Flowing Particle Bed Solarthermal Redox Process to Split Water

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Overview:
Year 3 of 3-Year Project

<table>
<thead>
<tr>
<th>Timeline</th>
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<tbody>
<tr>
<td>Project Start Date: 9/1/2014</td>
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<tr>
<td>Project End Date: 11/30/2017</td>
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<td>% Complete: 87%</td>
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<tr>
<th>Technical Barriers Addressed</th>
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<tr>
<td>S. High-temperature robust materials</td>
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<td>W. Materials and catalysts development</td>
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<td>X. Chemical reactor development and capital costs</td>
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<tr>
<th>Paid Partners</th>
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<tbody>
<tr>
<td>National Renewable Energy Laboratory (NREL), Golden, CO</td>
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<tr>
<td>• Solar testing facility and capabilities</td>
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<tr>
<td>Allan Lewandowski Solar Consulting, LLC</td>
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<td>• Solar field design consultation and modeling</td>
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<tr>
<td>Musgrave Group*, CU Boulder</td>
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<tr>
<td>• Active materials discovery and DFT modeling (*NSF/DOE Funding – joint FOA)</td>
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<tr>
<th>Collaborators</th>
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<tr>
<td>Australian National University (ANU), Canberra, AU</td>
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<tr>
<td>• Reactor models and receiver testing at solar simulator facility</td>
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<tr>
<td>Saudi Basic Industries Corporation (SABIC)</td>
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<tr>
<td>• Supplying equipment and materials characterization</td>
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<tr>
<td>Coorstek/Ceramatec</td>
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<tr>
<td>• Preparation of large spherical active materials</td>
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<td>• High temperature O₂ transport membrane</td>
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<th>Budget</th>
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<tr>
<td>Total project funding: $2,000,000</td>
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<td>Sub-contract to NREL: $450,000</td>
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<td>Total recipient cost share: $6,250</td>
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<td>Total funds received FY16: $687,055</td>
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<td>Total planned FY17: $455,901</td>
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**TRL 2 → TRL 3**
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 $\text{H}_2$/day at a cost < $2$/kg $\text{H}_2$

- 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\textsuperscript{th} and 200\textsuperscript{th} cycle and 2X targeted $\text{H}_2$ 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 $\text{H}_2$ 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\textsubscript{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

**Efficient, Cost-effective H₂ Production**

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**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 $\geq 150 \mu$mol H₂/g (100% done)
  - GNG2: Particles that produce $\geq 150 \mu$mol H₂/g and lose $\leq 10\%$ reactivity from 100th to 200th cycle (100% done)

**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 $\geq 25\%$ reduction in steam reactivity (100% done)

**Reactor Design**
- Construct particle flow system to test reactor design
  - M3.2: Evaluate diffusional limitations under inert gas with O₂ 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)

**On-Sun Production**
- Production of H₂ with reactive engineered particles (80% done)

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Ongoing updates to the process model and H2A
Accomplishments and Progress: Overall Process R&D

**Containment Materials R&D**

- Synthesized Al₂O₃, mullite, BN coated SiC
- Improved stability (>60%) with 10 nm Al₂O₃ coating shown with TGA
- Test system for coated tubes constructed

**Active Materials R&D**

- Demonstrated no loss in reactivity from 100th to 200th redox cycle while generating ~ 300 μmol H₂/g active material

**Overall System R&D**

- On-sun testing at NREL’s HFSF on target to meet final deliverable; 1.91L H₂ made in <3 hours

**SEOS for Recycled Inert Gas R&D**

- Demonstrated 12% efficiency with electrically heated high-temperature O₂ transport membrane
- Investigating effect of O₂ concentration on reduction kinetics and productivity

**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 H₂/8hr at NREL HFSF using Hercynite active materials

[Diagram of solar cavity receiver and redox fluidized beds]
Accomplishments and Progress: Temperature-Swing Process Design

- Continuous flowing particle bed hydrogen production process
- Solar radiation on reduction reactor only
- Reduction occurs at 1450°C
- Oxidation occurs at 1000°C
- Experimental implementation underway using 12 kW solar simulator at CU (pictured)
- 3L H₂ in 8 hours using Hercynite
Accomplishments and Progress: H2A Results

TEA predicts that NI and TS processes can produce H₂ at $2.00 /kg, and $1.98/kg, respectively.
Go/NoGo: Active Materials Robustness

Spray Dried Co$_{0.5}$Fe$_{0.5}$Al$_2$O$_4$

H$_2$ Production Cycles 97-99

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

299 µmole H$_2$/g

303 µmole H$_2$/g
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.

Impact of Inversion on Local Environment

Findings show promise for modeling of disordered systems without explicit calculations for every state.
Particle ALD is being used to study the stabilization effects of nano-scale diffusion barriers with atomic growth control.

- Mullite (3Al₂O₃:2SiO₂) and BN have been identified as a promising coating materials.
- H₂O 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 than 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-H₂ thermodynamic efficiency calculations showed the separation efficiency ($\eta_{sep}$) of inert gas and generated O₂ needs to be at least 10% to have an efficient process.
- Tested a high temperature (850°C) Ion Transport Membrane (ITM) to remove O₂ from inert gas.
- Compared energy requirement of separation to thermodynamic separation work to calculate $\eta_{sep}$.
- Experimental energy requirements are inflated to include thermal-to-electricity conversion ($\eta_{solar-to-electricity}$).

**O₂ concentration reduced to 15ppm from 1% O₂/N₂ mixture at 1 SLPM using ITM SEOS with 29% $\eta_{sep}$ (12% including thermal-to-electricity conversion)**
Accomplishments and Progress: Hercynite Materials Characterization

- Hercynite is formed by reacting $\text{Al}_2\text{O}_3$ and $\text{Fe}_3\text{O}_4$ to form the spinel phase
- $\text{Fe}_3\text{O}_4 + 3\text{Al}_2\text{O}_3 \rightarrow 3\text{FeAl}_2\text{O}_4 + \frac{1}{2}\text{O}_2$ \hspace{1cm} (R1)
- Hercynite materials is further reduced under $\text{O}_2$ vacancy mechanism
- $\text{FeAl}_2\text{O}_4 \rightarrow \text{FeAl}_2\text{O}_4 - \delta + \frac{\delta}{2}\text{O}_2$ \hspace{1cm} (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 $\text{H}_2\text{O}$ and $\text{CO}_2$ oxidation

Undoped hercynite undergoes an $\text{O}_2$ vacancy mechanism up to 1700 °C
Accomplishments and Progress: On-Sun Testing

After producing 1.91L H₂ in less than 3 hours, we are on-target to meet our end-of-project goal of 3L H₂ production in less than 8 hours.
Summary

• New process models using hybrid solar/electric reactors evaluated
• GNG of H₂ production of 150 µmol/g/cycle and less than 10% loss in reactivity met (~300 µmol H₂/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
• O₂ concentration reduced to 15ppm from 1% O₂/N₂ mixture at 1 SLPM using ITM SEOS with 12% ηsep including electricity use
• 1.91L H₂ made during 3 hours of testing at NREL’s HFSF, showing significant progress toward end-of-project goal
“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 H₂ 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 O₂ 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 m² are loaded into the lab-scale fluidized bed ALD reactor and a commercial tube might have an internal surface area of approximately 30 m². This is not a concern.
## Collaborations

<table>
<thead>
<tr>
<th>Fund-Receiving Collaborator</th>
<th>Project Roles</th>
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<tbody>
<tr>
<td>National Renewable Energy Laboratory (NREL) (sub)</td>
<td>High Flux Solar Furnace (HFSF) user facility for process demonstration</td>
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<tr>
<td>Musgrave Group, CU Boulder</td>
<td>Active materials discovery and DFT modeling through “sister” NSF project*</td>
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* Funds from Joint DOE/NSF FOA

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<th>Leveraged Collaborators (no funds from DOE)</th>
<th>Project Roles</th>
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<tr>
<td>Saudi Basic Industries Corporation (SABIC)</td>
<td>Materials characterization support; supplying equipment</td>
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<tr>
<td>Harper International Corporation</td>
<td>Active Materials Preparation; ITM SEOS Membrane</td>
</tr>
<tr>
<td>Australian National University (ANU)</td>
<td>Design and construction of pilot high-temperature solar/electric furnace</td>
</tr>
<tr>
<td>Harper International Corporation</td>
<td>Reactor models and receiver testing at solar simulator facility</td>
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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 H₂ 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

CU hybrid receiver (front with sliding CPC)

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

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 H₂

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

Efficiency Comparison:

<table>
<thead>
<tr>
<th></th>
<th>η solar collection</th>
<th>η PV STWS</th>
<th>η electrolysis</th>
<th>η overall</th>
</tr>
</thead>
<tbody>
<tr>
<td>PV</td>
<td>100%</td>
<td>20%</td>
<td>70%</td>
<td>14%</td>
</tr>
<tr>
<td>STWS</td>
<td>45%</td>
<td>60%</td>
<td></td>
<td>27%</td>
</tr>
<tr>
<td>Hybrid</td>
<td>η heat recuperation for ITM SEOS</td>
<td>η electric turbine</td>
<td>η electrical resistance</td>
<td>η overall (x 60% STWS)</td>
</tr>
<tr>
<td></td>
<td>90%</td>
<td>40%</td>
<td>100%</td>
<td>22%</td>
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<tr>
<td></td>
<td>80%</td>
<td>40%</td>
<td>100%</td>
<td>19%</td>
</tr>
<tr>
<td></td>
<td>70%</td>
<td>40%</td>
<td>100%</td>
<td>17%</td>
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Capital Comparison:
1) PV electrolysis is capital intensive – half the cost of a plant is PV and half is the electrolyzers;
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

- **AB₂O₄**

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

**Effect of δ on Eᵥ**
- 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

- **ABO₃**

**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/m²
- 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:

H₂ production at different SiC tube radii

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

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.

Accomplishments and Progress:

GNG: Long Term RedOX Testing

H₂ production at cycle 100: 299 µmol/g. At cycle 200: 303 µmol/g. Exceeds GNG target.