Flowing Particle Bed Solarthermal Redox Process to Split Water

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06/08/2017

Project ID: PD114

Overview:
Year 3 of 3-Year Project

Timeline

Project Start Date: 9/1/2014

Project End Date: 11/30/2017

% Complete: 87%

Technical Barriers Addressed

S. High-temperature robust materials

W. Materials and catalysts development

X. Chemical reactor development and capital costs

Paid Partners

National Renewable Energy Laboratory (NREL), Golden, CO

- Solar testing facility and capabilities

Allan Lewandowski Solar Consulting, LLC

- Solar field design consultation and modeling

Musgrave Group*, CU Boulder

- Active materials discovery and DFT modeling (*NSF/DOE Funding – joint FOA)

Collaborators

Australian National University (ANU), Canberra, AU

- Reactor models and receiver testing at solar simulator facility

Saudi Basic Industries Corporation (SABIC)

- Supplying equipment and materials characterization

Coorstek/Ceramatec

- Preparation of large spherical active materials
- High temperature O_2 transport membrane

TRL 2 → TRL 3

Budget

Total project funding: $2,000,000

Sub-contract to NREL: $450,000

Total recipient cost share: $6,250

Total funds received FY16: $687,055

Total planned FY17: $455,901

Relevance:
Renewable Efficient Hydrogen Generation

***Project Objective:* Design and test individual components of a novel flowing particle solarthermal water splitting system capable of producing 50,000 kg H_2/day at a cost < \$2/kg H_2**

- Identify and develop high-performance active material formulations
- Synthesize flowable, attrition-resistant, long-use spherical particles from low-cost precursors
- Demonstrate high-temperature tolerant, refractory, non-reactive containment materials
- Construct fluidized bed particle redox test system and test components of system
- Monitor progress toward cost target by incorporating experimental results into frequently updated detailed process model and H2A
- On-sun production for a full solar day
- Move from TRL 2 to TRL 3

This Reporting Period:

- ✓ Performed long-term stability tests of reactive materials showing no loss in reactivity between 100^{th} and 200^{th} cycle and 2X targeted H_2 production rate(**Barrier S**)
- ✓ Developed ALD barriers that improve high-temperature resistance of SiC to steam by >60%, 2X targeted impact (**Barrier S**)
- ✓ Demonstrated on-sun production of 1.91L standard L H_2 in less than 3 hours (**Barriers S and X**)
- ✓ Assessed economic viability of thermal energy storage to provide electricity for non-intermittent STWS (**Barrier X**)
- ✓ Completed study on effects of structure and magnetic ordering for 1343 materials (**Barrier W**)
- ✓ Continued testing of high temperature O_2 transport membrane for inert gas recycle (**Barrier X**)
- ✓ Completed construction of high-flux solar simulator to test hybrid reactor concept (**Barrier X**)

Approach:
Iterative Materials and Reactor Development

Reactive Materials

Produce and characterize reactive materials

- M1.2: Optimize perovskite and spinel material formulations (65% done)
- M1.4: Produce attrition resistant active materials (100% done)
- GNG1: Spray dried particles making ≥150 µmol H_2/g (100% done)
- GNG2: Particles that produce ≥150 µmol H_2/g and lose ≤10% reactivity from 100th to 200th cycle (100% done)

Efficient, Cost-effective H_2 Production

Reactor Design

Construct particle flow system to test reactor design

- M3.2: Evaluate diffusional limitations under inert gas with O_2 membrane (100% done)
- M3.3: Develop diffusional model for oxygen removal (30% done)
- M3.4: Operate reactor as a fluidized bed (80% done)
- GNG4: Operate particle flow redox system with >1g of active material (100% done)

Ongoing updates to the process model and H2A

Containment Materials

Develop redox compatible containment materials

- M2.1: Synthesis and characterization of coated SiC powders (80% done)
- M2.2: Selection of preferred coating material based on TGA results (80% done)
- M2.4: Coated containment tube system constructed (100% done)
- GNG3: Coated SiC with ≥25% reduction in steam reactivity (100% done)

On-Sun Production

Production of H_2 with reactive engineered particles (80% done)

Accomplishments and Progress: Overall Process R&D

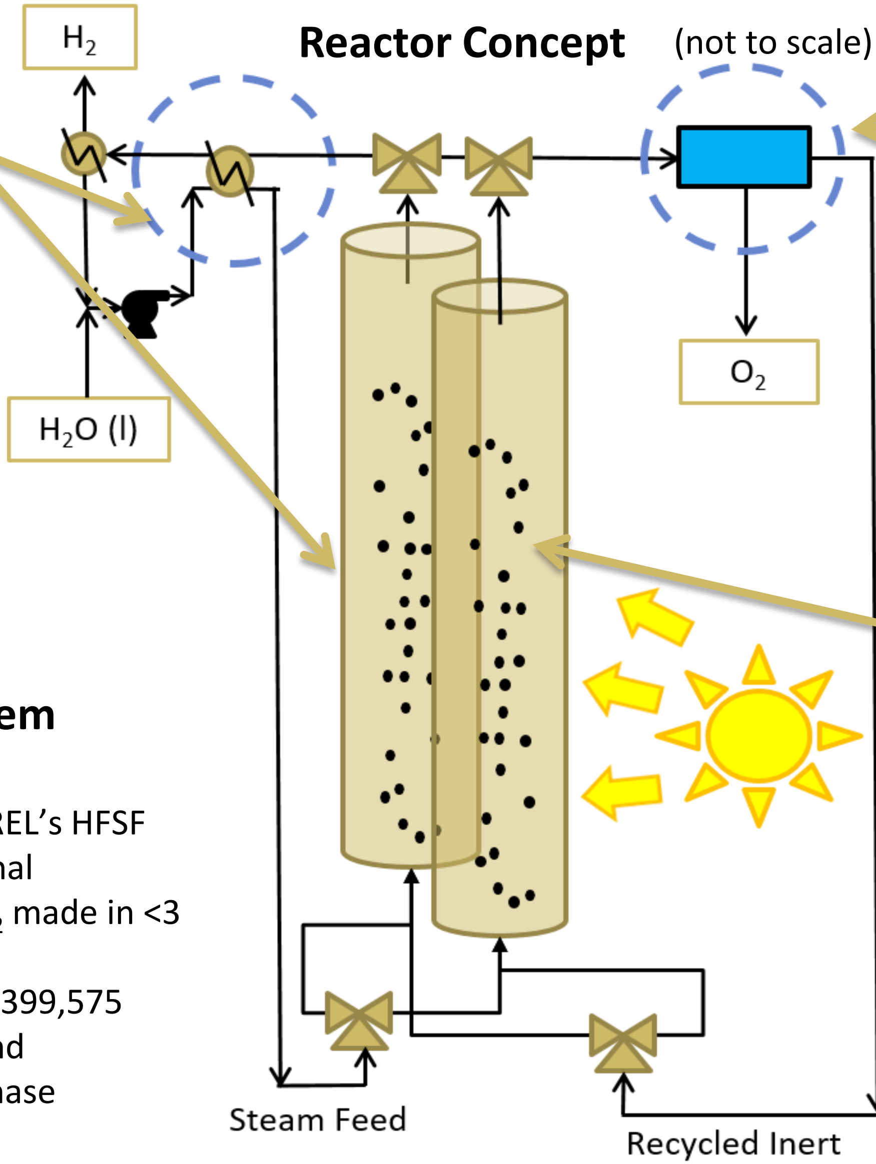
Containment Materials R&D

- Synthesized Al_2O_3, mullite, BN coated SiC
- Improved stability (>60%) with 10 nm Al_2O_3 coating shown with TGA
- Test system for coated tubes constructed

Overall System R&D

- On-sun testing at NREL's HFSF on target to meet final deliverable; 1.91L H_2 made in <3 hours
- Issued U.S. Patent 9,399,575 (2016): "Methods and apparatus for gas-phase reduction/oxidation processing".

Reactor Concept (not to scale)



SEOS for Recycled Inert Gas R&D

- Demonstrated 12% efficiency with electrically heated high-temperature O_2 transport membrane
- Investigating effect of O_2 concentration on reduction kinetics and productivity

Active Materials R&D

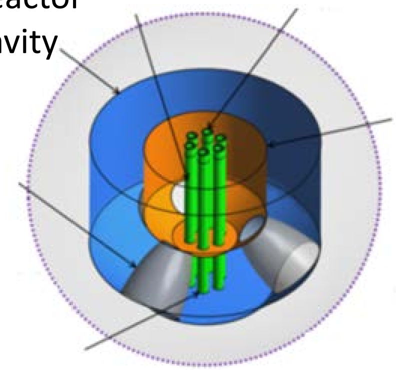
- Demonstrated no loss in reactivity from 100^{th} to 200^{th} redox cycle while generating ~ 300 μmol H_2/g active material

Multiple Fluid Beds in Solar Cavity (near-isothermal)

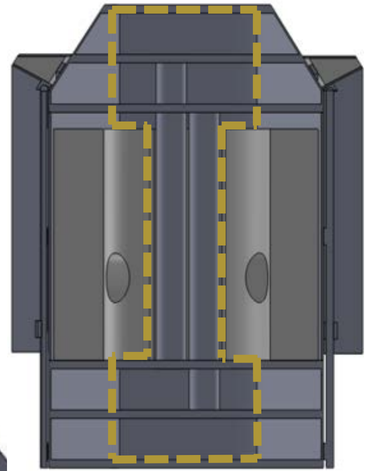
Accomplishments and Progress: Near-Isothermal Process Design

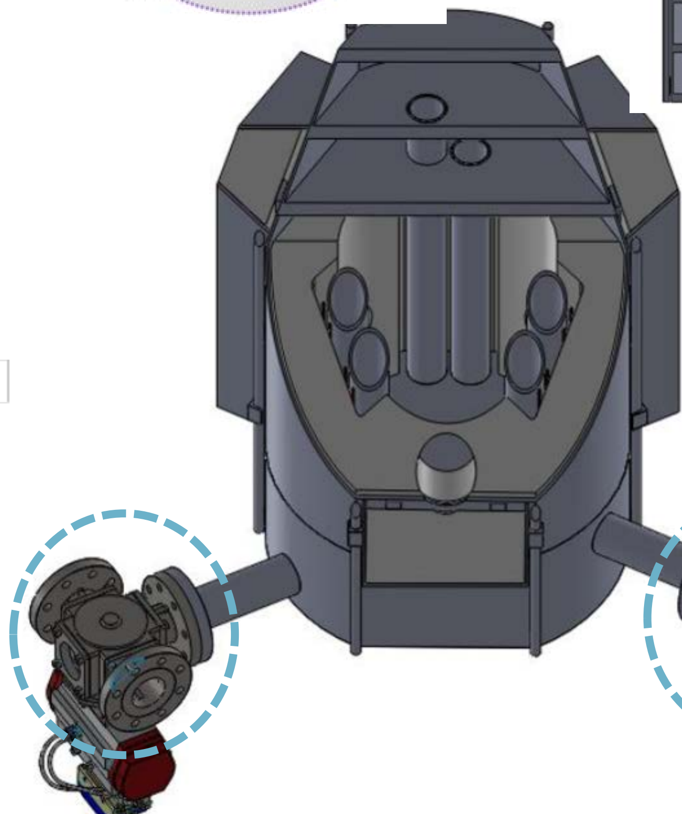
- Hybrid solar/electrical reactor for non-intermittent heating, 10 hr/d
- Renewable, storable electricity provided by heated molten salt using recuperated heat
- Membrane electricity calculated; experimental efficiency of 12%
- Redox reactors operate as fluidized beds within solar cavity
- No solids movement between reactors, simple design
- Reduction and oxidation occur at near 1450°C
- 3L H_2/8hr at NREL HFSF using Hercynite active materials

Reactor Cavity

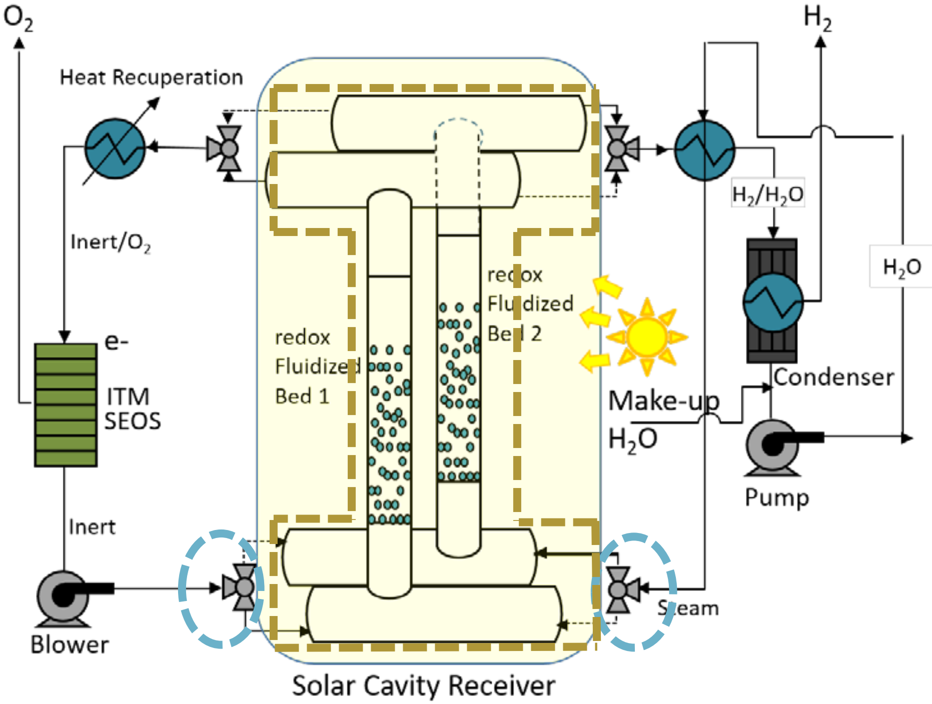


Receiver Vertical Cross-Section



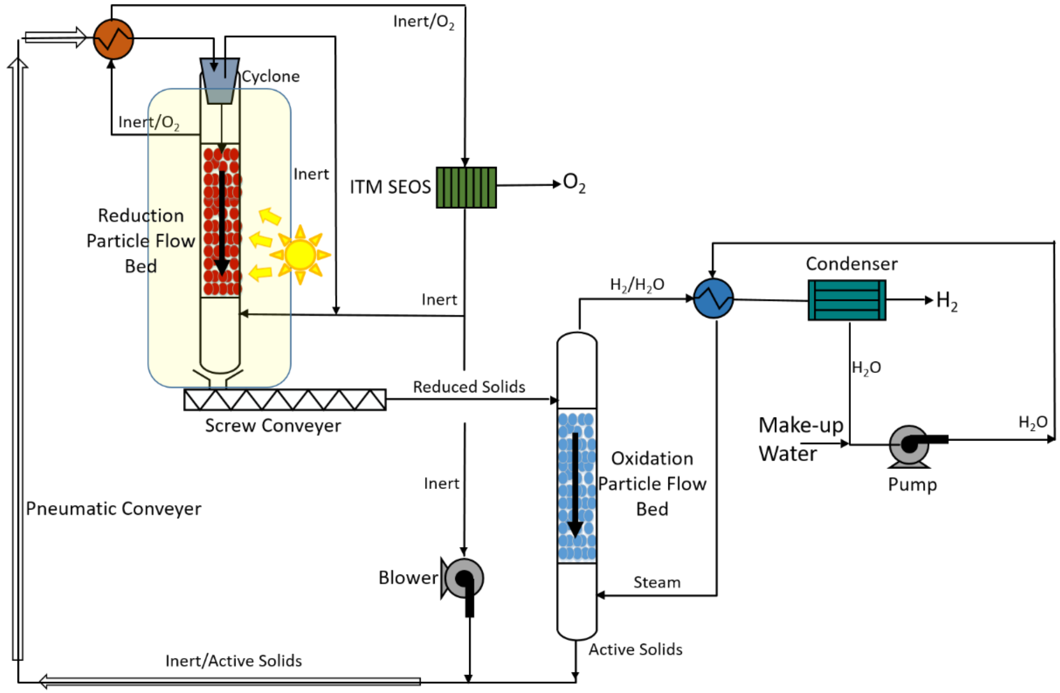


Receiver Horizontal Cross-Section



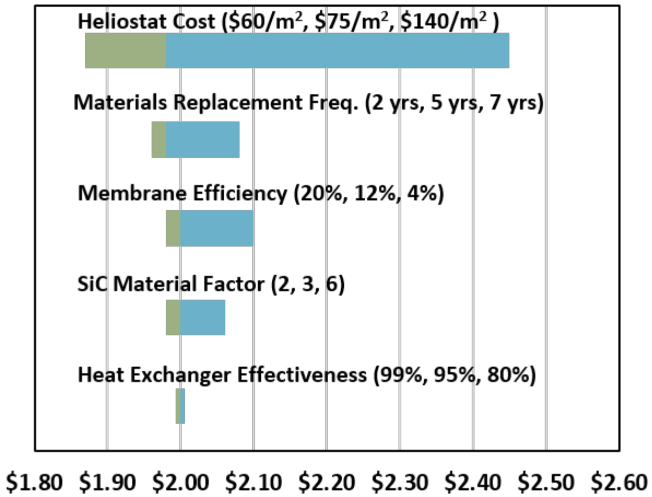
Accomplishments and Progress: Temperature-Swing Process Design

- Continuous flowing particle bed hydrogen production process
- Solar radiation on reduction reactor only
- Reduction occurs at 1450ºC
- Oxidation occurs at 1000ºC
- Experimental implementation underway using 12 kW solar simulator at CU (pictured)
- 3L H_2 in 8 hours using Hercynite

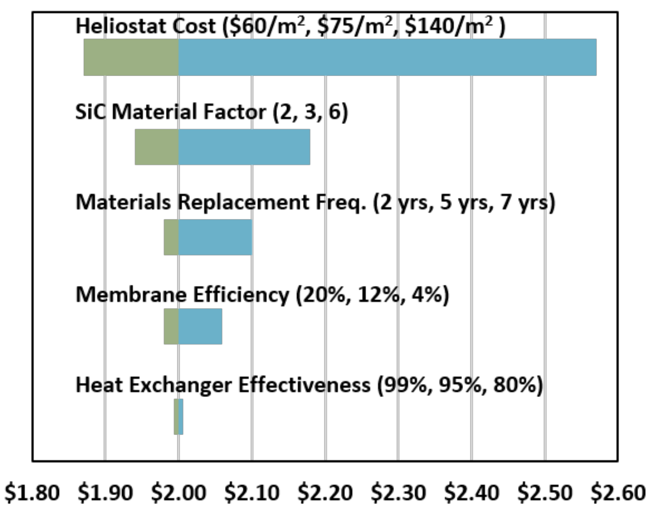


Accomplishments and Progress: H2A Results

Temperature-Swing



Near-Isothermal



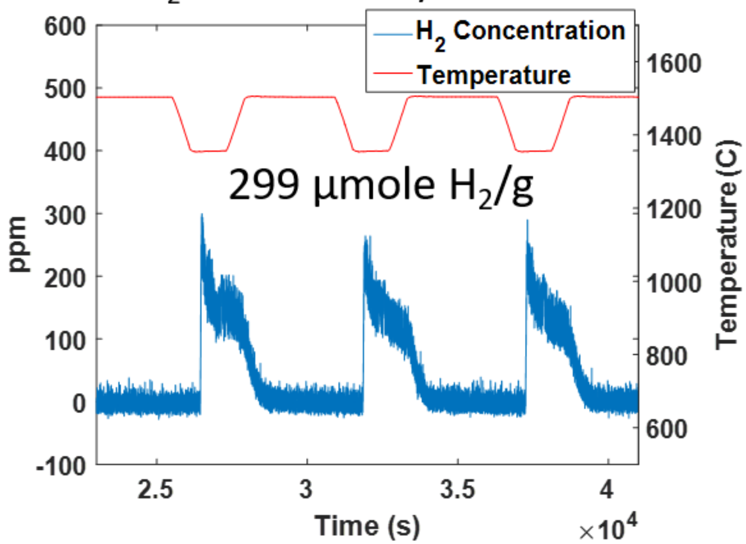
Cost Drivers	2015	2020	Ultimate
Heat exchanger effectiveness	85%	90%	95%
SiC material factor	6	5	3
Replacement frequency (years)	2	5	5
Material activity (µmol H_2/g)	354	389	425
Enthalpy of reaction (kJ/mol)	384	346	307
Heliostat cost ($/m^2)	$140	$75	$75
Hybrid Reactor Mark-up	1.5x	1.5x	1.25x
Cost H_2 Near-Isothermal ($/kg)	$8.79	$3.51	$2.00
Cost H_2 Temperature-Swing ($/kg)	$7.42	$2.61	$1.98

TEA predicts that NI and TS processes can produce H_2 at $2.00 /kg, and $1.98/kg, respectively

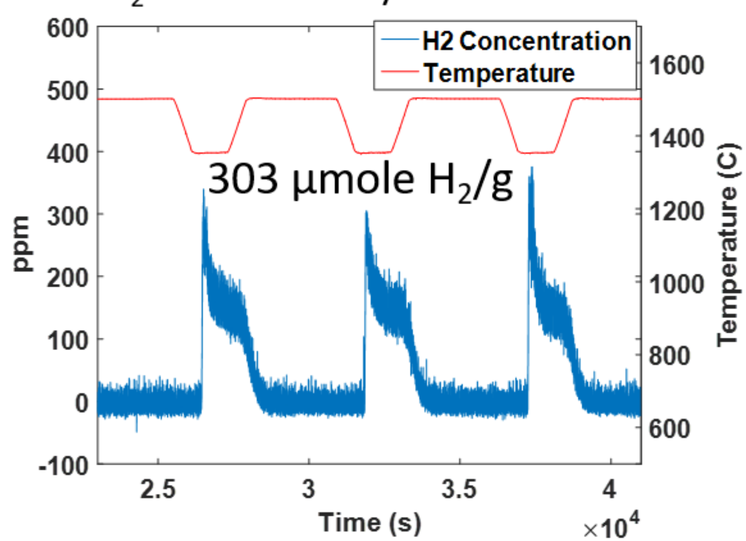
Go/NoGo: Active Materials Robustness

Spray Dried $Co_{.5}Fe_{.5}Al_2O_4$

H_2 Production Cycles 97-99



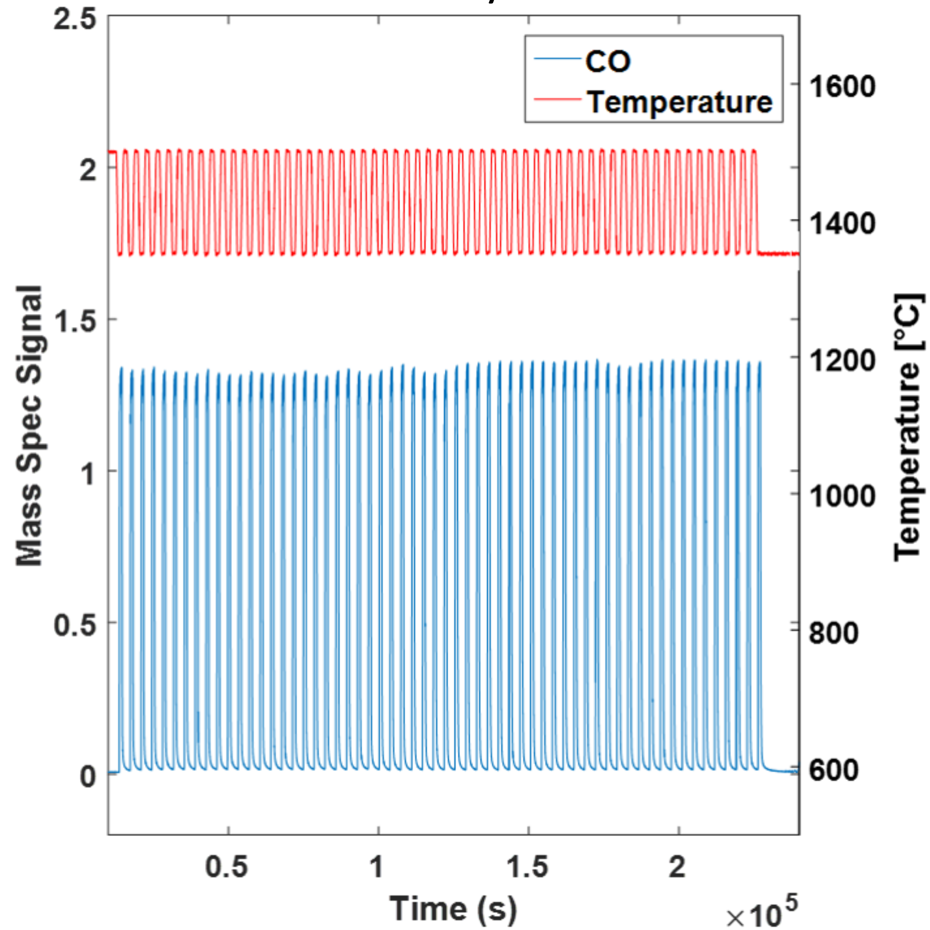
H_2 Production Cycles 201-203



Target: > 150 µmole H_2/g & < 10% activity loss between 100th and 200th cycle

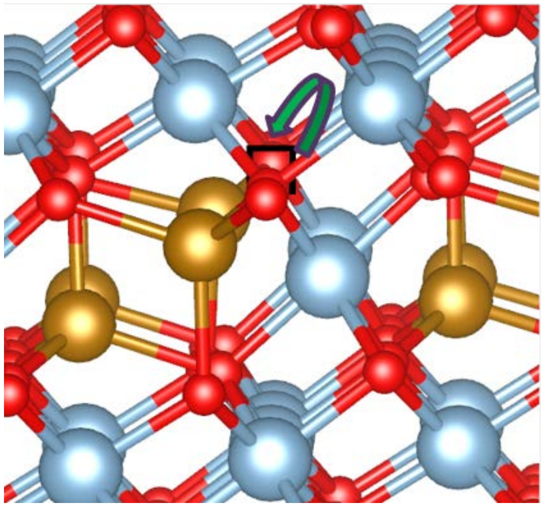
Actual: 300 µmole H_2/g and no activity loss

CO Production Cycles 141-200

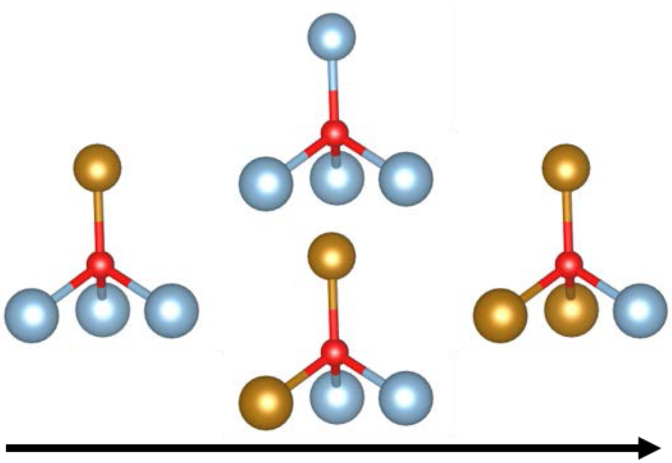


Accomplishments and Progress: Kinetic Modeling

Diffusion in Hercynite

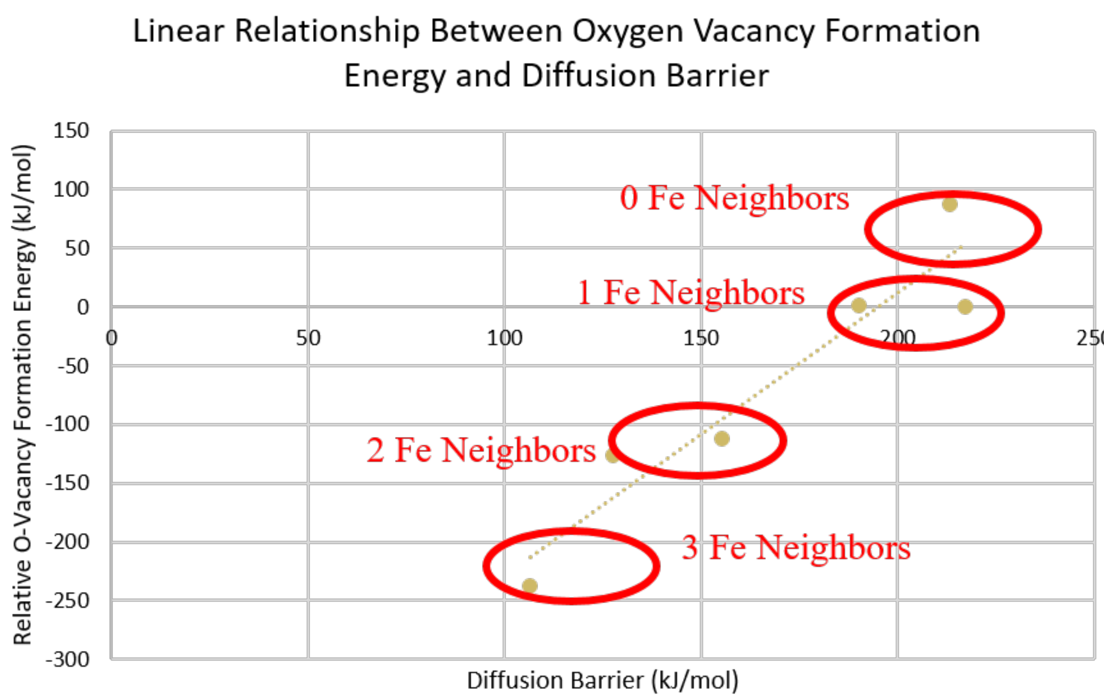


Impact of Inversion on Local Environment



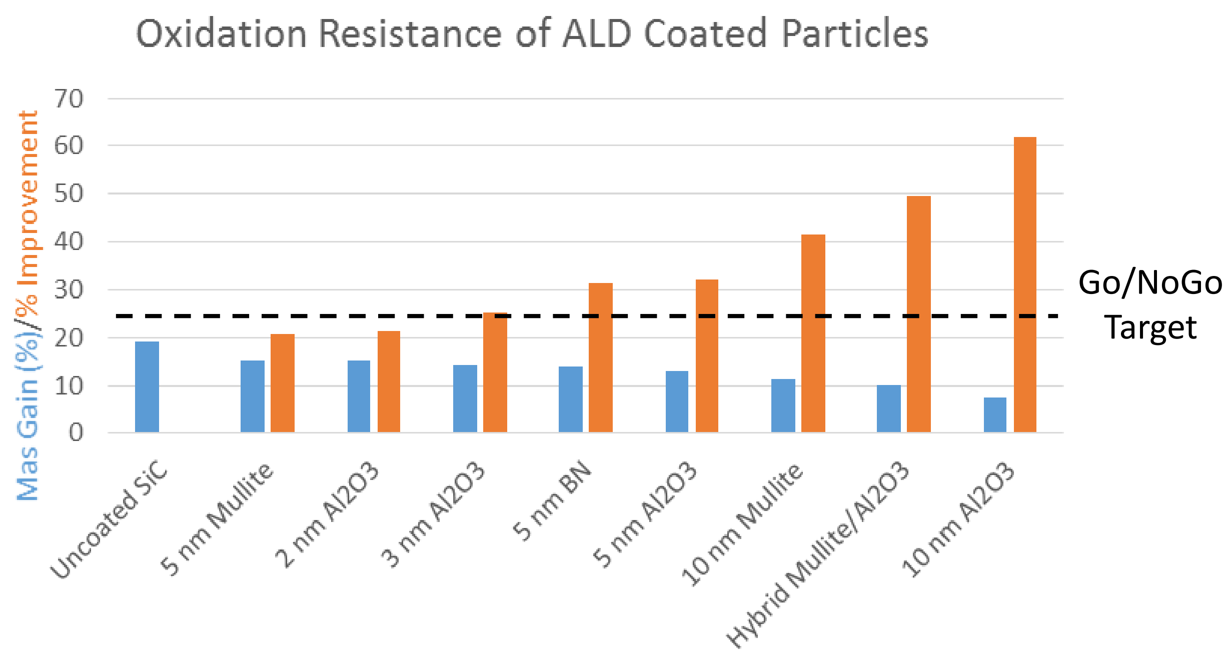
Increasing Inversion

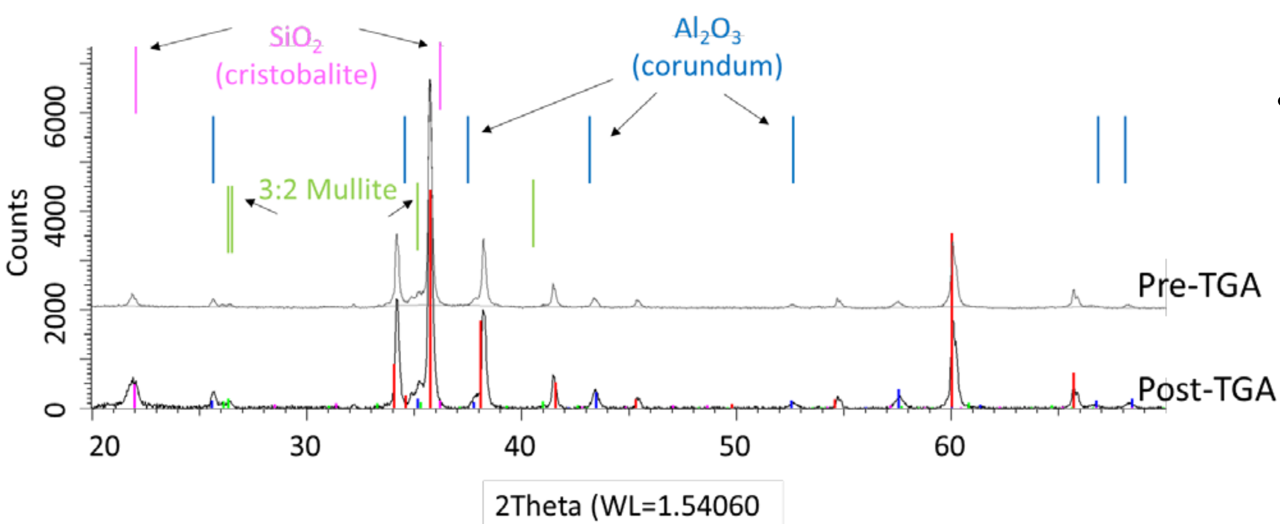
- Cation distribution in hercynite has a significant impact on the diffusion barrier
- Barrier shows strong correlation to both the oxygen vacancy formation energy, and the number of Fe cations that neighbor the diffusion site



Findings show promise for modeling of disordered systems without explicit calculations for every state.

Go/NoGo: SiC Steam Oxidation Resistance



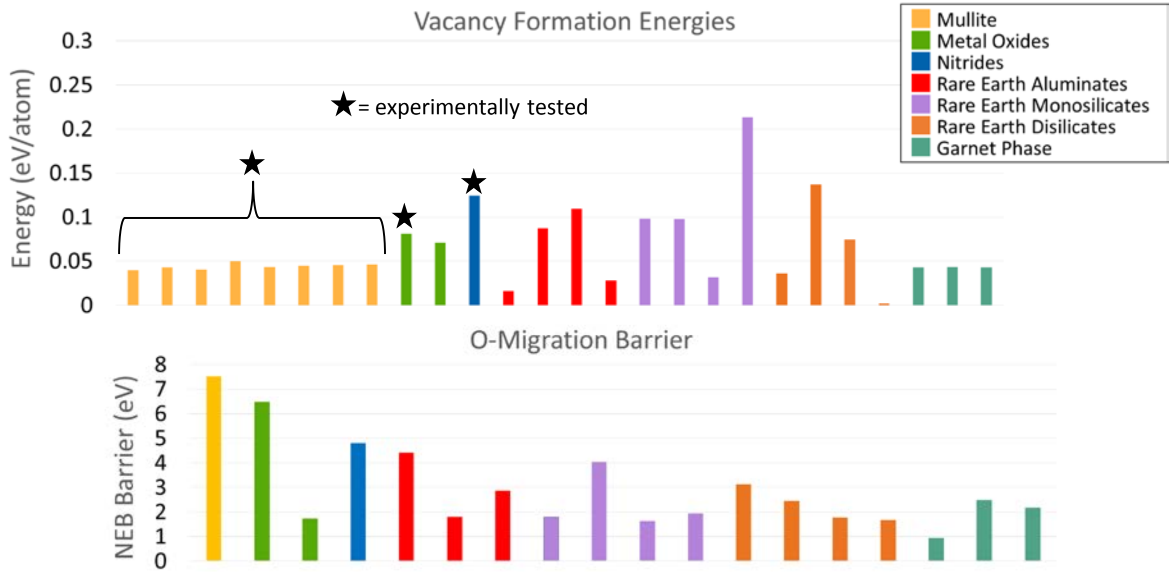


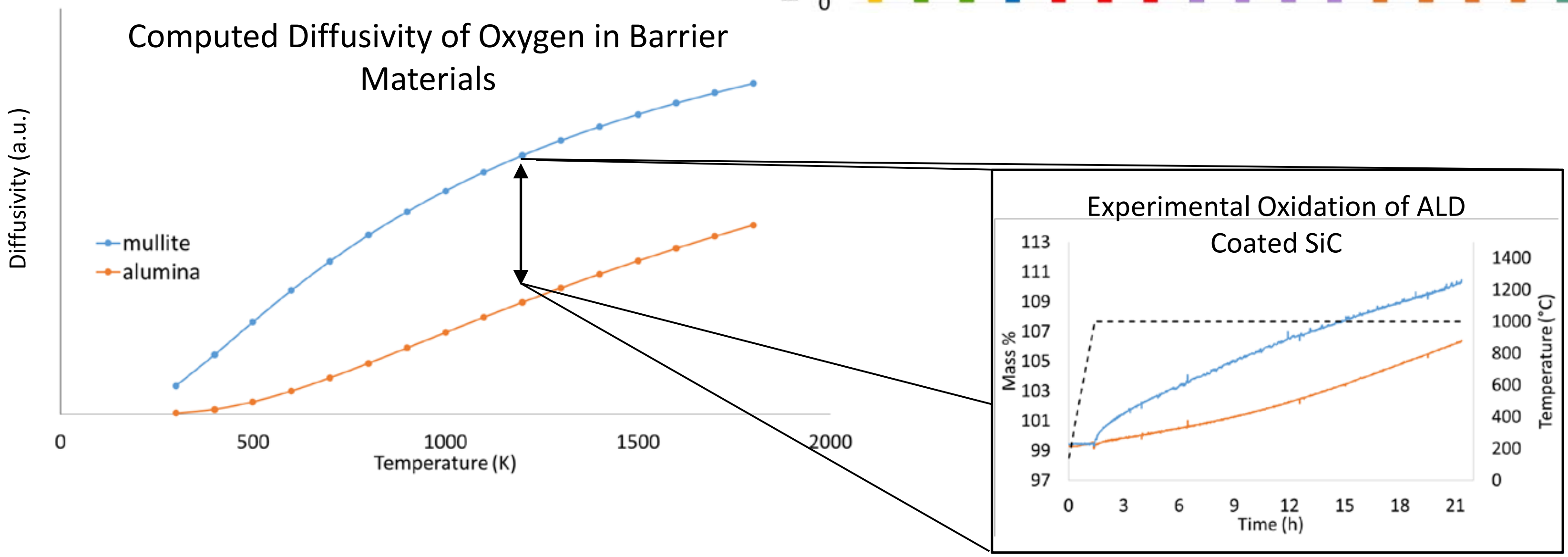
- Particle ALD is being used to study the stabilization effects of nano-scale diffusion barriers with atomic growth control
- Mullite ($3Al_2O_3$:$2SiO_2$) and BN have been identified as a promising coating materials
- H_2O exposure at 1000°C for 20 hours
- Increased film thickness improves performance
- Mullite films are able to match performance of alumina
- Preliminary BN films show reduced oxidation similar to alumina

ALD coatings show up to a 64% improvement to the oxidation resistance of SiC.

Accomplishments and Progress: Modeling for Coating Stability Analysis

- Density Functional Theory is being applied to model the chosen barrier materials
- Key metrics used to compare materials:
  - O/N vacancy formation energy
  - Oxygen hopping energy barriers
- We have performed calculations comparing mullite to bulk alumina, as well as a variety of materials receiving interest in EBC applications
  - 2 materials have been computationally determined to perform better that BN



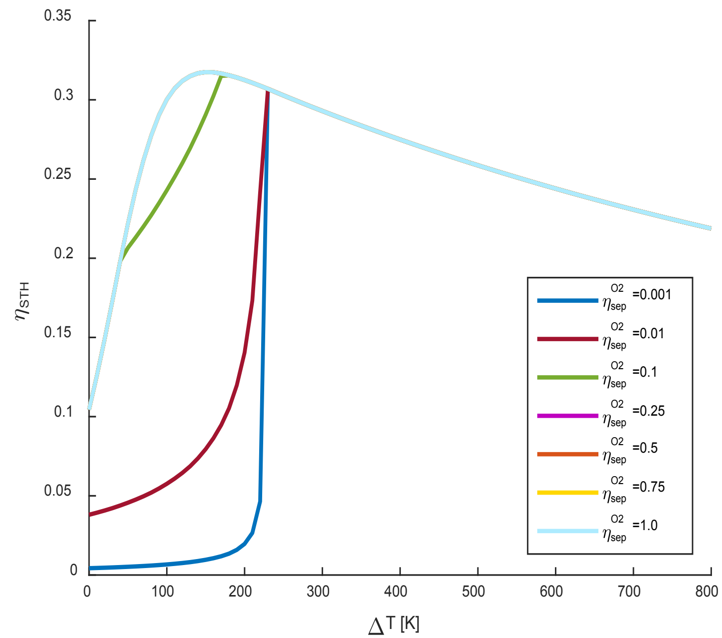


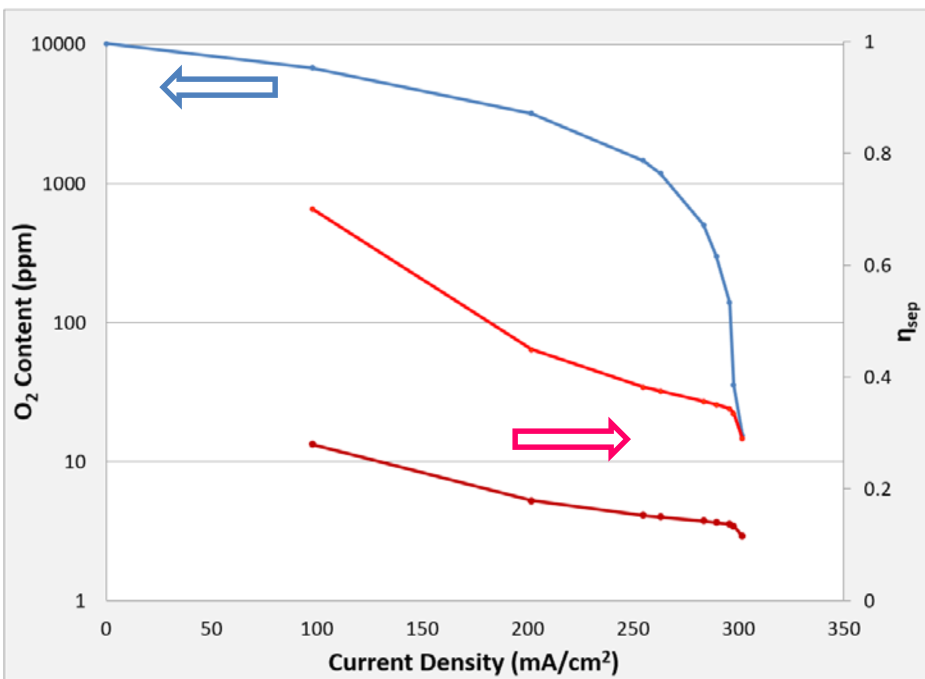
Computational results match well with experiments and have revealed metrics by which to theoretically screen barrier materials.

Accomplishments and Progress: ITM SEOS Membrane for Recycled Inert Gas Sweep

ITM SEOS Membrane Results

- Solar-to-H_2 thermodynamic efficiency calculations showed the separation efficiency (η_{sep}) of inert gas and generated O_2 needs to be at least 10% to have an efficient process.
- Tested a high temperature (850°C) Ion Transport Membrane (ITM) to remove O_2 from inert gas
- Compared energy requirement of separation to thermodynamic separation work to calculate η_{sep}
- Experimental energy requirements are inflated to include thermal-to-electricity conversion ($\eta_{solar\text{-}to\text{-}electricity}$)

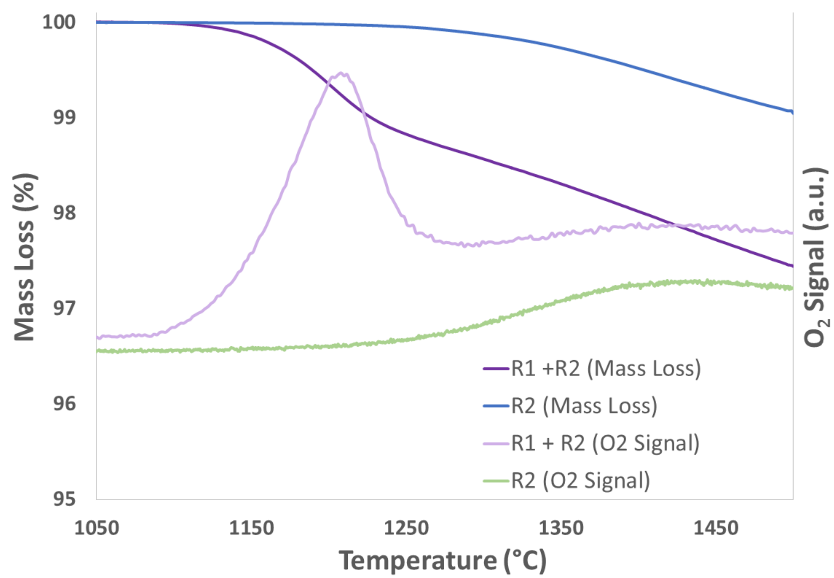


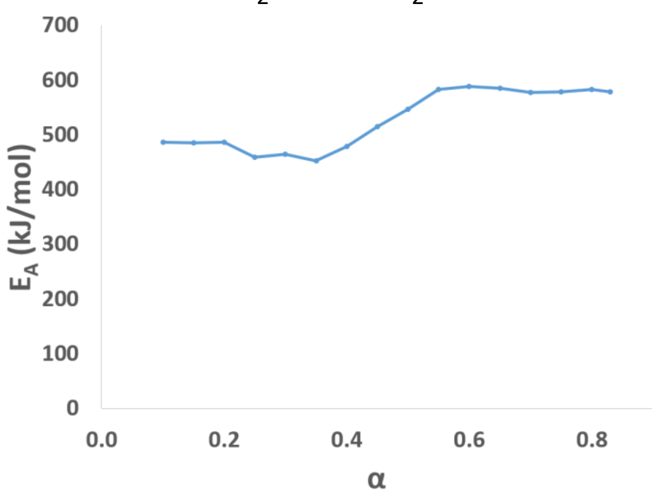


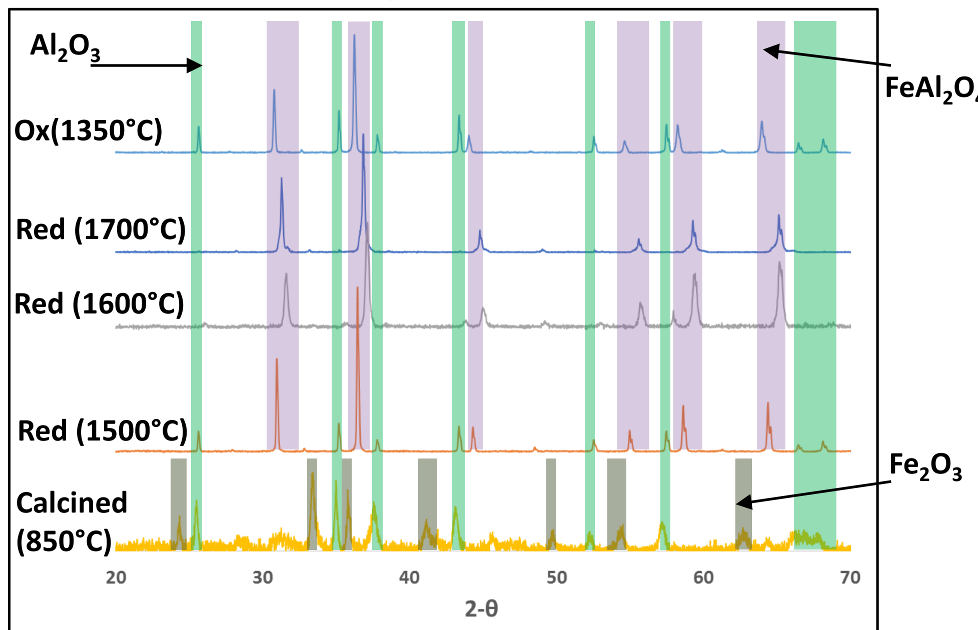
O_2 concentration reduced to 15ppm from 1% O_2/N_2 mixture at 1 SLPM using ITM SEOS with 29% η_{sep} (12% including thermal-to-electricity conversion)

Accomplishments and Progress: Hercynite Materials Characterization

- Hercynite is formed by reacting Al_2O_3 and Fe_3O_4 to form the spinel phase
- $Fe_3O_4 + 3Al_2O_3 \rightarrow 3FeAl_2O_4 + \frac{1}{2}O_2$ (R1)
- Hercynite materials is further reduced under O_2 vacancy mechanism
- $FeAl_2O_4 \rightarrow FeAl_2O_{4-\delta} + \frac{\delta}{2}O_2$ (R2)
- Apparent activation energies for R1 and R2 reactions were experimentally calculated using isoconversional methods
- XRD and TG analysis showed spinel phase is maintained after H_2O and CO_2 oxidation



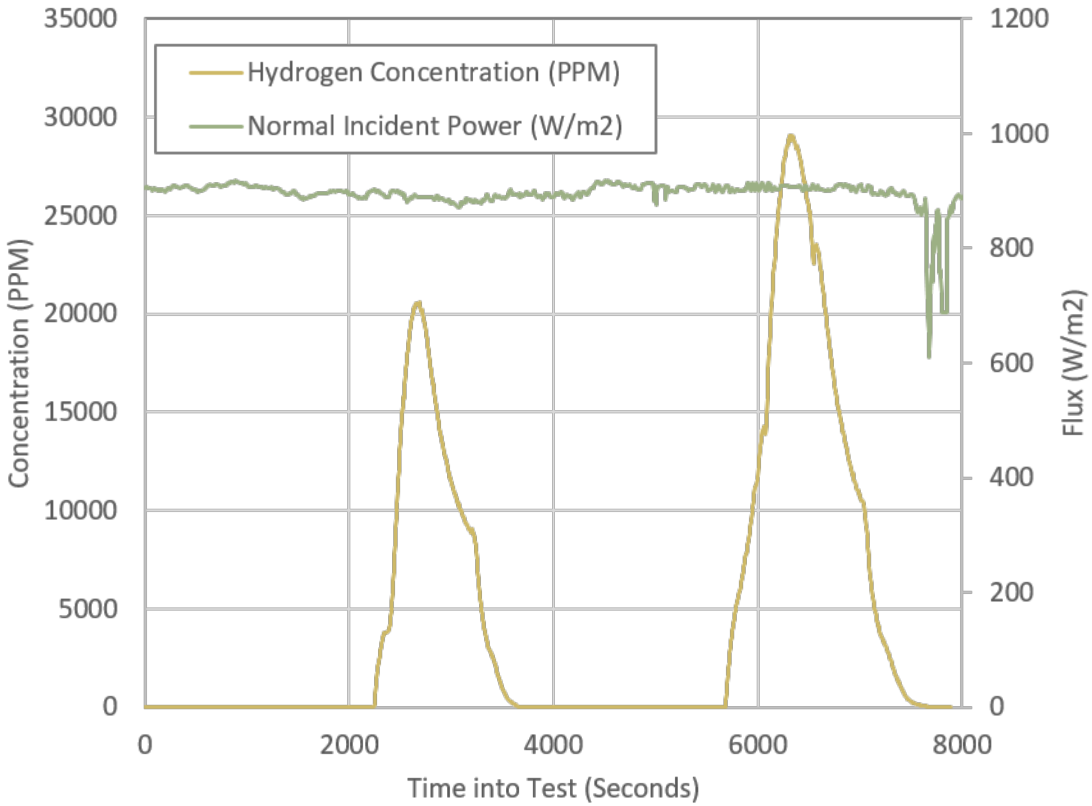


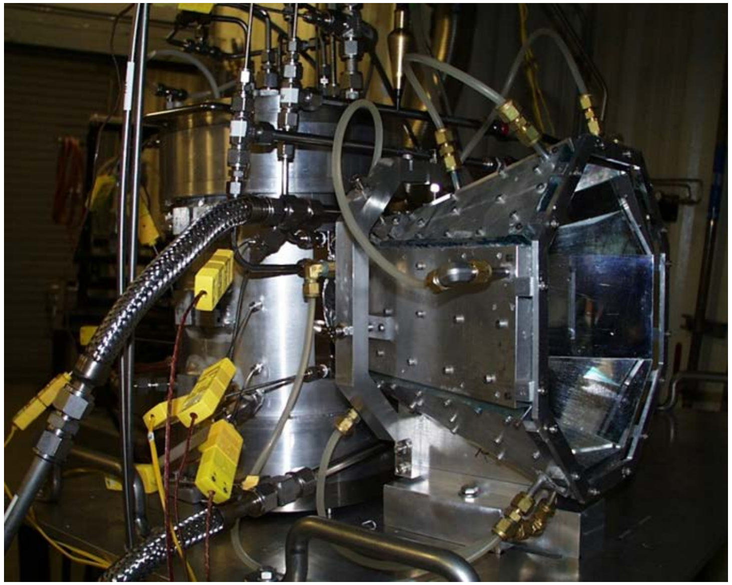


Undoped hercynite undergoes an O_2 vacancy mechanism up to 1700 °C

Accomplishments and Progress: On-Sun Testing

Data Summary for test on April 13th, 2017					
	Activity (μmol/g)	Total H_2 (μmol)	Total H_2 (L)	Peak Rate (μmol/g/s)	Oxidation Time (s)
Oxidation 1	367	29336	0.66	0.59	1316
Oxidation 2	697	55711	1.25	0.84	2010
Total H_2 for 2 cycles (L)			1.91	Time 2 cycles (h:mm:ss)	2:45:26
Expected H_2 for 4 cycles (L)			**3.81**	**Expected Time 4 cycles (h:mm:ss)**	**5:30:52**





After producing 1.91L H_2 in less than 3 hours, we are on-target to meet our end-of-project goal of 3L H_2 production in less than 8 hours

Summary

- New process models using hybrid solar/electric reactors evaluated
- GNG of H_2 production of 150 μmol/g/cycle and less than 10% loss in reactivity met (~300 μmol H_2/g/cycle and no loss between 100th and 200th cycle)
- Method of kinetic modeling of hercynite systems improved
- ALD coatings show up to 64% improvement in oxidation of SiC in steam environment (target was 25% improvement)
- Computational results for SiC coating stability match experimental results
- O_2 concentration reduced to 15ppm from 1% O_2/N_2 mixture at 1 SLPM using ITM SEOS with 12% η_{sep} including electricity use
- 1.91L H_2 made during 3 hours of testing at NREL's HFSF, showing significant progress toward end-of-project goal

AMR Reviewer Comments 2016

"It is recommended that the researchers improve the kinetics to decrease the cycle time."

- Fast kinetics and cycle time is one of many parameters that can have a profound impact on the technology's economic feasibility. We are examining the effect of dopants on kinetics with our NSF sister project, in addition to performing experiments to determine the kinetics of various materials. It is possible, perhaps even likely, that the material with the fastest kinetics will not be the best overall, therefore we must consider productivity, durability and other characteristics in addition to kinetics.

"The H2A analysis in 2015 indicated that heat exchanger effectiveness was by far the most critical factor in the final economics. This technical challenge seems to not have received attention."

- Heat exchanger effectiveness was found to have a smaller impact on the overall H_2 cost than any of the other variables presented in the tornado chart. This can be explained by the substantial efficiency advantage conferred by using recycled inert sweep gas and a high-temperature O_2 transport membrane. These two updates to the Aspen simulation make heat exchanger effectiveness a less important factor.

"Given the proposed size of the reactors, they need to present compelling evidence (examples) that atomic layer deposition (ALD) can be economically done on a system of this size, shape, etc."

- The process of ALD is independent of line-of-sight, so wherever precursor gas can flow surfaces can be coated. Therefore, one can easily coat the inside of tubes that can be heated. The time and precursor requirements for ALD are largely controlled by the surface area of the substrate making ALD highly scalable. For example approximately 60 m^2 are loaded into the lab-scale fluidized bed ALD reactor and a commercial tube might have an internal surface area of approximately 30 m^2. This is not a concern.

Collaborations

Fund-Receiving Collaborator	Project Roles
National Renewable Energy Laboratory (NREL) (sub)	High Flux Solar Furnace (HFSF) user facility for process demonstration
Musgrave Group, CU Boulder	Active materials discovery and DFT modeling through “sister” NSF project*

* Funds from Joint DOE/NSF FOA

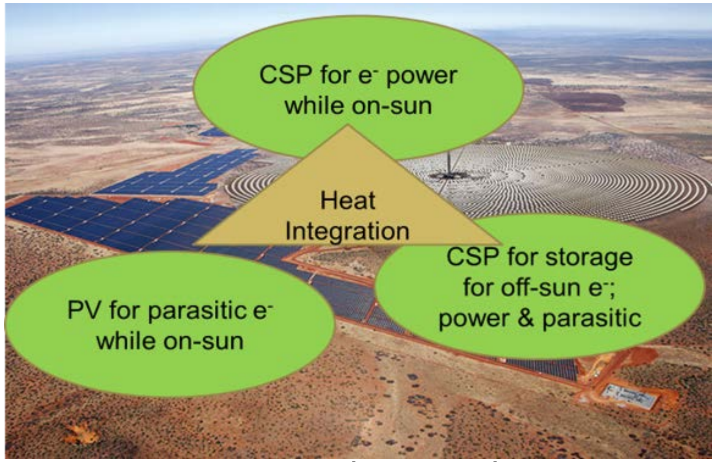
Leveraged Collaborators (no funds from DOE)	Project Roles
Saudi Basic Industries Corporation (SABIC)	Materials characterization support; supplying equipment
CoorsTek Amazing Solutions. / Ceramatec	Active Materials Preparation; ITM SEOS Membrane
Harper International Corporation	Design and construction of pilot high-temperature solar/electric furnace
Australian National University (ANU)	Reactor models and receiver testing at solar simulator facility

Proposed Future Work*

- Reactive Materials
  - Perform detailed thermodynamic and kinetic studies of active materials (M1.3 & M1.6)
  - Validate computation work of sister NSF project (M1.1 & M1.2)
    - Poster PD120
- Reactor Design
  - Operate reduction reactor tube under vacuum and evaluate diffusional limitations (M3.2)
  - Develop reactor concept for hybrid solar/electric water splitting
- Containment Materials Development
  - Synthesize ALD films on three SiC tubes having different thicknesses of coating material (M2.3)
  - Test coated tubes for stability in high temperature steam environment, and evaluate tested tubes using SEM, XRD and ICP (M2.5)
- Efficient H_2 production
  - Further refine AspenPlus model and H2A with experimental thermodynamic and kinetic results and optimal operating conditions (M5.1 & M5.2)

*Any proposed future work is subject to change based on funding levels

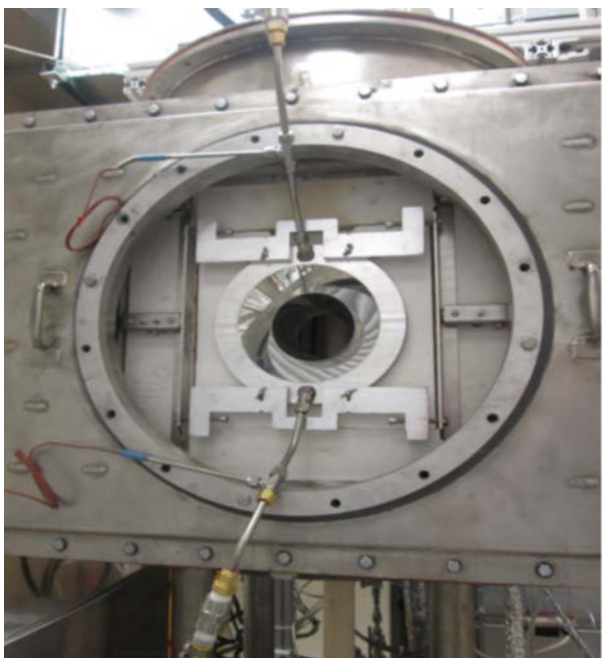
Proposed Future Work* – hybrid solar/electric receiver



Non-intermittent chemical processing

University of Colorado (CU) 10 kW_{th} HFSS

CU hybrid receiver (front with sliding CPC)

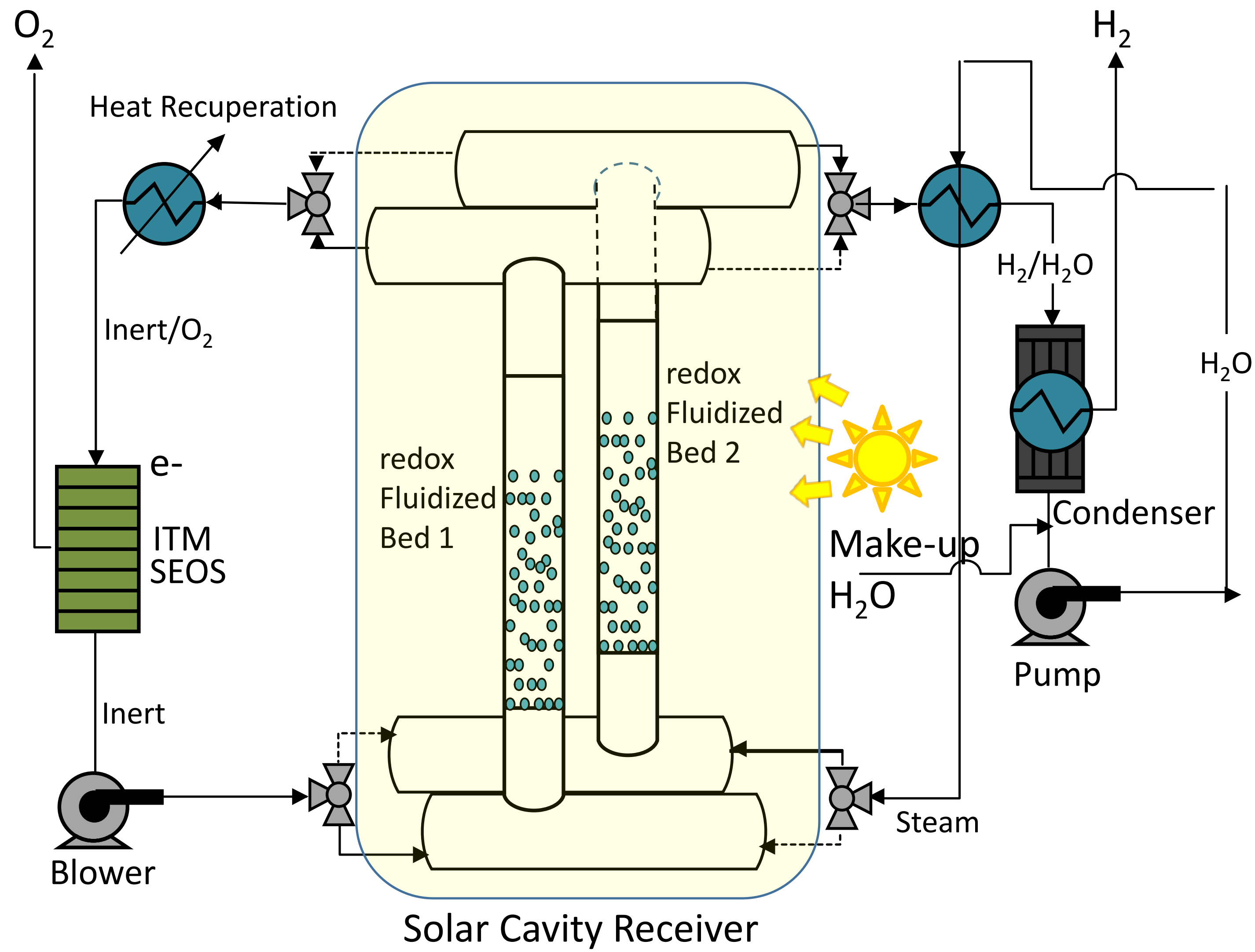


CU hybrid receiver (back showing xyz stand, etc.)

*Any proposed future work is subject to change based on funding levels

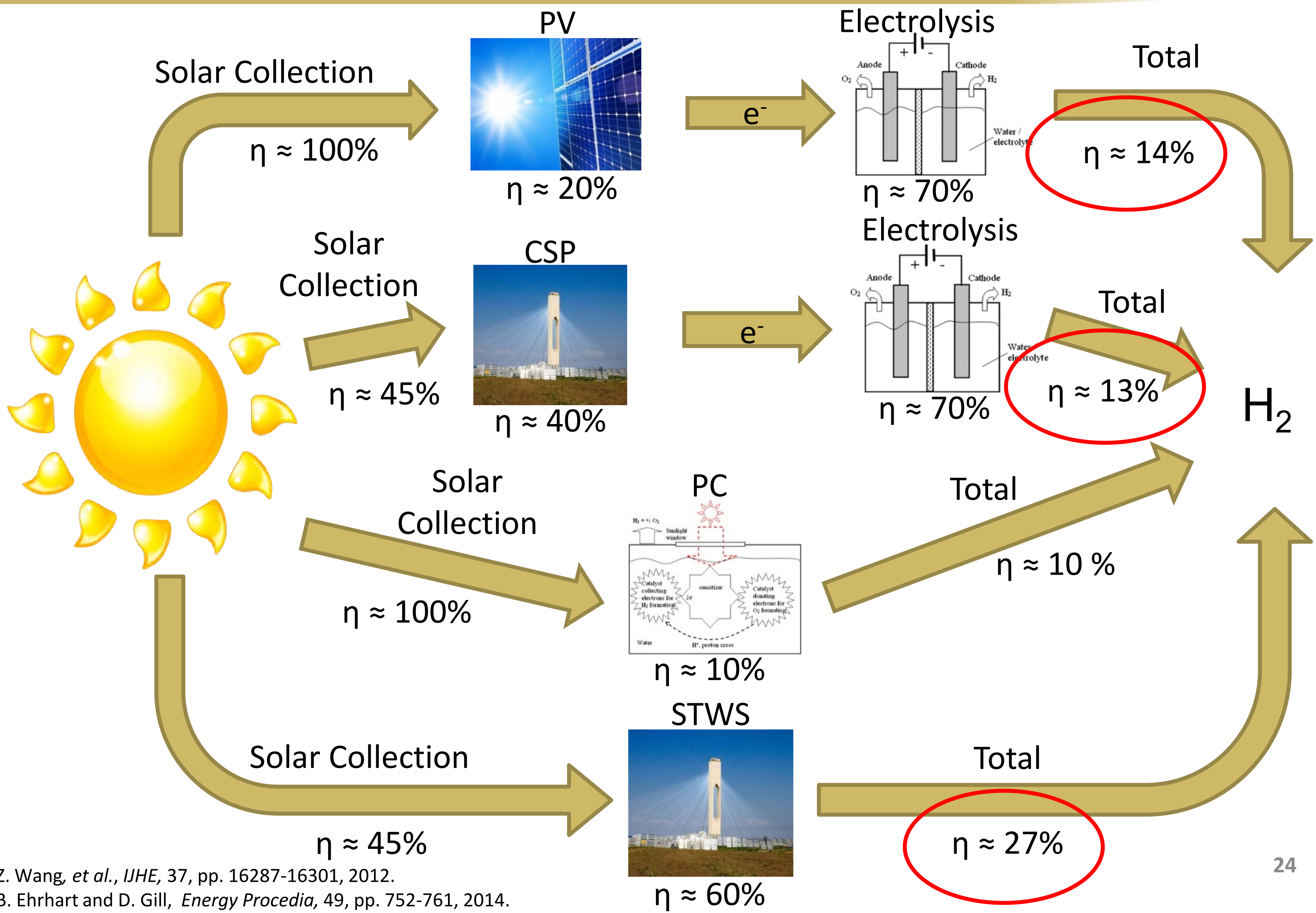
Acknowledgements

Backup Slides



Near-isothermal Single Cavity Dual Fluid Bed System
(Easily Made Hybrid by adding Electrical Resistance)

Efficiency is Important for Solar H_2



Z. Wang, *et al.*, *IJHE,* 37, pp. 16287-16301, 2012.
B. Ehrhart and D. Gill, *Energy Procedia,* 49, pp. 752-761, 2014.

Does Hybrid Solar/Electric make sense vs. Electrolysis for non-intermittent (10 hr per day) water splitting?

Efficiency Comparison:

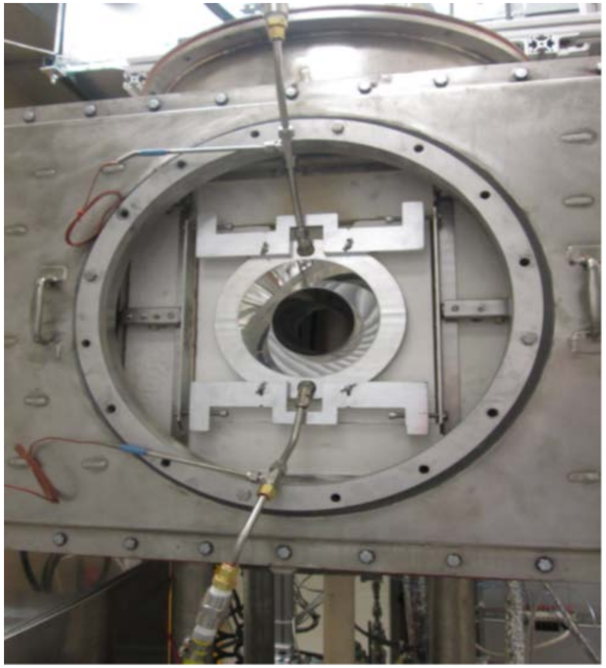
	η solar collection	η PV STWS	η elecrolysis	η overall
PV	100%	20%	70%	14%
STWS	45%	60%		27%
Hybid	**η heat recuperation for ITM SEOS**	**η electric turbine**	**η electrical resistance**	**η overall** (x 60% STWS)
	90%	40%	100%	22%
	80%	40%	100%	19%
	70%	40%	100%	17%

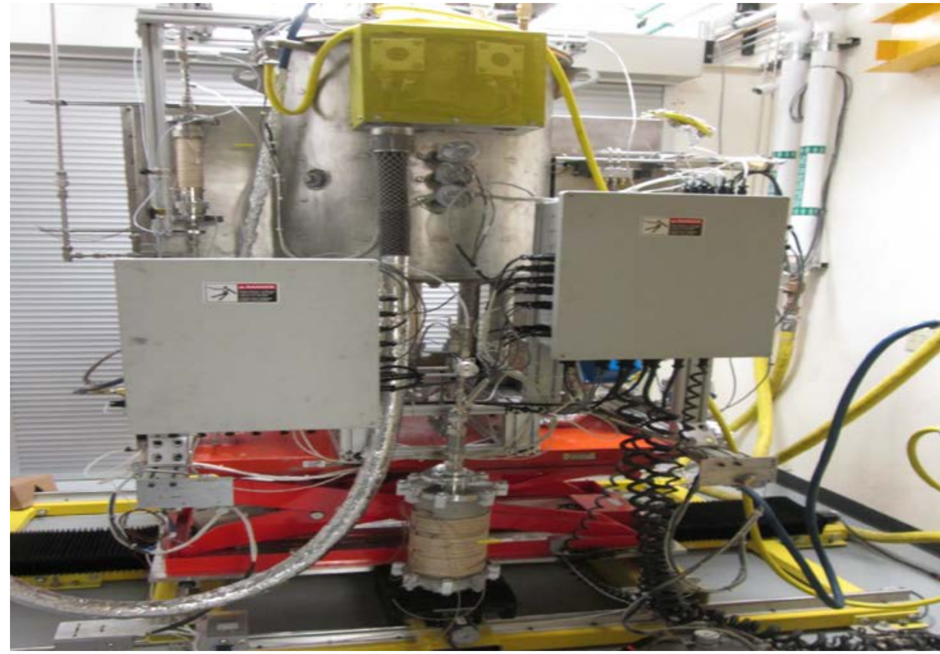
Capital Comparison:

1) PV electrolysis is capital intensive – half the cost of a plant is PV and half is the elecrolyzers;
2) Branz says cost of adding molten salt is 1/3 best possible cost of adding batteries;
3) Per Harper Int'l, adding electrical resistance with power supply to an already solarthermal receiver increases capital cost for an insulated solar reactor with sliding CPC already installed along with reactor tubes by 25 to 50% (max)

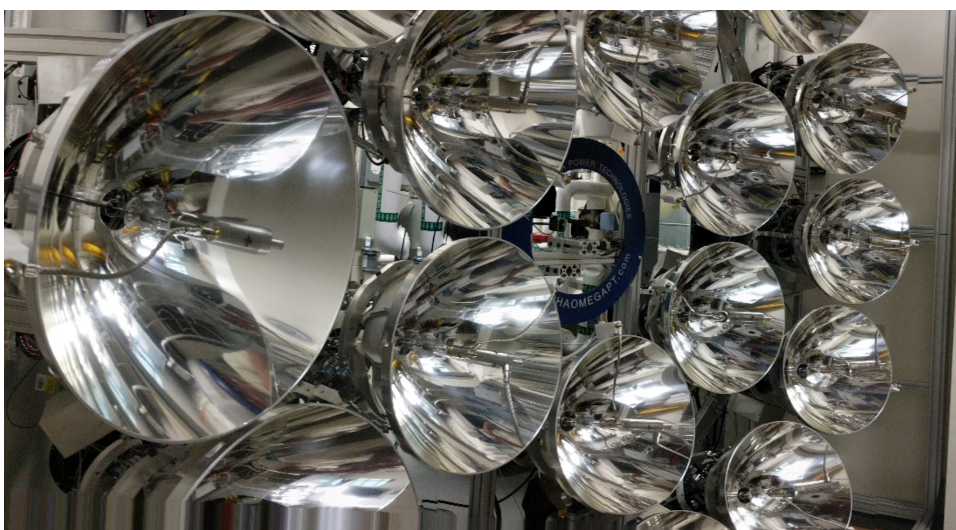
University of Colorado 12 kW$_{thermal}$ HFSS and Hybrid Solar/Electric Receiver

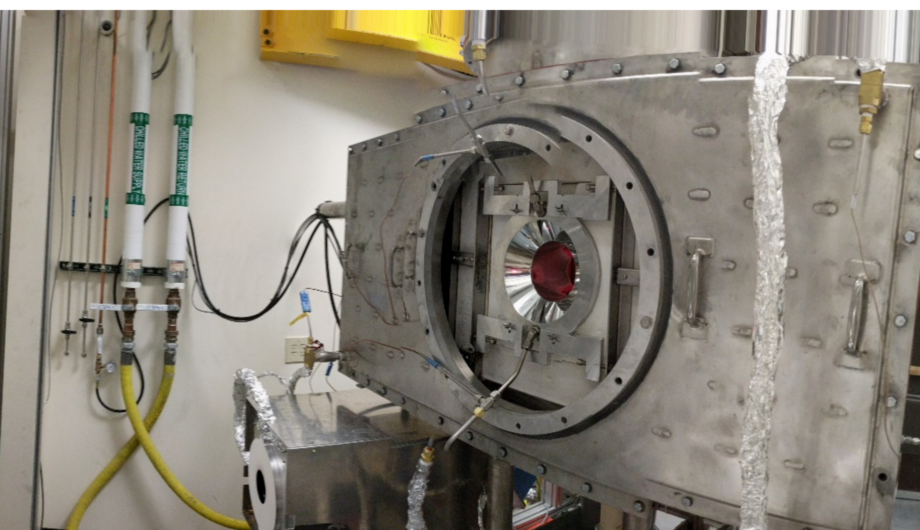
CU hybrid receiver (front with sliding CPC)





CU hybrid receiver (back showing xyz stand, etc.)

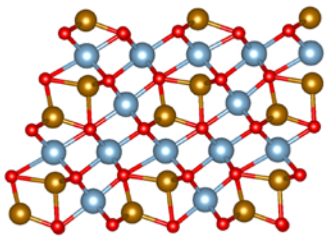




Accomplishments and Progress:
NSF "Sister" Project for STWS Materials Development

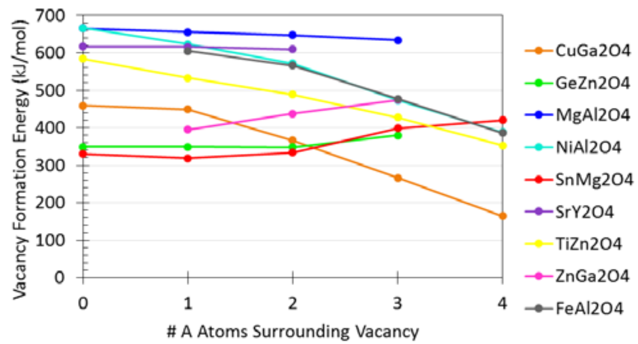
Spinel Screening

AB_2O_4

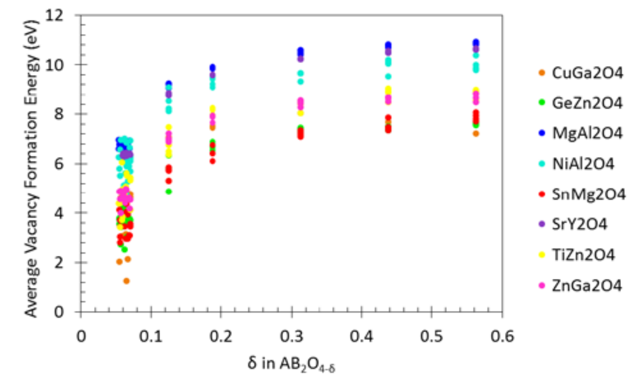


Legend:
- A Atom (Fe)
- B Atom (Al)
- Oxygen

Inversion Effect on Vacancy Formation Energy



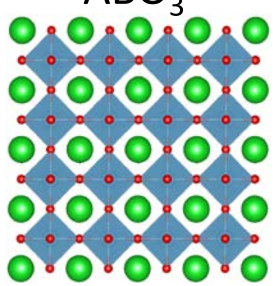
Effect of δ on E_v



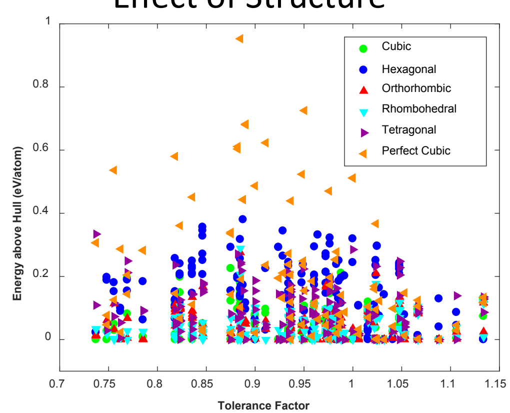
- Vacancy formation energy varies by up to 300 kJ/mol depending on cation environment
- Average vacancy formation energy changes similarly across spinels for increasing δ

Perovskite Screening

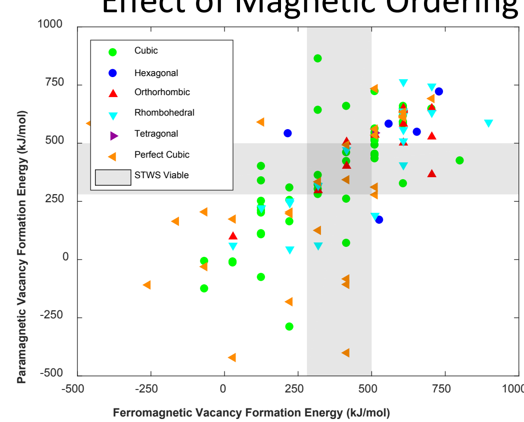
ABO_3



Effect of Structure



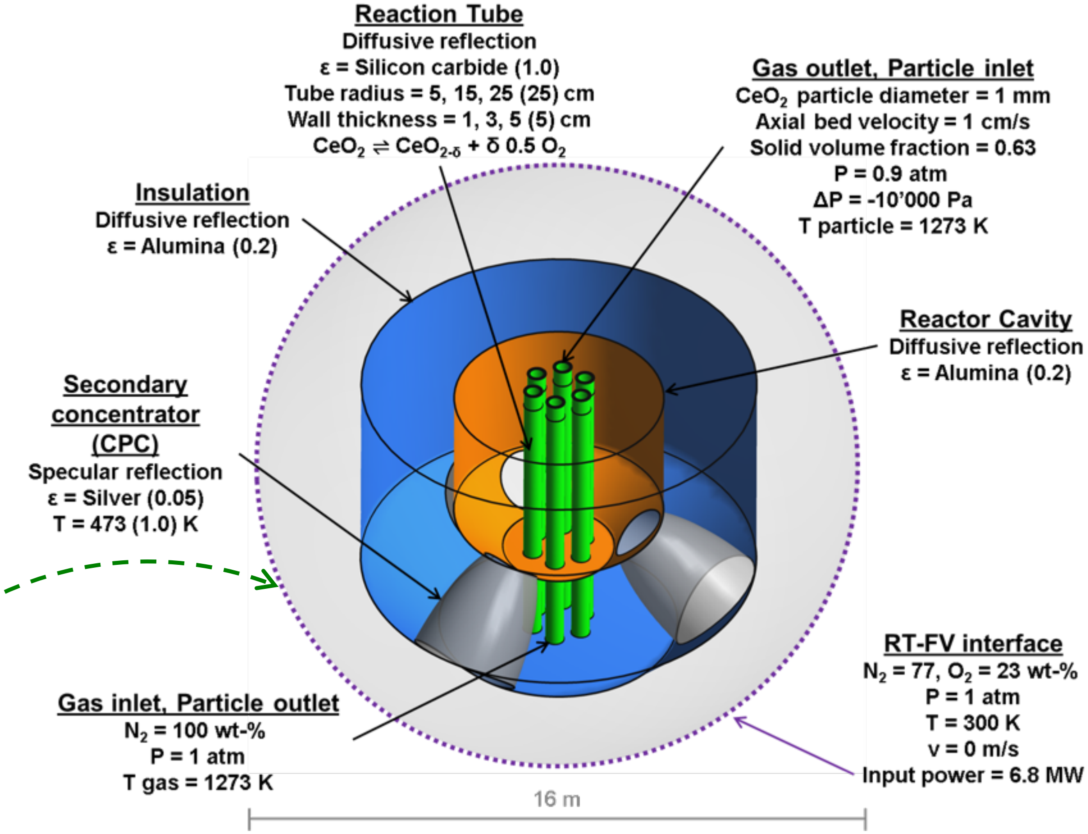
Effect of Magnetic Ordering



- Evaluated 1343 materials for the effect of structure and magnetic ordering on STWS behavior
- Found both factors to critically impact accuracy of predicted STWS ability

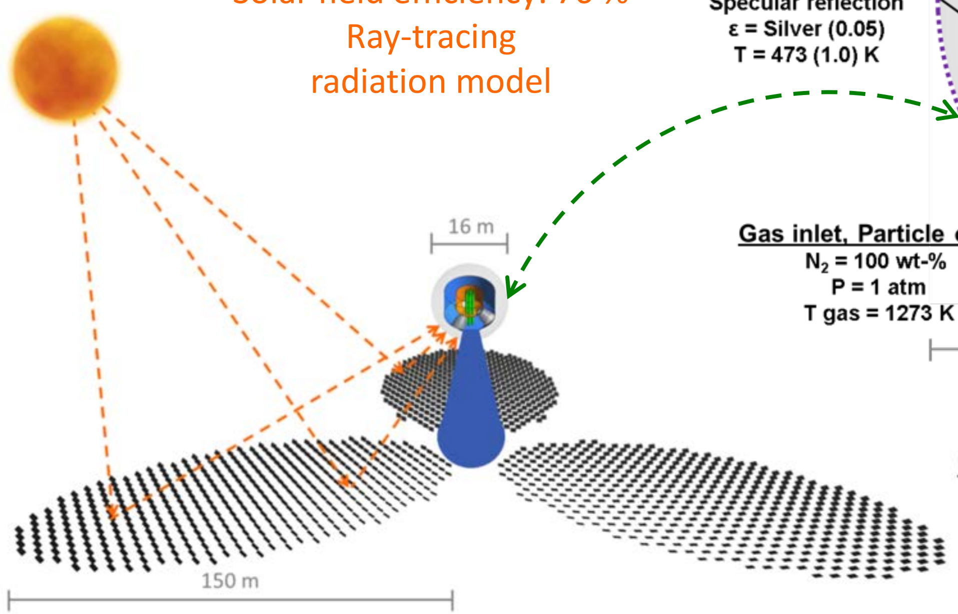
Accomplishments and Progress: Modeling of Solar-thermal Reactor Systems

Goal of this work: To simulate industrial-scale reactor for solar-thermal water splitting by catalytic particles



Heliostat-mirrors

Number: 469 X 3
Size: 4 X 4 m
DNI: 1000 W/m^2
Solar field efficiency: 76 %
Ray-tracing radiation model

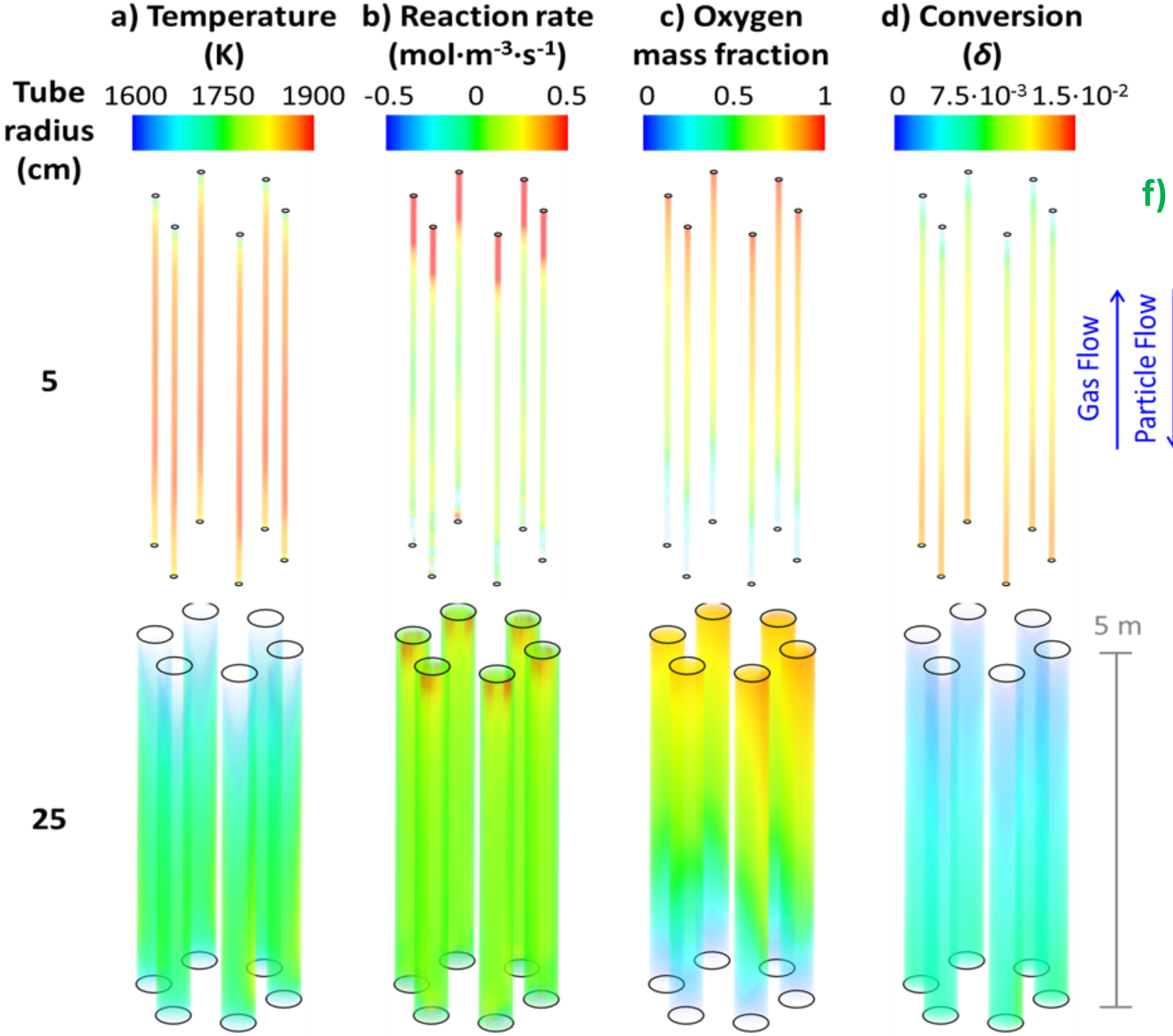


Chemical Reactor

Tower height: 75 m
Finite-volume radiation model

Ray-tracing and finite-volume methods coupled to model heliostat field and reactor

Accomplishments and Progress:
H_2 production at different SiC tube radii



e) Oxygen vacancy production rate (kmol/h)

f) Theoretical hydrogen Production rate (l/h)

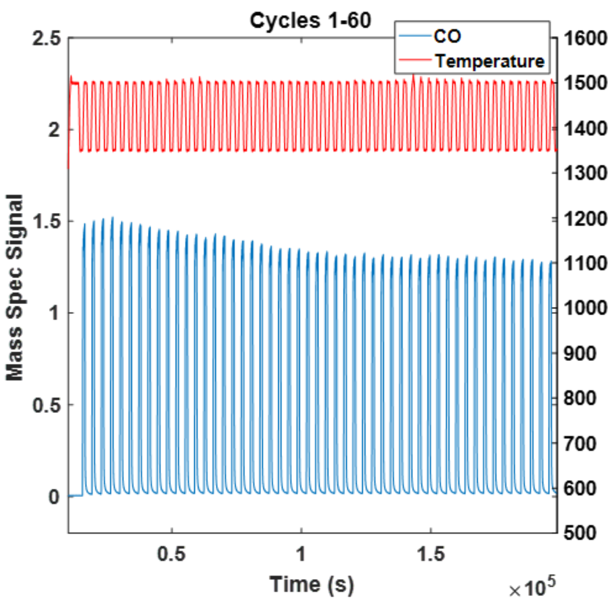
Tube radius (cm)	e)	f)
5	**0.3**	**$7.1 \cdot 10^3$**
25	**3.7**	**$8.3 \cdot 10^4$**

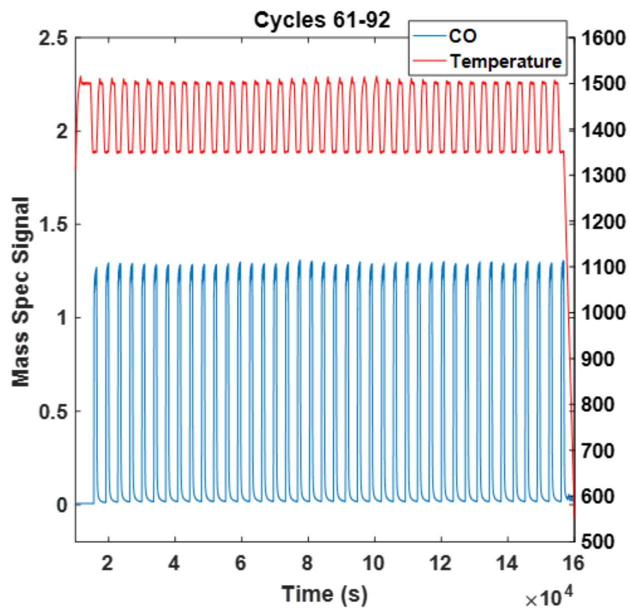
Gröhn, A.J., Lewandowski, A., Yang, R. & Weimer, A.W., (2016). Hybrid radiation modeling for multi-phase solar-thermal reactor systems operated at high-temperature. *Solar Energy*, **140**, 130-140.

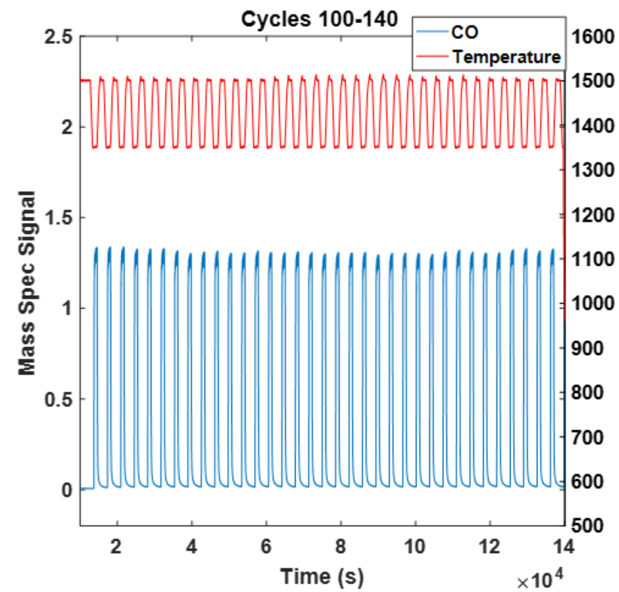
For tube radii of 5 cm and 25 cm, the calculated theoretical hydrogen production rates are $7.1*10^3$ L/hr and $8.3*10^4$ L/hr, respectively

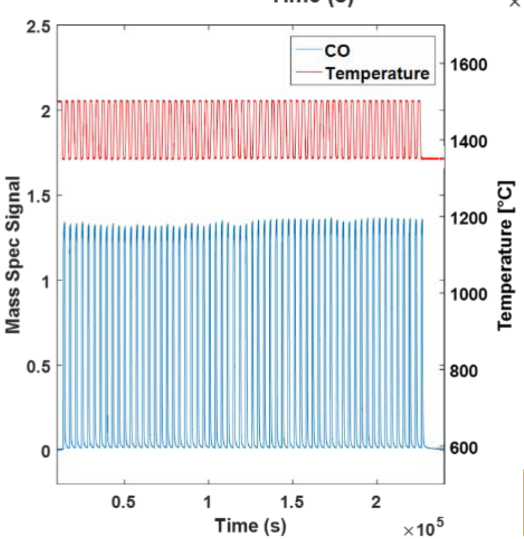
Accomplishments and Progress: GNG: Long Term RedOX Testing

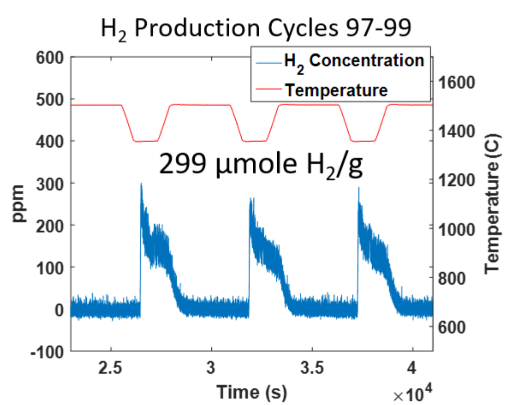
GNG2: Demonstrate the production of robust spray dried active materials that produce at least 150 µmol H2/g total and do not lose more than 10% of its reactivity between the 100th and 200th RedOx cycle material.

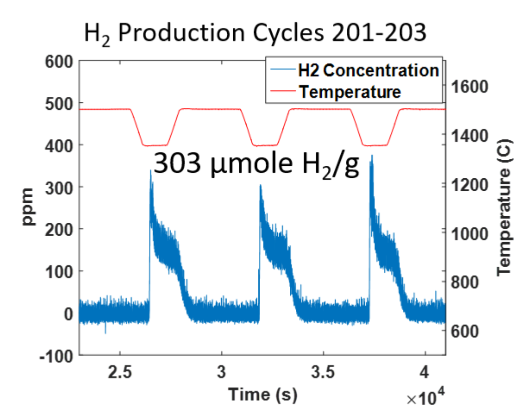












H_2 production at cycle 100: 299µmol/g. At cycle 200: 303µmol/g. Exceeds GNG target.