Flowing Particle Bed Solarthermal Redox Process to Split Water

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06/14/2018

Project ID: PD114

Overview:
Year 4 of 4-Year Project

Timeline

Project Start Date: 9/1/2014

Project End Date: 9/30/2018

% Complete: 93%

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)

TRL 2 → TRL 3

Technical Barriers Addressed

S. High-temperature robust materials

W. Materials and catalysts development

X. Chemical reactor development and capital costs

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

Budget

Total project funding: $2,000,000

Sub-contract to NREL: $450,000

Total recipient cost share: $6,250

Total funds received to date: $1,885,252

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 H2A
- On-sun production for a full solar day
- Move from TRL 2 to TRL 3

This Reporting Period:

- Four materials produced >200 µmol/g at T = 1450^{o}C
- O_2 concentration reduced to 15ppm from 1% at 1 SLPM using ITM SEOS with 29% η_{sep}
- Discovered hercynite undergoes O_2 vacancy mechanism when reduced and reoxidized
- Hercynite materials produced 280 µmol/g isothermally at 1700^{o}C in CU fluidized bed
- ALD costings show up to 64% improvement to oxidation resistance of SiC
- 4.22L H_2 produced in 8 hours testing at NREL's HFSF
- 3.23L H_2 produced in 6 hour continuous test at NREL's HFSF

Approach:
Iterative Materials and Reactor Development

Reactive Matierals

Reactor Design

Efficient, Cost-effective H_2 Production

Produce and test reactive materials

- M1.1: Develop hercynite material formulations (90% done)
- M1.2: Develop perovskite and spinel material formulations (90% done)
- M1.6: Kinetic studies on materials of interest (95% done)
- M1.7: Test materials for long-term reactivity (100% done)

Construct particle flow system to test reactor design

- M3.3: Develop diffusional model for oxygen removal (50% done)
- M3.4: Operate reactor as a fluidized bed (90% done)

Containment Materials

Ongoing updates to the process model and H2A

On-Sun Production

Develop redox compatible containment materials

- M2.1: Synthesis and characterization of coated SiC powders (90% done)
- M2.2: Selection of preferred coating material based on TGA results (95% done)
- M2.3: Synthesis of ALD coated SiC tubes (20% done)

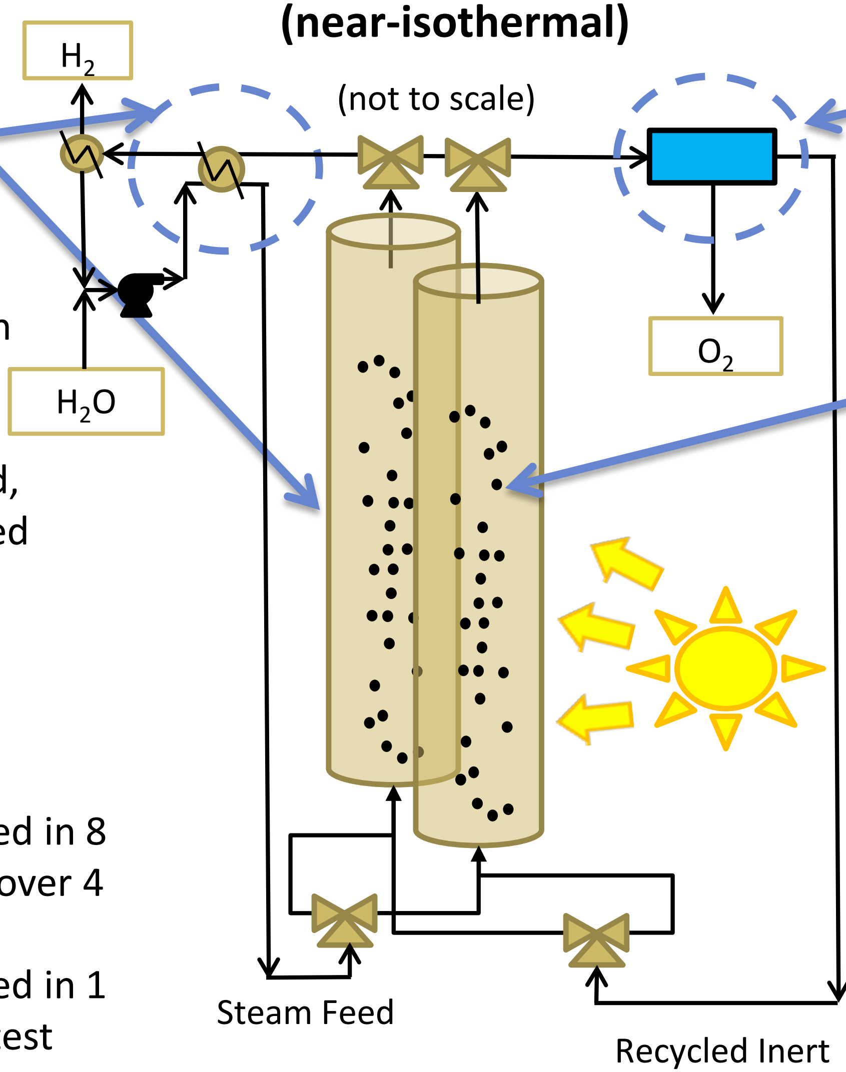
Production of H_2 with reactive engineered particles (100% done)

Accomplishments and Progress: Overall Process R & D

Multiple Fluid Beds in Solar Cavity (near-isothermal)

Containment Materials R&D

- ALD coatings provide up to 64% improvement on oxidation resistance
- SiC tubes coated, and will be tested at reaction conditions



SEOS for Recycled Inert Gas R&D

- O_2 conc reduced to 15 ppm from 1% with 29% η_{sep}

Active Materials R&D

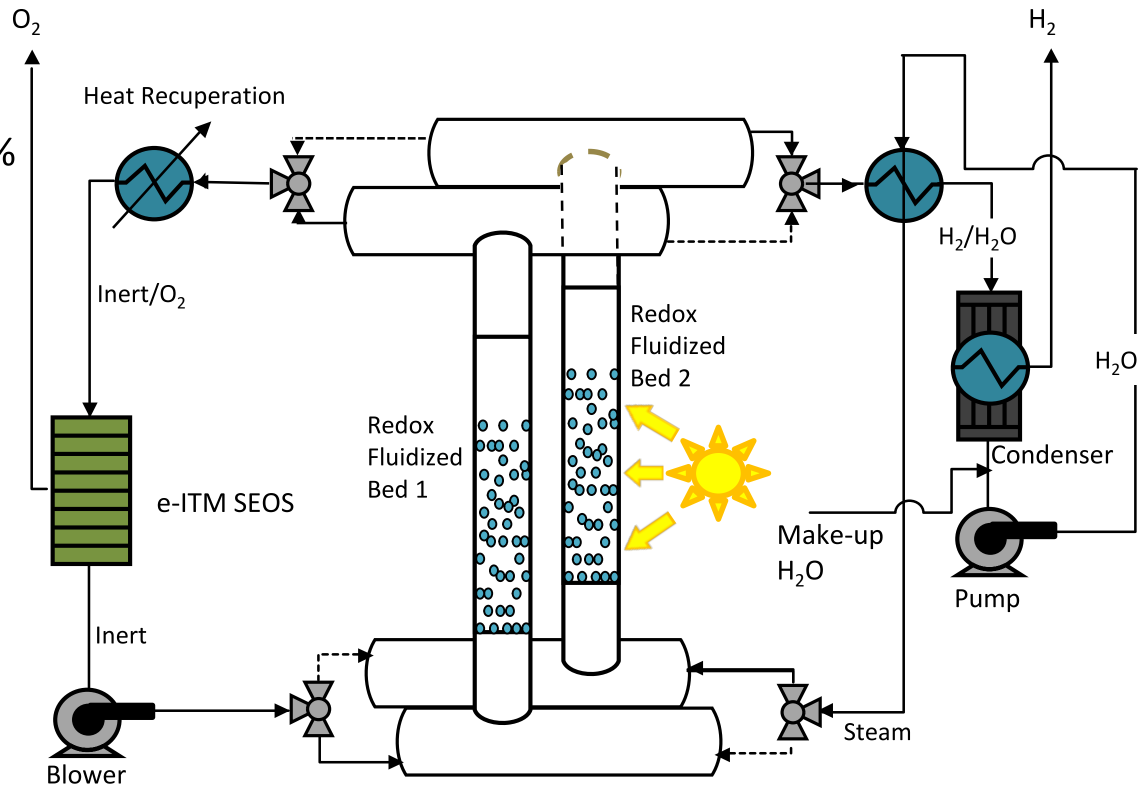
- 1.1M perovskites filtered to 27,015
- 116 ternary perovskites stable capable of driving STCH
- 425 double pervoskites screened
- Four materials produced >200 µmol/g at 1450°C
- Reliable, rapid kinetic screening technique developed
- Hercynite found to have O_2 vacancy mechanism

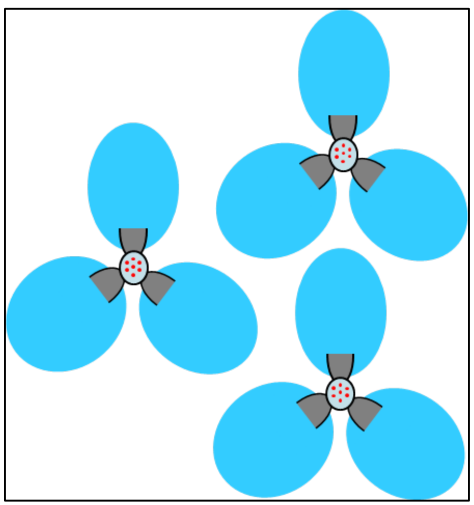
Overall System R&D

- 4.22L H_2 produced in 8 hours of testing over 4 days
- 3.23L H_2 produced in 1 day continuous test

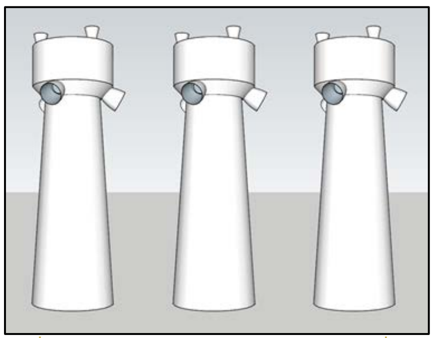
Accomplishments and Progress: Process Model

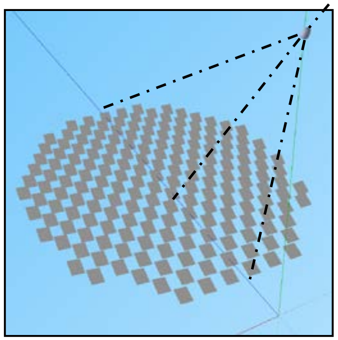
- Redox reactors operate as fluidized beds within solar cavity
- No solids movement between reactors, simple design
- Reduction and oxidation occur at near 1450°C
- Membrane experimental efficiency of 29%
- 570 μmol/g hercynite active material productivity
- Cost of ALD coatings and replacement included





Concept cartoon of new three-lobed solar field design with three central towers



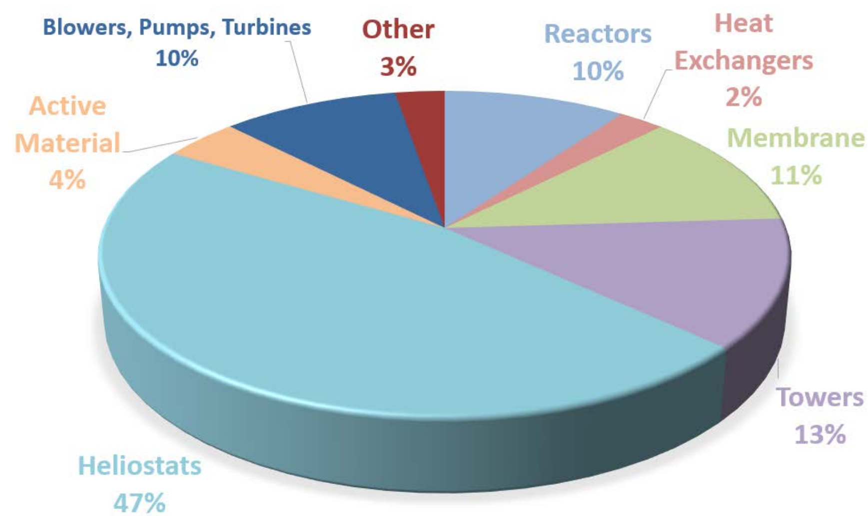


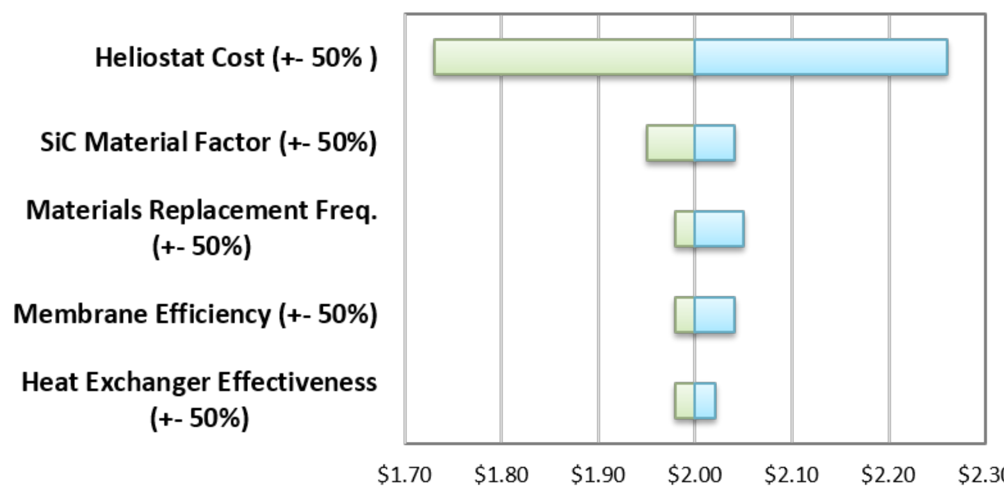
Accomplishments and Progress: H2A

Cost Drivers	Least Favorable	More Favorable	Most Favorable
Heat exchanger effectiveness	85%	90%	95%
SiC material factor	6	5	3
Replacement frequency (years)	2	5	7
Enthalpy of reaction (kJ/mol)	384	346	307
Heliostat cost ($/m^2)	$140	$75	$60
Cost H_2 ($/kg)	$8.70	$2.94	$2.00

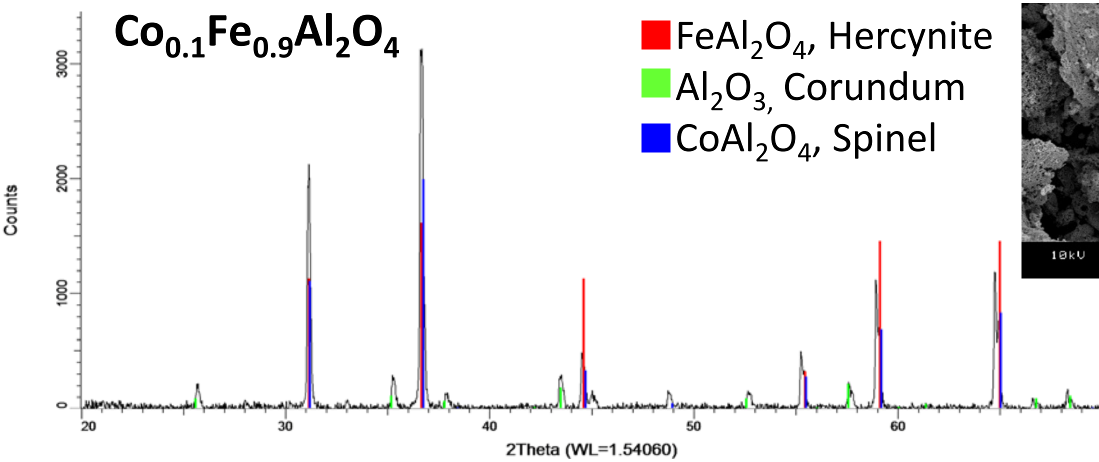
TEA predicts that process can produce H_2 at $2/kg assuming significant reduction in heliostat cost and improvements in active and containment materials

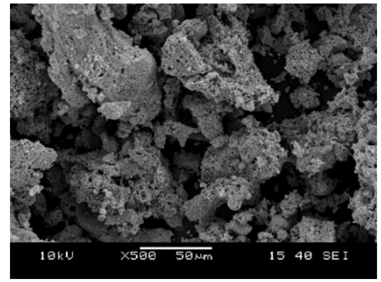
Direct Capital Cost Breakdown for $2/kg Cost Target





Accomplishments and Progress: Experimental Testing

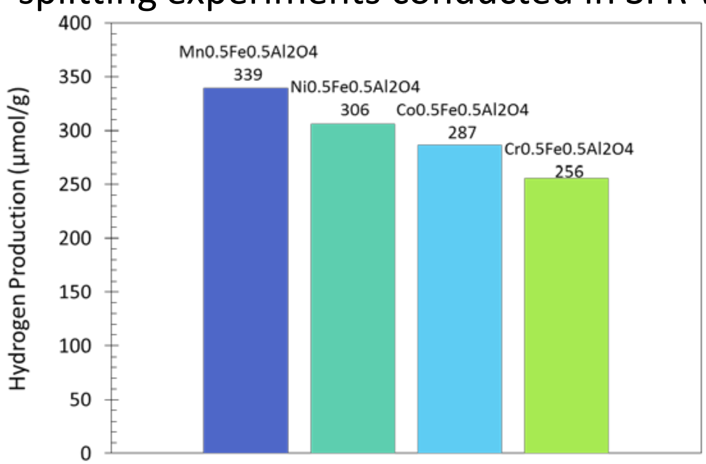


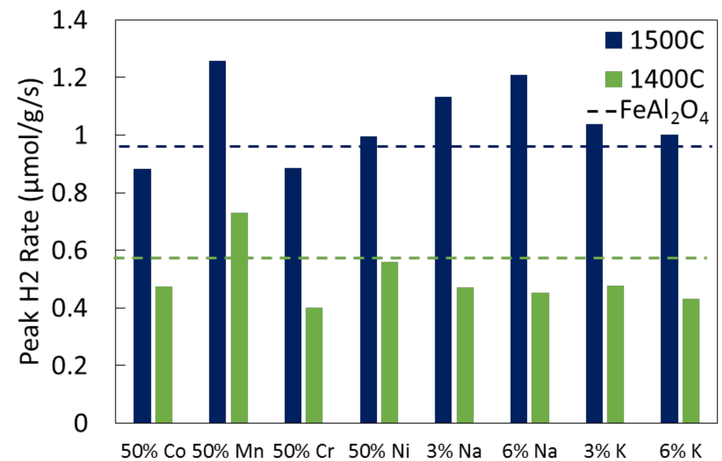


	ICP Molar Ratio	Target Ratio
Co	0.11	0.11
Fe	1	1
Al	1.78	2.22

Materials synthesized with citrate gel method and characterized with XRD, ICP, and SEM

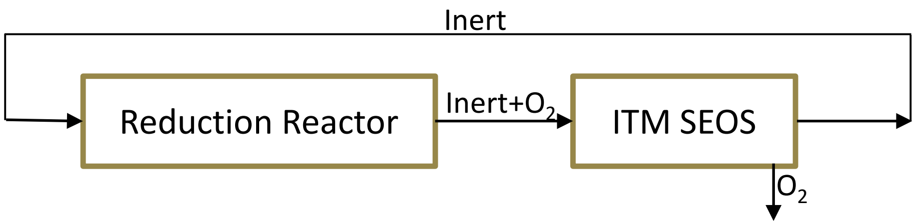
- Water splitting experiments conducted in SFR with 5 Cycles at 1450°C reduction, 1200°C oxidation

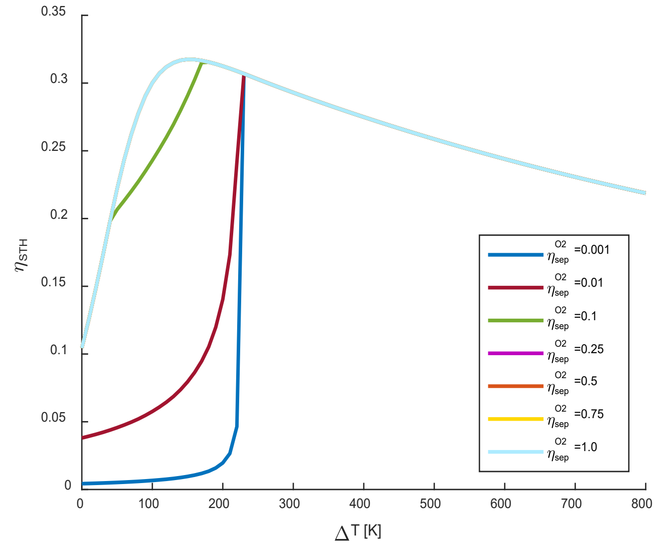




Four materials produced > 200 µmol/g at T_{red}=1450°C
$Mn_{0.5}Fe_{0.5}Al_2O_4$ shows the highest H_2 production of TM hercynite alloys and improved peak rate over undoped hercynite

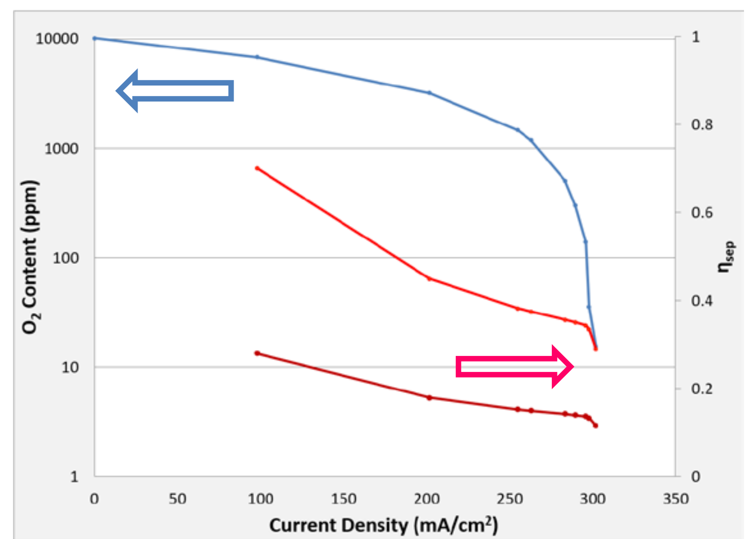
Accomplishments and Progress:
ITM SEOS Membrane for Recycled Inert Gas Sweep





<u>ITM SEOS Membrane Results</u>

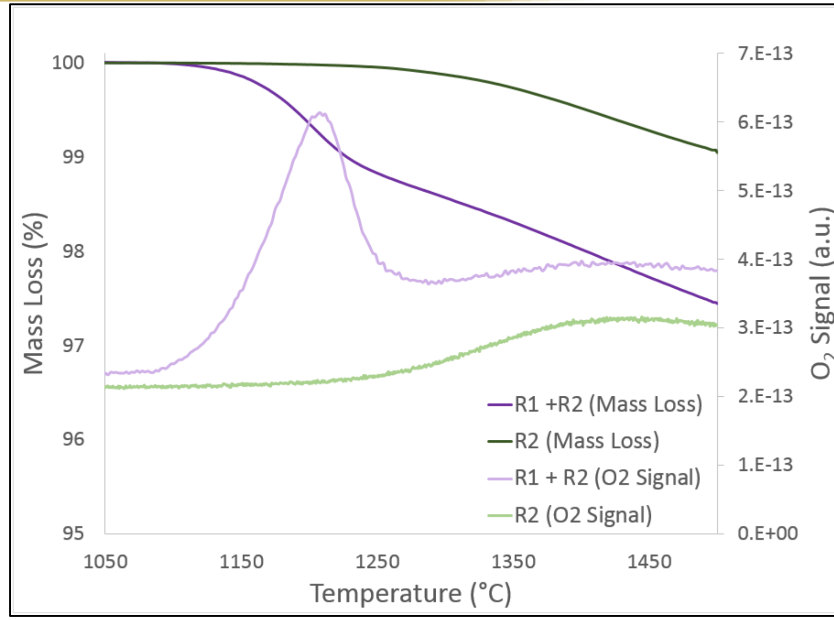
- Solar-to-H_2 thermodynamic efficiency calculations showed the separation efficiency (η_{sep}) of inert gas and generated O_2 needs to be at least 10% to have an efficient process.
- A high temperature (850°C) Ion Transport Membrane (ITM) Lab size unit was built in collaboration with Ceramatec
- Energy requirements for O_2 separation of ITM membrane was Compared to thermodynamic separation work to calculate η_{sep}
- Experimental energy requirements are inflated to include thermal-to-electricity conversion ($\eta_{solar\text{-}to\text{-}electricity}$)

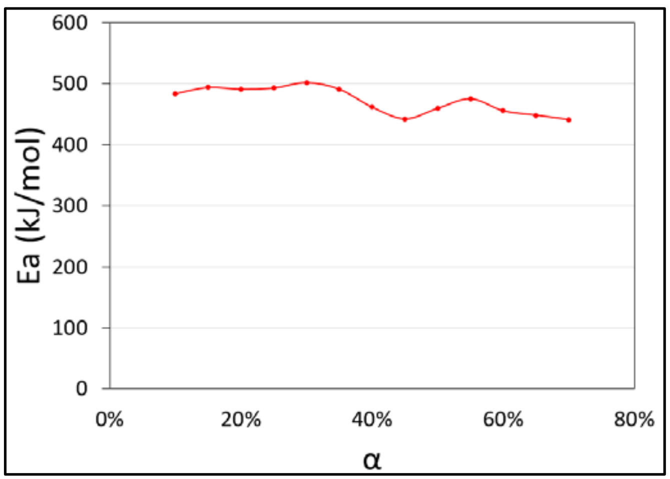


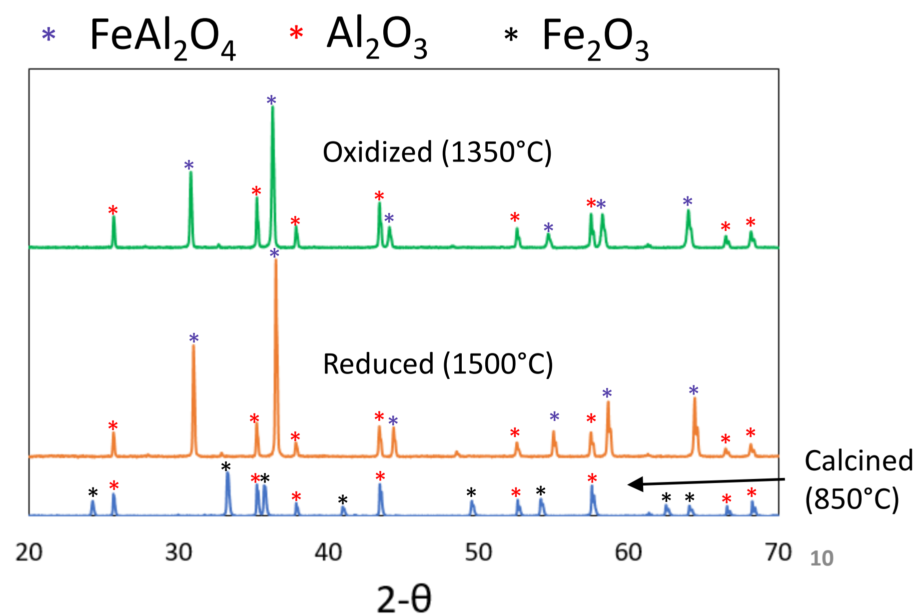
O_2 concentration reduced to 15ppm from 1% O_2/N_2 mixture at 1 SLPM using ITM SEOS with 29% η_{sep} (12% including thermal-to-electricity conversion)

Accomplishments and Progress: Hercynite Redox Reaction Mechanism

- 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



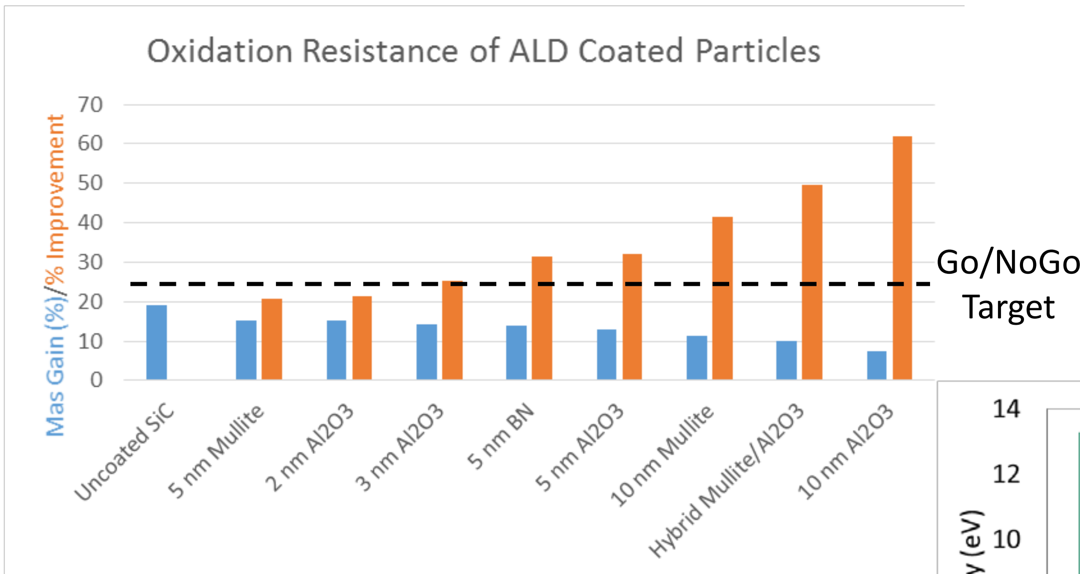




Undoped hercynite undergoes an O_2 vacancy mechanism when thermally reduced and oxidized with H_2O or CO_2

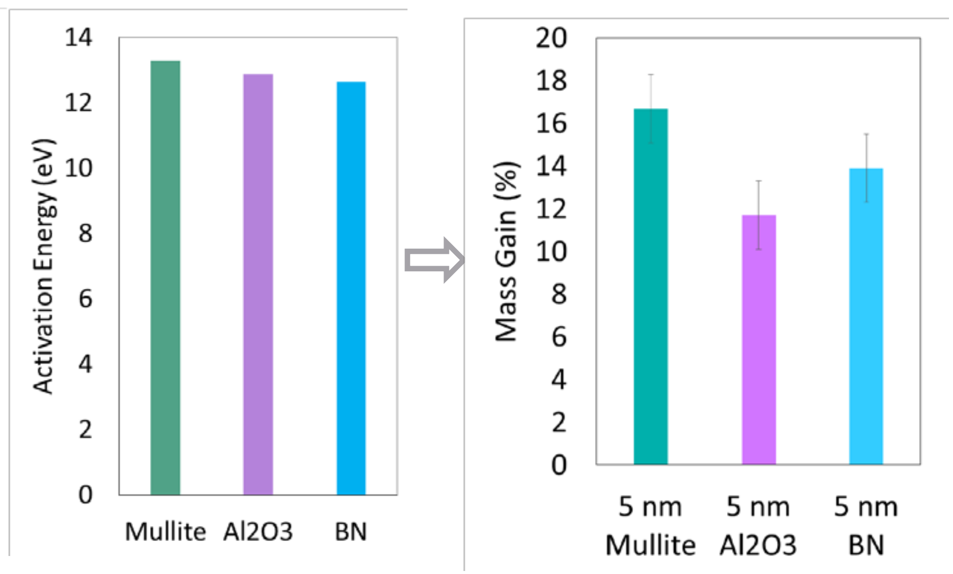
Accomplishments and Progress: SiC Steam Oxidation Resistance

- Particle ALD is being used to study the stabilization effects of nano-scale diffusion barriers with atomic growth control
- Mullite ($3Al_2O_3{:}2SiO_2$), alumina, and BN have developed and tested
- Mullite coatings were applied to SiC tubes that are currently installed in the reactor at NREL to study the durability of ALD films in solar applications



- Increased film thickness improves performance
- Mullite films with 1.5X thickness are able to match performance of alumina
- Preliminary BN films show reduced oxidation similar to alumina

- Computational determination of diffusion activation energy correlates well with experimental outcomes
- Three additional ALD films are currently being developed to further validate our computational method for screening film materials

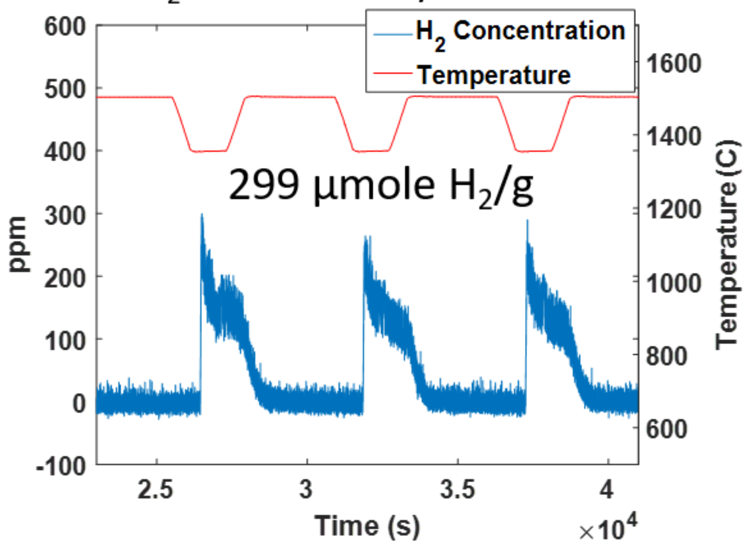


ALD coatings show up to a 64% improvement to the oxidation resistance of SiC.

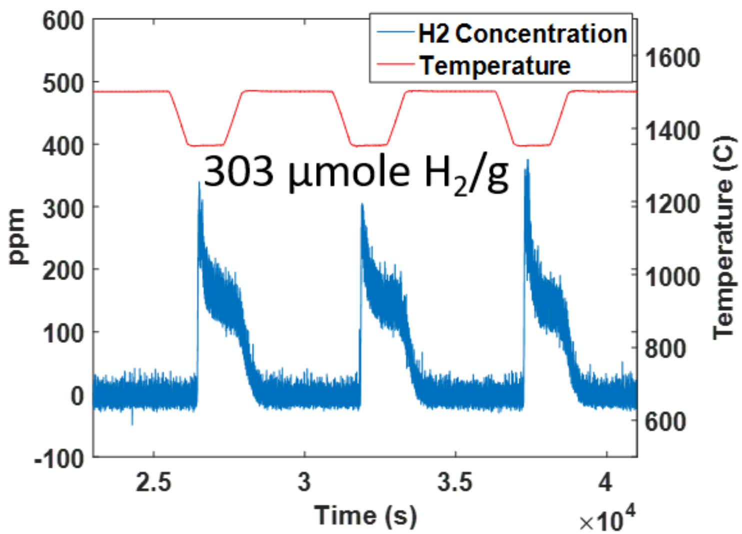
Accomplishments and Progress: Long Term Stability of Spinels

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

H_2 Production Cycles 97-99



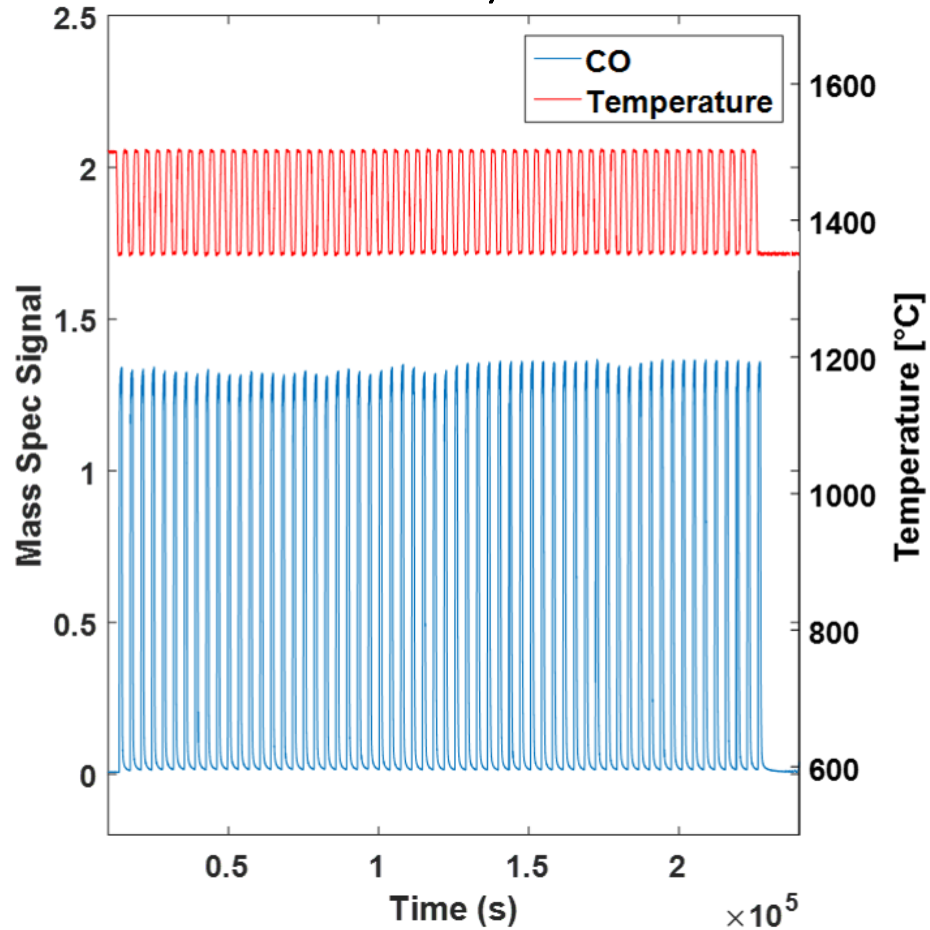
H_2 Production Cycles 201-203



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

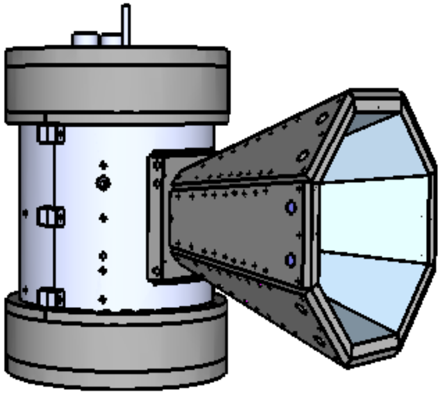
Actual: 300 µmole H_2/g and no activity loss

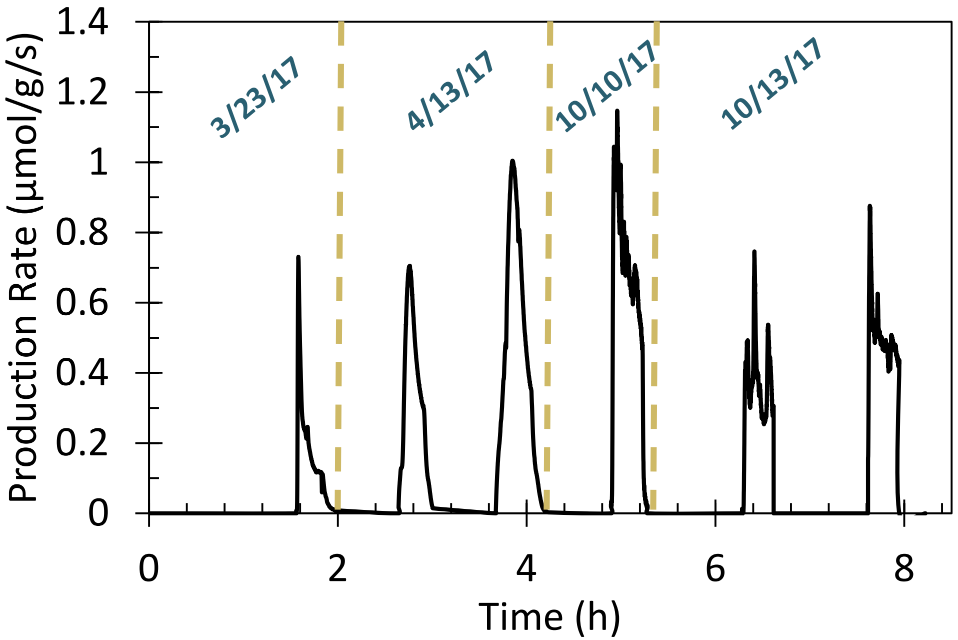
CO Production Cycles 141-200



Accomplishments and Progress: On-Sun Hydrogen Production

- Tests performed in NREL's 10 kW high-flux solar furnace
- Dual fluidized beds
- Two SiC tubes loaded with ~40g of hercynite each
- Steam fed from a humidification system
- In-situ MS
- Average H_2 productivity matches results of SFR testing at CU
    - CU SFR Average Productivity: 571 +/- 63
- 4.22L H_2 produced in 8 hours of testing (EERE goal: 3L in 8 hours)





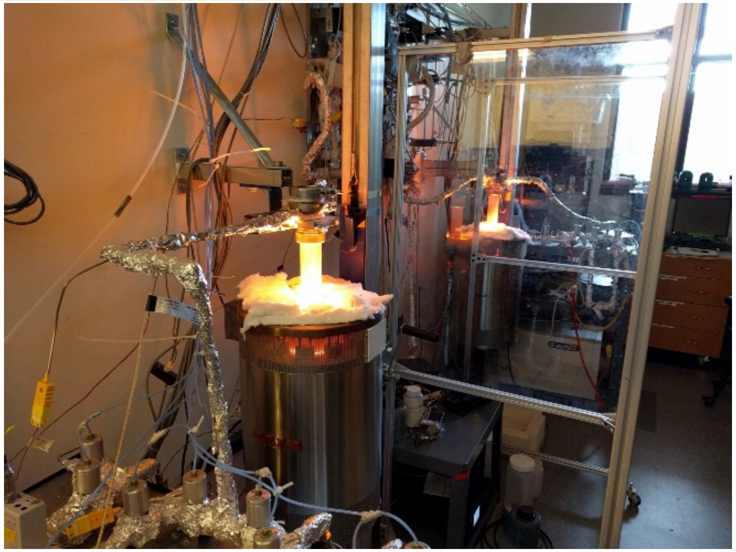
Cycle	Date	H_2 (L)	H_2 Productivity (µmol/g)
1	3/23/17	0.22	237
2	4/13/17	0.79	442
3	4/13/17	1.50	838
4	10/10/17	0.78	870
5	10/13/17	0.40	432
6	10/13/17	0.53	601
		Total H_2 4.23	Average Activity 570

4.22 L H_2 produced in 8 hours of testing at NREL's HFSF

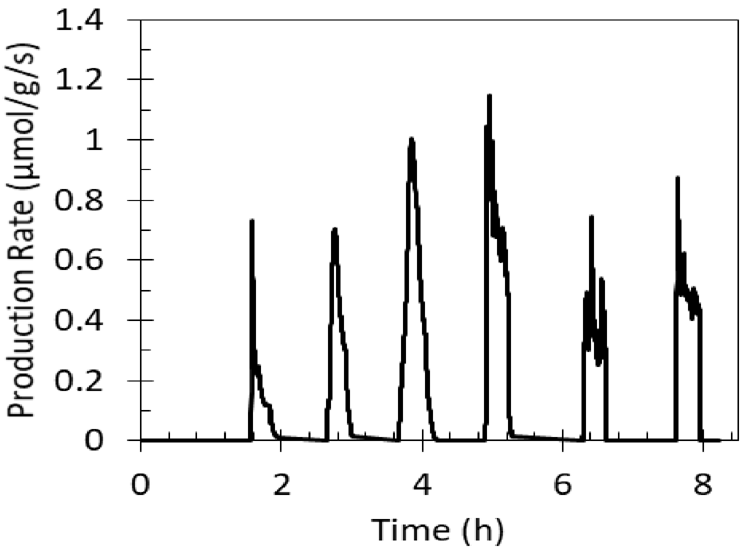
Accomplishments and Progress: On-Sun vs. In-Lab

- 800X scale up to NREL facility

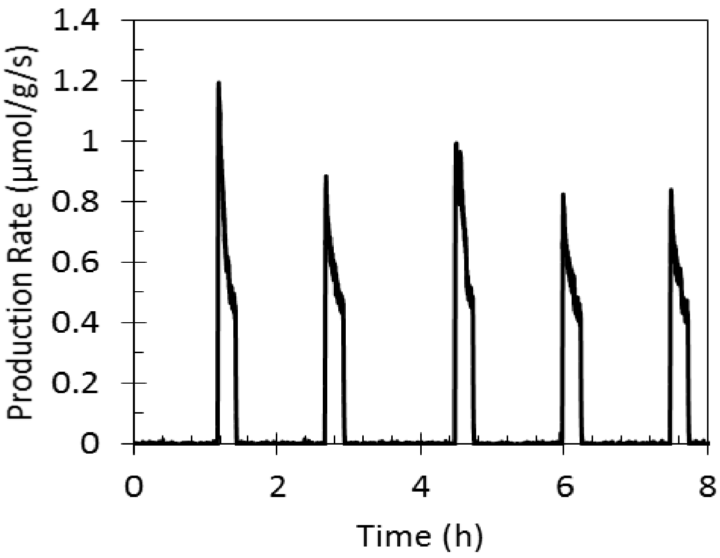
	Average H_2 Productivity (µmol/g)
SFR testing at CU	571 +/- 63
On-Sun testing at NREL	570 +/- 229



On-Sun Testing at NREL HFSF

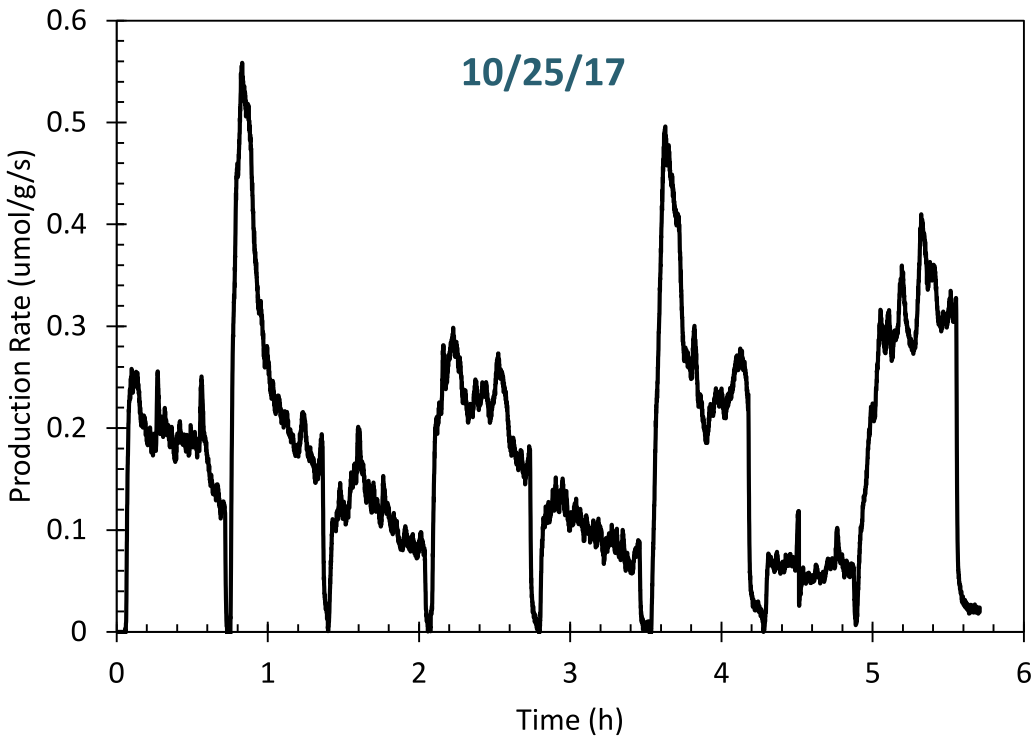


SFR Testing at CU



Accomplishments and Progress: On-Sun Hydrogen Production

- Tests performed in NREL's 10 kW high-flux solar furnace
- Same set-up as previous tests
- Dual fluidized beds; one reduces while the other oxidizes
- In previous studies, both tubes were reducing or oxidizing together
- 3.23 L H_2 produced in 6 hours of continuous testing
- Average productivity of 445 µmol/g/cycle



Cycle	Tube	H_2 (L)	H_2 Productivity (µmol/g)
1	1	0.39	445
1	2	0.56	610
2	1	0.23	265
2	2	0.48	521
3	1	0.21	237
3	2	0.59	650
4	1	0.13	150
4	2	0.62	681
		Total H_2 3.23	Average Activity 445

3.23 L H_2 produced in 6 hours in continuous test at NREL's HFSF

Summary

- Four materials produced > 200 µmol/g at T_{red}=1450°C. $Mn_{0.5}Fe_{0.5}Al_2O_4$ shows the highest H_2 production of TM hercynite alloys and improved peak rate over undoped hercynite
- 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)
- Undoped hercynite undergoes an O_2 vacancy mechanism when thermally reduced and oxidized with H_2O or CO_2
- Hercynite materials produced 280 µmoles of H_2/g isothermally at 1700 °C in the fluidized bed
- ALD coatings show up to a 64% improvement to the oxidation resistance of SiC
- 4.22L H_2 produced in 8 hours of testing at NREL's HFSF
- 3.23L H_2 produced in 6 hour continuous test at NREL's HFSF

AMR Reviewer Comments 2017

- *"The proposed work on detailed thermodynamic and kinetic optimization of current reactive materials is not likely to add much value given that more efficient water-splitting materials need to be discovered to achieve the DOE goals."*

  Our activity testing and techno-economic analysis has shown that hercynite is an economically viable material for solar-thermal water-splitting, although it is possible that better materials will be discovered. We feel that characterizing the thermodynamics and kinetics of hercynite will benefit the research community and move the technology closer to commercialization.

- *"It would have been… relevant to coat a slab of SiC with alumina and then allow the perovskite particles to fall against it, at temperature, followed by measurement of the persistence of the alumina coating at the impact site."*

  We plan to test the ALD-coated SiC tubes in the fluidized bed reactor at NREL. We will assess the extent of damage due to attrition from reactive materials and exposure to steam at high temperatures.

- *"The reactor designs were overly simple."*

  In year one of the project, we investigated optimal reactor design and scale-up for a fluidized bed system envisioned as a scaled-up version of the reactor in use at NREL. The model included the solar field, the CPCs, the reactor cavity and the fluidized bed reactors. It accounted for radiative, convective and conductive heat transfer as well as mass and momentum transfer within and in between the solid and fluid phases. We did not present this modeling in the previous year because it was included in our 2016 presentation.

- *"Material development was minimal. The project should have worked with SNL on material development."*

  Over the past year, we have developed new methods to screen materials rapidly based on kinetic properties. Additionally, we have synthesized and characterized 25 new spinel and perovskite formulations. Going forward, CU plans to collaborate with SNL on an EERE-funded STCH materials development project.

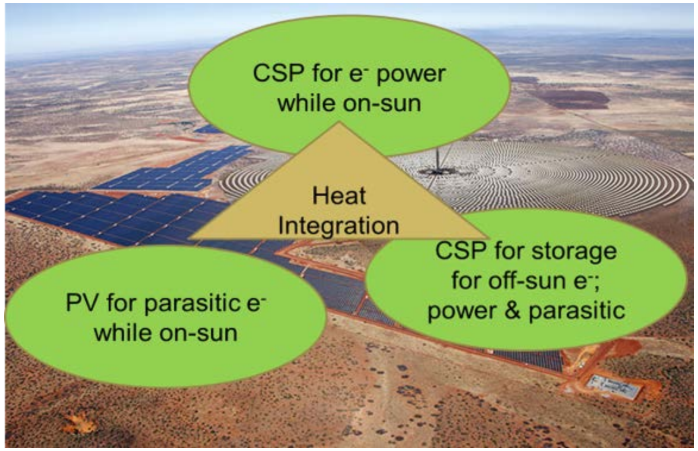
Collaborations

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*

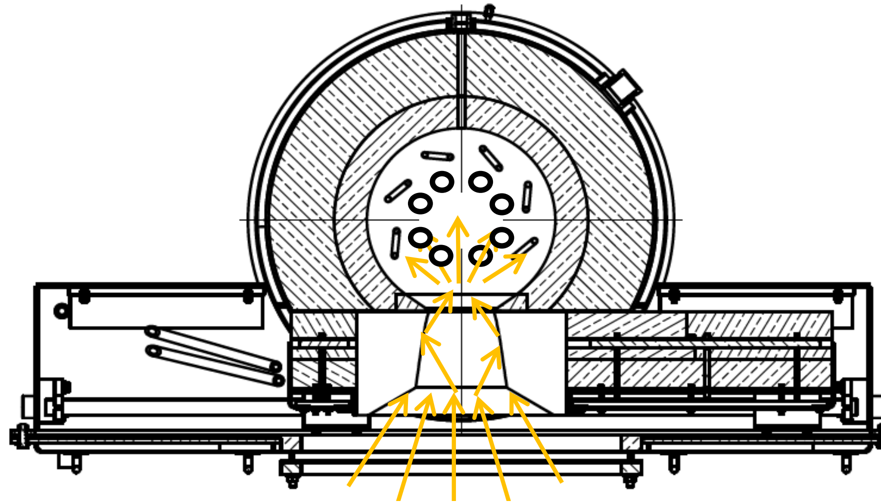
* Funds from Joint DOE/NSF FOA

Leveraged Collaborators (no funds from DOE)	Project Roles
Saudi Basic Industries Corporation (SABIC)	Materials characterization support; supplying equipment
CoorsTek / 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* – hybrid solar/electric receiver

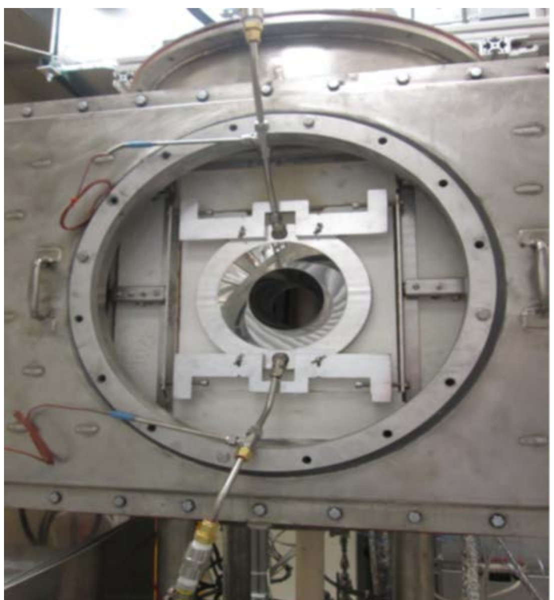


Non-intermittent chemical processing



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. Project is ending. Future work is outside scope of current project.

Acknowledgements

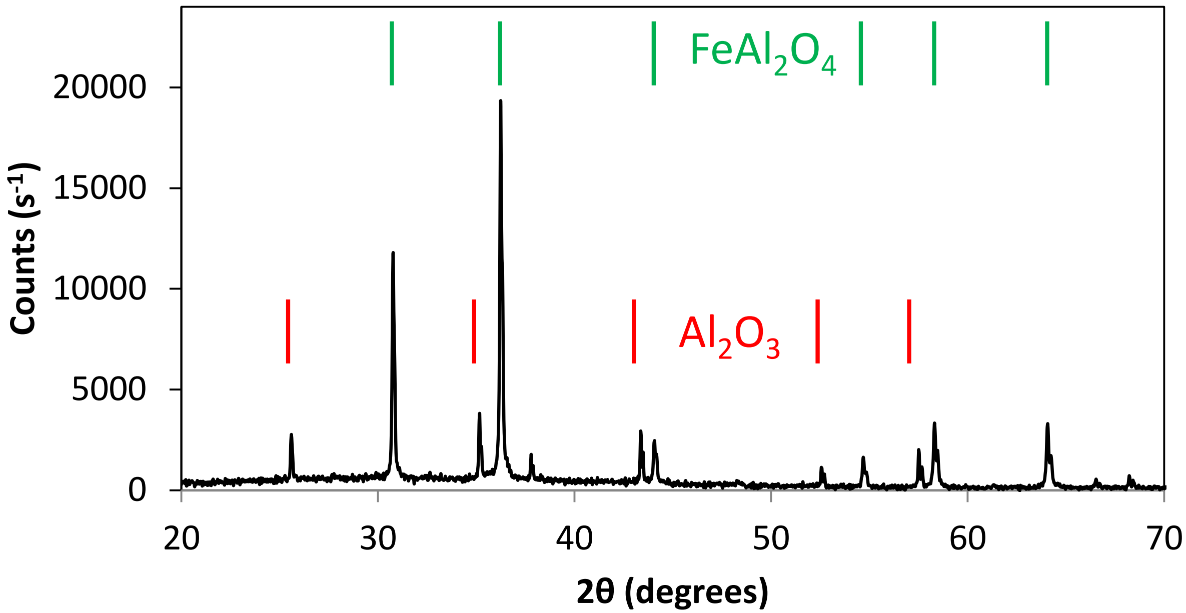
Backup Slides

Synthesis of Hercynite Particles

- Eirich Intensive Mixer Type RV02E used to fabricate hercynite particles
- Hercynite Precursors:
  - 2240g <10µm Al_2O_3 particles
  - 1760g <5µm Fe_2O_3 particles
  - 133g Corn Starch
  - 267g Maltodextrin
  - 300g Water

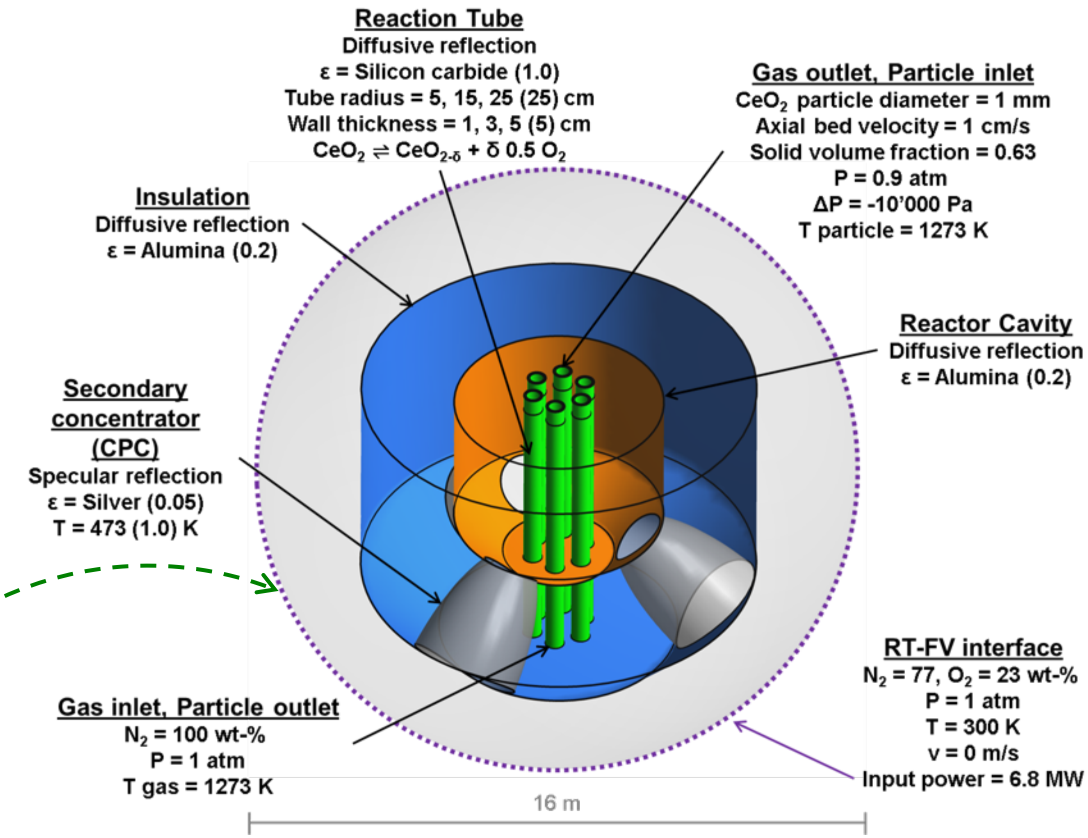
EIRICH Intensive Lab Mixer

- Dried at 150°C for 4 hours
- Pyrolyzed at 650°C for 2 hours
- Calcined at 1300°C under vacuum for 24 hours
- Mass loss heat treatment = ~5%
- Theoretical mass loss = 4.4%



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

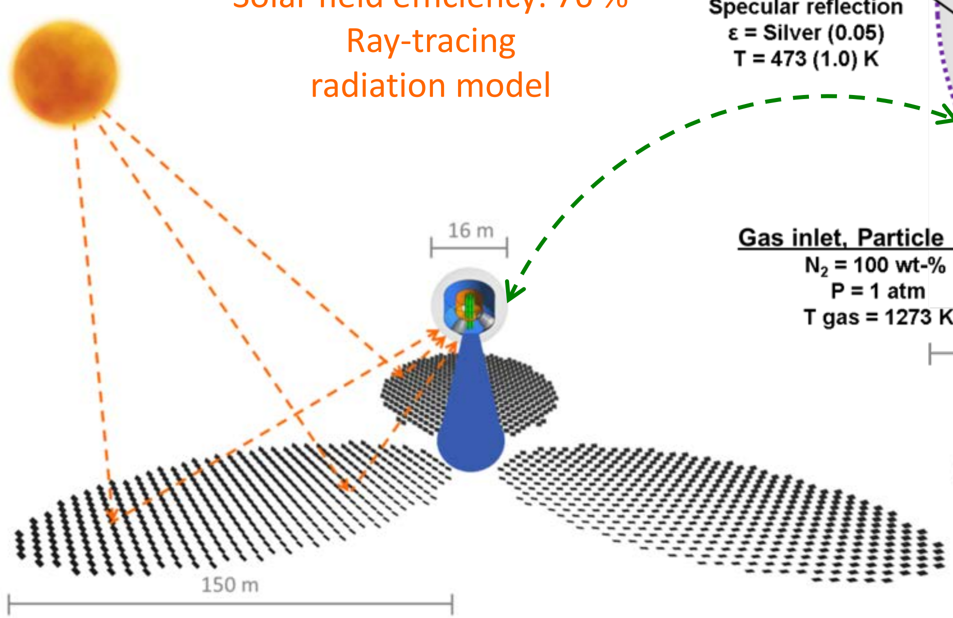
Number: 469 X 3

Size: 4 X 4 m

DNI: 1000 W/m^2

Solar field efficiency: 76 %

Ray-tracing radiation model



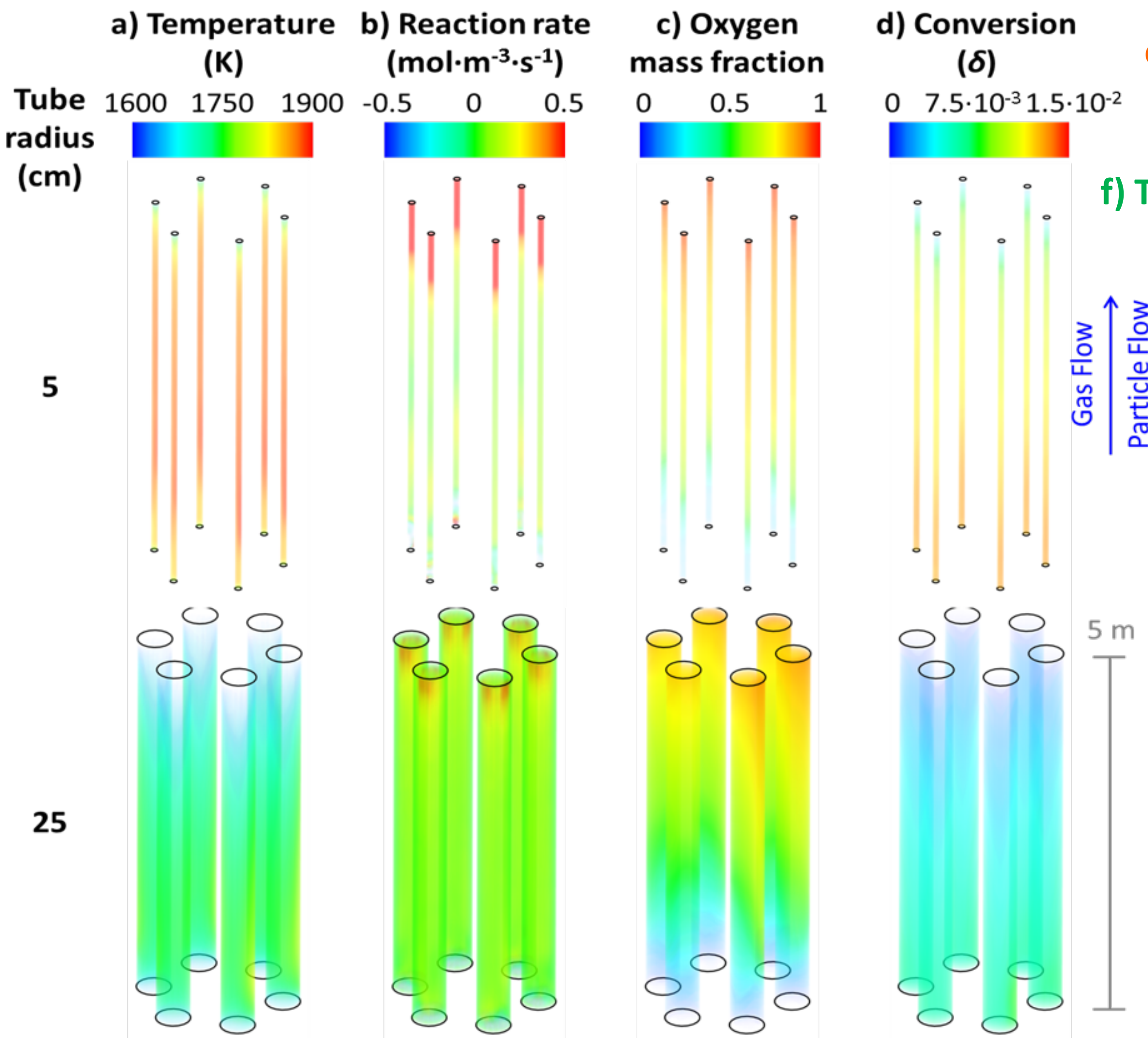
Chemical Reactor

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)
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*10³ L/hr and 8.3*10⁴ L/hr, respectively