Hybrid sensible/thermochemical storage of solar energy in cascades of redox-oxide-pair-based porous ceramics

Christos Agrafiotis, Andreas Becker, Lamark deOliveira, Martin Roeb, Christian Sattler

Institute of Solar Research
DLR/ Deutsches Zentrum für Luft- und Raumfahrt/
German Aerospace Center
Linder Höhe, 51147 Köln, Germany
Outline:

• Solar Energy Storage in air-operated Solar (Tower) Thermal Power Plants (STPPs)

• ThermoChemical Storage (TCS) principles and redox oxide pairs

• Some new ideas on redox-oxide-based porous ceramics for TCS in STPPs

• From laboratory to solar testing

• Conclusions, current and future work
Air-operated CSP Plants (Solar Tower Jülich/STJ)

- HTF: Air at atmospheric pressure, heated up to about 700ºC and then powering a steam generator.

- Sensible heat storage: TES by temperature increase (cp $\Delta T$)
From TES with sensible heat to hybrid sensible-thermochemical storage with redox oxides

Increase the volumetric storage density instead of the storage volume: “coat with/make of” honeycombs with redox oxide

Table 2.1: Metal Oxide Systems Applicable to TES Based on Thermodynamics Considerations

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Temperature (°C)</th>
<th>ΔH (kJ/mole)</th>
<th>Storage Density (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_4H_{10} \rightarrow 2.5C_2H_2 + 2.25O_2 )</td>
<td>110</td>
<td>126.0</td>
<td>279</td>
</tr>
<tr>
<td>( 2Li_2O \rightarrow 2Li_2O + O_2 )</td>
<td>150</td>
<td>68.2</td>
<td>1483</td>
</tr>
<tr>
<td>( 2MgO \rightarrow 2MgO + O_2 )</td>
<td>205</td>
<td>21.8</td>
<td>505</td>
</tr>
<tr>
<td>( 2PbO \rightarrow 2PbO + O_2 )</td>
<td>405</td>
<td>62.8</td>
<td>262</td>
</tr>
<tr>
<td>( 2PbO \rightarrow 2PbO + O_2 )</td>
<td>400</td>
<td>62.8</td>
<td>277</td>
</tr>
<tr>
<td>( 2BaO \rightarrow 2BaO + O_2 )</td>
<td>545</td>
<td>92.5</td>
<td>286</td>
</tr>
<tr>
<td>( 4MnO \rightarrow 2Mn_2O_3 + O_2 )</td>
<td>530</td>
<td>41.8</td>
<td>481</td>
</tr>
<tr>
<td>( 4CO \rightarrow 2CO_2 + O_2 )</td>
<td>678</td>
<td>35.2</td>
<td>123</td>
</tr>
<tr>
<td>( 38O_2 \rightarrow 38O_2 + O_2 )</td>
<td>883</td>
<td>72.3</td>
<td>474</td>
</tr>
<tr>
<td>( 2Co_2O_4 \rightarrow 6CoO + O_2 )</td>
<td>890</td>
<td>202.5</td>
<td>844</td>
</tr>
<tr>
<td>( 8H_2O \rightarrow 8H_2O + O_2 )</td>
<td>970</td>
<td>240.2</td>
<td>981</td>
</tr>
<tr>
<td>( 4MnO \rightarrow 4MnO + O_2 )</td>
<td>1000</td>
<td>31.9</td>
<td>202</td>
</tr>
<tr>
<td>( 4CoO \rightarrow 2Co_2O_3 + O_2 )</td>
<td>1120</td>
<td>64.5</td>
<td>811</td>
</tr>
<tr>
<td>( 6FeO_3 \rightarrow 4Fe_2O_3 + O_2 )</td>
<td>1400</td>
<td>79.2</td>
<td>496</td>
</tr>
<tr>
<td>( 2V_2O_5 \rightarrow 2V_2O_4 + O_2 )</td>
<td>1560</td>
<td>180.7</td>
<td>993</td>
</tr>
<tr>
<td>( 2MnO_3 \rightarrow 6MnO + O_2 )</td>
<td>1700</td>
<td>194.6</td>
<td>850</td>
</tr>
</tbody>
</table>

General Atomics: GA–C27137: THERMOCHEMICAL HEAT STORAGE FOR CONCENTRATED SOLAR POWER THERMOCHEMICAL SYSTEM REACTOR DESIGN FOR THERMAL ENERGY STORAGE ; Phase II Final Report, 2011
Cascaded ThermoChemical Storage (CTCS)

- A cascade of different redox oxide materials can be combined with various porous structures along as well “across” the reactor/heat exchanger.


Tests Scale Evolution (single-oxide or cascaded testing)

TGA

Lab-scale furnace test rig

Solar receivers
TGA (DSC) rig: Cyclic reduction – oxidation protocol
weight change (vs. stoichiometric) = f(T)

\[
\text{Reaction} \quad \quad \text{T}_{\text{red}} \, (\degree \text{C}) \quad \text{Max. wt. loss} \, (\%) \\
2 \text{BaO}_2 + \Delta \text{H} \rightarrow 2 \text{BaO} + \text{O}_2 \quad 690 \quad -9.45 \\
2 \text{Co}_3\text{O}_4 + \Delta \text{H} \rightarrow 6 \text{CoO} + \text{O}_2 \quad 870 \quad -6.64 \\
6 \text{Mn}_2\text{O}_3 + \Delta \text{H} \rightarrow 4 \text{Mn}_3\text{O}_4 + \text{O}_2 \quad 950 \quad -3.38 \\
4 \text{CuO} + \Delta \text{H} \rightarrow 2 \text{Cu}_2\text{O} + \text{O}_2 \quad 1030 \quad -10.01
\]
TGA: \( \text{Co}_3\text{O}_4 / \text{CoO} \)

- \( \text{Co}_3\text{O}_4 \) can operate in a quantitative, cyclic and fully reversible reduction/oxidation mode within 800-1000°C (950°C).
- As powder, coated on honeycombs/foams or shaped in foams.

TGA: Mn$_2$O$_3$/Mn$_3$O$_4$

- Mn$_2$O$_3$: reduction fast, stoichiometric; but large temperature “gap” between reduction ($\approx$950°C) - oxidation ($\approx$780-690°C) !!
- Very narrow temperature range ($\approx$690-750°C) within which Mn$_2$O$_3$ re-oxidation is significant.
- Mn$_2$O$_3$ re-oxidation is slow and needs extended dwell at the optimum temperature (range) for completion.
- Can be also achieved with slow rates and no dwell as shown below.
TGA: Other oxides

- **CuO/Cu$_2$O**: reduction temperature very close to m.p. of Cu$_2$O (shrinkage and sintering); could not work reproducibly even for few (5 cycles).
- **BaO$_2$/BaO**: BaO reacts with CO$_2$ present in air to BaCO$_3$
- **Perovskites**: loose/gain (little) weight continuously with T (perhaps plus in a cascade but ΔH also very low):

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔH (kJ/mol)</th>
<th>$T_{\text{red}}$ (°C)</th>
<th>$T_{\text{ox}}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 Co$_3$O$_4$ + ΔH → 6 CoO + O$_2$</td>
<td>202.5</td>
<td>895</td>
<td>875</td>
</tr>
<tr>
<td>6 Mn$_2$O$_3$ + ΔH → 4 Mn$_3$O$_4$ + O$_2$</td>
<td>31.9</td>
<td>950</td>
<td>720</td>
</tr>
</tbody>
</table>

- Favourable Ts for oxidation but entire cascade needs T > 950°C during reduction
Furnace test rig: “Visualization” of Hybrid Sensible-TCS vs. Sensible-only storage effect
Solar furnace test rig: Receiver – storage modules assembly; 1st tests: T along non-coated storage module (sensible-only storage)
Comparative testing of storage module and (SiC) receiver types (190 slm)

3 Cordierite foams
30 ppi; L = 12 cm

SiSiC honeycomb
90 cps; Schunk
Weight ≈1404 g
Length = 15 cm

3 SiSiC foams
10 ppi; ERBICOL
Weight ≈ 246 g
Length = 12 cm

ReSiC honeycomb
90 cps; Stobbe TC
Weight ≈ 584 g
Length = 10 cm

3 Cordierite foams
400 cps; L = 12 cm
Comparative performance of SiC receivers tested

T3≈1030°C  T3≈930°C  T3≈930°C
T5≈ 975°C   T5≈915°C  T5≈875°C
T6≈ 725°C   T6≈755°C  T6≈775°C
Conclusions:

• The construction modularity of the current state-of-the-art storage system in air-operated STPPs provides for implementation of concepts like **cascades of different redox oxide materials and spatial variation of solid material porosity in three dimensions**, to enhance utilization of heat transfer fluid and storage of its enthalpy.

• However: **limited variety of redox oxides available** within the particular temperature range. **Co$_3$O$_4$**: the most “reliable”, demonstrating full, quantitative cyclability within a narrow temperature range (“model system”).

• **Mn$_2$O$_3$**: low cooling rates required for oxidation; large “temperature gap” between reduction/oxidation temperature. This “disadvantage” though, can be rendered to benefit within a cascaded structure.

• Relatively high reduction temperatures of both Co$_3$O$_4$ ($T_{\text{red}} \approx 895^\circ\text{C}$) and Mn$_2$O$_3$ ($T_{\text{red}} \approx 950^\circ\text{C}$).

• Could be achieved in the solar furnace with currently available SiSiC honeycomb receivers: capability of solar-heating incoming air to $\approx 1050^\circ\text{C}$, and two cordierite foams downstream ($\approx 8$ cm) to $\approx 950^\circ\text{C}$ demonstrated.
Acknowledgements:

• To EU for financing this work under the MARIE CURIE ACTION Intra-European Fellowships (IEF) Call: FP7-PEOPLE-2011-IEF, Grant 300194: Thermochemical Storage of Solar Heat via Advanced Reactors/Heat exchangers based on Ceramic Foams (STOLARFOAM)

• To DLR Programmdirektion Energie (PD-E) for funding through Project Thermochemical storage for CSP-applications based on Redox-Reactions – from materials to processes (REDOXSTORE).
Thank you for your attention!

- christos.agrafiotis@dlr.de
- martin.roeb@dlr.de
- christian.sattler@dlr.de