SAND2014-17185R

Solar Hydrogen Production with a Metal Oxide-Based Thermochemical Cycle

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Project Start Date: October 1, 2008

Project End Date: September 30, 2014 (project continuation and direction determined annually by DOE)

Overall Objectives

- Verify the potential for a solar thermochemical hydrogen production cycle based on a two-step, non-volatile metal oxide to be competitive in the long term.
- Develop a high-temperature solar receiver-reactor (SRR) and redox material for hydrogen production with a projected cost of $3.00/gge at the plant gate by 2020.

Fiscal Year (FY) 2014 Objectives

- Discover and characterize novel perovskite materials for a two-step, non-volatile metal oxide water-splitting thermochemical cycle.
- Calculate theoretical system efficiency for various SRR operating scenarios that meet or exceed a STH conversion ratio of 26%.
- Formulate and refine particle-based SRR designs and assess feasibility.
- Construct an engineering test stand and evaluate particle conveyance and pressure separation concepts under vacuum at elevated temperature.
- Conduct H2Av3 analysis of a central receiver-based particle SRR producing 100,000 kg H_2/day and identify a clear path towards meeting DOE projected cost targets for H_2.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(S) High-Temperature Robust Materials.
(T) Coupling Concentrated Solar Energy and Thermochemical Cycles.
(X) Chemical Reactor Development and Capital Costs.
(AC) Solar Receiver and Reactor Interface Development.

Technical Targets

This project is conducting fundamental studies on materials for use in concentrated solar power applications and designing reactor concepts that, when combined, will produce H_2 from thermochemical water-splitting (WS) cycles. Insights gained from these studies will be applied toward the design and optimization of an SRR that meets the following ultimate DOE hydrogen production targets:

- Hydrogen Cost: \$2/kg H_2
- Material of Reaction Cost: \$11K/yr TPD H_2
- STH Conversion Ratio: 26%
- 1-Sun Hydrogen Production Rate: 2.1×10^{-6} kg/s m^2

FY 2014 Accomplishments

- Synthesized 30 different redox materials using AB(Mn or Fe)O_3 perovskite oxides (A = Ca, La, Sr, or mixtures thereof; B = Ce, Ti, or Zr). Compounds were screened for water-splitting activity using TGA methodologies. Finding a more effective redox material increases the likelihood of meeting the DOE targets for material cost and STH conversion ratio.
- Developed a thermodynamic model for SLMA2 (see Acronyms for definition) based on P_{O2}-δ-T data. Predicted the optimal operating temperature (ΔT), O_2 pressure (vacuum), and heat recovery effectiveness required for SLMA2 to meet or exceed a STH conversion ratio greater than 20%. We predict that near-term DOE technical targets for solar H_2 can be achieved in a two-step high temperature thermochemical cycle using SLMA2.
- Derived performance criteria and thermodynamic properties for an "ideal" non-stoichiometric oxide. This hypothetical material strikes a balance between the solar energy required to heat oxide versus steam, and thus is predicted to cycle at an *optimal* reactor efficiency. Identifying such criteria is key to meeting the long-term DOE STH conversion ratio target of 26%.
- Advanced Sandia's particle bed reactor concept to include a novel and game-changing approach—cascading pressure thermal reduction—enabling ultra-low O_2 pressure under thermal reduction in vacuum. This discovery is critical to achieving a STH conversion ratio greater than 20% for state-of-the-art perovskites.
- Designed a particle elevator for a 3-5 kW-scale engineering test stand. Construction is under way. When completed, it will be integrated into a fully functioning SRR. Knowledge gained from operating this reactor will be used to analytically up-scale our technology to a 100,000 kg H_2/day centralized plant.
- Analyzed H_2 cost for a central receiver-based particle SRR operating at 100,000 kg H_2/day capacity. Plant design incorporates a full field beam-down optical layout for each of many 5 MW central receivers. Analysis reveals the importance of reactor efficiency to meeting DOE ultimate cost targets due to the high capital cost of solar collection.

Introduction

This research and development project is focused on the advancement of a technology that produces hydrogen at a cost that is competitive with fossil-based fuels for transportation. A two-step, solar-driven WS thermochemical cycle is theoretically capable of achieving a STH conversion ratio (i.e. conversion efficiency) that exceeds the DOE target of 26% at a scale large enough to support an industrialized economy (1). The challenge is to transition this technology from the laboratory to the marketplace and produce H_2 at a cost that meets or exceeds the DOE target of \$2/kg H_2.

Conceptually, heat derived from concentrated solar energy can be used to reduce a metal oxide at high temperature producing O_2 (step 1). The reduced metal oxide is then taken "off sun" and re-oxidized at lower temperature by exposure to H_2O, thus producing H_2 (step 2) and completing the cycle. The ultimate commercial success of solar thermochemical H_2 production is contingent upon developing suitable redox active materials and incorporating them into an efficient SRR. There are numerous material chemistries that have attributes suitable for inclusion in a thermochemical H_2 production system (2–4). The challenge is to identify an optimally-performing material. In addition, the development of redox material and SRR are not mutually exclusive, but must be conducted in parallel (5). To maximize the probability of success, this project also addresses the reactor- and system-level challenges related to the design of an efficient particle-based SRR concept (6).

Approach

Thermochemical WS reactors are heat engines that convert concentrated solar energy (heat) to chemical work. Our approach is to discover novel materials to accomplish the WS chemistry and pair these with a novel SRR that, when combined, can achieve an unprecedented STH conversion ratio. The material discovery work involves expanding our understanding of the underlying thermodynamics and kinetics in order to make performance improvements and/or formulate new, more redox-active compositions. Sandia's patented SRR technology is based on a moving bed of packed particles that embodies all of the design attributes essential for achieving high efficiency operation: 1) sensible heat recovery; 2) spatial separation of pressure, temperature, and reaction products; 3) continuous on sun operation; and 4) direct absorption of solar radiation by the redox-active material. Research efforts are focused on validating design concepts and deriving optimal operating conditions through detailed systems modeling.

Results

In this project year, Sandia advanced the understanding of perovskite oxides as a class of materials for solar H_2 production, as well as identified the characteristics of an ideal redox material that can be incorporated into Sandia's SRR. Thirty different perovskite formulations were synthesized and screened. Our principle focus in FY 2014 was on chemical modifications of Mn- and Fe- based perovskites according to the following elemental substitutions: AB(Mn or Fe)O_3 oxides; A = Ca, La, Sr, or mixtures thereof; B = Ce, Ti, or Zr. We found that many of these compounds readily reduce at temperatures well below that of CeO_2 (T_{RED}<1000°C), and possess redox capacities in excess of CeO_2 (i.e. reduce more deeply, $\delta >> 0.1$). Unfortunately, none of these materials performed WS chemistry better than the family of SLMA compounds we discovered last year (4). Nonetheless, we are encouraged by the fact that simple modifications of AB(Mn or Fe)O_3 oxides yield redox-active materials, and maintain the position that perovskite oxides hold great promise for meeting DOE targets.

In FY 2014, we developed specifications for an ideal non-stoichiometric oxide for use in high temperature WS cycles (summarized in figure 1a). Here, seven key characteristics of redox-active materials are defined, such as WS temperature (T_{WS}), extent of oxygen non-stoichiometry in reduction (δ), H_2O/H_2 ratio during WS, etc. These values (or limiting ranges) were determined by high-level theoretical analysis of Sandia's SRR using known properties for CeO_2 and SLMA2 that revealed the controlling factors for STH conversion ratio. With CeO_2, efficiency is dominated by oxide heating. For SLMA2, it is dominated by steam heating. Therefore, we postulate that the ideal material properties lie between these two.

We also discovered a new descriptor to aid in material screening, defined as "T_{OR}". This is the temperature at which O_2 begins to evolve from the solid and is strongly correlated to reduction enthalpy, WS activity, and process viability. With this descriptor, we can accelerate screening in both the TGA and SFR. Shown in figure 1b is the O_2 evolution rate measured as a function of temperature during thermal reduction for several perovskite formulations tested in FY 2014. It is clear that some of our newest Mn-based compounds readily reduce, as evidenced by a $T_{OR}<600°C$ that is well below SLMA2 or CeO_2. We also know that the reduction enthalpy for SLMA2<CeO_2, and therefore deduce that high T_{OR} suggest high reduction enthalpy. Not surprisingly, T_{OR} also strongly correlates to WS activity. The data in figure 1c and 1d provide evidence for this. Equilibrium data for SLMA2 and CeO_2 under various WS conditions are shown in these two plots. For an O atom from a H_2O molecule to go into the solid (thereby making H_2), the end-state δ curve (colored lines) must lie below that of a dashed curve for a specific WS condition (T_{WS} and H_2O/H_2 ratio). Ceria's T_{OR} (1220°C) is higher than SLMA2 (865°C). And by comparison, a larger collection of colored lines for CeO_2 (figure 1d) lie below a H_2O/H_2 ratio of 10/1 than for SLMA2 (figure 1c). This implies that the driving force for WS on reduced CeO_2 is greater than SLMA2. Therefore, high T_{OR} *also* indicates high WS activity. More importantly from a screening perspective, if T_{OR} is too low (below 700°C), as is the case for $SrZr_{0.3}Mn_{0.7}O_3$ and $CaTi_{0.4}Mn_{0.6}O_3$, the oxide will not split water. We believe that the ideal redox material will have a T_{OR} bounded by the grey shaded area in figure 1b.

This year we derived a thermodynamic expression for SLMA2 from fitting a solid solution model to TGA measurements. The results, presented in figure 2a, allow us to calculate the chemical state of SLMA2(P_{O2}, δ, T_{TR}) given any two of these parameters. The model also predicts enthalpy and entropy of reduction as a function of oxygen non-stoichiometry. With this model we have mapped the theoretical STH efficiency for SLMA2, shown in figure 2b, as a function of temperature separation (ΔT), heat recuperation effectiveness (ε_{GG} and ε_R), and O_2 pressure in reduction (p_{TR} Pa) at T_{TR}=1450°C. It is evident from the efficiency profiles in figure 2b that SLMA2 can meet or exceed the 2020 DOE target for STH conversion efficiency in Sandia's SRR. By using SLMA2 to decrease the thermal reduction temperature (T_{TR}) while maintaining a $\Delta\delta$>CeO_2, we achieve high STH efficiency *without* relying on solid-solid heat recovery ($\varepsilon_R=0$); a much less demanding reactor condition than proposed for high-STH operation with CeO_2 (6). In addition, the gas-gas heat recovery effectiveness (ε_{GG}) has been limited to exchanger temperatures less than 1000°C, an important design consideration given the difficulty of ultra-high temperature heat exchange.

In FY 2014, we made a groundbreaking improvement to the packed bed reactor design; the invention of a multi-stage thermal reduction process via pressure cascade (shown schematically in figure 3). This approach enables hitherto unfeasibly low thermal reduction pressures (i.e. high vacuum). Achieving ultra-low O_2 pressure (p_{TR}) during reduction is critically important to high STH efficiency operation (see figure 2b). The practical challenges to reaching low p_{TR} are extremely large O_2 flow velocities, and correspondingly large pumping speeds, required for a multi-MW tower SRR. In fact, the desired extent of reduction requires $p_{TR}<10$ Pa, a physical impossibility in a single-chambered reactor using existing pumping technology. The improved cascade approach performs the thermal reduction in multiple chambers, each operating at a successively lower pressure. The packed particle bed design inherently provides for the required pneumatic sealing between chambers. The data in figure 3b show the outstanding potential for decreasing p_{TR} via cascading pressure thermal reduction. One order of magnitude p_{TR} decrease can be achieved in only five stages, each operating at the same pumping speed. In a ceria based cycle for example, a 10 fold p_{TR} decrease corresponds to a 45% relative efficiency increase. Furthermore, because ultra-low p_{TR} is accessible via the new cascade approach, technically challenging high-temperature solid-solid heat recovery is no longer vital for efficient reactor design, representing a significant design innovation and simplification.

Finally, in FY 2014 we incorporated our extensive theoretical understanding of this process into the design of a 3-5 kW-scale engineering test stand. The particle elevator and apparatus for testing radiative heat transfer into particle beds is shown in figure 4. When completed, this prototype will be used to evaluate all reactor functions, first individually and then within a fully integrated system inclusive of continuous operation and hydrogen production under simulated solar radiation. Data collected from this instrument will be used to further refine reactor designs, and analytically up-scale Sandia's technology to a 5 MW centralized tower system.

Conclusions and Future Directions

- Discover additional perovskite and phase-change type oxides with ideal properties identified in FY 2014 for improved WS activity.
- Construct and test a functional SRR test stand sized for 3-5 kW with two reduction chambers.
- Design tower and field configurations compatible with multiple reduction chambers.

FY 2014 Publications/Presentations

1. "Cascading Pressure Thermal Reduction for Efficient Solar Fuel Production", I. Ermanoski, *International Journal of Hydrogen Energy*, in press (2014).
2. "Efficiency Maximization in Solar Thermochemical Fuel Production: Challenging the Concept of Isothermal Water Splitting", I. Ermanoski, J.E. Miller, M.D. Allendorf, *Physical Chemistry Chemical Physics*, **16** (2014) 8418.
3. "Annual Average Efficiency of a Solar-Thermochemical Reactor", I. Ermanoski and N.P. Siegel, *Energy Procedia*, **49** (2014) 1932.
4. "Advancing Oxide Materials for Thermochemical Production of Solar Fuels", J.E. Miller, A. Ambrosini, E.N. Coker, M.D. Allendorf, A.H. McDaniel, *Energy Procedia*, **49** (2014) 2019.
5. "Nonstoichiometric Perovskite Oxides for Solar Thermochemical H_2 and CO Production", A.H. McDaniel, A. Ambrosini, E.N. Coker, J.E. Miller, W.C. Chueh, R. O'Hayre, J. Tong, *Energy Procedia,* **49** (2014) 2009.
6. "Considerations in the Design of Materials for Solar-Driven Fuel Production Using Metal-Oxide Thermochemical Cycles", J.E. Miller, A.H. McDaniel, M.D. Allendorf, *Advanced Energy Materials,* **4,** (2), (2014) 1300469. DOI:10.1002/aenm.201300469.
7. "Perovskite-Type Oxides for Efficient Energy Conversion and Storage", J. Tong. Invited seminar at Institute of Engineering Thermophysics, Chinese Academy of Sciences, China, 23 June, 2014.
8. "Solar Thermochemical Water Splitting: Advances in Materials and Methods", A.H. McDaniel, M.D. Allendorf, I. Ermanoski, A. Ambrosini, E.N. Coker and J.E. Miller, W.C. Chueh, R. O'Hayre, J. Tong. Invited seminar at CIMTEC 2014 6th Forum on New Materials, Montecatini Terme, Italy, 15-19 June, 2014.
9. "Solar Chemistry and Fuel Production", N.P. Siegel. Presented at the Chemical Engineering Spring Seminar Series, Bucknell University, Lewisburg, PA, USA, 25 February, 2014.
10. "The Water Splitting Kinetics of Two-Step Solar Thermochemical Process With CeO_2", D. Arifin, A.H. McDaniel, A.W. Weimer. Presented at the annual meeting of the AIChE, San Francisco, CA, USA, 3-8 November, 2013.
11. "A Detailed Mechanism of Solar Thermochemical Carbon Dioxide Splitting With CeO_2", D. Arifin, A.H. McDaniel, A.W. Weimer. Presented at the annual meeting of the AIChE, San Francisco, CA, USA, 3-8 November, 2013.
12. "High Temperature Solar Fuel Production Using Solid State Ionic Materials", J. Tong, R. O'Hayre. Presented at the annual meeting of Center for Revolutionary Photoconversion, Denver, CO, USA, 12-15 August 2013.

References

1. N. P. Siegel, J. E. Miller, I. Ermanoski, R. B. Diver, and E. B. Stechel, *Ind. Eng. Chem. Res.*, **52**, 3276–3286 (2013).
2. W. C. Chueh and S. M. Haile, *Philos. Trans. R. Soc. Math. Phys. Eng. Sci.*, **368**, 3269–3294 (2010).
3. R. B. Diver, J. E. Miller, M. D. Allendorf, N. P. Siegel, and R. E. Hogan, *J. Sol. Energy Eng.*, **130**, 041001(1)–041001(8) (2008).
4. A. H. McDaniel, E. C. Miller, D. Arifin, A. Ambrosini, E. N. Coker, R. O'Hayre, W. C. Chueh, and J. Tong, *Energy Environ. Sci.*, **6**, 2424–2428 (2013).
5. J. E. Miller, A. H. McDaniel, and M. D. Allendorf, *Adv. Energy Mater.*, **4**, 1300469 (2014).
6. I. Ermanoski, N. P. Siegel, and E. B. Stechel, *J. Sol. Energy Eng.*, **135**, 031002 (2013).
7. I. Ermanoski, J. E. Miller, and M. D. Allendorf, *Phys. Chem. Chem. Phys.*, **16**, 8418 (2014).

Acronyms

FY = fiscal year.
SCM = strontium cerium manganate.
SFR = stagnation flow reactor.
SLMA = general term to describe $Sr_xLa_{1-x}Mn_yAl_{1-y}O_3$ perovskite compositions.
SLMA2 = $Sr_{0.6}La_{0.4}Mn_{0.6}Al_{0.4}O_3$.
SRR = solar receiver-reactor.
STH = solar-to-hydrogen.
TGA = thermogravimetric analyzer.
T_{OR} = onset temperature for oxygen evolution measured during thermal reduction.
T_{OXD} = the oxide re-oxidation temperature, usually in the range 800-1200°C.
T_{RED} = the oxide thermal reduction temperature, usually in the range 1300-1600°C.
WS = water-splitting.
η_R = reactor efficiency defined as the molar H_2 production rate × H_2 lower heating value divided by the solar energy flux at the reactor aperture.
p_{TR} = the partial pressure of O_2 in the reduction zone.
ε_R = solid-solid heat recuperator effectiveness.
ε_{GG} = gas-gas heat recuperator effectiveness.
δ = extent of oxygen non-stoichiometry in $ABO_{3-\delta}$ or $CeO_{2-\delta}$

Figure Captions

Figure 1. (a) Range of material properties derived for an ideal non-stoichiometric oxide (see text). (b) O_2 production rate, normalized to material mass, as a function of temperature measured during thermal reduction under a flow of He gas for several representative perovskite formulations (see legend). Dark vertical lines denote the onset temperature for O_2 evolution, which strongly correlates to the reduction enthalpy (ΔH_{TR}) and WS activity. Shaded box represents a temperature region where the ideal material will begin to evolve O_2. (c, d) Thermodynamic data for SLMA2, CeO_2, and H_2O plotted as a function of WS temperature (T_{WS}), oxygen non-stoichiometry (δ), and H_2O/H_2 ratio. For H_2 production (i.e. water splitting) to be thermodynamically favored at a particular H_2O/H_2 ratio and temperature, the solid colored lines for the final state δ must lie below the dashed lines (see text).

Figure 2. (a) P_{O2}-δ-T relationship map for SLMA2. Solid markers are experimental data measured by TGA, lines are fits to a solid solution model. (b) Predicted STH efficiency as a function of the temperature difference between T_{RED} and T_{OXD} (ΔT) for SLMA2 at various O_2

partial pressures under reduction (p_{TR}, Pa). Practical limits are assigned to the gas-gas (ε_{GG}) heat recovery effectiveness, and no credit is taken for solid-solid (ε_R) heat recovery (see inset). The thermodynamic model derived for SLMA2 was incorporated into this calculation (7). At a $p_{TR}<3$ Pa, SLMA2 is predicted to exceed the DOE 2020 STH efficiency target in Sandia's particle-based SRR.

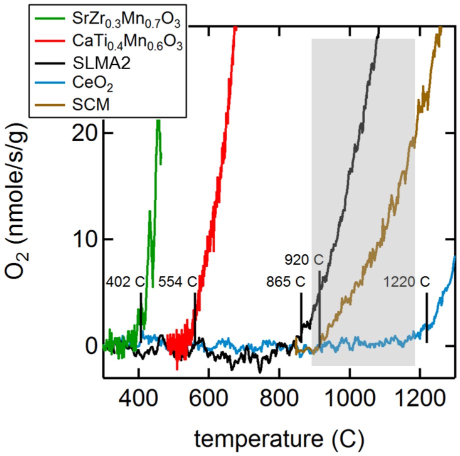
Figure 3. (a) Conceptual schematic of the 3-5 kW-scale engineering test stand under construction at Sandia. The sketch shows salient features of the device including two thermal reduction chambers and the particle elevator. (b) A simple schematic illustration of a cascading pressure reactor along with a graph showing the pumping advantage realized by using a multi-chambered approach. The ratio of $p_{TR,0}/p_{TR,i}$ (where TR,0 is the first chamber) is plotted as a function of the number of reduction chambers (i). One order of magnitude reduction in p_{TR} is achieved using only 5 chambers (calculation based on CeO_2 and other limiting factors such as solar concentration ratio and practical gas pumping speeds.)

Figure 4. (a) Schematic and image of Bucknell's test platform designed to study radiant heat transfer into particle beds. The platform consists of a windowed aperture (hemispherical quartz dome) attached to an insulated housing, and operates under vacuum with minimal attenuation of incident radiant energy. Approximately 100 cm^3 of particles can be placed in the cavity. (b) Schematic and image of Sandia's particle elevator. When complete, approximately 10 kg of redox-active particles can be transported, under vacuum at high temperature (<1000°C), to adjacent oxidation and reduction chambers (not shown). The moving packed particle bed is key to achieving ultra-low O_2 pressure during reduction and continuous on-sun operation.

(a)

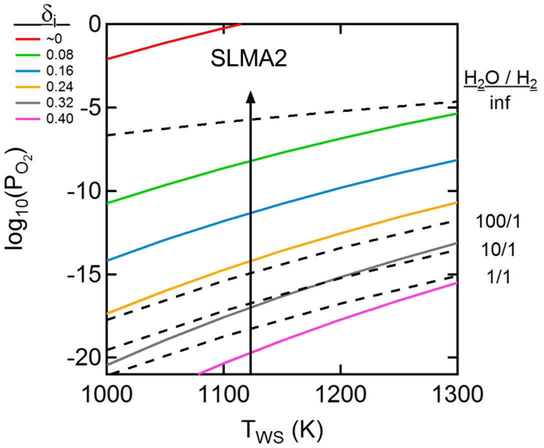
prop.	SLMA	IDEAL	CeO_2
T_{OR}	865°C	900-1200°C	1220°C
T_{WS}	900°C	750-900°C	1000°C
δ	0.30	SLMA	0.08
H_2O/H_2	200/1	CeO_2	10/1
*$Rate_{WS}$	~0.04 s^{-1}	CeO_2	~0.01 s^{-1}
*ΔH_{TR}	220-320	350-400	400-500
*ΔS_{TR}	100-130	~CeO_2	200-300

* Rate=pseudo first order, $\Delta H(\delta)$=kJ/mol O, $\Delta S(\delta)$=J/K mol O

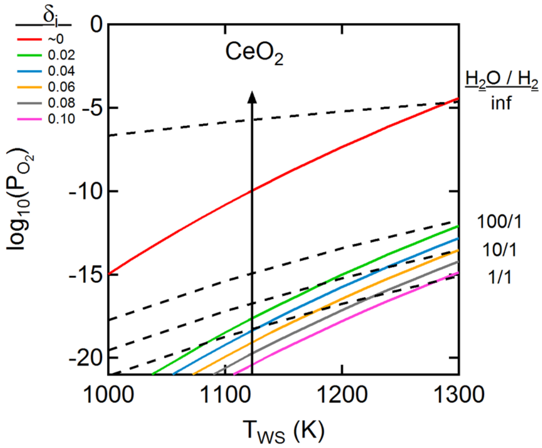


(b)

(c)



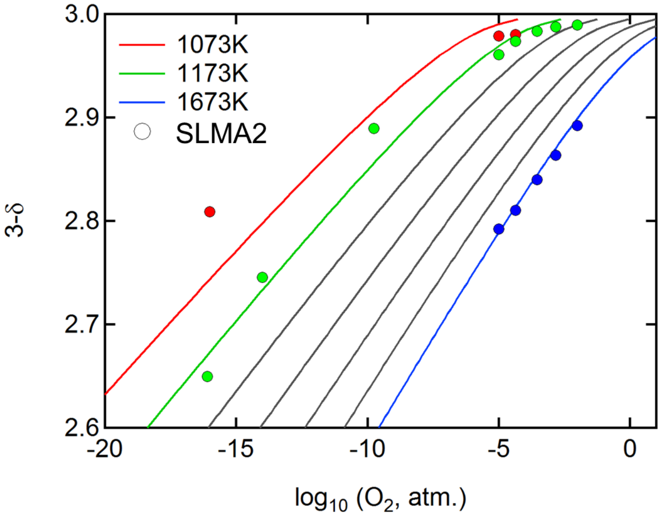
η_{STH} dominated by steam heating.



(d)

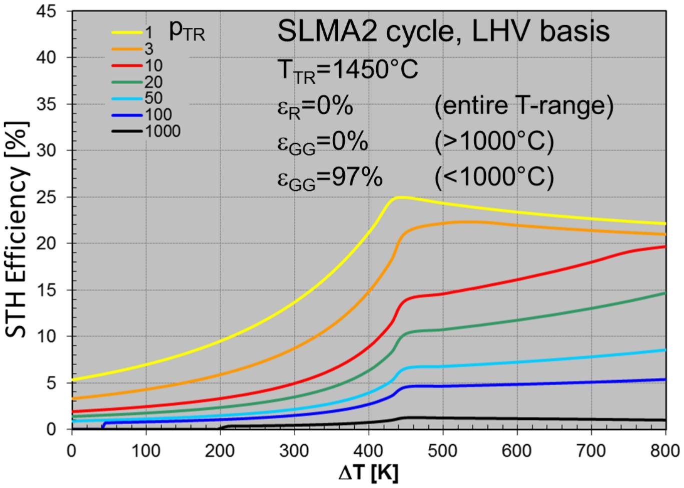
η_{STH} dominated by oxide heating.

(a)

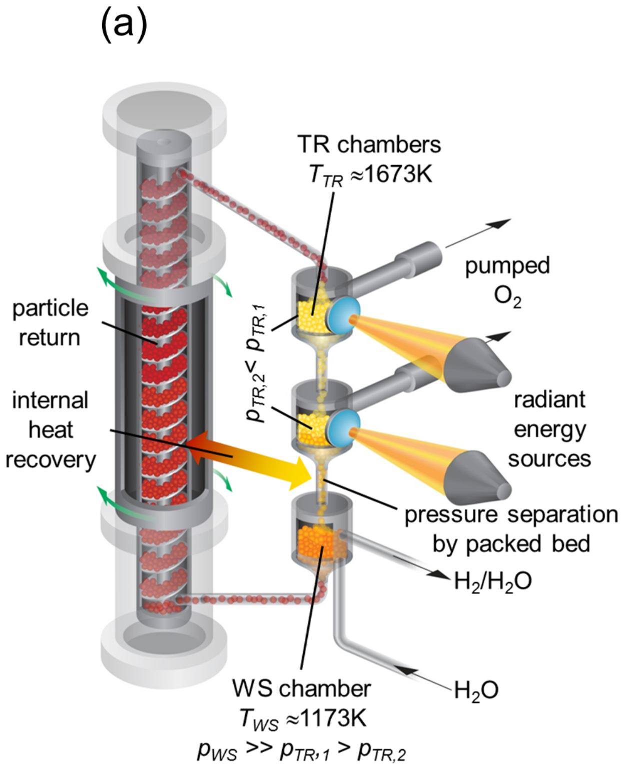


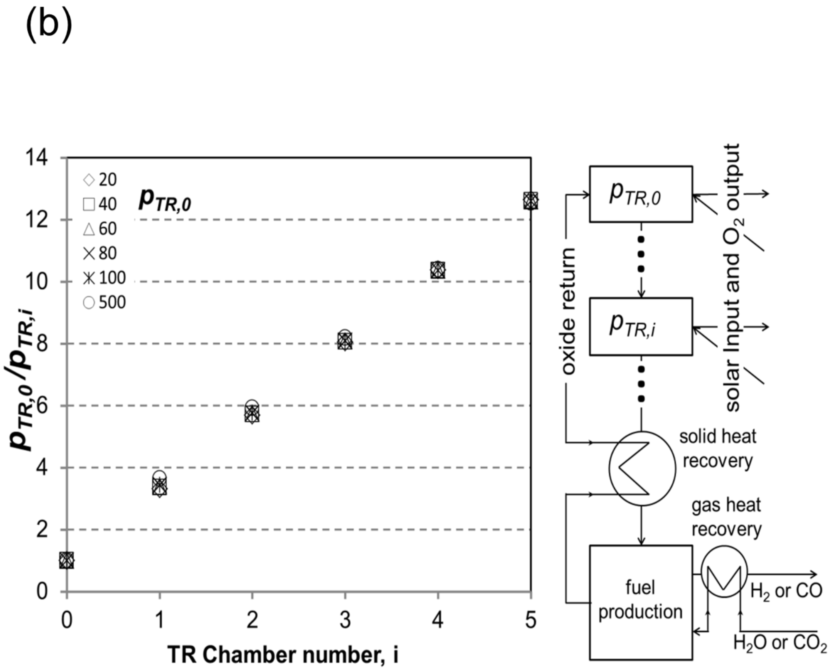
$$MO_{3-\delta_i} + \frac{(\delta_i - \delta_f)}{2} O_2 \rightarrow MO_{3-\delta_f}$$

(b)

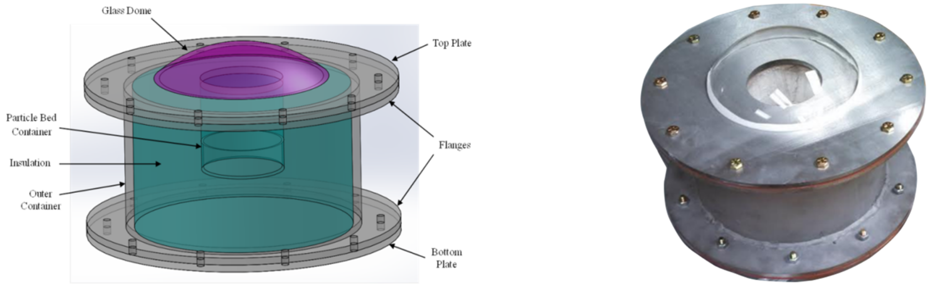


DOE 2020 target for STH ratio = 20%


(a)
TR chambers
T_{TR} ≈1673K
pumped
O_2
particle return
$p_{TR,2} < p_{TR,1}$
internal heat recovery
radiant energy sources
pressure separation by packed bed
H_2/H_2O
H_2O
WS chamber
T_{WS} ≈1173K
$p_{WS} >> p_{TR,1} > p_{TR,2}$


(b)
◇ 20
□ 40
△ 60
× 80
✻ 100
○ 500
$p_{TR,0}$
$p_{TR,0}/p_{TR,i}$
0
2
4
6
8
10
12
14
0
1
2
3
4
5
TR Chamber number, i
$p_{TR,0}$
$p_{TR,i}$
oxide return
solar Input and O_2 output
solid heat recovery
gas heat recovery
fuel production
H_2 or CO
H_2O or CO_2

(a)


Glass Dome
Top Plate
Particle Bed Container
Insulation
Outer Container
Flanges
Bottom Plate

(b)