Solar-thermal Ferrite-Based Water Splitting Cycles

May 19, 2009

Jonathan Scheffe, Melinda M. Channel, Alan W. Weimer

Department of Chemical and Biological Engineering
University of Colorado at Boulder.

Project ID No. PD_10_Weimer

This presentation does not contain any proprietary, confidential or otherwise restricted information
Overview

Timeline
- 6-1-2005
- 9-30-2010
- 75% completed

Budget
- Total Project Funding
  - $900,000 DOE
  - $225,000 Cost share
- Funds received in FY09
  - $0

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
Swiss Federal Research Institute (ETH Zurich)
Objectives

• Research and develop a cost effective ($4/kg H_2 at plant gate) ferrite-based solar-thermal thermochemical water – splitting cycle through theoretical and experimental investigation

• Based on the above, develop a process flow diagram and carry out an economic analysis of the best process option
Relevance – Simple 2-Step Thermochemical H\textsubscript{2}O Splitting Cycle

\[ \text{Thermal Reduction (TR)} \]

\[ \text{Water Oxidation (WO)} \]

\[ \text{M} = \text{Co, Ni, Zn, Mg} \]
Fe$_3$O$_4$ Redox Thermodynamics

\[ 2\text{Fe}_3\text{O}_4 \rightarrow 6\text{FeO} + \text{O}_2 \]

\[ 3\text{FeO} + \text{H}_2\text{O} (g) \rightarrow \text{Fe}_3\text{O}_4 + \text{H}_2 \]

\[ \Delta G \text{ (kcal/mol)} \]

Temperature (°C)
Co$_3$O$_4$ Redox Thermodynamics

\[ 2\text{Co}_3\text{O}_4 \rightarrow \text{6CoO} + \text{O}_2 \]

\[ \Delta G = \text{kcal/mol} \]
CoFe$_2$O$_4$ Redox Thermodynamics

\[ 2\text{CoFe}_2\text{O}_4 \rightarrow 2\text{CoO} + 4\text{FeO} + \text{O}_2 \]

\[ \text{CoO} + 2\text{FeO} + \text{H}_2\text{O}(g) \rightarrow \text{CoFe}_2\text{O}_4 + \text{H}_2 \]

\[ \Delta G \text{ (kcal/mol)} \]

\[ \text{Temperature (°C)} \]
Approach - Free Energy Minimization

Theoretical Limit (P = 0.001 Mpa)

\[ \text{MFe}_2\text{O}_4 \rightarrow \text{Products} \]

\[ \text{NiFe}_2\text{O}_4 \]

\[ \text{CoFe}_2\text{O}_4 \]

\[ \text{Co Ferrite} \]

\[ \text{Ni Ferrite} \]

\[ \text{Products} \]

(100% conversion)
• Particle ALD will provide for ultra-high surface area ferrite materials having enhanced reaction rates
Approach - ALD of $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$

- Calcination
- Thermal Reduction $1200 \, ^\circ\text{C} - 1400 \, ^\circ\text{C}$
- $\text{(CoO)}(2\text{FeO})$
Results - *In Situ* Mass Spectrometry – Particle ALD Synthesis of CoFe$_2$O$_4$
Results - Self Limiting Cobalt Oxide Chemistry

Cobalt Oxide Film

\( \text{ZrO}_2 \)

5 nm

Heat Treated in \( N_2 \)

200 Coating Cycles

 Counts per Second

20 30 40 50

2\( \theta \)
Results – Self-limiting iron oxide ALD; Energy Dispersive Spectroscopy (EDS) Confirms the Presence of Iron

Amorphous Fe$_2$O$_3$ confirmed by XPS
TEM Image of CoFe$_2$O$_4$ on Porous ZrO$_2$ Support

CoFe$_2$O$_4$ film

ZrO$_2$

10 nm

Intensity (counts/s)

2$\Theta$ (degrees)

Reduced 1500 °C
Calcined 1200 °C
CoFe$_2$O$_4$ on ZrO$_2$
Water Splitting Reactor

Ar/H₂O from bubbler

4-way valve

ZrO₂ crucible

Ar (diluant)

Ar (purge)

reactor bypass

Mullite reaction tube

to MS

to pump

P

4-way valve

P
Results - Conversion is Greater for ALD samples

Co$_{0.95}$Fe$_{2.05}$O$_4$ – ALD, 2.2% Loading
conversion = 52.2% (1.30E-3 moles H$_2$/g)

Co$_{1.13}$Fe$_{1.87}$O$_4$ – ALD, 4.7% Loading
conversion = 46.0% (1.15E-3 moles H$_2$/g)

Co$_{0.95}$Fe$_{2.05}$O$_4$ – coprecip
conversion = 13.7% (3.42E-4 moles H$_2$/g)

WO Temp = 1000 °C
TR Temp = 1400 °C
Results - Maximum Conversion Observed with a Co Stoichiometry Near 1.0

Moles H₂/g ferrite

x, in CoₓFe₃₋ₓO₄

CoFe₂O₄

Experimental
Theoretical
Approach - Demonstrate One Low-T Redox Cycle for CoFe$_2$O$_4$ (alumina support)

~ 1 hr/cycle – TGA, using co-precipitated ferrite

$O_2$ begins to evolve slightly after 900 °C

$H_2$ evolution

Reduction Step

Oxidation Step
Results - Samples are Stable After 8 Cycles
Approach – General Economics

- Central Production Facility supplying H₂ at 300psig
- Produce 100,000 kg H₂/day, operating 8 hours/day, 365 days/yr.
- Calculate the necessary solar field requirements using Soltrace based on AspenPlus™ simulations and measured irradiance data for Daggett, CA (annual average).
- Evaluate a base case and byproduct case for 35%, 70%, and 100% theoretical maximum conversions of NiFe₂O₄ in the solar reduction step.
- Size and cost all capital items for variable production rates; Estimate operating costs in line with the general H2A assumptions
- Base case provides for no byproducts and no carbon avoidance credits
- O₂ and electricity are produced in the byproduct case and will be sold for allowable H2A credit; no carbon avoidance credits
- Back-calculate the allowable capital cost of NiFe₂O₄ for all cases to produce H₂ having an H2A selling price of targeted $4, $7 and $11/kg H₂
Major Operating Assumptions

- **2008 Case**
  - $180/m² heliostat cost

- **2012 Case**
  - $140/m² heliostat cost

- **2017 Case**
  - $80/m² heliostat cost
  - No heat recovery between redox steps

- **By-product cases**
  - O₂ sold for $0.02/kg (H2A)
  - Electricity (heat removal) sold for $0.07/kWhr (H2A)
  - No carbon avoidance credits

- **Solar Reactor**
  - 1400°C
  - O₂ removed with vacuum pump system
  - Moving bed of ferrite within Silicon Carbide tubes
  - 8 cycles per day
Approach - Base Case Process Flow Diagram

- NiFe$_2$O$_4$
- O$_2$
- NiFe$_2$O$_4$ Reduced Ferrite
- Moving Bed Reactor Tubes
- 1400°C
- Adiabatic Storage
- 1000°C
- H$_2$ Synthesis Reactor
- Water
- H$_2$
- Adiabatic Storage
- 1000°C
- NiFe$_2$O$_4$
Results - AspenPlus™ Base Case
Results – Solar field design

Solar field design by Mr. Allan Lewandowski

- 100,000 kg/day $H_2$; 70% conversion $\text{NiFe}_2\text{O}_4$
- 2,821 GWhr/yr required, Daggett, CA (annual $\eta = 43.6\%$)
- Five 258 m tall towers; [CPC] = 3x; 3 fields/tower
- 2.33 Million m$^2$ total heliostat area
- $C = 3868$ suns net concentration, receiver $T = 1400^\circ\text{C}$
- Requires 261 acres of land
- 280 Mw$\text{th}$ power to each solar reactor
2017 Capital Cost Breakdown

**Base Case**
TCI $605M
70% Conversion
H2 $4/kg
Allowed Ferrite Cost: $57/kg

**Current Material Costs:**
NiO $22/kg
Fe$_2$O$_3$ $2/kg
Then, NiFe$_2$O$_4$ $8.67/kg
2017 Capital Cost Breakdown

By-product Case
TCI $654M
70% Conversion
H₂ $4/kg
Allowed Ferrite Cost: $69/kg

Annual Revenue:
H₂: $146M (93%)
O₂: $5.8M (4%)
7.94 kg/kg H₂
Electricity: $5.2M (3%)
1.99 kWhr/kg H₂
70% Conversion Ferrite Purchase Cost

Ferrite Purchase Cost ($/kg)

H2 Selling Price ($/kg)

- 2008 $11
- 2012 $7
- 2017 $4

$8.67/kg ferrite materials cost

Base Case
By-product
# Results - Ferrite Cost ($/kg)

<table>
<thead>
<tr>
<th></th>
<th>H2 Selling Price ($/kg)</th>
<th>Allowable Ferrite Purchase Cost ($/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>35% Reduction Conversion</td>
</tr>
<tr>
<td><strong>Base Case</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2008</td>
<td>$11</td>
<td>$107</td>
</tr>
<tr>
<td>2012</td>
<td>$7</td>
<td>$37</td>
</tr>
<tr>
<td>2017</td>
<td>$4</td>
<td>$5</td>
</tr>
<tr>
<td><strong>By-product Case</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2008</td>
<td>$11</td>
<td>$116</td>
</tr>
<tr>
<td>2012</td>
<td>$7</td>
<td>$47</td>
</tr>
<tr>
<td>2017</td>
<td>$4</td>
<td>$14</td>
</tr>
<tr>
<td><strong>Byproducts</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electricity (kWhr/kg H2)</td>
<td>4.42</td>
<td>1.99</td>
</tr>
<tr>
<td>O2 (kg/kg H2)</td>
<td></td>
<td>7.94</td>
</tr>
</tbody>
</table>
## Results – Cycle Efficiencies

<table>
<thead>
<tr>
<th>Case</th>
<th>Reduction</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>35%</td>
<td>70%</td>
</tr>
<tr>
<td><strong>Base Case</strong></td>
<td>LHV</td>
<td>31.7%</td>
</tr>
<tr>
<td></td>
<td>HHV</td>
<td>37.4%</td>
</tr>
<tr>
<td><strong>By-product Case</strong></td>
<td>LHV</td>
<td>35.8%</td>
</tr>
<tr>
<td></td>
<td>HHV</td>
<td>41.5%</td>
</tr>
</tbody>
</table>
Summary

• The nickel ferrite water-splitting cycle appears to meet the 2017 $4/kg H₂ plant gate DOE solar thermochemical target and is potentially the most economical solar process evaluated to date.

• Ferrite materials based on Particle-ALD react faster and at lower temperatures (most likely due to a reduction in diffusional resistances), reducing materials of construction concerns and cycle times.

• More experimental work needs to be completed to verify the reactions and conversions.
Proposed Future Work

• Compare ALD produced CoFe$_2$O$_4$, NiFe$_2$O$_4$ and ZnFe$_2$O$_4$ ferrites experimentally
• Demonstrate ability to cycle ALD-based ferrites through multiple redox reactions
• Evaluate methods for producing low cost ALD ferrite materials using non-ZrO2 high surface area substrates
• Development of stationary processing methods with superior heat integration and simplicity suitable for large-scale processing
Collaborations

- ETH-Zurich (Swiss Federal Research Institute)
  - ETH students & facilities involved
- Sandia / NSF
  - PhD student spent two summers working in their lab ($25M Grand Challenge – interested in ALD ferrites)
- ALD NanoSolutions, Inc. (Broomfield, CO)
  - agreed to produce larger quantities of ALD ferrite materials for the project
- Sundrop Fuels (Louisville, CO)
  - interested in on-sun demonstration at their solar pilot facility
Acknowledgements

• DOE Hydrogen Production Program
• Dr. Mark Allendorf and Dr. Tony McDaniel, SNL
• Mr. Carl Bingham, NREL
• Mr. Allan Lewandowski, consultant
• Prof. Aldo Steinfeld, ETH Zurich
Approach - More FeO generated with CoFe$_2$O$_4$

For $T < 1400^\circ$C, focus on ferrite materials to maximize $H_2$ synthesis.
Approach - more $H_2$ generated with $CoFe_2O_4$

- 1400 °C Thermal Reduction
- 1000 °C Water Oxidation

For $T < 1400$°C, focus on ferrite materials to maximize $H_2$ synthesis.
Results - Optimize H$_2$O Flow

- H$_2$O Concentration
- Reactor Pressure (Torr)
- H$_2$O Residence Time (ms)

Response: moles H$_2$ evolved

<table>
<thead>
<tr>
<th>H$_2$O Residence Time (ms)</th>
<th>5.4</th>
<th>52.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor Pressure (Torr)</td>
<td>30</td>
<td>130</td>
</tr>
<tr>
<td>H$_2$O Concentration</td>
<td>10%</td>
<td>1%</td>
</tr>
</tbody>
</table>

- Optimize H$_2$O Flow
Results - $[\text{H}_2\text{O}]$ Affects Oxidation Rate

Pressure = 80 Torr
WO Temp = 1000 $^\circ$C

H$_2$O adsorption limited

 Bulk diffusion limited
Results - Largest \( \text{H}_2 \) Responses (\( \mu \)moles \( \text{H}_2 \)) seen at Highest \([\text{H}_2\text{O}]\)
<table>
<thead>
<tr>
<th>Material Description</th>
<th>Hydrogen Generation</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiFe$_2$O$_4$ (from SB Han 2007) – Solid state synthesis</td>
<td>1.97 E-5 moles H$_2$/gram ferrite</td>
</tr>
<tr>
<td>CoFe$_2$O$_4$ (9% loading) on Al$_2$O$_3$ - ALD</td>
<td>1.89 E-4 moles H$_2$/gram ferrite</td>
</tr>
<tr>
<td>Completely achieving thermodynamic limit for CoFe$_2$O$_4$ reduction</td>
<td>2.5 E-3 moles H$_2$/gram ferrite</td>
</tr>
</tbody>
</table>

~10X H$_2$ generation relative to solid state synthesis
### Results - Annual Reduction Energy Requirements

\[ \text{NiFe}_2\text{O}_4 \rightarrow 1.2 \text{ FeO} + 0.4 \text{ Fe}_2\text{O}_3 + \text{ NiO} + 0.3 \text{ O}_2 \]
\[ \Delta H_{\text{rxn}} = 214,612.9 \text{ J/mol} \quad \text{(FactSage™ results at 0.1 MPa & 1400°C)} \]

<table>
<thead>
<tr>
<th>Solar Reactor (GWhr/yr)</th>
<th>Reduction Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>35%</td>
</tr>
<tr>
<td><strong>Heat of Reaction</strong></td>
<td>1,799</td>
</tr>
<tr>
<td><strong>Sensible Heat</strong></td>
<td>2,044</td>
</tr>
<tr>
<td><strong>Total Energy Required</strong></td>
<td>3,843</td>
</tr>
</tbody>
</table>

Cavity operates at \(~3,800 \text{ suns, losses are primarily radiative.\)}}