Solar-thermal ALD Ferrite-Based Water Splitting Cycles

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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

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

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

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

M = Co, Mn, Ni, Zn, or other transition metals
Ferrite Cycle Challenges

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

\[(\text{CoO})(\text{FeO})(\text{Fe}_2\text{O}_3)\] (solid solution)

Slag Phase (liquid)

![Graph showing the phases and mole fractions of CoO, FeO, and Fe$_2$O$_3$ vs. temperature.](image)
Weakness Identified (H2A related) –
“…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..“

Weakness Addressed
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 H₂/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<sub>th</sub> delivered to each solar reactor
- Net concentration 3,868 suns with an annual $\eta = 40.2\%$
## Results – Process Efficiencies

<table>
<thead>
<tr>
<th>Source</th>
<th>Efficiency, $\eta$</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Heliostat Field</strong> (Solar to Receiver)</td>
<td>40.2%</td>
<td>Soltrace</td>
</tr>
<tr>
<td><strong>Thermal</strong></td>
<td>51.7%</td>
<td></td>
</tr>
<tr>
<td><strong>STCH</strong></td>
<td>20.8%</td>
<td></td>
</tr>
</tbody>
</table>
H2A Results – 100,000 kg H$_2$/day (central)

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

![Graph showing H$_2$ selling price over cycles/day with key requirements listed.]
H2A Results – 100,000 kg H₂/day (central)

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

Graph showing the selling price of H₂ over time with different cycles/day.

- 2015: ~12 min cycles
- 2020: ~2 min cycles
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?

CoO
Fe₂O₃
CoO
Fe₂O₃

CoFe₂O₄

Thermal Reduction
1200 to 1500 °C

O₂

(H₂)

H₂O oxidation
900 to 1400 °C

(CoO)(1.4FeO)(0.3Fe₂O₃)
Support and EDS Mapping
(CoFe$_2$O$_4$ thin ALD films)

Low X bulk m-ZrO$_2$ Support  High X bulk m-ZrO$_2$ Support

EDS Zr map  EDS Fe map
ALD CoFe$_2$O$_4$ on ZrO$_2$ Supports

- ZrO$_2$ support; 50 m$^2$/g as received
- 2 nm CoFe$_2$O$_4$ film via ALD
- Raman Spectra confirm CoFe$_2$O$_4$

Scheffe, J.R. et al., in press, Chemistry of Materials (2011)
CO$_2$/H$_2$O 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

- 50% conversion achieved in < 23 s for thin film
  - High surface area, likely no oxide film diffusion limitation
  - No noticeable deactivation for ALD CoFe₂O₄ films/ZrO₂

WS @ 600°C, CR (ALD coated CoFe₂O₄/ZrO₂)

Peak H₂ Rate 40 μmol H₂/s/g in 20 s
Sintering and Phase Segregation During High Temperature Cycling (1450°C reduction)

Grain Growth and Sintering

Phase Segregation

Pre-Processing

Post-Processing
**H₂O Oxidation Behavior Comparison**

- Similar amount of H₂ produced by both structures/cycle.
- Peak rate analysis indicates differences between sintered ALD and co-precipitate composite structures.
  - Greater peak H₂ production rate (~10 X) for sintered ALD film
ALD Rate comparison – thin film vs. aggregates

- More \( \text{H}_2 \) produced using thin films/cycle (~ 2X)
- Peak rate analysis indicates differences between intact thin films and sintered ALD structures.
  - Greater peak \( \text{H}_2 \) production rate (~ 10 X) for ALD thin film
ALD Rate comparison – thin film vs. bulk prepared

Chemical Reduction (ALD thin film)

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

Thermal Reduction (co-precipitated; bulk prepared)
H2A Results – 100,000 kg H₂/day (central)

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

2015
~12 min cycles

2020
~2 min cycles
Spinel

Hercynite

FeAl$_2$O$_4$

CoAl$_2$O$_4$

No Apparent “Slag” Phase

~ 250°C Lower T

Reduction

Hercynite: 940°C

Ferrite: 1190°C

“Hercynite Cycle”

Advantages

MFe$_2$O$_4$+3Al$_2$O$_3$ \rightarrow MAI$_2$O$_4$+2Fe$_2$AlO$_4$+1/2O$_2$

MAI$_2$O$_4$+2Fe$_2$AlO$_4$+H$_2$O \rightarrow MFe$_2$O$_4$+3Al$_2$O$_3$+H$_2$

H$_2$O \rightarrow H$_2$+1/2O$_2$

(Powder XRD Confirms “Hercynite”)
“Hercynite” vs. Ferrite Cycle H₂ Production (oxidation @1000°C)

CoFe₂O₄/Al₂O₃ ("hercynite cycle")

CoFe₂O₄/ZrO₂ (conventional ferrite cycle)

Comparative Reduction Step

FACTSage™ Free Energy Minimization

~5 kg CeO₂ reduced @ 1600°C
~0.3 kg NiFe₂O₄/Al₂O₃ @ 1450°C

Equivalent H₂ Production

“hercynite”

ferrite
ceria
H2A Results – 100,000 kg H₂/day (central)

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

![Graph showing the decrease in H₂ selling price over time with key requirements highlighted.](image-url)

- 2015: ~12 min cycles
- 2020: ~2 min cycles

H₂ Selling Price ($/kg) vs. # Cycles/day

0 100 200 300 400 500

$8 $7 $6 $5 $4 $3 $2

100,000 kg H₂/day (central)
Multi-tube Cavity/Receiver Reactor

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

9.7 mm ID x 12.7 mm OD Hexoloy® SiC tubes
H2A Results – 100,000 kg H₂/day (central)

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

# Cycles/day

H₂ Selling Price ($/kg)

- 2015
- 2020

~12 min cycles
~2 min cycles
Novel Skeletal Al$_2$O$_3$ 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](image-url)

**Graph:**

- Oxidation temperature, °C
- Surface area, m$^2$/g
- Pore volume, cm$^3$/g

**Legend:**

- Large Pore Volume
- Large Pores
- Easily Controlled High Surface Area > 100m$^2$/g
ALD CoFe$_2$O$_4$ Film on Skeletal Al$_2$O$_3$

~ 20 wt% ferrite
"Hercynite" H₂O splitting cycle demonstrated w/ 1160°C/800°C redox cycle!

Coated Nanoparticle Al₂O₃

Coated Skeletal Al₂O₃

Metal alloys may potentially be used for structural containment!
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 TIAAX review
- The team has demonstrated that H2 can be produced with reduction T < 1200°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 H₂ & Desalinated H₂O

900,000 kg H₂O/day

800,000 kg O₂/day

100,000 kg H₂/day

698 GWhr/yr

2332 GWhr/yr

Steam

Condensate

Distilled H₂O

Potable

to multiple-effects;

2.1 M gal H₂O/day

(8 M kg/day)

Salt Concentrate

Triple-effect Evaporator

0.35 kg steam/kg water evaporated

Sea/brackish Water Feed
Opportunity

- An opportunity exists for widespread application in the Mohave Desert where a hybrid process produces renewable \( \text{H}_2 \) via water splitting with a multiple-effect evaporator process producing distilled/potable water from sea water – interfaced for efficient heat integration
  - Pathway to renewable \( \text{H}_2 \)
  - Pathway to reduced GHGs
  - Pathway to potable \( \text{H}_2\text{O} \) supplies
Major Accomplishments since May, 2010

• Demonstrated synthesis of skeletal Al$_2$O$_3$ substrate, subsequent ferrite ALD nanocoating and “hercynite” thermochemical cycling to split water at 1160ºC,

• H2A analysis independently reviewed by TIAAX, 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)
Approach - Free Energy Minimization
Theoretical Limit (P = 0.001 MPa)

\[ M\text{Fe}_2\text{O}_4(\text{Fe}^{3+}) \rightarrow [(\text{MO})(1.12\text{FeO}) + 0.44\text{Fe}_2\text{O}_3 ](\text{Fe}^{2+}) + 0.28 \text{O}_2 \]
Operating “Sweet Spot”

Energy Absorption Efficiency

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

(ideal optics)

C~4,000 suns is required
• 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**

\[
\text{NiFe}_2\text{O}_4 + 0.67 \text{ZrO}_2 \rightarrow \text{MeO (Fe}^{2+}+\text{Fe}^{3+}+\text{Ni}^{2+}) + 0.67 \text{ZrO}_2 + \frac{1}{2}x \text{O}_2 \\
\text{MeO (Fe}^{2+}+\text{Fe}^{3+}+\text{Ni}^{2+}) + 0.67 \text{ZrO}_2 + x \text{H}_2\text{O} \rightarrow \text{NiFe}_2\text{O}_4 + 0.67 \text{ZrO}_2 + x \text{H}_2
\]

<table>
<thead>
<tr>
<th>Oxidation Temperature</th>
<th>800°C</th>
<th>900°C</th>
<th>1,000°C</th>
<th>1,100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moles H₂ Produced</td>
<td>0.50</td>
<td>0.49</td>
<td>0.46</td>
<td>0.41</td>
</tr>
<tr>
<td>Solar Energy Required (GWhr/yr)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Overall Heat of Reaction</td>
<td>1,837</td>
<td>1,892</td>
<td><strong>1,993</strong></td>
<td>2,231</td>
</tr>
<tr>
<td>Sensible Heat Required</td>
<td>1,520</td>
<td>1,520</td>
<td>1,311</td>
<td>1,141</td>
</tr>
<tr>
<td>Total Solar Energy Required</td>
<td>3,582</td>
<td>3,412</td>
<td><strong>3,304</strong></td>
<td>3,372</td>
</tr>
</tbody>
</table>
Predicted FACTSage™

“Hercynite” & Ferrite Cycle Oxidation Performance (1000°C)

Experimental Validation
CO₂ Splitting with nano Al₂O₃ Powder Support

1450 °C reduction

900 °C CO₂ oxidation

wt % T(°C)