Solarthermal Redox-based Water Splitting Cycles

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Overview

Timeline

• Start: 6-1-2005
• End: 9-30-2013
• 80% completed

Budget

• Total Project Funding
  2005-2011: $1,210K DOE
  $347,500 Cost Share
• Funds received in FY12
  $217,000 (subcontract from SNL)
  $  54,250 Cost Share
• Planned FY2013 Funding
  $250,000 (subcontract from SNL)

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)
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: ($14.80/kg H₂ in 2015; $3.70/kg H₂ in 2020; ultimately $2/kg H₂)

Milestone – “Synthesize a cobalt ferrite/alumina “hercynite” active material by ALD using polymer templates. Demonstrate isothermal redox water-splitting in a stagnation flow reactor at a temperature of 1350°C yielding a H₂ production per gram of total mass of active material > 100 µmoles/g active material.” (> 200 µmoles/g active material achieved in 3/2013)
Approach

- Ceria redox is considered base material for comparative water splitting (WS) performance – fast kinetics & robust
- Evaluate “doped” CeO$_2$, compared to base
- Evaluate “hercynite cycle” materials, i.e. ferrite/alumina reaction
  - Temperature Swing redox (TS)
  - Isothermal redox (IS)
- Model multi-tube fixed reactor configuration for efficiency estimates & “best” design
- Evaluate effect of increased pressure (P) and temperature (T) on increasing the slower oxidation rates measured at Sandia National Labs in 2012
- Validate high productivity “hercynite cycle” data obtained on-sun at NREL in 2012 (145 µmole H$_2$/g total)
Accomplishments & Progress

Stagnation Flow Reactor for Materials Characterization

- CeO$_2$
- “Hercynite”
- T-Swing redox
- Isothermal redox

O$_2$ Analyzer
Steam Generator
Furnace 25 – 1700°C
Ceria 1500°C/1200°C (redox)

Water Injection

[H₂O] = 50%
P = 760 Torr

159.1 15.7 µmoles H₂/g

H₂ generated: 147.05 µmol/g

H₂ generated: 153.47 µmol/g

H₂ generated: 176.90 µmol/g

420 s
Ceria 1350°C/1000°C (redox)

[H$_2$O] = 50%
P=760 Torr

16.4 3.6 µmoles H$_2$/g

H$_2$ generated:
20.18 µmol/g

H$_2$ generated:
16.10 µmol/g

H$_2$ generated:
13.03 µmol/g
Zr Substitution Beneficial to Reduction

Experiments run at Sandia National Laboratories
Zr Substitution Beneficial to Oxidation

Experiments run at Sandia National Laboratories
“Hercynite Cycle”

MFe$_2$O$_4$ + 3Al$_2$O$_3$ → H$_2$ + O$_2$ + MAI$_2$O$_4$ + 2FeAl$_2$O$_4$

- Reduced and oxidized moieties are stabilized in two different compounds;
- Compound formation is more thermodynamically favorable than solid solution formation;
- Higher T and P should increase oxidation rate.

M (typical) = Co or Ni
“Hercynite Cycle” Robustness

Chemistry Validated via Raman:
Micrographs of Active Nanostructured “Hercynite” Materials


Cross-sectioned Particle
Skeletal γ-Al$_2$O$_3$
(80 m$^2$/g; 1 cm$^3$/g pore volume);

19.8 wt% CoFe$_2$O$_4$ on Al$_2$O$_3$

Reduction temperature is dictated by reduction enthalpy of the active material

However water is not reacting in the gas phase, need to consider three phases:
- Gas, Surface and Solid

\[ \Delta G = P \Delta V - T \Delta S + \sum_{j=1}^{M} \mu_j \Delta N_j \]

\( N_x \) on the surface is related to \( P_x \):

\[ N_x = a \cdot P_x \]

By altering pressure, the free energy can become favorable

\[ \mu_{MO_{x-1}} N_{MO_{x-1}} + \mu_{H_2O} N_{H_2O} = \mu_{MO_x} N_{MO_x} + \mu_{H_2} N_{H_2} \]
“Hercynite Cycle” Isothermal Water Splitting

\[ T_{\text{red}} = T_{\text{ox}} = 1350 \, ^{\circ}\text{C} \]

760 Torr

50% \([\text{H}_2\text{O}]\]

1 hour reduction

25 min oxidation

47% Active

102 \pm 18 \text{ } \mu\text{mol H}_2/\text{g}

All material has been aged by running > 150 water splitting cycles prior to use.
## Hercynite Isothermal Summary @ 1350°C

<table>
<thead>
<tr>
<th>% [H₂O]</th>
<th>P (_{\text{H₂O}}) (Torr)</th>
<th>(\text{H}_2) production (^a) ((\mu\text{mol/g})) (^b)</th>
<th>Peak rate (^b) ((\mu\text{mol/g/s}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>33</td>
<td>253.3</td>
<td>40 ± 9</td>
<td>0.06 ± 0.02</td>
</tr>
<tr>
<td>40</td>
<td>325.7</td>
<td>72 ± 8</td>
<td>0.15 ± 0.07</td>
</tr>
<tr>
<td>50</td>
<td>380</td>
<td>102 ± 18</td>
<td>0.35 ± 0.18</td>
</tr>
</tbody>
</table>

\(^a\) Error was calculated at 95% confidence level.
\(^b\) Rates represent \(\mu\text{mol H}_2/\text{g}\) of total material. Multiply by 2.13 to get \(\mu\text{mol H}_2/\text{g}\) active material.

- Increased H₂O pressure increases total H₂ produced
- Increased H₂O pressure increases peak rates of H₂ production
- Increased H₂O pressure decreases time for complete re-oxidation.
Temperature Swing vs. Isothermal Water Splitting

P = 760 Torr, [H2O] = 50%

- 1350/1000 °C Isothermal H2
- 1500/1200 °C H2
- 1350 °C Isothermal H2

1450 °C
372 µmoles H2/g active material

174.5 µmol H2/g

372 s
## Water Splitting Comparisons

<table>
<thead>
<tr>
<th>Temp Swing (TS) &amp; Isothermal (IT) (Red/Ox); Temperature (°C)</th>
<th>CeO₂ (µmole/g)</th>
<th>Nanostructured “Hercynite” (µmole/g); x 2.13 / g active</th>
<th>CeO₂ Peak Rate (µmole/g/s)</th>
<th>Nanostructured “Hercynite” Peak Rate (µmole/g/s); x 2.13 / g active</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500/1200</td>
<td>159.1 ± 15.7</td>
<td>93.7 ± 19.2</td>
<td>1.28 (avg)</td>
<td>0.32 (avg)</td>
</tr>
<tr>
<td>1350/1000</td>
<td>16.4 ± 3.6</td>
<td>31.4 ± 2.3</td>
<td>0.15 (avg)</td>
<td>0.03 (avg)</td>
</tr>
<tr>
<td>1350/1350</td>
<td></td>
<td>102 ± 18</td>
<td></td>
<td>0.55 ± 0.16</td>
</tr>
<tr>
<td>1450/1450</td>
<td></td>
<td>167.4 (avg)</td>
<td></td>
<td>1.34 (avg)</td>
</tr>
</tbody>
</table>

P = 760 Torr; [H₂O] = 50%

- At high reduction T, TS CeO₂ produces ~ equal H₂ as IT “hercynite cycle” per total g of material (“hercynite cycle” produces about 2X more on active material basis).
- At low reduction T, IT “hercynite cycle” produces ~ 5X more H₂ compared to CeO₂ and ~10X more on basis of active material.
- IT “hercynite cycle” produces substantially more H₂ than TS “hercynite cycle”. 
Isothermal Redox Similar to PSA

Insulated, Absorbing Cavity w/ Multi-tubular Fixed Beds

Top-Down View

- Potentially faster redox switching
- Fewer concerns with thermal shock

Pseudo-Side View

900 – 1100 °C

1300 – 1500 °C
3D Monte Carlo ray-tracing model:
• Provides profiles of absorbed solar energy on all surfaces from defined solar profile at aperture

3D transient CFD model:
• Fluid flow through packed bed
• Convective / conductive / radiative heat transfer in packed bed and cavity
• Natural convection in cavity space
• Kinetic reaction rates = f (T, local fluid composition, reaction extent)
• Equilibrium limitations via kinetic rates of reverse reactions

Objectives
• Develop steady state & dynamic models of a multi-tube solar receiver
• Identify parameters controlling receiver efficiency
• Identify optimal tube/cavity configurations & solar flux input
• Quantify impacts of isothermal operation on receiver efficiency
Isothermal redox Efficiency Calculations

Time-averaged receiver efficiency based on transient H₂ production

\[ \eta = \frac{\int_{\text{cycle}} \dot{n}_{H_2} LHV_{H_2} \, dt}{\int_{\text{cycle}} P_{\text{solar}} \, dt + \int_{\text{cycle}} E_{O_2} \dot{n}_{O_2} \, dt} = \frac{\text{Heating value of H}_2 \text{ produced}}{\text{Solar energy + Energy to separate O}_2 \text{ from inert}} = \frac{LHV_{H_2} \bar{\eta}_{H_2,i}}{P_{\text{solar}} + E_{O_2} \bar{\eta}_{O_2}} \]

Battery Limits

“Hercynite Cycle”

- 4 kW solar input
- Adiabatic external boundaries
- 6 cm square aperture
- 6 min cycle time
- Flux - Solar beam width / direction optimized independently for each design

<table>
<thead>
<tr>
<th>r cavity (cm)</th>
<th>h cavity (cm)</th>
<th>r tube (cm)</th>
<th>mol CoFe₂O₄ per tube</th>
<th>sccm H₂O per tube</th>
<th>Maximum T (°C)</th>
<th>Average T (°C)</th>
<th>η_{LHV H₂}</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.6</td>
<td>18</td>
<td>2.3</td>
<td>2.6</td>
<td>1</td>
<td>1620</td>
<td>1532</td>
<td>5.5</td>
</tr>
<tr>
<td>20.1</td>
<td>22</td>
<td>3.3</td>
<td>6.3</td>
<td>6</td>
<td>1427</td>
<td>1257</td>
<td>16.7</td>
</tr>
</tbody>
</table>

\( \eta_{LHV H₂} \) increases with a decreased surface/volume ratio for solar reactor
• High-flux Solar Furnace On-sun Operations at NREL

• Laser-assisted Stagnation Flow Reactor Operations at Sandia – Livermore (one Ph.D. student in-place at all times)
Proposed Future Work

- Evaluate isothermal redox at $T > 1450^\circ C$; $P > 760$ Torr; and $[H_2O] = 100$
- Evaluate improved compositions approaching stoichiometric $CoFe_2O_4/Al_2O_3 = 3$
- Develop reaction kinetics rate expressions for “hercynite cycle” active materials
- Incorporate improved reduction and oxidation reaction kinetics into the multi-tubular receiver model; update model
- Demonstrate isothermal redox on-sun
- Evaluate a high-T oxygen transport membrane for $O_2$ removal during redox cycling (ITM-SEOS)
- Carry out H2A Analysis for Isothermal Redox Processing
Proposed Future Work

- Synthesize Micro-containers of Nano-sized Active Materials & test in a Particle Flow Reactor

- Particle ALD can be used to produce nano-coated nano-particles that are then spray dried/calcined to 60 microns

\[
\text{CoFe}_2\text{O}_4/\text{Al}_2\text{O}_3 = 1/3 \text{ (molar)}
\]

<table>
<thead>
<tr>
<th>dp Al(2)O(3) (nm)</th>
<th>CoFe(2)O(4) Film Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1.7</td>
</tr>
<tr>
<td>40</td>
<td>3.3</td>
</tr>
<tr>
<td>150</td>
<td>12.5</td>
</tr>
</tbody>
</table>

Spray Dried

Calcined
(Typical \(d_{50}\) = 60-80 µm)

Or, directly spray dry nano Al\(2\)O\(3\), Fe\(2\)O\(3\) and CoO
Summary

- Zr-doped CeO$_2$ increases H$_2$ productivity by ~ 20% over undoped CeO$_2$;

- Hercynite cycle nanostructured active materials operating isothermally at 1450°C have comparable peak reaction rates and H$_2$ production rates/g compared to Zr-doped CeO$_2$ reduced at 1500°C and oxidized at 1200°C. On the basis of g active materials only, hercynite cycle materials are 2X performance - demonstrated 372 μmoles H$_2$/g active material.

- Hercynite cycle nanostructured active materials operating isothermally at 1350°C have 5X peak reaction rates and H$_2$ production rates/g compared to CeO$_2$ reduced at 1350°C and oxidized at 1000°C. On the basis of g active materials only, hercynite cycle materials are 10X H$_2$ production performance.
• Active “hercynite cycle” nanostructures maintained their redox activity for over 150 cycles, after 1st cycle;

• Increased $[\text{H}_2\text{O}]$, operating P and operating T increase total $\text{H}_2$ produced, increase the peak rate of $\text{H}_2$ production, and decrease the time for complete re-oxidation for isothermal “hercynite cycle” materials; and

• A small adiabatic 4-kW$_\text{thermal}$ solarthermal multi-tube fixed bed reactor operating isothermally with “hercynite cycle” materials is predicted to have a $\eta_{\text{LHV H}_2} > 15\%$. 
Acknowledgements:

• 16 Peer-reviewed scientific papers published in 2012;
• 7 already published in 2013 (+ 3 in press)
• 4 U.S. Patents issued in 2012; 1 Issued thus far in 2013
• Three Ph.D. students won 1st, 2nd, and 3rd Place Posters and an U/G student took 1st Place at 2012 Annual AIChE Meeting (Pittsburgh)
SurroundSun™ Multi-tubular Switching Redox Reactor/Receiver

CoFe₂O₄ + 3 Al₂O₃ \rightarrow CoAl₂O₄ + 2Fe₂AlO₄ + 1/2O₂
CoAl₂O₄ + 2Fe₂AlO₄ + H₂O \rightarrow CoFe₂O₄ + 3 Al₂O₃ + H₂

1st Half Cycle

H₂O \rightarrow H₂ + 1/2O₂

University of Colorado
Multi-tube Solar Receiver/Reactor
1350°C/1000°C Redox (P=1120 Torr; 50% [H₂O])

Nanostructured ALD “Hercynite” Materials

Averaged H₂ Production Rate

CoFe₂O₄ + 3 Al₂O₃ + excess Al₂O₃ ➔
145 µmole/g total
309 µmole/g active material
732 µmole/g ferrite
47 % active material

Higher P favors higher productivity (need to validate)

Integrated H₂ production in µmole/g ferrite

Laser-Assisted redox at SNL (2012)

Nanostructured “hercynite cycle” active materials

Fast Reduction Kinetics & Oxygen Exchange

Slow CO₂ oxidation @ 1000°C & 600 Torr

Need to determine impact of higher T & P on oxidation rate

Arifin, D. et al., Energy & Environmental Science 5, 9438-9443 (2012)
Film thickness is uniform throughout the entire sample.

5.2 nm film (1.2 Å/cycle)

HRTEM Alumina Coated Silica (40 nm)

Film thickness is uniform throughout the entire sample of primary particles; coated in a fluidized bed.

5.2 nm film (1.2 Å/cycle)

7 nm Primary TiO$_2$ Particle Nanocoated

Cross-section HRTEM Image of an Al$_2$O$_3$ (15 Å) ALD Coated 7 nm TiO$_2$ Nanoparticle Processed in a Fluidized Bed Reactor