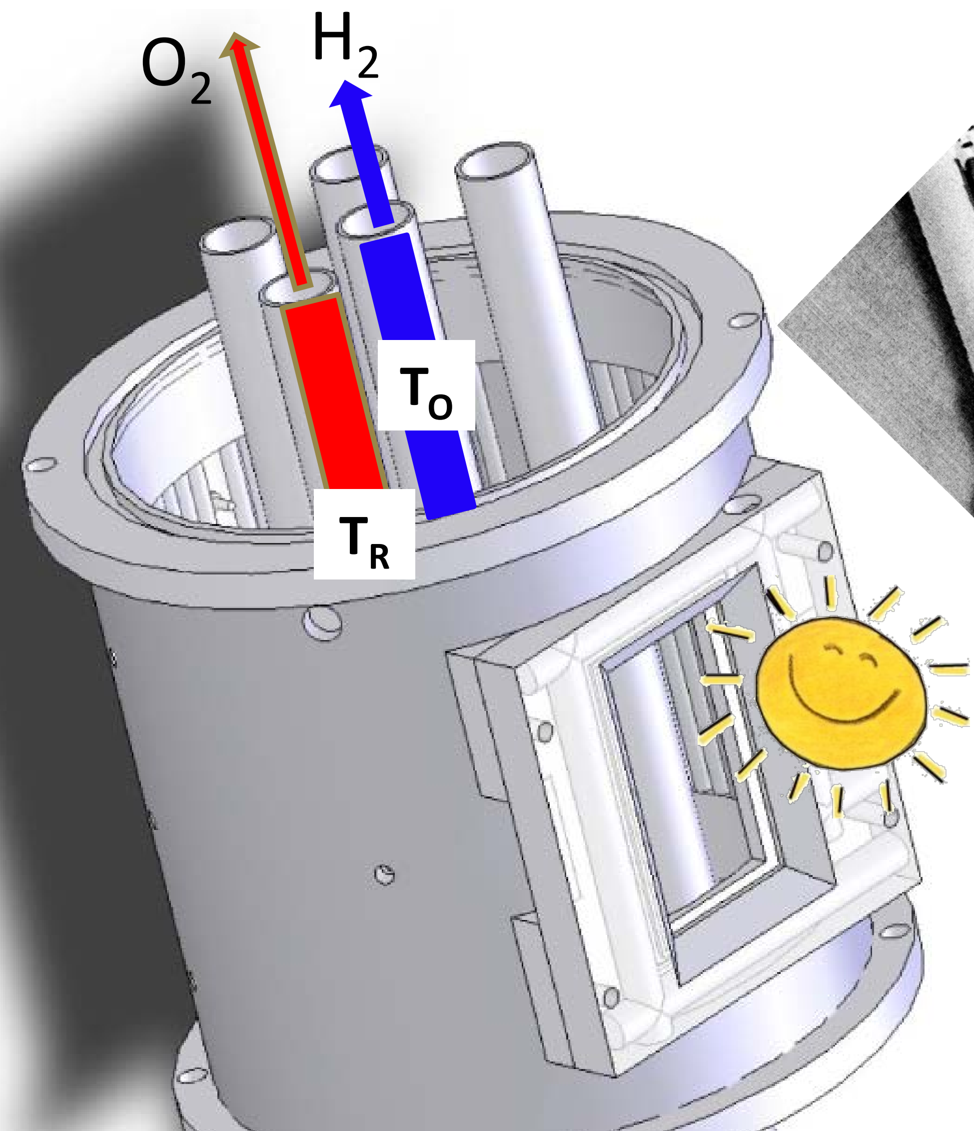
Comparative Reduction Step FACTSage™ Free Energy Minimization

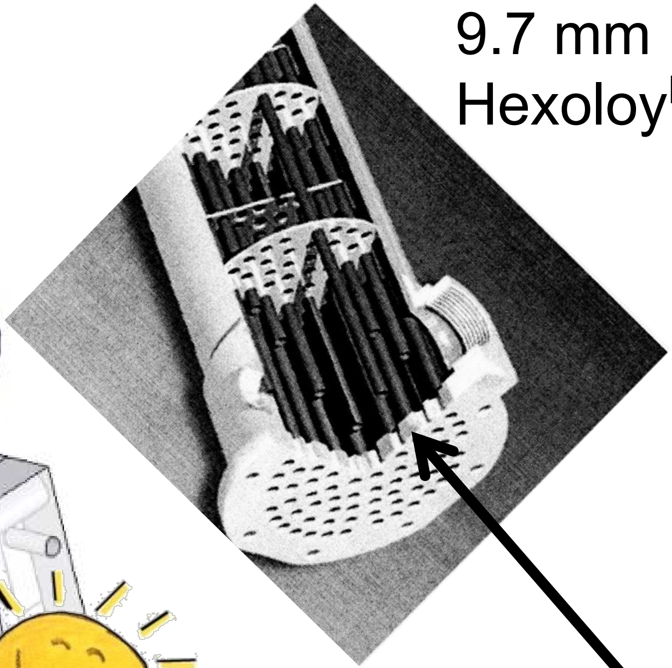


H2A Results – 100,000 kg H_2/day (central)



Multi-tube Cavity/Receiver Reactor

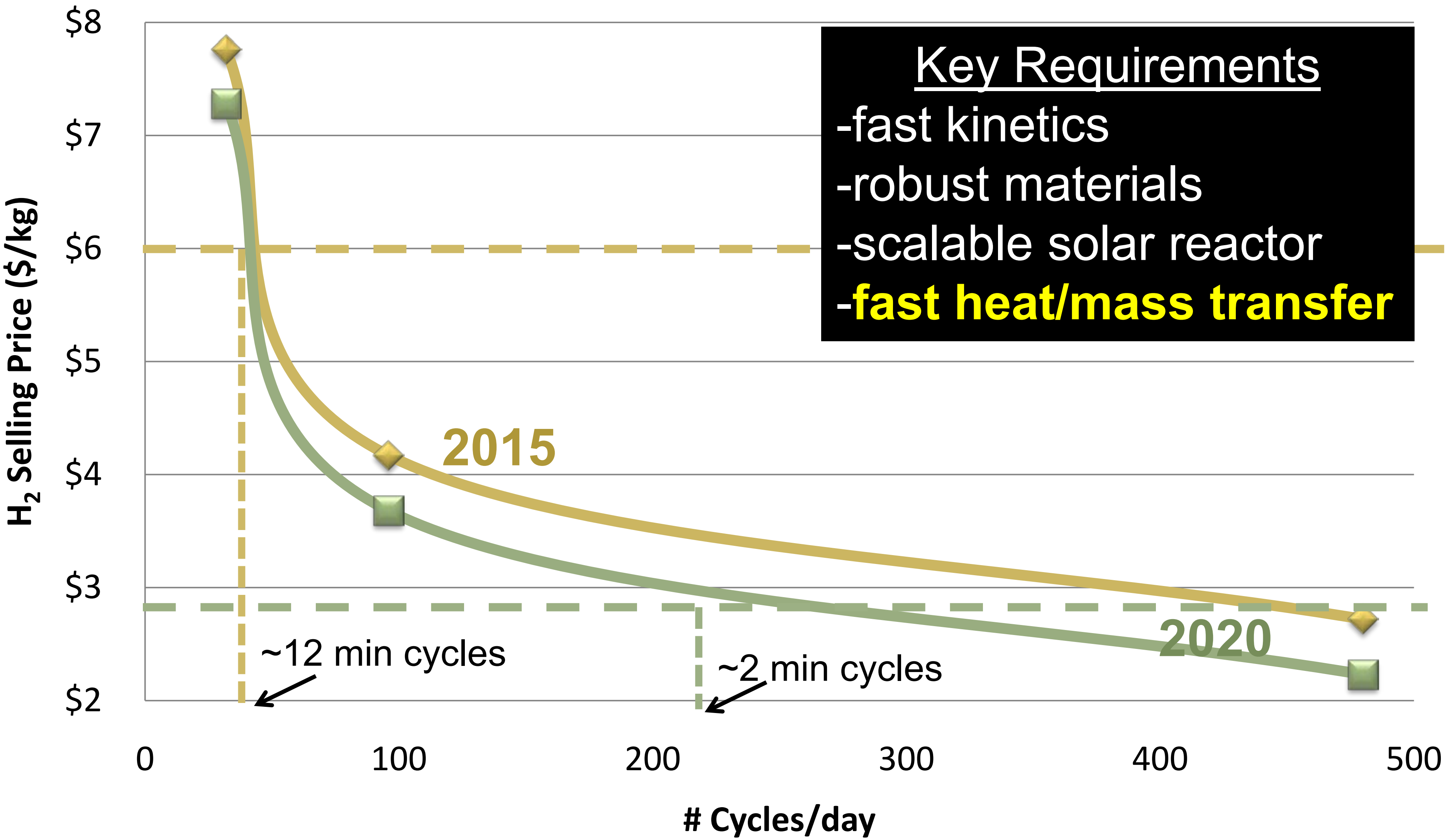




9.7 mm ID x 12.7 mm OD
HexoloyÈ SiC tubes

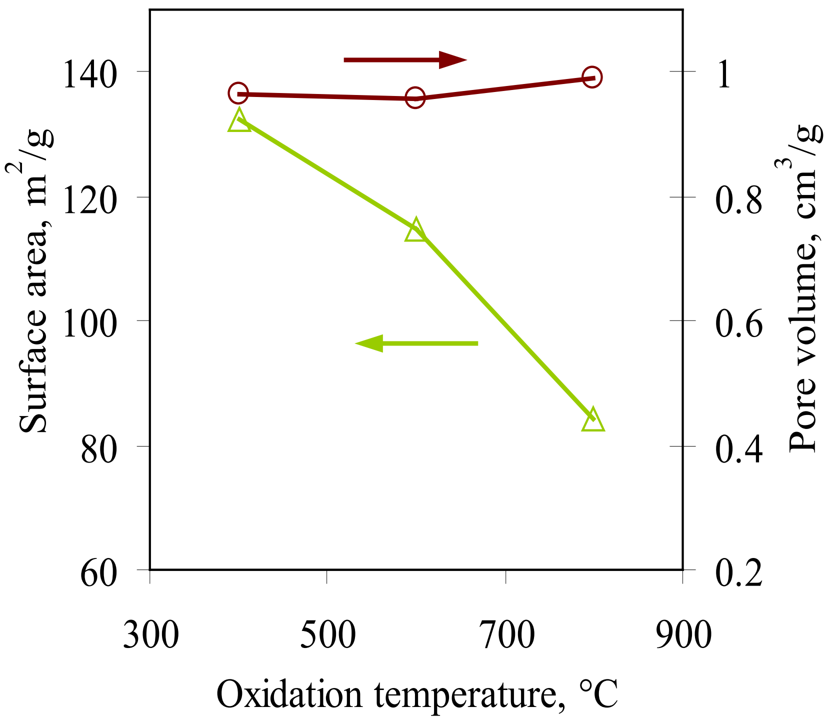
Active ferrite/"hercynite" cycle materials packed in small diameter SiC tubes in bundles

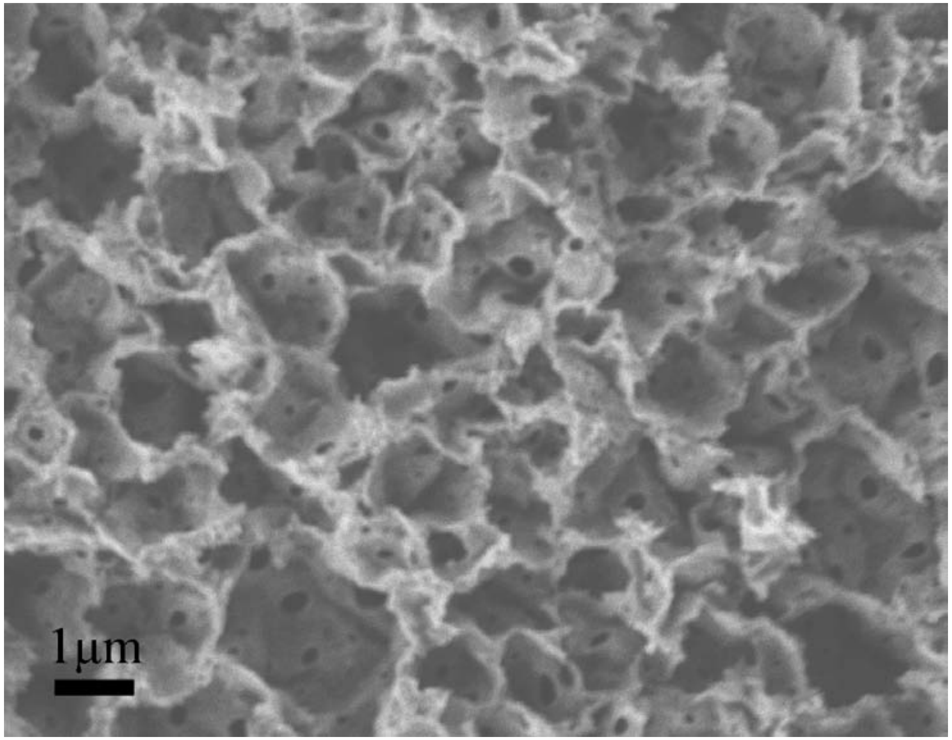
H2A Results – 100,000 kg H_2/day (central)



Novel Skeletal Al_2O_3 Support Material (promotes heat/mass transfer)

- Large Pore Volume
- Large Pores
- Easily Controlled High Surface Area > 100m^2/g

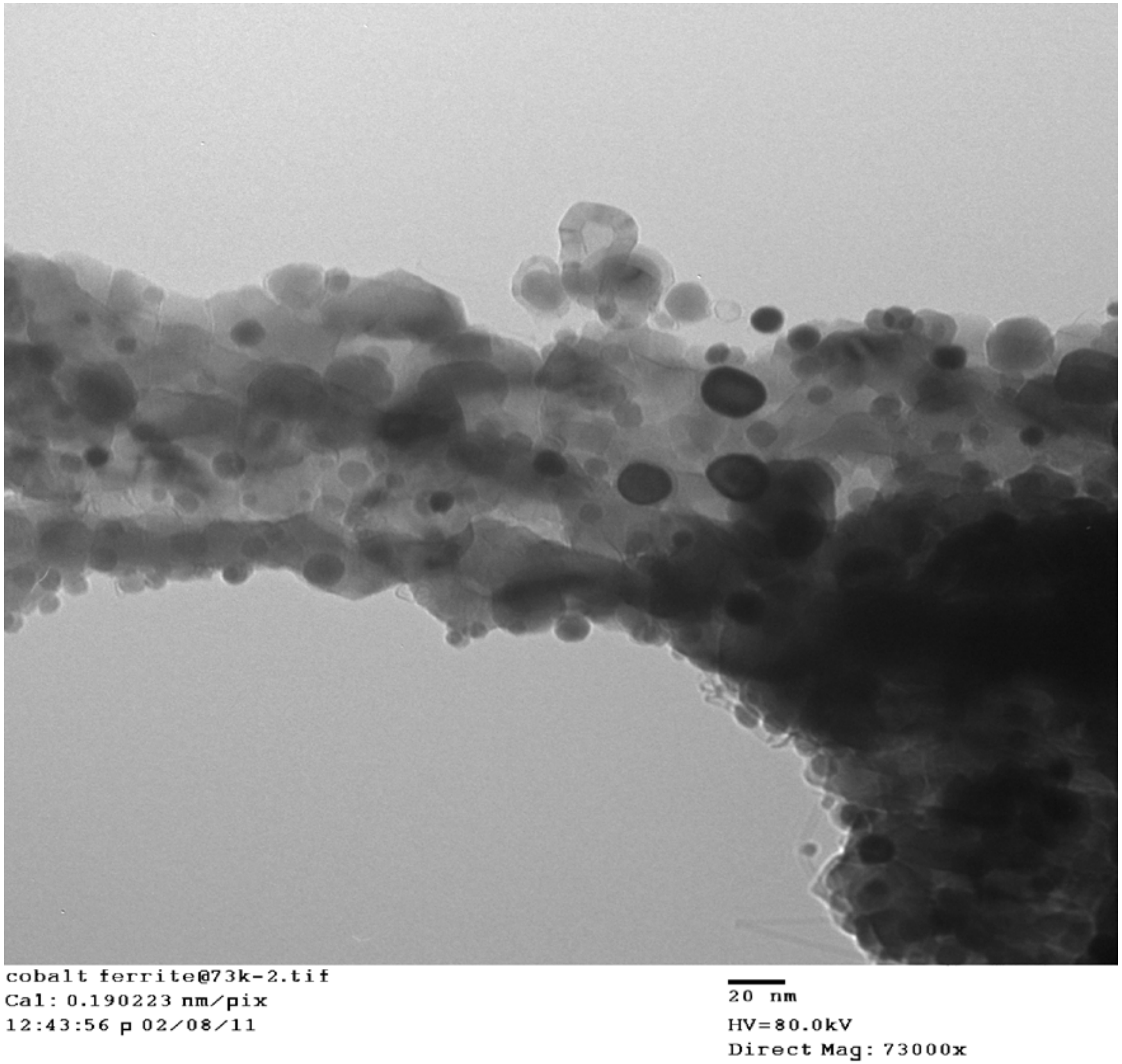




Cross sectioned surface of alumina support material

ALD $CoFe_2O_4$ Film on Skeletal Al_2O_3

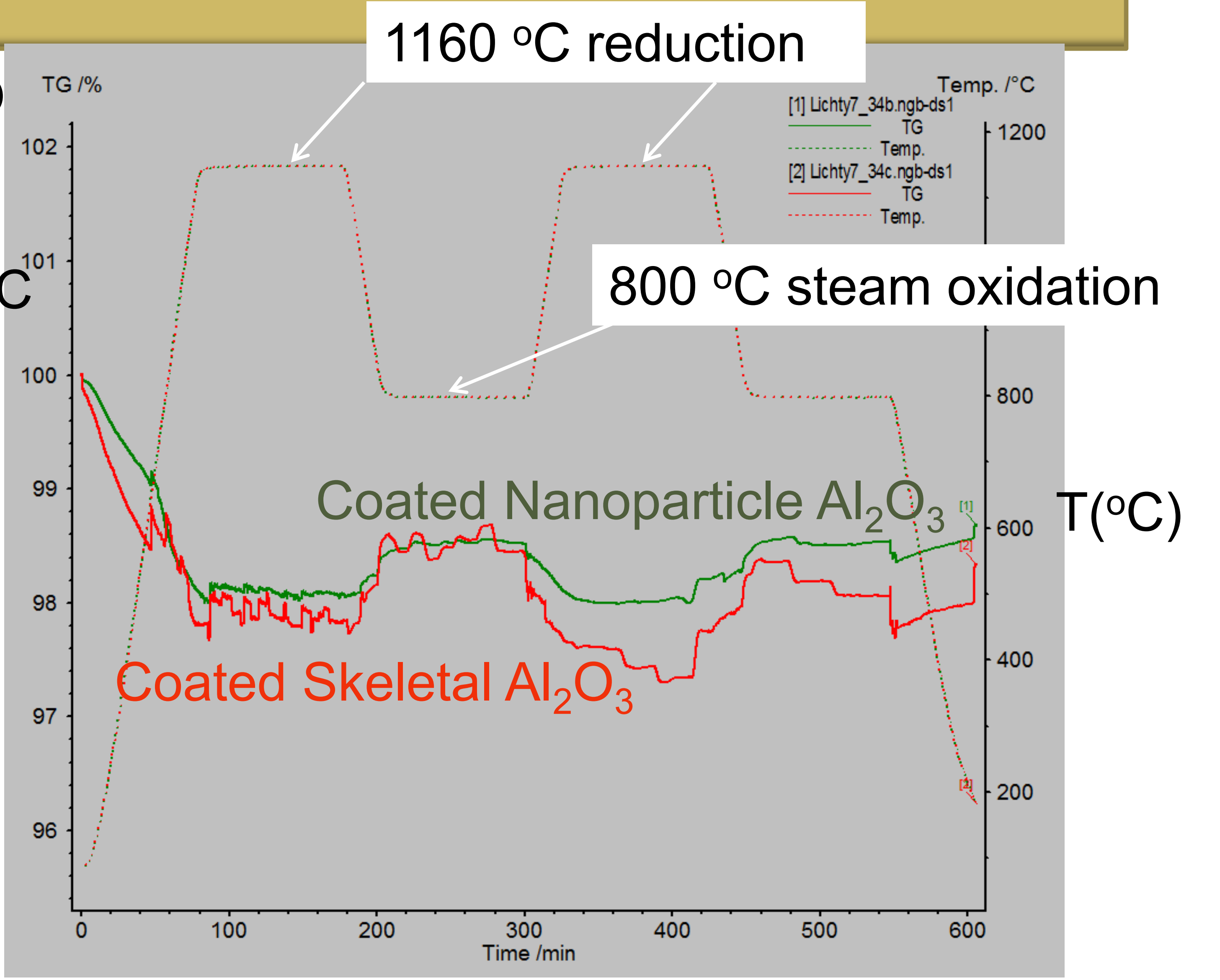
~ 20 wt% ferrite



H_2O Splitting w/Skeletal Al_2O_3

"Hercynite" H_2O splitting cycle demonstrated w/ 1160°C/800°C redox cycle!

Metal alloys may potentially be used for structural containment!



Address Identified Weakness

Weakness Identified –

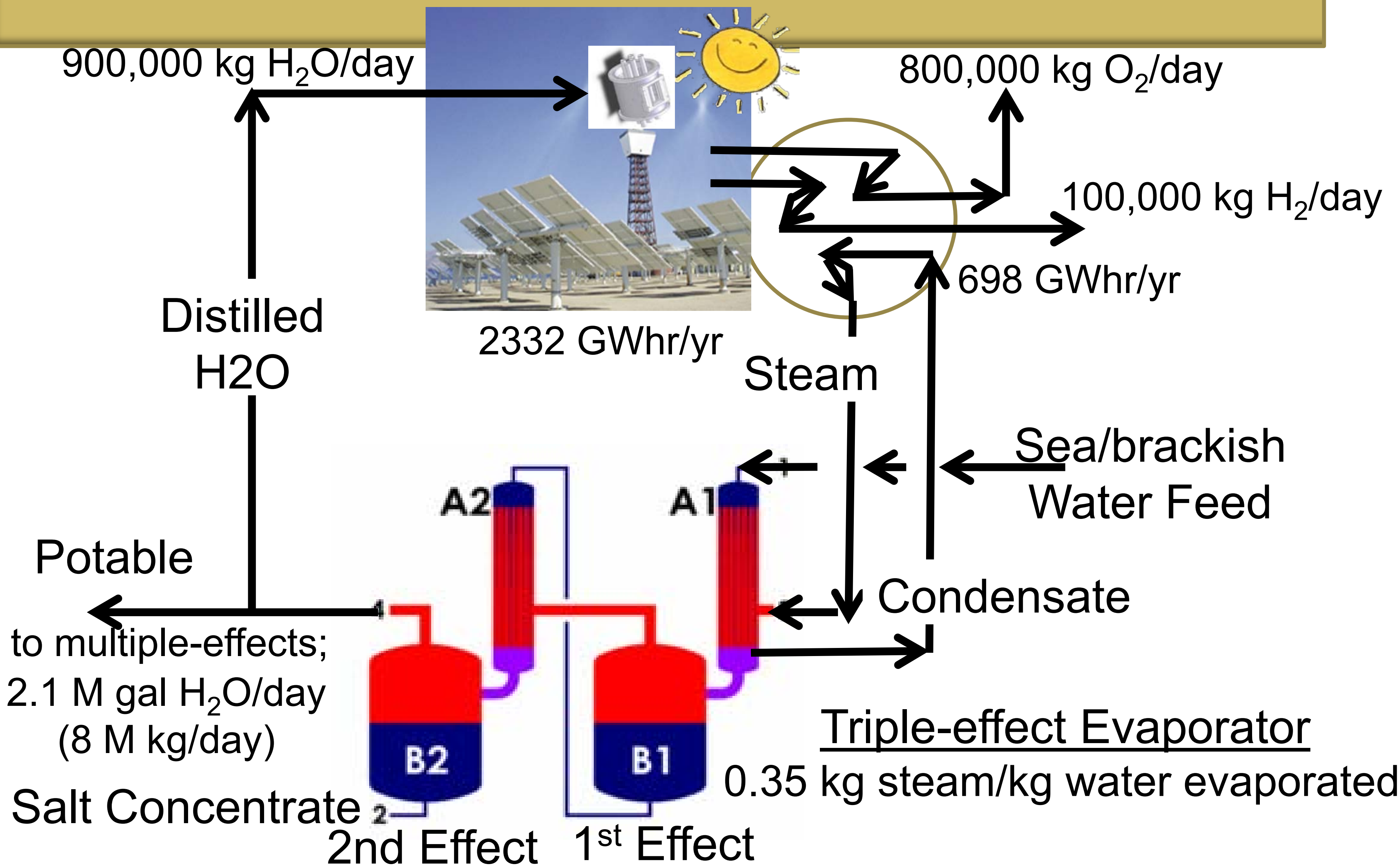
"There is a sense that this project is not likely to produce a practical option for hydrogen generation"

Weakness Addressed

- H2A economics indicates that the thin film ferrite cycle is projected to achieve both the 2015 and 2020 base case assumption H2A targets – per TIAX review
- The team has demonstrated that H_2 can be produced with reduction $T < 1200^{o}C$ using the "hercynite"cycle - having a stable solid intermediate, opening the door to a potentially efficient and robust process using metal alloy containment materials

Hybrid Solarthermal Process

Renewable H_2 & Desalinated H_2O



Opportunity

- An opportunity exists for widespread application in the Mohave Desert where a hybrid process produces renewable H_2 via water splitting with a multiple-effect evaporator process producing distilled/potable water from sea water – interfaced for efficient heat integration
  - Pathway to renewable H_2
  - Pathway to reduced GHGs
  - Pathway to potable H_2O supplies

Major Accomplishments since May, 2010

- Demonstrated synthesis of skeletal Al_2O_3 substrate, subsequent ferrite ALD nanocoating and "hercynite" thermochemical cycling to split water at 1160^{o}C,
- H2A analysis independently reviewed by TIAX, the DOE contractor for these comparative assessments,
- In the process of constructing an automated system to carry out continuous redox cycling

Summary/Future Work

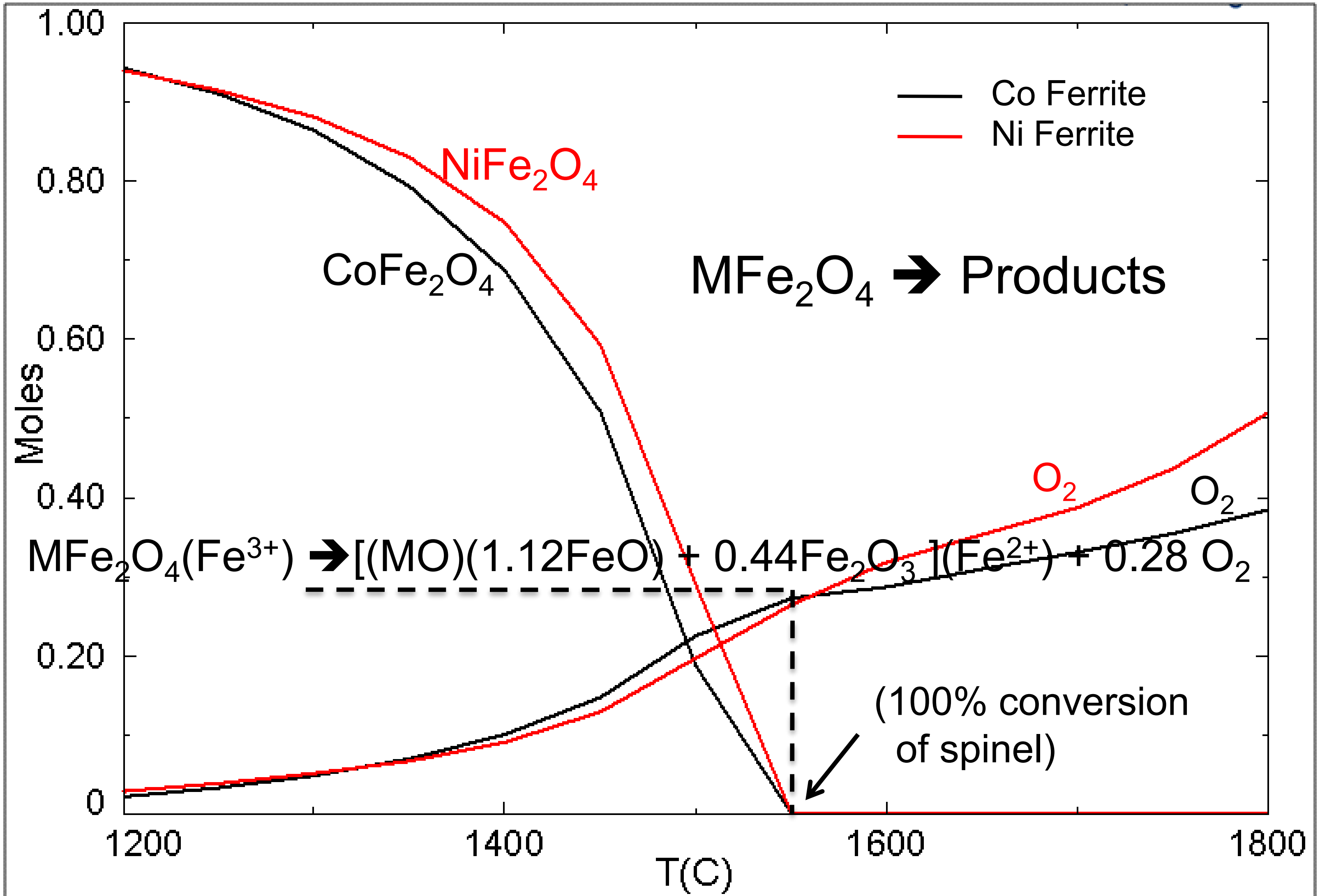
- ALD materials remain active for up to 30 water spitting cycles with no sign of deactivation after initial aggregation
- ALD thin films are ~ 100X more active than conventionally produced bulk ferrites
- “Hercynite” route potentially has significant advantages in terms of reduced reduction temperature and larger operating window
- H2A economics assessment by outside reviewer indicates a positive outcome if technology can be demonstrated
- Key is materials maintaining thin active layer supporting fast redox cycling; focus is materials development and demonstrated stability
- Will demonstrate the “hercynite cycle” in one reaction tube on-sun at the NREL HFSF

Acknowledgements

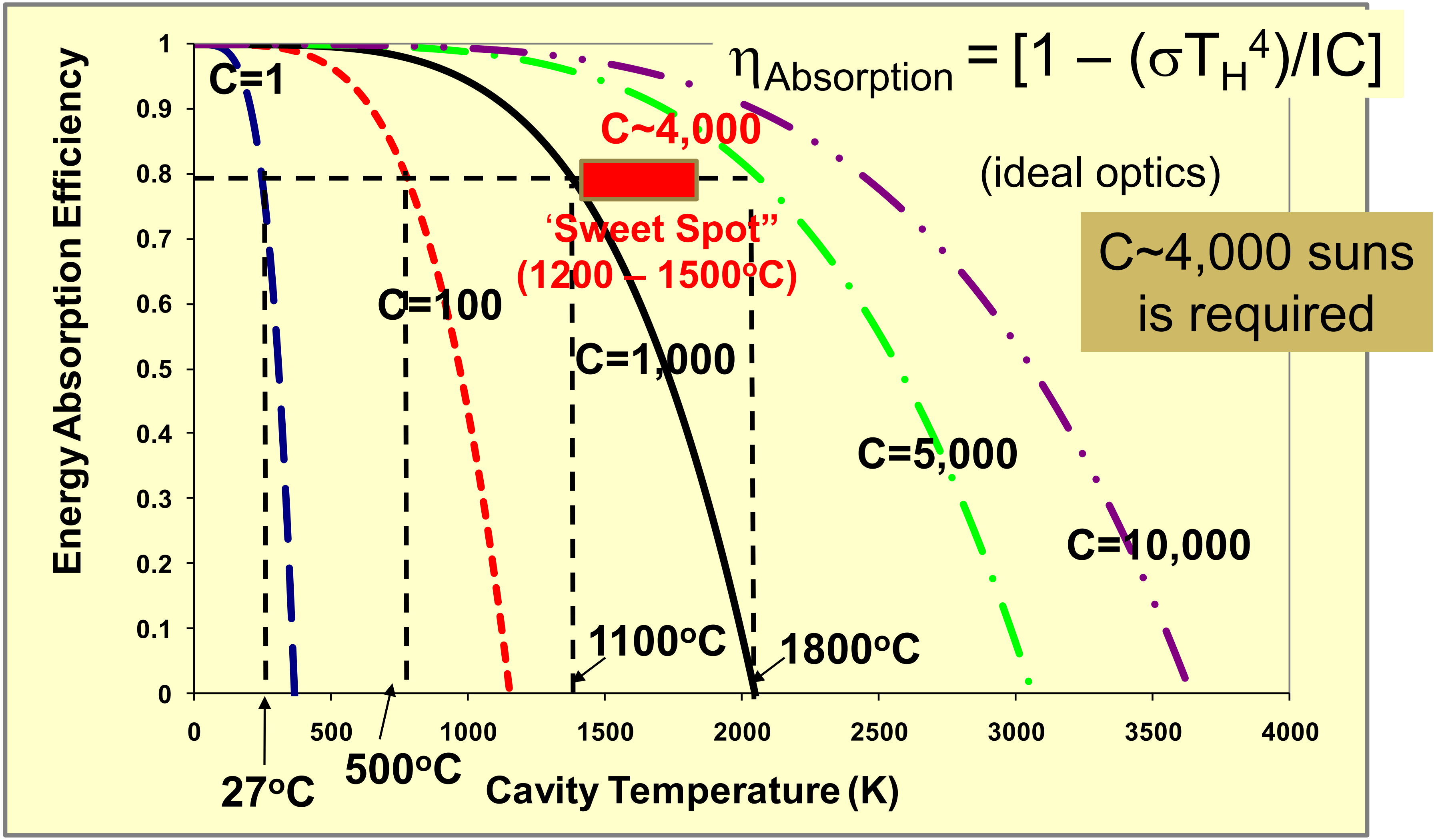
7 Peer-reviewed Scientific Papers (2010/2011)
2 U.S. Patent Filings (2010)

Supplemental Slides

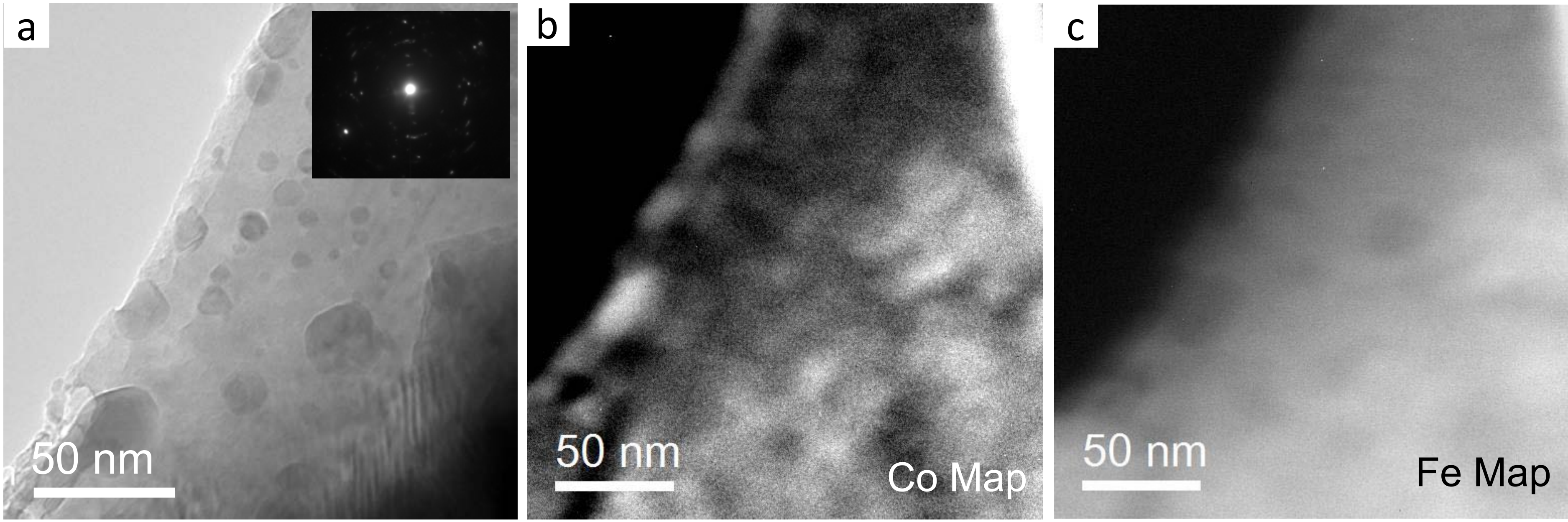
Approach - Free Energy Minimization Theoretical Limit (P = 0.001 MPa)



Operating “Sweet Spot”



ALD $CoFe_2O_4$ /ZrO2 Thermally Reduced



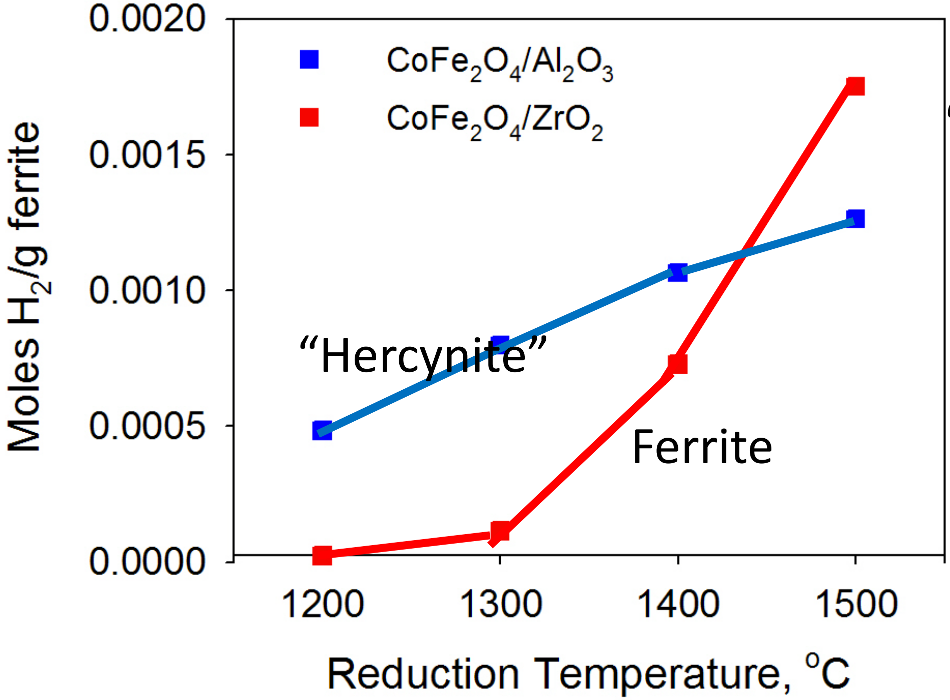
- ZrO_2 observed by Raman after thermal treatment (sample sinters; confirmed by BET)
- Nonetheless, material remains active after 25 cycles with no observed deactivation

Results - Annual Reduction Energy Requirements

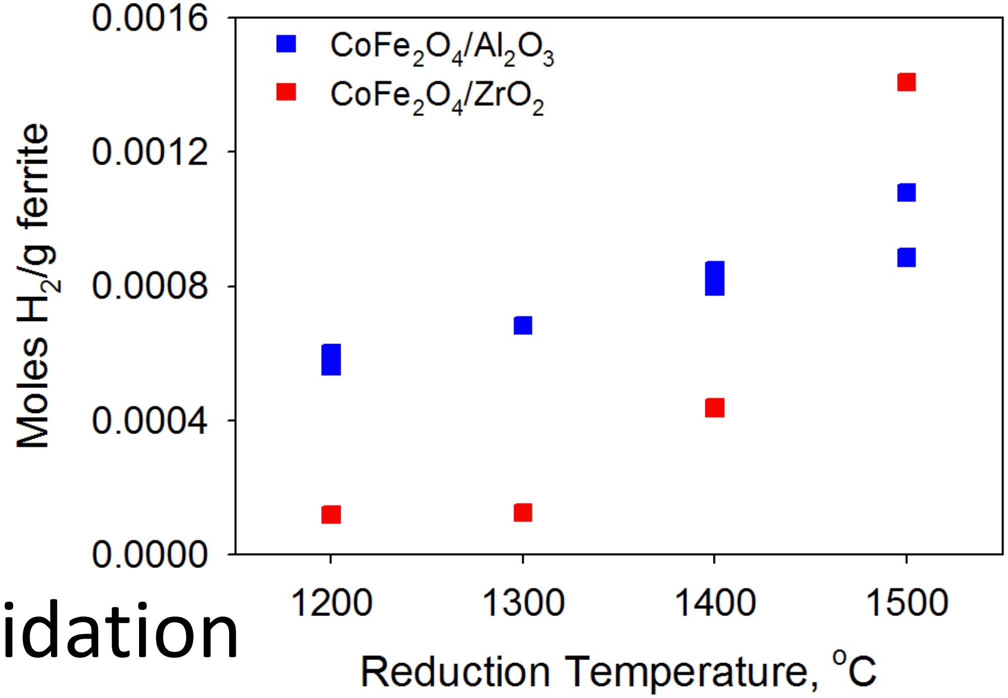
Total Solar Heat Input Required without Heat Integration

$NiFe_2O_4 + 0.67\ ZrO_2 \rightarrow MeO\ (Fe^{2+}+Fe^{3+}+Ni^{2+}) + 0.67\ ZrO_2 + ½x\ O_2$				
$MeO\ (Fe^{2+}+Fe^{3+}+Ni^{2+}) + 0.67\ ZrO_2 + x\ H_2O \rightarrow NiFe_2O_4 + 0.67\ ZrO_2 + x\ H_2$				
Oxidation Temperature	**800°C**	**900°**	**1,000°C**	**1,100°C**
Moles H_2 Produced	0.50	0.49	0.46	0.41
Solar Energy Required (GWhr/yr)				
Overall Heat of Reaction	1,837	1,892	1,993	2,231
Sensible Heat Required	1,520	1,520	1,311	1,141
Total Solar Energy Required	3,582	3,412	3,304	3,372

"Hercynite" & Ferrite Cycle Oxidation Performance (1000°C)



Predicted FACTSage™



Experimental Validation

CO_2 Splitting with nano Al_2O_3 Powder Support