Comparing the solar-to-fuel energy conversion efficiency of ceria and perovskite based thermochemical redox cycles for splitting H2O and CO2

Author(s):
Muhich, Christopher L.; Blaser, Samuel; Hoes, Marie C.; Steinfeld, Aldo

Publication Date:
2018-10-11

Permanent Link:
https://doi.org/10.3929/ethz-b-000292879

Originally published in:

Rights / License:
Creative Commons Attribution 4.0 International
Comparing the solar-to-fuel energy conversion efficiency of ceria and perovskite based thermochemical redox cycles for splitting H₂O and CO₂

Christopher L. Muhich a,*, Samuel Blaser b, Marie C. Hoes b, Aldo Steinfeld b

a School for the Engineering of Matter, Transport, & Energy, Arizona State University, 551 E. Tyler Mall, Tempe, AZ, 85287, USA
b Department of Mechanical and Process Engineering, ETH Zurich, Sonneggstrasse 3, 8092 Zurich, Switzerland

Article info
Article history:
Received 16 April 2018
Received in revised form 6 August 2018
Accepted 19 August 2018
Available online 19 September 2018

Keywords:
Solar thermochemical water splitting
Solar thermochemical carbon dioxide splitting
Efficiency analysis
Redox cycling
Renewable fuels

Abstract
A thermodynamic analysis was conducted on a solar thermochemical plant for syngas generation via H₂O/CO₂-splitting redox cycles in order to determine the performance of six candidate redox materials under an array of operation conditions. The values obtained for the solar-to-fuel energy conversion efficiency are higher in relative order Zr-doped CeO₂ > undoped CeO₂ > La₀.₆Ca₀.₄MnO₃ > La₀.₆Ca₀.₄Mn₀.₆Al₀.₄O₃ > La₀.₆Sr₀.₄MnO₃ > La₀.₆Sr₀.₄Mn₀.₆Al₀.₄O₃. This ordering is attributed to their relative reducibility and re-oxidizability, where the doped and undoped ceria, that favor oxidation, outperform perovskites, that favor reduction and therefore require high flowrates of excess H₂O and CO₂ during re-oxidation. Solids-solid heat recuperation during the temperature swing between the redox steps is crucial, particularly for ceria because of its low specific oxygen exchange capacity per mole and cycle. Conversely, the efficiencies of the perovskites are more dependent on gas-gas heat recuperation due to the massive excess of H₂O/CO₂. Redox material thermodynamics and plant/reactor performance are closely coupled, and must be considered together to maximize efficiency. Overall, we find that Zr-CeO₂ is the most promising redox material, while perovskites which seem promising due to high H₂/CO production capacities under large H₂O/CO₂ flow rates, perform poorly from an efficiency perspective due to the high heating duties, especially for steam.

© 2018 The Author(s). Published by Elsevier Ltd on behalf of Hydrogen Energy Publications LLC. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

Introduction
Concentrated solar thermochemical gas splitting (STGS) of H₂O and/or CO₂ is a promising approach for renewable H₂ and/or CO production because of its high theoretical solar-to-fuel energy conversion efficiency (h_solar-to-fuel) as a result of the utilization of the entire solar spectrum [1–5]. The h_solar-to-fuel is the ratio of the energy stored in the fuel to the solar energy required to produce the fuel [6]. In two-step STGS, concentrated sunlight drives the reduction of a metal oxide at T_red, releasing O₂, as shown in Eq. (1). In a second step, the reduced
<table>
<thead>
<tr>
<th>Nomenclature</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>reactor/material surface absorptivity</td>
</tr>
<tr>
<td>δ_{red}</td>
<td>reduction extents after reduction</td>
</tr>
<tr>
<td>δ_{ox}</td>
<td>reduction extents after oxidation</td>
</tr>
<tr>
<td>Δδ</td>
<td>change in reduction extent between reduction and oxidation</td>
</tr>
<tr>
<td>ΔH_{red}</td>
<td>enthalpy of reduction (kJ/mol)</td>
</tr>
<tr>
<td>ε</td>
<td>emissivity</td>
</tr>
<tr>
<td>ε_{gg}</td>
<td>gas-gas heat exchanger effectiveness</td>
</tr>
<tr>
<td>ε_{ss}</td>
<td>effectiveness of the solids heat exchanger</td>
</tr>
<tr>
<td>η_{O2-rem}</td>
<td>O₂ removal efficiency</td>
</tr>
<tr>
<td>η_{optic}</td>
<td>efficiency of optical collection</td>
</tr>
<tr>
<td>η_{sep}</td>
<td>efficiency of gas separation</td>
</tr>
<tr>
<td>η_{solar-to-fuel}</td>
<td>solar to fuel efficiency</td>
</tr>
<tr>
<td>A_{reactor}</td>
<td>aperture area (m)</td>
</tr>
<tr>
<td>C</td>
<td>solar concentration ratio</td>
</tr>
<tr>
<td>cP_{solid}</td>
<td>heat capacity of the solid (kJ/mol)</td>
</tr>
<tr>
<td>DNI</td>
<td>direct normal solar irradiance (W/m²)</td>
</tr>
<tr>
<td>h</td>
<td>effective hight to solids lifting per cycle (m)</td>
</tr>
<tr>
<td>h_{Conv}</td>
<td>convective heat transfer coefficient (kW/m² K)</td>
</tr>
<tr>
<td>HHV\textsubscript{H₂}</td>
<td>higher heating value of hydrogen (kJ/mol)</td>
</tr>
<tr>
<td>I_{solar}</td>
<td>direct normal solar irradiance (kW/m²)</td>
</tr>
<tr>
<td>K_{dissoc}</td>
<td>equilibrium constant for H₂O or CO₂ dissociation</td>
</tr>
<tr>
<td>MO_{x-red}</td>
<td>oxidized metal oxide</td>
</tr>
<tr>
<td>MO_{x-reduced}</td>
<td>reduced metal oxide</td>
</tr>
<tr>
<td>N</td>
<td>molar flowrate (mol/s)</td>
</tr>
<tr>
<td>P_{amb}</td>
<td>ambient pressure (bar)</td>
</tr>
<tr>
<td>P_{red}</td>
<td>pressure of reduction (bar)</td>
</tr>
<tr>
<td>P_{ox}</td>
<td>equivalent oxygen partial pressure in the oxidation chamber (bar)</td>
</tr>
<tr>
<td>P_{Ox, min}</td>
<td>minimum oxidation partial pressure required to drive the oxidation reaction forward (bar)</td>
</tr>
<tr>
<td>Q_{aux}</td>
<td>energy to run auxiliary processes (kW)</td>
</tr>
<tr>
<td>Q_{Conv}</td>
<td>heat lost to convection (kW)</td>
</tr>
<tr>
<td>Q_{gas}</td>
<td>energy of heating unreacted H₂O/CO₂ (kW)</td>
</tr>
<tr>
<td>Q_{H₂Ox}</td>
<td>heat released during the exothermic oxidation reaction(kW)</td>
</tr>
<tr>
<td>Q_{mech}</td>
<td>energy for moving the solids (kW)</td>
</tr>
<tr>
<td>Q_{mol}</td>
<td>heat needed to produce 1 mol of the fuel (kW)</td>
</tr>
<tr>
<td>Q_{o₂}</td>
<td>sensible heat recoverable from the oxygen gas exiting the reduction chamber (kW)</td>
</tr>
<tr>
<td>Q_{O2-rem}</td>
<td>energy to remove oxygen (kW)</td>
</tr>
<tr>
<td>Q_{rad}</td>
<td>re-radiated heat (kW)</td>
</tr>
<tr>
<td>Q_{Sc}</td>
<td>heat not recuperated by the solid-solid heat exchanger (kW)</td>
</tr>
<tr>
<td>Q_{sep}</td>
<td>energy for separating the product H₂/H₂O or CO/CO₂ mixtures (kW)</td>
</tr>
<tr>
<td>Q_{SH}</td>
<td>energy to heat the solids (kW)</td>
</tr>
<tr>
<td>Q_{solar}</td>
<td>total solar energy input (kW)</td>
</tr>
<tr>
<td>Q_{TC}</td>
<td>heat required for the thermochemical process (kW)</td>
</tr>
<tr>
<td>S</td>
<td>excess H₂O/CO₂</td>
</tr>
<tr>
<td>T_{amb}</td>
<td>ambient temperature (K)</td>
</tr>
<tr>
<td>T_{ox}</td>
<td>temperature of oxidation (K)</td>
</tr>
<tr>
<td>T_{red}</td>
<td>temperature of reduction (K)</td>
</tr>
<tr>
<td>T_{wall}</td>
<td>reactor wall temperature of reduction (K)</td>
</tr>
</tbody>
</table>

Material is re-oxidized by H₂O and/or CO₂, liberating the desired H₂ and/or CO, as shown in Eq. 2a and b:

\[
\text{MO}_{x-red} \rightarrow \text{MO}_{x-reduced} + \frac{\Delta \delta}{2} O \quad (1)
\]

\[
\text{MO}_{x-red} + \Delta \delta H₂O \rightarrow \text{MO}_{x-reduced} + \Delta \delta H₂ \quad (2a)
\]

\[
\text{MO}_{x-red} + \Delta \delta CO₂ \rightarrow \text{MO}_{x-reduced} + \Delta \delta CO \quad (2b)
\]

where δ_{red} and δ_{ox} are the reduction extents after reduction and oxidation, respectively, and Δδ = δ_{red} − δ_{ox}. The thermodynamic properties of the O-carrying metal oxide dictate the temperatures and pressures required for reduction and oxidation and the fuel production per cycle. These properties, therefore, critically influence the overall efficiency of the process. Several redox materials have been investigated for use in STGS cycles, including aluminate base spinels [7-9], ceria and doped ceria [3,10-19], and perovskites [20-24], which reduce through the formation of O-vacancies in the lattice that are filled upon re-oxidation rather than by decomposition/oxidation into a new phase. O-vacancy materials have lower H₂ or CO production capacities than phase change materials such as ZnO [25,26], or Fe₂O₄ [27] because the entire material does not reduce. Instead, the un-reduced material stabilizes the reduced material, thus preventing metal or metal oxide gas formation or melting which is common among the phase change material and is undesirable due to materials handling challenges. Therefore, we restrict this work to O-vacancy materials. However, we note that others have investigated the thermodynamics of decomposition based reactions [12,25,28,29], and multi-step (> 2) cycles such as the copper–chlorine or hydrogen sulfide cycles [30-34].

Among O-vacancy materials, ceria has become the standard for STGS because of its rapid reaction kinetics and stability over a range of reduction extents [3,4,35-39], which is dictated by both the temperature and the oxygen partial pressure in the system. However, it requires relatively high reduction temperatures (~1773 K) to achieve substantial reduction extents [3,10-13]. Ceria has been doped with Hf and Zr to increase the reducibility of ceria, while other single element doping strategies have not been effective [3,14-19,40]. Recently perovskites, particularly those based on lanthanum manganates (La\textsubscript{1-x}Mn\textsubscript{x}O\textsubscript{3}, for example where X = Ca, Ga, Sr, and Y = Mn, Al) have attracted interest because they reduce under less extreme conditions than ceria and have been shown to produce more hydrogen than ceria when reduced at lower temperatures (<1673 K) under large H₂O or CO flows [20-24,41]. In general, STGS redox materials face a dual challenge: reduce substantially at low temperatures and high oxygen partial pressures (pO₂), and re-oxidize completely with low H₂O/CO₂ excesses at high temperatures. The latter is incommensurate with the former due to contradictory thermodynamic forces [42]. Along the continuum of possible materials properties, ceria materials favor the re-oxidation reaction while perovskites favor the reduction reaction. Because both reactions cannot be favored at once, analysis of the usefulness of an active material should not simply be based on the quantity of H₂/CO it is capable of generating after reduction at high temperatures and oxidation.
under high excesses of H₂O/CO₂ at low temperatures. Rather the active material should be judged based on its \( \eta_{\text{solar-to-fuel}} \). The analysis of materials based on their \( \eta_{\text{solar-to-fuel}} \) is not as simple as Eqs. (1) and (2) suggest. An entire solar plant must be considered which takes into account the various ancillary processes which enable the redox cycle [3]. Sunlight must be collected, concentrated, and delivered to a solar reactor. During reduction, O₂ must be removed to maintain the pO₂ at a level sufficiently low for reduction to proceed. During oxidation, H₂O/CO₂ must be supplied and H₂/CO removed. The metal oxide must be heated and cooled between the reduction and oxidation reactions. The energy penalties associated with each of these general terms and with the temperature swing are affected by the operating points of the system i.e. the reduction and oxidation temperatures and pressures, and the quantity of excess H₂O/CO₂ [43]. Additionally, the effectiveness of the plant, i.e. the solar delivery system and heat recuperation, has a large impact on overall performance [44]. The selection of optimal operating points for a given material, and thus the determination of the maximum \( \eta_{\text{solar-to-fuel}} \) is further complicated by the non-intuitive interactions of the operating points and materials properties [12]. As a simple example, a decrease in the oxidation temperature lowers the required H₂O flow rate and steam heat duty, but increases the energy required to re-heat the metal oxide from the oxidation temperature to the reduction temperature; which of these has a larger effect on the \( \eta_{\text{solar-to-fuel}} \) depends on the heat capacity of the material, its re-oxidation thermodynamics, and the operating points [12].

Previous work has investigated some of these interactions to understand the effect of operation/system conditions for selected redox materials. Most models take a thermodynamic equilibrium approach and investigate a wide variety of behaviors such as the effects of various operational points (i.e. temperatures and pressure of the various reactions) [12,43,45–48], and the reactor system variables such as heat recovery effectiveness or method to remove O₂ [44,49–52]. Work has also been conducted into the effect of various materials using an entropy based method [53] and in systems based methods [12,23,54], which is the method we follow. In most cases, undoped ceria (CeO₂) was used as the redox material because its reduction extent (\( \delta \)) is well documented across a wide range of temperatures and oxygen partial pressure [13]. Some works have investigated zirconia doped ceria (Zr-CeO₂) [54], perovskites [23], and ferrites [12]. A wide variety of assumptions have been made about the solar reactor, reduction/oxidation conditions, heat recuperation, the oxidizing gas/active material contacting patterns, which makes a comparison difficult.

In this contribution we expand upon the previous work by using a comprehensive system model to compare \( \eta_{\text{solar-to-fuel}} \) of CeO₂, Zr-CeO₂ and several perovskites enabling us to fairly compare materials under various operating points and solar plant assumptions while minimizing the risk of selecting conditions which favor one material over another. Doped lanthanum manganates (La\(_{0.6}X\(_{0.4}\)Mn\(_{0.6}Y\(_{0.4}\)O\(_{3-a}\)) where \( X = \text{Ca or Sr}, \text{and } Y = \text{Al or Mn} \) were chosen as the perovskites because they have well characterized non-stoichiometries (\( \delta \)) and reduction thermodynamics at the temperatures relevant to STGS [23]. We find that, in almost all cases, the materials have relative \( \eta_{\text{solar-to-fuel}} \) of Zr-CeO₂ > CeO₂ > \( \text{La}_{0.6}\text{Ca}_{0.4}\text{Mn}_0\text{.6} \text{Al}_0\text{.4} \text{O}_3 \) (LCM) > \( \text{La}_{0.6}\text{Ca}_{0.6}\text{Mn}_0\text{.6} \text{Al}_0\text{.4} \text{O}_3 \) (LCMA) > \( \text{La}_{0.6}\text{Sr}_{0.4}\text{Mn}_0\text{.6} \text{Al}_0\text{.4} \text{O}_3 \) (LSM). We also discuss how system and operation points interact with materials choices and make recommendations for further materials and reactor design points.

**Modeling system efficiency**

In order to determine the relative efficiencies of various STGS redox materials we implemented a thermodynamic model based on energy and mass balances in Matlab®. This model enabled us to identify optimal system operating points of various materials and plant assumptions and analyze their \( \eta_{\text{solar-to-fuel}} \). Fig. 1 shows a general diagram of the system, which was defined as generally as possible to minimize system specific considerations. The system model, including the equations for calculating heat sources, sinks and flow rates, is described in detail in Section Thermodynamic model while the re-oxidation conditions and model inputs, including materials and systems properties, are described in Sections Determination of reduction extents and excess H₂O flow rates and Model parameters, respectively. The systems model is based on the works of Ermanoski et al. [43] and Ehrhart et al., [12] therefore we provide only an overview of the model. For a complete discussion of the model see Ehrhart et al. [12].

**Thermodynamic model**

The STGS model determines the \( \eta_{\text{solar-to-fuel}} \) for a set of materials in a solar plant with various system characteristics and at various operating conditions by calculating the ratio of the energy stored in the produced H₂ or CO to the solar energy required to produce it. This model operates under the assumption that concentrated sunlight is the only energy source.
input. We write the equations in terms of H₂O splitting, and comment on any changes or modifications necessary for CO₂ splitting to avoid redundancy. The overall figure of merit for the system is the \( \eta_{\text{solar-to-fuel}} \) defined by Eq. (3), where the energy stored in H₂ is a product of the H₂ molar flowrate \( (N_{H_2}) \) and the higher heating value of hydrogen (HHV\(_{H_2}\)), and Q\(_{\text{solar}}\) is the total solar energy input. For CO₂ splitting the combustion enthalpy of CO at room temperature is used.

\[
\eta_{\text{solar-to-fuel}} = \frac{N_{H_2} \cdot \text{HHV}_{H_2}}{Q_{\text{solar}}} \tag{3}
\]

Our analysis was conducted using a 1 mol/s flow basis of H₂/CO₂ where all other flows were scaled to meet this requirement. The system is assumed to operate at steady-state and thermodynamic equilibrium, meaning that all heat and mass fluxes are time independent. This enables the determination of the maximum \( \eta_{\text{solar-to-fuel}} \) for the materials because continuous production minimizes losses associated with moving materials and start up and cool down processes. Any kinetic impediments to the chemical reactions or heat transfer limitations only suppress the overall efficiency, and are therefore neglected from this analysis.

**Solar concentration**
The total solar energy delivered to the STGS plant must be sufficient to drive the thermochemical process (Q\(_{TC}\)), and to compensate for losses during collection, namely re-radiation (Q\(_{\text{read}}\)) and convective losses (Q\(_{\text{conv}}\)), as shown in Eq. (4).

\[
Q_{\text{solar}} = Q_{TC} + Q_{\text{read}} + Q_{\text{conv}} = \alpha \cdot C \cdot \eta_{\text{optic}} \cdot \eta_{\text{reactor}} \tag{4}
\]

The energy is delivered to the system through the solar receiver’s aperture and is a product of the reactor/material surface absorptivity (\( \alpha \)), direct normal solar irradiance DNI (\( I_{\text{solar}} \)), solar concentration ratio (C), aperture area (A\(_{\text{reactor}}\)) and optical efficiency (\( \eta_{\text{optic}} \)). The assumed values of these and all other general system parameters are shown in Table 1. These values were chosen to be consistent with previous models [12,43] based on experimental or theoretical work [55]. We note that optical efficiencies vary greatly and systems range from 60% [56] to up to 90% [57,58] depending on the design. We have chosen the upper value, based on a single reflection and high cleanliness factor, for use in this work. Any degradation in the optical performance will suppress the overall efficiency but the relative behavior of the materials will remain the same.

**Table 1 – Parameters describing the solar plant.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha ) (absorptivity)</td>
<td>0.95</td>
</tr>
<tr>
<td>( \varepsilon ) (emissivity)</td>
<td>0.05</td>
</tr>
<tr>
<td>( h_{\text{conv}} ) (convective loss coefficient)</td>
<td>0.0482 [kW/m²°C]</td>
</tr>
<tr>
<td>( \eta_{\text{optic}} ) (optics efficiency)</td>
<td>0.9</td>
</tr>
<tr>
<td>C (Concentration ratio)</td>
<td>3000</td>
</tr>
<tr>
<td>( T_{\text{wall}} ) (reactor wall temperature)</td>
<td>( T_{\text{red}} + 20 ) [K]</td>
</tr>
<tr>
<td>( I_{\text{solar}} ) (direct normal solar irradiance)</td>
<td>1 [kW/m²]</td>
</tr>
<tr>
<td>( h ) (effective height of solids lifting per cycle)</td>
<td>10 m</td>
</tr>
<tr>
<td>( \eta_{\text{mech}} ) (thermal-to-mechanical energy efficiency)</td>
<td>0.15</td>
</tr>
</tbody>
</table>

The solar concentration losses by re-radiation and convection through the aperture are calculated in Eqs. (5) and (6), respectively. The temperature of the reactor wall (\( T_{\text{wall}} \)) is assumed to be 20 K higher than the desired reduction reactor temperature. By combining Eqs. (4)–(6), the required aperture area is easily calculated by Eq. (7). Therefore, the only remaining quantity needed to calculate the total solar energy input is the heat necessary to drive the thermochemical process (Q\(_{TC}\)).

\[
Q_{\text{read}} = A_{\text{reactor}} \cdot \varepsilon \cdot T_{\text{wall}}^4 \tag{5}
\]

\[
Q_{\text{conv}} = A_{\text{reactor}} \cdot h_{\text{conv}} \cdot (T_{\text{wall}} - T_{\text{amb}}) \tag{6}
\]

\[
Q_{TC} = A_{\text{reactor}} \left[ 2 \cdot C \cdot I_{\text{solar}} \cdot \eta_{\text{optic}} - \varepsilon \cdot T_{\text{wall}}^4 - h_{\text{conv}} \cdot (T_{\text{wall}} - T_{\text{amb}}) \right] \tag{7}
\]

**Thermal cycling requirements**
The Q\(_{TC}\) is a product of the flow rate of H₂ or CO (set to be 1 mol/s) and the heat needed to produce 1 mol of the fuel (Q\(_{\text{mol}}\)), as shown in Eq. (8). Therefore, only Q\(_{\text{mol}}\) must be determined to calculate the \( \eta_{\text{solar-to-fuel}} \). Q\(_{\text{mol}}\) includes the energy required to drive the reduction (\( \Delta H_{\text{red}} \)), heat the cycling metal oxide (Q\(_{\text{OX}}\)), and to run auxiliary processes (Q\(_{\text{aux}}\)), as shown in Eq. (9). The energy required to drive the H₂O splitting reaction, i.e. Eq. (2), is provided by the energy stored in the reduced metal oxide (\( \Delta H_{\text{red}} \)) and is determined from the partial molar reduction thermodynamics of the active material.

\[
Q_{\text{TC}} = \eta_{\text{reactor}} \cdot Q_{\text{mol}} \tag{8}
\]

\[
Q_{\text{mol}} = \Delta H_{\text{red}} + Q_{\text{OX}} + Q_{\text{aux}} \tag{9}
\]

The solid heating duty (Q\(_{\text{SH}}\)) depends on the heat capacity of the solid (cp\(_{\text{solid}}\)), the temperature swing between reduction and oxidation steps, and the flow rate of solids, Eq. (10). The molar flow rate of solids required to generate 1 mol of H₂/CO is equal to the change in reduction extent between reactions (Δ\( \delta \)), as shown in Eq. (2). A heat exchanger with a heat recuperation effectiveness \( \varepsilon_{\text{rec}} \) transfers heat between the solids cooling to the oxidation temperature and those heating to the reduction temperature. Therefore, only the quantity of heat not recovered must be provided by the high quality solar heat to re-heat the oxidized solid to the reduction temperature. The unrecovered solids cooling energy can be used to run auxiliary processes, such as H₂O or CO₂ heating, as discussed in the next section.

\[
Q_{\text{SH}} = c_{\text{p, solid}} \cdot (T_{\text{red}} - T_{\text{ox}}) \cdot (1 - \varepsilon_{\text{rec}}) / \Delta \delta \tag{10}
\]

**Auxiliary heat requirements**

Additional energy (Q\(_{\text{aux}}\)) is required to drive auxiliary processes which enable STGS, including removing the oxygen from the reduction chamber (Q\(_{\text{O2-rem}}\)), heating unreacted H₂O/CO₂ to the oxidation temperature (Q\(_{\text{gas}}\)), any mechanical work (Q\(_{\text{mech}}\)), and separating the product H₂/H₂O or CO/CO₂ mixture (Q\(_{\text{sep}}\)).

\[
Q_{\text{aux}} = Q_{\text{O2-rem}} + Q_{\text{gas}} + Q_{\text{mech}} + Q_{\text{sep}} - Q_{\text{OX}} - Q_{\text{C}} - Q_{\text{D2}} \quad \text{if } Q_{\text{aux}} > 0 \tag{11a}
\]

\[
Q_{\text{aux}} = 0 \quad \text{if } Q_{\text{O2-rem}} + Q_{\text{gas}} + Q_{\text{mech}} + Q_{\text{sep}} - Q_{\text{OX}} - Q_{\text{C}} - Q_{\text{D2}} < 0 \tag{11b}
\]
However, there are available heat benefits which can provide energy for these processes, namely heat released during the exothermic oxidation reaction \(Q_{\text{OX}}\), heat not recuperated by the solid-solid heat exchanger \(Q_{\text{s,s}}\), and the sensible heat of the oxygen gas exiting the reduction chamber \(Q_{\text{O2-rem}}\). The sources of these heat benefits are at a lower temperature than the reduction chamber or the solids heater, and thus cannot be used to provide energy for these purposes. Therefore, any heat benefits greater than those required to run the lower temperature auxiliary processes must be rejected (Eq. (11b)); in other words, \(Q_{\text{aux}}\) must always be positive or zero.

We assume that the energy required to remove \(O_2\) from the system \(Q_{\text{O2-rem}}\) is equivalent to the work required to compress \(O_2\) from the reduction pressure to the ambient pressure, and then adjusted by some \(O_2\) removal efficiency \(\eta_{\text{O2-rem}}\) which includes the heat to work conversion, as shown in Eq. (12). While this equation is the thermodynamic requirement for pumping, it represents the minimum work required to remove \(O_2\) from the system (before inflation). We do not suggest that \(O_2\) is necessarily removed by vacuum pumping because there are multiple other methods of \(O_2\) removal [51,59]; rather we use this formulation for convenience.

\[
Q_{\text{O2-rem}} = \frac{1}{2} R T_{\text{amb}} \ln \left( \frac{P_{\text{amb}0}}{P_{\text{pred}}} \right) \frac{1}{\eta_{\text{O2-rem}}} \tag{12}
\]

The oxidizing gas heating requirement is determined by the moles of \(H_2O/CO_2\) required and the energy required to heat the gas to the oxidation temperature, as shown in Eq. (13a) and b for \(H_2O\) and \(CO_2\) respectively. Any excess \(H_2O/CO_2\) required to drive the oxidation reaction forward is also considered. All reactant gas and product \(H_2/\text{excess } H_2O\) or \(CO/\text{excess } CO_2\) cooling is assumed to occur in a heat exchanger with an effectiveness of \(\varepsilon\). The total energy required to heat \(H_2O/CO_2\) is:

\[
Q_{\text{aux}}(H_2O) = \left( c_{pW}\ast(T_{\text{O2}} - T_{\text{amb}}) + \Delta H_{\text{O2}} + \int_{T_{\text{O2}}}^{T_{\text{amb}}} c_{p\text{Steam}} dT \right) + (1 - \varepsilon_g) \ast \left( c_{pW}\ast(T_{\text{O2}} - T_{\text{amb}}) + \Delta H_{\text{O2}} \right) + \int_{T_{\text{O2}}}^{T_{\text{amb}}} c_{p\text{Steam}} dT - \varepsilon_g \ast \int_{T_{\text{O2}}}^{T_{\text{amb}}} c_{pH_2} dT \tag{13a}
\]

\[
Q_{\text{aux}}(CO_2) = \int_{T_{\text{amb}}}^{T_{\text{O2}}} c_{pCO_2} dT + (1 - \varepsilon_g) \ast \left( \int_{T_{\text{O2}}}^{T_{\text{amb}}} c_{pCO_2} dT \right) - \varepsilon_g \ast \int_{T_{\text{O2}}}^{T_{\text{amb}}} c_{pCO_2} dT \tag{13b}
\]

A mechanical work requirement is included in a simple manner as shown by Eq. (14). This was chosen to depend on the quantity of solid cycled to produce 1 mol of fuel and is inflated by a mechanical efficiency, which accounts for heat to mechanical work conversion losses. Here we assume that the work stems from having to lift solids, as would be the case in a particle based reactor. While this is included for completeness, it has very little effect on the overall system, contributing almost nothing to the total energy requirements (see below), and only decreases the \(\eta_{\text{solar-to-fuel}}\) by 0.08% for the base case of ceria.

\[
Q_{\text{mech}} = \frac{M_{\text{solid}} \ast g \ast h}{\Delta S_{\text{mech}}} \tag{14}
\]

We assume that product (\(CO\) or \(H_2\)) and reactant gases (\(CO_2\) or \(H_2O\)) are separated at a temperature \(T_{\text{sep}}\) of 298 K. \(H_2\) and \(H_2O\) have a natural phase separation without energy investment (i.e. \(Q_{\text{sep}} = 0\)). However, \(CO\) and \(CO_2\) must be separated by a different means. We calculate the separation work using the second law of thermodynamics and the entropy of separating the gases multiplied by a separation efficiency \(\eta_{\text{sep}}\), as shown in Eq. (15). Here \(n\) is the flow rate of the various streams entering or leaving the separator, \(\Delta S_{\text{mix}}\) is the entropy of mixing ideal gases of the various streams, and \(CO\) stream, \(CO_2\) stream and unsep stream indicators correspond to the CO rich and \(CO_2\) rich streams leaving the separator and the stream entering the separator respectively. The streams exiting the \(CO/CO_2\) separator are assumed to be 99% pure \(CO\) or \(CO_2\) and 100% pure \(CO_2\). The flow rates are determined from a simple mass balance.

\[
Q_{\text{sep}} = \frac{T_{\text{sep}} \ast \Delta S_{\text{mix}}}{\eta_{\text{sep}}} = T_{\text{sep}} \ast (n_{\text{CO stream}} \Delta S_{\text{mix CO stream}} + n_{\text{CO2 stream}} \Delta S_{\text{mix CO2 stream}} - n_{\text{unsep stream}} \Delta S_{\text{mix unsep stream}}) \ast \frac{1}{\eta_{\text{sep}}} \tag{15}
\]

The sensible heat recoverable from \(O_2\) \(Q_{\text{O2}}\), the heat released during re-oxidation, and the solids cooling enthalpy are calculated from Eqs. (16)–(18), respectively. They are determined from the simple sensible heat equation, reaction energies, and from the energy left in the solids after they cool down to the oxidation temperature, which is equivalent to the energy needed to re-heat the material.

\[
Q_{\text{O2}} = \frac{1}{2} \int_{T_{\text{O2}}}^{T_{\text{red}}} c_{pO_2} dT \tag{16}
\]

\[
Q_{\text{OX}}(H_2O) = -\Delta H_{\text{red}} - \Delta H_{\text{H}_2O}^r \tag{17a}
\]

\[
Q_{\text{OX}}(CO_2) = -\Delta H_{\text{red}} - \Delta H_{\text{CO}_2}^r + \Delta H_{\text{CO}}^r \tag{17b}
\]

\[
Q_{\text{SC}} = Q_{\text{SH}} \tag{18}
\]

**Determination of reduction extents and excess \(H_2O\) flow rates**

The calculation of the mass and energy flow rates depend on the reduction extents of the metal oxide before and after the reduction and oxidation reactions. The extent of reduction after the reduction \(\theta_{\text{red}}\) is determined by the reduction temperature and \(O_2\) partial pressure. It is described by the thermodynamic reduction behavior of the material, from which temperature, \(O_2\) partial pressure, and reduction extent relationships can be developed as discussed in Section Model.
parameters. However, the determination of reduction extent after oxidation ($\delta_{\text{red}}$) is more complicated. We assume that the oxidation reaction occurs in a countercurrent reactor, and that there is intimate gas/solid contact and thermodynamic equilibrium at the ends of the reactor. This configuration ensures that the exiting $\text{H}_2\text{O}/\text{H}_2$ or $\text{CO}_2/\text{CO}$ mixture is exposed to the strongest reducing agent, and the exiting metal oxide is exposed to the strongest oxidizing gas mixture, which results in the highest possible reaction extents of both metal oxide re-oxidation and $\text{H}_2\text{O}/\text{CO}_2$ conversion. Under these assumptions, the strongest reducing agent, and the exiting metal oxide is the $\text{CO}_2/\text{CO}$ mixture. Because we assume that the metal oxide where $K_{\text{dissoc}}$ is the equilibrium constant for $\text{H}_2\text{O} \leftrightarrow \text{CO}_2$ oxidation and $\text{H}_2\text{O}/\text{CO}_2$ conversion. Under these assumptions, the $\text{O}_2$ partial pressure of the re-oxidized metal oxide is equal to the equilibrium $p_{\text{O}_2}$ of the unreacted $\text{H}_2\text{O}$ or $\text{CO}_2$ at the oxidation temperature $(T_{\text{ox}})$, which is easily calculated as:

$$p_{\text{ox}} = \left(\frac{K_{\text{dissoc}}(T_{\text{ox}})}{2}\right)^{1/3}$$

where $K_{\text{dissoc}}$ is the equilibrium constant for $\text{H}_2\text{O}$ or $\text{CO}_2$ dissociation at the oxidation temperature, and $p_{\text{amb}}$ is the pressure of the $\text{H}_2\text{O}$ or $\text{CO}_2$ entering the oxidation chamber, assumed to be ambient pressure. The $\delta_{\text{ox}}$ of the material is subsequently determined from equilibrium data using $T_{\text{ox}}$ and $p_{\text{ox}}$.

Similarly, the $p_{\text{O}_2}$ of the reduced material entering the oxidation chamber is equal to that of the exiting $\text{H}_2\text{O}/\text{H}_2$ or $\text{CO}_2/\text{CO}$ mixture. Because we assume that the metal oxide does not re-oxidize during the temperature swing, $\delta_{\text{red}}$ remains unchanged and the $p_{\text{O}_2}$ at gas outlet of the oxidation chamber $(p_{\text{oxMin}})$ is determined using the thermodynamic relationship at $\delta_{\text{ox}}$ and $T_{\text{ox}}$. The $\text{H}_2\text{O}/\text{H}_2$ or $\text{CO}_2/\text{CO}$ ratio $(S)$ is then calculated using $p_{\text{oxMin}}$ and thermodynamic data for gas splitting:

$$S = \frac{1}{K_{\text{dissoc}}(T_{\text{ox}})}$$

### Model parameters

To determine the $\eta_{\text{solar-to-fuel}}$ for a material, the thermodynamic behavior of the material and several system specifications must be known. The required material information includes the thermodynamic correlation between temperature, oxygen partial pressure and reduction extent, enthalpy of reaction and heat capacity. The system specific parameters include the efficiency of heat recuperation ($\varepsilon_{\text{gg}}$ and $\varepsilon_{\text{ss}}$), $\text{O}_2$ removal efficiency ($\eta_{\text{O}_2\text{-rem}}$) and the parameters, listed in Table 1. All gas phase and $\text{H}_2\text{O}/\text{CO}_2$ heat capacities and formation energies were calculated based on formulas taken from the NIST Chemistry WebBook [60,61].

### Material properties

The experimentally determined dependence of metal oxide reduction extents on temperature and pressure is not available across the wide range necessary for the analysis in this work. Therefore, we calculated it from the partial molar entropies and enthalpies of reduction, which are available for the six materials studied here. We use the reduction thermodynamics as developed by Panlener et al. for ceria [13], Takacs et al. for $\text{Zr-GeO}_2$ [62], and Takacs et al. for the perovskites [23]. The oxygen partial pressure at various reduction extents and temperatures was tabulated for each material using Eq. (21), except for LSMA which used a defect model based approach to determine $p_{\text{O}_2}$ due to unphysical behavior using Eq. (21). For details on relating the defect model, partial molar properties, temperature and pressure see Takacs et al. [23] The $p_{\text{O}_2}$ at a desired temperature and non-stoichiometry, or the non-stoichiometry at a desired temperature and oxygen partial pressure, were calculated by interpolating between the entries in the table.

$$p_{\text{O}_2} = \exp\left[\frac{2\gamma\Delta h(\delta)}{R(T^* - T)} - \frac{\Delta s(\delta)}{R}\right]$$

(21)

The enthalpy of reduction was taken as the average partial molar reduction enthalpy. The heat capacity for ceria was taken to be 80 J/mol K [63] and was assumed to be the same for $\text{Zr-GeO}_2$. The heat capacity of perovskites was chosen to be 140 J/mol K because it is the value for many La-based perovskites [64–67] including Sr doped LaMnO$_3$ [68] at elevated temperatures, and because perovskites show general uniformity in their heat capacities [64–68].

### System parameters

In this work we investigate systems with reduction temperatures of 1573–1773 K, and oxidation temperatures decreasing from the reduction temperature to 773 K. This temperature was selected as a minimum oxidation temperature because below this point kinetics are likely to require long oxidation times. Additionally, such large temperature swings are likely to induce thermal stresses in the material and structures, decreasing their lifetimes.

We also investigate the effect of heat recuperation and $\text{O}_2$ removal and separation efficiencies on the relative behaviors of the materials. Heat recuperation was considered to be from 0% to 90% effective, while $\text{O}_2$ removal and $\text{CO}/\text{CO}_2$ separation were considered to be 1%–50% effective. While it is obvious that more efficient and effective auxiliary processes result in higher $\eta_{\text{solar-to-fuel}}$, it is unlikely that a commercial system would achieve effectiveness and efficiency higher than 90%. By investigating the effects of various system parameters, we are able to determine if the optimal material is system dependent, and if so, where the various materials perform best.

### Results

The $\eta_{\text{solar-to-fuel}}$ was calculated for each material under a variety of system assumptions (i.e. heat recovery effectiveness and $\text{O}_2$ removal and separation efficiency) and process conditions (reduction and oxidation temperatures and $\text{O}_2$ partial pressure during reduction). Each operation and system parameter was varied, having either an optimistic, neutral or pessimistic value, as is shown in Table 2. The optimistic value has been chosen to be higher than that which is currently experimentally demonstrated to show the potential of STGS, in particular for the case of solid/solid heating and $\text{O}_2$ removal. In all cases, the oxidation temperature was varied and the steam excess was calculated to give the highest $\eta_{\text{solar-to-fuel}}$ possible. We first describe the efficiency of ceria based STGS...
system, followed by the efficiencies of the other redox materials in comparison to ceria.

The efficiency of ceria based STGS

The solar to hydrogen efficiency of a solar thermochemical H$_2$O splitting plant is determined as a function of the temperature swing between the reduction and oxidation steps, as shown in Fig. 2a, under the neutral system conditions of $\epsilon_{gg} = 0.5$, $\eta_{rem} = 0.05$, $T_{red} = 1673$ K, and $P_{O_2} = 10^{-3}$ bar. The $\eta_{solar-to-fuel}$ initially increases from 0% under isothermal conditions to a maximum of 15.9% at an optimal value ($\Delta T_{opt}$) of 340 K. A further increase in the temperature swing results in a decrease in the $\eta_{solar-to-fuel}$. Across the range of temperature swings, the H$_2$ generated per mole of ceria is small, achieving a maximum $\Delta T = 0.017$ at $\Delta T_{opt}$ and 0.018 when re-oxidized at 773 K, the lowest allowed reduction temperature, as is shown from Fig. 2b. This is due to the fact that ceria does not reduce significantly even at 1773 K because of its high reduction enthalpy.

The presence of a $\Delta T_{opt}$ arises from competing heat requirements. At low $\Delta T$’s large quantities of steam have to be heated to the oxidation temperature to drive the H$_2$O splitting reaction forward, as shown in Fig. 2c. Additionally, the energy required to heat each mole of H$_2$O is high due to high oxidation temperature. As $\Delta T$ increases the energy required per mole of H$_2$O decreases because the oxidation temperature is lower, and less H$_2$O is required to re-oxidize the material, as shown in Fig. 2d. At the optimal operating point for ceria under these system assumptions, an excess of roughly 16.5 mol of H$_2$O are needed for each mole of H$_2$ produced. By increasing $\Delta T$ further the steam excess is decreased, achieving full conversion (a required steam excess of <10% of the produced H$_2$) at $\Delta T = 630$ K.

At $\Delta T > \Delta T_{opt}$, the heating of solids becomes the dominate term and controls the $\eta_{solar-to-fuel}$. At low $\Delta T$, the solar energy required to re-heat the solids is recoverable by driving the auxiliary processes such as steam heating. As $\Delta T$ increases the auxiliary heating requirements decrease, while the energy stored in the solids increases. Eventually, more sensible energy is stored in the solids than is required to drive auxiliary processes and the additional heat is rejected. At $\Delta T$ higher than this point the solids heating energy is wasted and the $\eta_{solar-to-fuel}$ decreases. $\Delta T_{opt}$ occurs at the point where the heating requirements balance. In other words, at $\Delta T < \Delta T_{opt}$ extra solar energy must be supplied to heat H$_2$O, while $\Delta T > \Delta T_{opt}$ require extra solids heating energy and heat is rejected. This finding and analysis is in agreement with previous work [12].

A solar thermochemical CO$_2$ splitting plant behaves similarly to a H$_2$O splitting plant. The results of the simulations are shown in Fig. 3. Due to the similarity of the plant behavior, we confine ourselves to discussing the differences. The overall $\eta_{solar-to-fuel}$ of the plant is 14.8% which occurs at a $T_{opt} = 380$ K, as shown in Fig. 3a. This is a slightly lower efficiency and larger optimal temperature swing than for H$_2$O splitting (15.9% and 340 K respectively). The lowered efficiency arises from the higher excess of CO$_2$ required to drive re-oxidation and additional work required for separation (which is 103 kJ/mol at $T_{opt}$). At the optimal operating point, 23 mol of excess CO$_2$ is required, as compared to only 16.5 excess moles of H$_2$O, which corresponds to heating duties of 607 kJ/mol for CO and 742 kJ/mol for H$_2$ respectively. At the optimal temperature for H$_2$O splitting a 40 mol excess of CO$_2$ is required, leading to a heating duty of 1078 kJ/mol. These requirements suppress the optimal oxidation temperature to decrease the required excess of CO$_2$, which increases the solids heating duty. The higher CO$_2$ excess required is because splitting H$_2$O is less exergonically unfavorable than splitting CO$_2$.

Effect of various system and operating conditions on ceria based STGS

Additional simulations of the ceria based system were conducted under different system and operation point assumptions. We investigated the effects of changing either one or two system assumptions in the efficiency model to determine not only the individual effects but also determine if there are correlations between the effects. Only the information from the optimal operating point are described as the behavior and trends are similar to that of the exemplary neutral operating point case. The results of the H$_2$O and CO$_2$ splitting systems are shown in Fig. 4 and Fig. 5, respectively, where the diagonal elements (i.e., those running from the upper left corner to the lower right corner) of the heat map show the effect of altering one assumption, and the off-diagonal elements correspond to two altered assumptions. We first describe single assumption effects before describing correlated effects, starting with the H$_2$O splitting system before extending the discussion to CO generation.

Of the five assumptions about the H$_2$O splitting system, the solid-solid heat recuperation has the largest effect on the $\eta_{solar-to-fuel}$ of a ceria based system. Additionally, the reduction temperature and pressure also play a large role in determining the overall $\eta_{solar-to-fuel}$. The pump efficiency and gas-gas heat recuperation effectiveness have a lower effect, and exhibit “on-off” behavior. As Fig. 4a shows, increasing (decreasing) the solid-solid heat recuperation effectiveness from 0.5 to 0.9 (0.0) increases (decreases) the solar efficiency from 15.7% to 30.3% (10.4%). The large dependency of $\eta_{solar-to-fuel}$ on solids heat recuperation arises from the low H$_2$ production capacity of ceria, see Fig. 4b, which therefore requires many moles of ceria to be cycled for each mole of H$_2$ produced and an associated large quantity of heat. This is of critical importance.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Pessimistic</th>
<th>Neutral</th>
<th>Optimistic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduction temperature ($T_{red}$)</td>
<td>1573 K</td>
<td>1673 K</td>
<td>1773 K</td>
</tr>
<tr>
<td>Reduction O$_2$</td>
<td>10$^{-3}$bar</td>
<td>10$^{-4}$bar</td>
<td>10$^{-5}$bar</td>
</tr>
<tr>
<td>Solid-solid heat recuperation effectiveness ($\epsilon_{ss}$)</td>
<td>0%</td>
<td>50%</td>
<td>90%</td>
</tr>
<tr>
<td>Gas-gas heat recuperation effectiveness ($\epsilon_{gg}$)</td>
<td>0%</td>
<td>50%</td>
<td>90%</td>
</tr>
<tr>
<td>O$<em>2$ removal efficiency ($\eta</em>{O_2-rem}$)</td>
<td>1%</td>
<td>5%</td>
<td>10%</td>
</tr>
<tr>
<td>CO/CO$<em>2$ separation efficiency ($\eta</em>{sep}$)</td>
<td>1%</td>
<td>10%</td>
<td>50%</td>
</tr>
</tbody>
</table>
because efficient solid/solid heat recuperation is technically challenging. Depending on the reactor design, solid heat recuperation may range from 0% in designs with fixed monolithic structures [37] to 50% in design with rotating components [69,70] and higher values in designs with moving particles [71–73]. This work is not alone in identifying the criticality of solid-solid heat recuperation, its findings merely reaffirm the point. For similar reasons, the optimal temperature swings, shown in Fig. 4c, are relatively low and therefore the temperature over which the solids must be re-heated is minimized.

Decreasing the reduction pressure or increasing the reduction temperature to 1 Pa or 1773 K, respectively, increases the $\eta_{\text{solar-to-fuel}}$ to roughly 21.75%. Conversely increasing the pressure or decreasing the temperature to 100 Pa or 1373 K, respectively, decreases efficiency to ~10%. These modifications, especially the adaption of the optimistic assumption, have a smaller effect than that of altering the solid-solid heating.

The gas-gas effectiveness and O2 removal efficiency have a much smaller effect on the $\eta_{\text{solar-to-fuel}}$ of ceria and increasing/decreasing the values does not give symmetric behavior. While increasing the gas-gas heat recuperation efficiency increases the efficiency of the system (from 15.7% at $\varepsilon_{gg} = 0.5$ to 18.4% at $\varepsilon_{gg} = 0.9$), eliminating the gas-gas heat recuperation only decreases the $\eta_{\text{solar-to-fuel}}$ by 1% (14.7%). This suggest that while any level of solids heat recover is good, there is a minimum gas-gas heat recovery necessary to significantly affect the overall efficiency of the system. We attribute this to the fact that little excess steam is required to drive the H2O splitting reaction (see Fig. 4b) because of the strongly oxidizing nature of reduced CeO2. Conversely, the O2 removal is only a drag on the overall system efficiency. Improvements to the O2 removal efficiencies above 5% effects little improvement in $\eta_{\text{solar-to-fuel}}$, resulting in a $\eta_{\text{solar-to-fuel}}$ increase from 15.7% to 15.9% at a $\eta_{\text{O2-rem}}$ of 10%. However, a decrease in the removal efficiency to 1% decreases the $\eta_{\text{solar-to-fuel}}$ to 12.6%. Therefore, it is necessary that the O2 removal system be somewhat efficient. While it is unlikely that vacuum pumping is capable of achieving such efficiencies at low pressures, methods such as electrochemical O2 pumping, or thermochemical oxygen pumping, which does not require heat to work conversation, may be capable of achieve these efficiencies [74].

---

**Fig. 2** — Solar thermal water splitting a) efficiency of CeO2, b) required excess steam flow and change in the non-stoichiometry, and c) & d) associated energy requirements over a range of temperature swings. d) highlights the heat requirements in c). The plant and system operation points were: $\varepsilon_{gg} = \varepsilon_{ss} = 0.5$, $\eta_{\text{O2-rem}} = 0.05$, $T_{\text{red}} = 1673$ K, $P_{\text{red}} = 10^{-4}$ bar.
Improving two system variables at once has, unsurprisingly, a beneficial effect, while combined poor system performance has a larger deleterious effect. However, the effect of improving only the solid-solid heat recuperation has more of a beneficial impact on the system than improving any other two system metrics. This shows the imperative of having solid-solid heat recuperation when the active material is ceria.

As discussed above, the CO₂ splitting plant behaves similarly to the H₂O splitting plant. We find that the CO₂ splitting plant is slightly less efficient than the H₂O splitting plant and operates with a higher temperature swing, as shown in Fig. 5a and b, because higher CO₂ flow rates are required than H₂O to reoxidize CeO₂, as shown in Fig. 5. This however does not alter the finding that the solid-solid heat recuperation has the largest effect on the \( \eta_{\text{solar-to-fuel}} \). Additionally, we find that while a higher separation efficiency is better, it has only a minor influence on the overall system efficiency.

Overall, we conclude that having a high solids heat recuperation effectiveness is highly desirable, while reduction temperature and pressure should be increased and decreased, respectively, as much as possible. The O₂ removal system merely needs to be able to achieve reasonable (-5%) efficiency, with the caveat that below this value the pumping begins to have a detrimental effect. Especially efficient gas-gas heat recuperation or CO₂ separation is worthwhile only if it is highly effective.

**Solar-to-fuel energy conversion efficiency of various redox materials**

In addition to ceria, we investigated the \( \eta_{\text{solar-to-fuel}} \) of Zr-CeO₂, LSMA, LSM40, LCMA, and LCM40. The \( \eta_{\text{solar-to-fuel}} \) and associated metrics for the base case assumptions about the solar plant (i.e. \( \varepsilon_{gg} = \varepsilon_{ss} = 0.5 \), \( \eta_{O_2\text{-rem}} = 0.05 \), \( \eta_{sep} = 0.1 \), \( T_{red} = 1673 \text{ K} \), \( P_{red} = 10^{-3}\text{ bar} \)) are shown in Fig. 6a for a range of temperature swings. Under these conditions, only Zr-CeO₂ achieves higher system efficiencies than ceria, while the four perovskites perform significantly worse. Within the perovskites, those containing Ca achieve higher efficiencies than those containing Sr, and the materials without Al (LSM40/LCM40) perform better than those that do.

In all cases the efficiencies converge to \(-0.3\%\) at \( \Delta T = 0 \). This is because the material does not change temperature and therefore the materials act merely to separate O₂ evolution...
and H₂ evolution rather than to facilitate water splitting. The pO₂ in the system is set during oxygen removal and all materials reduce accordingly. In the re-oxidation step, sufficient H₂O enters the system so that the effective pO₂ is equal to the pO₂ of the materials, which are all identical as the temperature has not changed. At \( T = 0 \), the steam heating term dominates the heat input, as seen in Fig. 2c and d, and therefore the materials dependent effects are negligible on the overall system efficiency. The relative solar-to-fuel of the materials comes from the trade-off between the H₂ produced per cycle and the steam requirements. Zr-CeO₂, which performs better than ceria at \( T > 570 \) K, has a higher H₂ production capacity and steam requirement than CeO₂ at all \( T \). At low non-zero \( T \), Zr-CO₂ requires substantially more steam than CeO₂, and the rate of the decrease of steam required with the temperature swing is lower (Fig. 6b). This arises from the fact that CeO₂ re-oxidation is more exothermic than Zr-CeO₂, and CeO₂ is therefore a stronger reducing agent than Zr-CO₂. Because the steam heating duty initially controls the overall system efficiency, ceria initially has a higher \( \eta_{\text{solar-to-fuel}} \) than Zr-CeO₂. However, Zr-CeO₂ achieves higher reduction extents than CeO₂, and therefore has a higher production capacity per cycle (seen in Fig. 6c). This cannot compensate for the high required H₂O excess at low \( T \); however, at larger \( T \) where the efficiency is controlled by solids heating, the higher production capacity per cycle of Zr-CeO₂ results in lower material flow rates and solid heating requirements as compared to CeO₂. This results in Zr-CeO₂ having a higher \( \eta_{\text{solar-to-fuel}} \) than CeO₂.
The perovskites have larger production capacities than either ceria or Zr-CeO₂, because they have lower reduction enthalpies and thus reduce more easily. However, this comes at the cost of higher steam requirements during oxidation. At most the perovskites have production capacity seven times higher than the ceria materials, which is dwarfed by the steam requirement which is several orders of magnitude higher than the ceria materials. Within the perovskites, those with lower steam requirements had higher $h_{\text{solar-to-fuel}}$, as shown in Fig. 6b. The relative $h_{\text{solar-to-fuel}}$ ordering for the perovskites is LCM40 > LCMA > LSM40 > LSMA. We attribute the better performance of Ca containing perovskites to their higher reduction energy as compared to the Sr containing perovskites. Similarly, the Al containing perovskites have lower partial molar reduction enthalpies than their non-Al containing counter parts at high degrees of reduction where the required steam excess is determined, meaning that Al containing perovskites require more steam and thus have lower $h_{\text{solar-to-fuel}}$.

It is worth noting that LSMA, in addition to being the lowest efficiency material, requires more H₂O/CO₂ as $D_T$ increases which is the opposite of the other materials. This arises from its low partial molar reduction enthalpy and entropy at the degrees of non-stoichiometry achieved at the reduction temperature and pressure (~0.1), as measured by Takacs et al. [23]. The resulting free energy of re-oxidation by H₂O/CO₂ becomes less negative at larger $D_T$ because the re-oxidation enthalpy (~-260 kJ/mol) is only slightly larger in magnitude than the enthalpy of splitting the gases; this small energetic driving force cannot compensate for the entropy loss of gas reduction and therefore higher H₂O/CO₂ ratios are required as $D_T$ increases to drive the reaction forward.

Fig. 5 – A heat map of the effect of altering system and operational parameters on the performance of a CO₂ splitting plant with CeO₂ active material. a) The solar to CO efficiency ($h_{\text{solar-to-fuel}}$), b) optimal temperature swing ($D_{T_{\text{opt}}}$), c) excess CO₂ to CO ratio ($s$), d) change in oxidation state between the reduction and oxidation reaction ($\Delta \delta$). The diagonal elements show altering only one parameter, off diagonal elements show the effects of altering two parameters, the upper right corner shows the base case ($\varepsilon_{gg} = \varepsilon_{ss} = 0.5$, $\eta_{pump} = 0.05$, $T_{\text{red}} = 1673$ K, $P_{O_2} = 10^{-4}$ bar, and $\eta_{\text{sep}} = 0.1$. Pluses or minuses correspond to the pessimistic and optimistic cases, which are 0.0 or 0.9 for heat recuperation ($\varepsilon_{gg}$ and $\varepsilon_{ss}$), 0.01 or 0.1 for O₂ removal efficiency ($\eta_{O_2-\text{rem}}$), $10^{-5}$ and $10^{-3}$ bar for reduction O₂ partial pressure ($P_{O_2}$), 1573 or 1773 K for reduction temperature ($T_{\text{red}}$), and 0.01 and 0.5 for separation efficiency ($\eta_{\text{sep}}$), respectively.
System effects
We investigated the behavior of all of the materials under a wide range of solar plant and operating condition assumptions. The results of the H2O splitting plant are shown in Fig. 7, while the CO2 plant is shown in Fig. 8. In general, the findings reported above, that the materials have relative $\eta_{\text{solar-to-fuel}}$ of $\text{Zr-CeO}_2 > \text{CeO}_2 > \text{LCM40} > \text{LCMA} > \text{LSM40} > \text{LSMA}$ for H2O splitting, hold under most of the conditions considered. However, for some conditions CeO2 outperforms Zr-CeO2 for CO2 splitting. Therefore, we will only discuss general behaviors across the operation points, focusing on H2O splitting and then commenting on CO2 splitting.

Zr-CeO2 has similar trends to undoped ceria, in that the solid-solid heat recuperation effectiveness has the largest effect on efficiency, which is unsurprising given their similar composition and thermodynamics. The only major difference is that Zr-CeO2 generally has a higher solar conversion efficiency for H2O splitting. The doped material shows the highest efficiency when the solid heat recuperation is high. This is logical because the material must be looped many times to produce each mole of H2, owing to the low, but higher than CeO2, production capacity per cycle. The re-oxidation temperatures of Zr-CeO2 are all lower than those of CeO2 and even reach the minimum allowed oxidation temperature of 773 K for high solids heat recuperation and low O2 removal efficiency.

In some cases, however, CeO2 has a higher $\eta_{\text{solar-to-fuel}}$ than Zr-CeO2 for CO2 splitting. This occurs in the cases of high solids reheating effectiveness or in some cases with poor gas-gas heat recuperation. This is once again logical because Zr-CeO2 requires more CO2 to drive reoxidation than undoped CeO2. Therefore, when the gas-gas heat recuperation is poor, the higher energy requirement associated with flowing more CO2 outweighs the higher production capacity of Zr-CeO2.

Fig. 6 – The effect of altering the redox material in a STGS plant for generating H2 (a–c) or CO (d–f). a and d) The solar to fuel efficiency, b) and e required steam flow, and c) and f) change in the non-stoichiometry over a range of temperature swings of CeO2, Zr-CeO2, LCM40, LCMA, LSM40, LSMA. The plant and system operation points were: $\varepsilon_{\text{gg}} = \varepsilon_{\text{ss}} = 0.5$, $\eta_{\text{O2-rem}} = 0.05$, $\eta_{\text{sep}} = 0.1$ (CO production), $T_{\text{red}} = 1673$ K, $P_{\text{red}} = 10^{-4}$ bar.
Fig. 7 – The effects of altering system and operational parameters on the performance of a water splitting plant with various active materials: a) CeO₂, b) Zr-CeO₂, c) LCM40, d) LCMA, e) LSM40 and f) LSMA. The diagonal elements show altering only one parameter, (with the altered parameter shown in the corner) off diagonal elements show the effects of altering two parameters, and the upper right corner shows the base case ($\varepsilon_{gg} = \varepsilon_{ss} = 0.5$, $\eta_{\text{pump}} = 0.05$, $T_{\text{red}} = 1673$ K, and $P_{O_2} = 10^{-4}$ bar). Pluses or minuses correspond to the pessimistic and optimistic cases, which are 0.0 or 0.9 for heat recuperation ($\varepsilon_{\text{gg}}$ and $\varepsilon_{\text{ss}}$), 0.01 or 0.1 for O₂ removal efficiency ($\eta_{\text{O}_2\text{-rem}}$), $10^{-5}$ and $10^{-3}$ bar for reduction O₂ partial pressure ($P_{O_2}$), and 1573 or 1773 K for reduction temperature ($T_{\text{red}}$), respectively. Dark colors represent low values and bright colors are high values.
The effects of altering system and operational parameters on the performance of a CO₂ splitting plant with various active materials: a) CeO₂, b) Zr-CeO₂, c) LCM40, d) LCMA, e) LSM40 and f) LSMA. The diagonal elements show altering only one parameter (with the altered parameter shown), off diagonal elements show the effects of altering two parameters, and the upper right corner shows the base case ($\varepsilon_{gg} = \varepsilon_{ss} = 0.5$, $\eta_{pump} = 0.05$, $T_{red} = 1673$ K, $h_{sep} = 0.1$ and $P_{O_2} = 10^{-4}$ bar). Pluses or minuses correspond to the pessimistic and optimistic cases, which are 0.0 or 0.9 for heat recuperation ($\varepsilon_{gg}$ and $\varepsilon_{ss}$), 0.01 or 0.1 for O₂ removal efficiency ($\eta_{O_2}$-rem), 0.05 or 0.5 for separation efficiency ($\eta_{sep} = 0.1$), $10^{-5}$ and $10^{-3}$ bar for reduction O₂ partial pressure ($P_{O_2}$), and 1573 or 1773 K for reduction temperature ($T_{red}$), respectively. Dark colors represent low values and bright colors are high values.
Similarly, when the solid-solid heat recuperation is high, the solids re-heating requirements of CeO₂ are decreased and therefore the low production capacity effects are diminished. Once again the higher CO₂ flowrates of Zr-CeO₂ cause the lower η_{solar-to-fuel}. The perovskites behave differently than the ceria based materials. This is because they are much poorer reducing agents than the ceria materials, and H₂O heating is the major controller of overall system efficiency. This is seen in the fact that the H₂O flow rates are very high and that minimum possible oxidation temperature (773K) is the optimal ΔT for almost all cases, See SI Fig. S1–S5. Therefore, perovskite materials are affected strongly by a different set of system and operating conditions than the ceria materials. Rather than solid heat recuperation being the most important factor, reduction temperature and pressure, and the gas-gas heat recuperation controls the efficiency of perovskite processes. LCM40 and LSM40 both require a high reduction temperature and low reduction oxygen partial pressure in order to achieve moderate efficiencies. Without a high reduction temperature and low reduction P_{O2} these cycles perform very poorly (< 10% η_{solar-to-fuel}). Highly effective steam heat recovery also improves the overall efficiency, however without it the cycles are still capable of producing H₂ at a reasonable efficiency. This is because under high T_{Req} or low P_{O2} conditions the material reduces significantly, and thus has a higher driving force for re-oxidation, and, therefore, the quantity of H₂O required to generate a mole of H₂ is low compared to the other investigated conditions. The aluminum containing perovskites (LCMA and LSMA) require very effective gaseous heat recovery to perform even modestly well, and even then their η_{solar-to-fuel} is low. This arises from the fact that these materials require more than a 50 times excess of steam to re-oxidize the material under all conditions, and therefore it is logical that high gaseous heat recovery is necessary for even minimal η_{solar-to-fuel}. This finding shows the need for a system based analysis of new STGS materials, because while the perovskites, LSMA in particular, have gained significant attention due to high H₂ production capacities, our system efficiency model suggest that they will not result in high η_{solar-to-fuel}.

The trends discussed above for H₂O splitting hold for CO₂ splitting for the perovskites (see SI Fig. S6–S10). Because the efficiency of these materials was already controlled by gas heating for H₂O, which is a more oxidizing gas, using a less oxidizing gas (CO₂) which requires higher gas flow rates only exacerbates the situation. For CO₂ splitting, all perovskites exhibit poor η_{solar-to-fuel}, except in cases where there is excellent gas-gas heat recuperation, and even then a low oxygen partial pressure or high reduction temperature are required.

Discussion

In all but three H₂O splitting configurations investigated (out of 121 total), Zr-CeO₂ outperformed un-doped ceria by 3–5% η_{solar-to-fuel}. Even in the three cases where CeO₂ showed better performance the difference was less than 1% η_{solar-to-fuel}. The most even performance between the two occurred for the low O₂ removal efficiency case (η_{O2-rem} = 1%) where neither material had a η_{solar-to-fuel} of more than 14%. Therefore, assuming that the kinetics are roughly similar, or that they can be designed around, we suggest that Zr-CeO₂ materials are superior in terms of overall hydrogen production efficiencies. When the system is used to drive CO₂ splitting, the better material is more dependent on the system parameters, where CeO₂ outperforms Zr-CeO₂ when there is high solids heat recovery, or under the most pessimistic assumptions. Conversely, there are only two cases where a perovskite, namely LCM40 and LCMA outperform CeO₂ for H₂O splitting, and this is where the gas-gas heat recuperation is very effective (90%) but the solid-solid recuperation is not (0%). This also is logical because the perovskites are not very sensitive to solids heat recuperation but are very sensitive to gas heat recuperation while the opposite is true for CeO₂. Even under these conditions, Zr-CeO₂ outperforms the perovskites. The fact that the perovskites only outperform ceria where they are at their best and ceria is at its worst, suggests that perovskites may not be optimal for STGS systems because they require steam excesses that are far too high. Similarly, the perovskites never outperform CeO₂ or Zr-CeO₂ for CO₂ splitting, once again because CO₂ splitting requires larger excesses of the oxidizing gases, which is the weak point of perovskites, even for H₂O splitting. Overall, the best performing material, Zr-CeO₂ which is only slightly better than un-doped ceria, is the material with balanced thermodynamic properties which slightly favor the oxidation reaction.

Conclusions

In this work, we used a thermodynamic model to determine the solar-to-fuel energy conversion efficiency of six redox materials for thermochemically splitting H₂O and CO₂. We showed that the materials have relative performances of Zr-CeO₂ > CeO₂ > La₀.₆Ca₀.₄Mn₀.₆Al₀.₄O₃ > La₀.₆Sr₀.₄Mn₀.₆Al₀.₄O₃ > La₀.₆Sr₀.₄Mn₀.₆Al₀.₄O₃ > La₀.₆Sr₀.₄Mn₀.₆Al₀.₄O₃ and that this ordering is relatively independent of system parameters or operating points, with the caveat that CeO₂ outperforms Zr-CeO₂ for CO₂ splitting in systems with high solids heating recuperation. However, while the system parameters and operating points have little effect on the overall conclusion, the different materials are more or less sensitive to different parameters. The performance of ceria based materials (Zr-CeO₂ and CeO₂) are most influenced by the solid-solid heat recuperation, while the LCM and LSM are correlated to reduction temperature and O₂ partial pressure, and LCMA and LSMA are correlated to gas-gas heat recuperation. We attribute these effects to the re-oxidizability of the materials. The perovskites, which are appealing at first glance due to their high reducibility, require vast excesses of steam to drive re-oxidation and H₂ or CO generation, and are therefore highly limited by factors affecting re-oxidation. The ceria materials are limited by their reduction extents, and therefore their production capacity. Based on these finding we draw two general conclusions. 1) The redox material behavior dictates the requirements of the solar plant. This means that the system needs to be designed around the material, i.e. the system priorities high solid-solid heat recuperation for the ceria materials or high gas-gas heat recuperation for the LCM or LSM. 2) The search for new
materials should concentrate on those that slightly favor the oxidation reaction, not the reduction reaction, as it has been previously thought; these new materials should oxidize well while not requiring reduction temperatures in excess of 1600 °C. Even at low temperatures the CeO₂ and Zr-CeO₂ have higher efficiencies than the perovskites which favor reduction. This is because the steam heating requirements quickly negate the benefits of additional production capacity. Overall, we have shown that STGS can achieve high internal-to-fuel with available redox materials for solar reactors operating at optimal reduction temperature and pressure conditions and with adequate heat recovery.

Acknowledgements

We gratefully acknowledge the financial support by the Swiss National Science Foundation (Grant No. 200021_162435), the Swiss State Secretariat for Education, Research and Innovation (SERI) under contract number 16.0183, and the EU’s Horizon 2020 research and innovation program (INSHIP – No. 731287).

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.ijhydene.2018.08.137.

REFERENCES


[68] Szewczyk A, Gutowska M, Dabrowski B. Specific heat and phase diagram of heavily doped La$_{1-x}$Sr$_x$MnO$_3$ (0.45 $\leq x \leq 1.0$). Phys Rev B 2005;72:224429.


