The Zn-based Thermochemical Cycle for Splitting H₂O and CO₂

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Outline

- Zn/ZnO Thermochemical Cycle
- Second-Law Analysis
- Solar Reactor Technology
  - PSI’s Rotary Reactor
  - Challenges and Solutions
- Heat Transfer Modeling
  - 10 kW → 100 kW → 1000 kW
- Experimental Validation
  - 10 kW Reactor Prototype
- Scale-up Reactor Design
  - 100 kW Pilot Plant
- Life Cycle Analysis
- Economics
- Conclusions & Outlook
Solar H₂ and CO Production via Two-Step Zn/ZnO Cycle

Concentrated Solar Energy

**Step 1: Dissociation**

\[ \text{ZnO} \rightarrow \text{Zn} + \frac{1}{2} \text{O}_2 \]

\[ \Delta H = 557 \text{ kJ/mol}, T_H > 2000 \text{ K} \]

**SOLAR REACTOR**

**Step 2: Hydrolysis**

\[ \text{Zn} + \text{H}_2\text{O} \rightarrow \text{ZnO} + \text{H}_2 \]

\[ \Delta H = -62 \text{ kJ/mol}, T_L = 700 \text{ K} \]

**HYDROLYSER**

**FUEL CELL**

H₂O Splitting with Zn/ZnO Redox Reactions

Concentrated Solar Energy
**CO₂ Splitting with Zn/ZnO Redox Reactions**

**Step 1: Dissociation**

ZnO \rightarrow Zn + \frac{1}{2} O₂  
\( \Delta H = 557 \text{ kJ/mol}, T_\text{TH} > 2000 \text{ K} \)

**Step 2: Reduction**

Zn + CO₂ \rightarrow ZnO + CO  
\( \Delta H = -67 \text{ kJ/mol}, T_\text{L} = 400 \text{ K} \)

**Fuel Cell or Combustion**

**H₂O/CO₂ Splitting with Zn/ZnO Redox Reactions**

**Step 1: Dissociation**

ZnO \rightarrow Zn + \frac{1}{2} O₂  
\( \Delta H = 557 \text{ kJ/mol}, T_\text{TH} > 2000 \text{ K} \)

**Step 2: Reduction**

2Zn + H₂O + CO₂ \rightarrow 2ZnO + H₂ + CO  
\( \Delta H = -67 \text{ kJ/mol}, T_\text{L} = 400 \text{ K} \)

**Liquid Fuels**

**Partners:** ETH Zurich & PSI  
**Funding:** ETH, PSI, Baugarten Foundation
Concentrated Solar Energy

\[ \Delta H_{\text{ZnO} @ 300K \rightarrow \text{Zn} + \frac{1}{2} \text{O}_2 @ 2000K} = 557 \text{ kJ/mol} \]

\[ \eta_{\text{absorption}} = \frac{\Delta H_{\text{rxn}}}{Q_{\text{solar}}} = 1 - \frac{\sigma T^4}{I C} = 82\% \]

\[ Q_{\text{solar}} = 680 \text{ kJ/mol} \]

\[ Q_{\text{rad}} = 123 \text{ kJ/mol} \]

\[ I = 1 \text{ kW/m}^2 \]

\[ C = 5000 \]

\[ Q_{\text{quench}} = \Delta H_{\text{Zn} + \frac{1}{2} \text{O}_2 @ 2000K \rightarrow \text{Zn} + \frac{1}{2} \text{O}_2 @ 300K} = -209 \text{ kJ/mol} \]

\[ W_{\text{FC}} = \Delta G_{\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} @ 300K} = 237 \text{ kJ/mol} \]

\[ Q_{\text{WS}} = \Delta H_{\text{Zn} + \frac{1}{2} \text{O}_2 \rightarrow \text{ZnO} + \text{H}_2} = -62 \text{ kJ/mol} \]

\[ Q_{\text{hydrolyser}} = (\Delta H - \Delta G) = -49 \text{ kJ/mol} \]

\[ \eta_{\text{exergy}} = \frac{W_{\text{FC}}}{Q_{\text{solar}}} = 35\% \ (82\%) \]

Solar Thermal Dissociation of ZnO

Solar reactor technology
- PSI’s 10 kW solar reactor prototype
- Direct-irradiated rotary cavity reactor

Solar furnace, PSI, Switzerland

Solar simulator, PSI, Switzerland

### 10 kW Solar Reactor Prototype

- ZnO container
- Screw feeder
- Rotary joint
- Data acquisition
- Reaction chamber
- Ceramic insulation
- Water-cooled front
- Quartz window
- Gas nozzles (radial and tangential inert gas flows)
- Water-cooled aperture

**Partners:** PSI & ETH Zurich  
**Funding:** SFOE, ETH, PSI

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### Solar Reactor Technology

#### Design challenges

**Materials**
- Lining of reactor walls
- Thermal insulation
- $T > 2000$ K
- Thermal shock resistant
- Chemically stable
- Mechanically stable

**Window**
- 2000-5000 kW/m²
- Protection against deposition of condensing gases

**Gas Separation**
- Product gas separation $[\text{Zn(g)} / \text{O}_2]$ at high temperatures $> 1000$ K
- Inert gas $[\text{Ar}]$ separation and recycling

**Conveying**
- Particles $[\text{ZnO}]$ feeding
- Products $[\text{Zn}]$ removal

**Partners:** PSI & ETH Zurich  
**Funding:** SFOE, ETH, PSI

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Solar Reactor Technology

High-temperature cavity wall materials and insulation

Sintered ZnO tiles (3.7 mm thick)
- Sintered ZnO tiles
  - 80%Al₂O₃-20%SiO₂
  - 95%Al₂O₃-5%Y₂O₃

Sintered Al₂O₃ tiles (7 mm thick)
- Sintered Al₂O₃ tiles
  - Al₂O₃ tiles
  - Alumina insulation
  - CMC

Challenge

- Effective removal of solid products (scraper)
Solar Reactor Technology

Typical experiment at PSI's solar furnace

Operating conditions
- Concentration: 3500 suns
- Temperature: >2000 K
- Power: 10 kW

Video
- Reactor to focus
- Flux map meas.
- Open shutter
- Reactor heat-up
- Feed cycle
- Pyrometer meas.

Challenges
- Window protection
- Zn-O₂ separation (inert gas)
- Annular quench
- Tubular quench

Partners: PSI & ETH Zurich
Funding: SFOE, ETH, PSI
Solar Reactor Technology

Aerodynamic window protection

- Precipitation on the window due to pressure fluctuations (clogging of outlet)

100 kW Scaled-up Reactor

Window protection

Challenge
- Avoid precipitation of condensable Zn(g) on window

Solution
- Aerodynamic window protection using inert gas (Ar) streams:
  - Radial / tangential flows
- Flow visualization & CFD
Solar Reactor Technology

Zn-O₂ separation

Solar Thermogravimeter (Solar TG)

ZnO(s) → Zn(g) + ½ O₂

Quench unit

• Three zone approach
• Quench units D34 and D15

Nominal flows
• RF (reacting flow): 7 l/min
• AF (annular flow): 7 l/min
• QF (quench flow): 24.5 l/min

Partners: PSI & ETH Zurich
Funding: SFOE, ETH, PSI

• J. Materials Science 43 (2008) 4729–4736
Solar Experimental Results

Quench units D34 and D15 compared to Solar TG

- Zinc yield > 50% (filter: > 60%)

Solar Reactor Modeling

Kinetic analysis of ZnO dissociation in a packed-bed

Solar Reactor Modeling
Kinetic analysis of ZnO dissociation in a packed-bed

Surface temperature and weight loss vs. time

Arrhenius plot yielding

\[ E_a = 361 \text{ kJ mol}^{-1} \]
\[ k_0 = 14.03 \times 10^6 \pm 2.73 \times 10^6 \text{ kg m}^{-2} \text{ s}^{-1} \]

\[ \frac{dm}{dt} = k_0 e^{-\frac{E_a}{RT}} \]

Comparison with theoretical results and with other studies

\( E_{a,th} = 356 \text{ kJ mol}^{-1}, E_{a,exp} = 361 \text{ kJ mol}^{-1} \)

\[ k_0,th = 5.99 \times 10^6 \text{ kg m}^{-2} \text{ s}^{-1} \]
\[ k_0,exp = 14.03 \times 10^6 \text{ kg m}^{-2} \text{ s}^{-1} \]
Solar Reactor Modeling

Transient heat transfer model

- Numerical reactor model developed at PSI & ETH
- Transient model considering:
  - Radiative, conductive and convective heat transfer
  - Kinetics of ZnO dissociation occurring in a shrinking bed under an ablation regime

\[ q_{\text{radiating}} = -c_v \Delta T \frac{dT}{dt} \]
\[ T^\prime = \frac{1}{h} \]

Energy conservation
\[ \rho c_p \frac{dT}{dt} - V \left( k_e \nabla T \right) + q_{\text{boundary}} \]

Boundary conditions
- cavity inner surfaces
  \[ k_e \nabla T \cdot n = k_e (T - T_{\text{ref}}) + q_{\text{absorbing}} \]
- outer surfaces
  \[ k_e V \nabla T \cdot n = k_e (T_{\text{ref}} - T) + \varepsilon \sigma (T_{\text{ref}}^4 - T^4) \]

Initial condition
\[ T(x, r, t=0) = T_0 \]


Typical Experimental Run at PSI’s High-Flux Solar Simulator

- 5 feed cycles: 120 g ZnO each
- \( T_{\text{ref}} \)
- \( T_{\text{ref}} \)
- \( T_{\text{ref}} \)
- \( T_{\text{ref}} \)
- \( T_{\text{ref}} \)

**Solar Reactor Modeling**

**Experimental validation**

**Temperature profiles**

9 feed cycles: 131 g ZnO each

<table>
<thead>
<tr>
<th># feed-cycles</th>
<th>Measured (g)</th>
<th>Calculated (g)</th>
</tr>
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<tbody>
<tr>
<td>3</td>
<td>68.5 ± 5.2</td>
<td>63.9</td>
</tr>
<tr>
<td>5</td>
<td>59.5 ± 6.8</td>
<td>54.0</td>
</tr>
<tr>
<td>7</td>
<td>148.4 ± 28.8</td>
<td>223.3</td>
</tr>
<tr>
<td>9</td>
<td>224.2 ± 49.5</td>
<td>197.1</td>
</tr>
</tbody>
</table>

**Mass of ZnO dissociated**


**Solar Reactor Modeling**

**Energy balance**

- Max. solar-to-chemical energy conversion efficiency: ~3%

Solar Reactor Modeling

Theoretical efficiency of 10 kW, 100 kW, and 1000 kW reactors

Solar-to-chemical efficiency vs. ZnO surface temperature

- Efficiency optimized by
  - minimizing water-cooled components
  - increasing ZnO surface temperature (→ materials issues)

Solar Thermal Dissociation of ZnO

10 kW reactor prototype
- Solar thermal dissociation of ZnO demonstrated:
  - Experimental runs > 4 h; up to 9 semi-continuous feed cycles
  - Transient heat transfer model validated

Scale-up to 100 kW pilot plant
- Demonstration scheduled for June/July 2011:
  - Testing at 1 MW Solar Furnace, Odeillo, France

- Chemical Energy J. 150, 502-508, 2009
PROMES-CNRS Odeillo: 1 MW Solar Furnace (MWSF)
Heliostat field, parabolic concentrator, tower

Elevation view of the Odeillo MWSF facility

Partners: PSI & ETH Zurich
Funding: SFOE, ETH, PSI
100 kW Scaled-up Reactor

Heat transfer model

- Reactor dimensions:

<table>
<thead>
<tr>
<th></th>
<th>100 kW</th>
<th>10 kW</th>
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<tbody>
<tr>
<td>Cavity diameter</td>
<td>580</td>
<td>160</td>
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<tr>
<td>Cavity length</td>
<td>750</td>
<td>230</td>
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<tr>
<td>Reactor outlet diameter</td>
<td>110/37</td>
<td>80/15</td>
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<tr>
<td>Al2O3 tiles thickness</td>
<td>12.7</td>
<td>7</td>
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<tr>
<td>Outer shell diameter</td>
<td>1080</td>
<td>200</td>
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<tr>
<td>Aperture diameter</td>
<td>190</td>
<td>60</td>
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<tr>
<td>Window diameter</td>
<td>520</td>
<td>160</td>
</tr>
<tr>
<td>Average concentration ratio</td>
<td>3500</td>
<td>3500</td>
</tr>
</tbody>
</table>

- Reactor modeled for two consecutive days of operation:
  - Power increased linearly over a 1-hr span
  - Nominal power kept constant for 8 hours
  - No incident power during 15 hours to simulate overnight condition
100 kW Scaled-up Reactor
Thermal performance predictions

- Assumptions (ideal case): 100% ZnO dissociation, 100% Zn yield

<table>
<thead>
<tr>
<th>Reactor efficiency</th>
<th>Day 1</th>
<th>Day 2</th>
<th>%</th>
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</thead>
<tbody>
<tr>
<td>Average reaction rate</td>
<td>25.4</td>
<td>25.7</td>
<td>kg h⁻¹</td>
</tr>
</tbody>
</table>

| External incoming radiation | Q<sub>total</sub> | 232.8 | 232.8 | kW |
| Passed through aperture | Q<sub>aperture</sub> | 100.0 | 100.0 | kW |

Energy flows
- Chemical energy
- Radiation losses
  - Convective reradiation
  - External reradiation
  - Window reradiation
- Reflection losses
  - Window reflections
  - Inner reflections
- Conduction losses
  - Front shield
  - Aperture
  - Quench unit
- Convective losses
- Reactor sensible heat

Q<sub>chemical</sub> = enthalpy of reaction + sensible heat
Q<sub>total</sub> = total radiative power incident on window’s outer surface

Challenge
- Reduce thermal load
- Reradiation = 26.3%
- Reflections = 15.6%

Solution
- Water-cooled front cone with reflecting ceramic coating
- T<sub>front cone</sub> > 2200 K

Partners: PSI & ETH Zurich
Funding: SFOE, ETH, PSI
\[ \varepsilon = 0.1 \]
\[ D_0 = 19 \text{ cm} \]
\[ D_i = 28 \text{ cm} \]
\[ L = 25.4 \text{ cm} \]
\[ \Phi = 43 \text{ deg} \]
\[ C_{\text{CPC}} = 2.2 \]

- **Secondary concentrator: CPC**
  - Compound Parabolic Concentrator
  - Prevent Zn vapor from condensing on cold CPC surface
- **Water-cooled front cone**

**Baseline design**
- High reradiation
- Low conduction
- \( \eta_{\text{reactor}} = 23\% \)

**Water-cooled cone**
- Low reradiation
- High conduction
- \( \eta_{\text{reactor}} = 21\% \)

- Redistribution of heat losses

**100 kW Scaled-up Reactor**

- **Front cone: alternative designs**
- Radiation reflected and absorbed by front cone significantly reduced
- Total input power, \( Q_{\text{solar}} \), decreases by more than 40%
- Required number of heliostats reduces from 22 to 12
- Investment cost reduced

**100 kW Scaled-up Reactor**

- **Compound Parabolic Concentrator (CPC)**
  - Absorbed by cone + aperture
  - Passing through the reactor aperture
  - \( \eta_{\text{reactor}} = 38\% \)
100 kW Scaled-up Reactor
Simplified process scheme

- Concentrated thermal radiation
- Solar reactor
- Rotating scraper
- Screw mantle
- ZnO container
- Gas analysis
- Flow controllers
- Gas supply

Detailed design finalized in December 2010
Fabrication of reactor and peripherals until April 2011

Partners: PSI & ETH Zurich
Funding: SFOE, ETH, PSI
100 kW Scaled-up Reactor
High temperature materials

Reliable reactor materials for applications at T > 2000 K

- Ceramic wall materials:
  - ZnO and Al₂O₃ tiles
  - Al₂O₃–SiO₂ insulation (1800°C / 1400°C)

- Cylindrical shape → hexagonal shape:
  - Mechanical stability for rotary motion

100 kW Scaled-up Reactor
Zn-O₂ gas separation

Rapid quench

- Dilution with cold inert gas (Ar)
- High Zn yield → high dilution
- Future: Recycling of Ar for process economics

Reactor operating strategy

- Annular quench:
  Feeder remains at cavity exit (semi-continuous mode)
- Tubular quench (modular units):
  Feeder remains fully retracted (batch mode)
1st Priority: Reliable reactor operation at high temperatures
- Front cone heat removal
- Window protection
- High-temperature materials
- Particle feeding and removal

2nd Priority: Gas separation and efficiency
- Separation of Zn and O₂ by rapid quench
- Zn yield > 50%; \( \eta_{\text{reactor}} > 5\% \)

Life Cycle Analysis (LCA)
Well-to-wheel analysis for solar-produced H₂ used in a fuel cell car

Production of energy carrier
- Thermal ZnO dissociation (STD)
- Carbo-thermic ZnO reduction (SCR)
- Thermal electricity prod. (STE)

Transport
- Zn transport
- Hydrogen pipeline
- Hydrolysis
- Electrolysis
- HVDC

Further processing and use
- Hydrogen distribution
- Fuel cell car
- Electrolysis

11 MWₜ (50 MWₜₚ) PS10, Seville, Spain
ES-CH: 1650 km
Michelin-PSI “Hy-Light” Fuel Cell Car

ES
DE
CH
IT
AT
FR
Life Cycle Analysis (LCA)
Well-to-tank analysis for solar-produced H₂: GHG emissions

- Radiative forcing in g CO₂-equivalents (time horizon 100 years)

<table>
<thead>
<tr>
<th>Solar technologies</th>
<th>Solar Thermal Dissociation</th>
<th>Solar Carbothermic Reduction (cc: charcoal; hc: hardcoal)</th>
<th>Solar Thermal Electricity</th>
<th>Steam Methane Reforming</th>
<th>Coal Gasification (Advanced)</th>
<th>Electrolysis (Hydro/Nuclear)</th>
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Economic Analysis
H₂ supply costs in car tank: Variation of interest rate (IR)

- CSP technologies

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IR Reference: 15% 15% 8% 10% (Reference hydrogen infrastructure: 18%)
Conclusions & Outlook

Conclusions

- Zn-based thermochemical cycle for splitting H₂O and CO₂
- 1st step: Solar thermal dissociation of ZnO
- Solar reactor technology from prototype (10 kW) to pilot plant (100 kW)
- 2nd step: Reduction of CO₂ and H₂O with Zn

Outlook

- Pilot plant demonstrations 2011 & 2012
- Development of conceptual design for industrial solar Zn production plant based on CSP tower technology
- Analysis of system economics