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Advancing oxide materials for thermochemical production of solar fuels

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Abstract

Two-step metal-oxide based thermochemical cycles show great promise for the production of the synthetic fuel precursors CO and H_2 from CO_2 and H_2O, respectively. The basic properties that define an ideal material and key traits of the materials for successful implementation will be established. To the first level, an ideal material is defined by thermodynamic properties. The thermodynamics establish the conditions under which the reaction will proceed, and if it will, also define the upper efficiency limit of the process. The efficiency that is realized in practice is a function of the reaction extent and the reactor in which the process is implemented. The possible reaction extent is also limited by the thermodynamics, e.g. the temperature and oxygen partial pressure, but may also be limited by other factors such as thermal and mass transport. Transport, in turn, is influenced by fundamental material properties as well as by the reactor configuration and material geometry. Beyond these considerations, a suitable thermochemical material will be stable to physical and chemical degradation (e.g. erosion, volatilization, sintering, formation of undesirable phases, etc.) over many thousands of cycles and hours of operation. In light of this discussion possible routes to improved materials will be discussed including chemical modifications to known materials, improved structures, and the discovery of new materials for this application. Finally we will report results for new materials that have higher capacities (reaction extents) and faster reaction kinetics than the accepted state-of-the art materials for two step metal oxide thermochemical cycles evaluated under similar conditions.

Keywords: metal oxides; thermochemical cycles; hydrogen; solar fuels

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1. Introduction

The conversion of solar energy to chemical energy through synthetic means, i.e. the production of solar fuels from CO_2 and H_2O, is analogous to biofuel technology at a high level and hence offers many of the same advantages, but with the potential for higher efficiency. As such, the potential impact of solar fuels as a companion or alternative technology to transportation biofuel production is large [1]. Solar-driven electrolysis of water to produce H_2 (which can be further reacted with CO_2) provides a relatively mature technology baseline for solar fuels. The solar thermochemical approach is a potentially capable of delivering an annual average solar to fuel efficiency (AASFE) of > 20% for the production of both H_2 and/or CO from H_2O and/or CO_2, respectively. To achieve this result a thermal efficiency (η_{th}) in excess of 36% is required. Although the technology is advancing, realizing this level of performance will require advances in both materials and solar reactor systems [2]. If the CO and H_2 are to be further converted to hydrocarbons, improvements in balance of plant components, e.g. separation technologies, will also be beneficial [3]. Here we identify some of the key attributes of active metal oxide materials for two-step thermochemical cycles and then move to illustrating strategies for developing improved materials. We close with a brief summary of very positive results obtained with a new material currently under investigation in our laboratories.

Nomenclature

AASFE	annual average ratio of energy in produced fuel (HHV) to solar energy incident on collector
HHV	higher heating value
η_{HHV}	thermal efficiency, ratio of energy in produced fuel (HHV) to net thermal energy input into reactor
η_{TH}	thermodynamic efficiency, ratio of work potential of fuel ($\Delta G°$ at 298K) to net thermal energy input into reactor. Note this is similar but slightly smaller than η_{HHV}.
T_{TR}	thermodynamically defined minimum reduction temperature
T_{OX}	thermodynamically defined maximum oxidation temperature
SLMA4664	$Sr_{0.4}La_{0.6}Mn_{0.6}Al_{0.4}O_3$
SLMA6464	$Sr_{0.6}La_{0.4}Mn_{0.6}Al_{0.4}O_3$
SLMA4646	$Sr_{0.4}La_{0.6}Mn_{0.4}Al_{0.6}O_3$

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2. Considerations for materials choice and design

Two-step metal oxide thermochemical cycles accomplish the splitting of water or carbon dioxide by dividing the difficult thermolysis reaction (H_2O + heat → H_2 + ½ O_2) into two reactions that can be accomplished under less extreme conditions. The first reaction is a thermal reduction of the solid that liberates oxygen ($1/\delta$ MO_x + heat → $MO_{x-\delta}$ + ½ O_2); the second reaction is an oxidation of the reduced solid with steam or carbon dioxide that yields H_2 or CO and restores the oxide to its original state ($1/\delta$ $MO_{x-\delta}$ + H_2O → $1/\delta$ MO_x + H_2 + heat). In an ideal system these two reactions can be repeated cyclically and indefinitely to produce H_2 and O_2 (CO and O_2) continually, and in isolation from one, another utilizing only heat as an energy source. Important chemical and physical attributes influencing the performance of materials relative to this ideal and that should be considerations in any materials development effort are discussed below. The discussion is limited to solid metal oxide chemistries.

2.1. Thermodynamics

The thermodynamics of two-step thermochemical cycles are presented in detail elsewhere [4]. We briefly present select points and implications here; for this discussion, ideal behavior and perfect thermal recuperation between reaction steps has been generally assumed.

For any reaction cycle, at any condition (e.g. temperature), the thermodynamics of the individual reactions (in this case reduction and oxidation) must sum to the thermodynamics of the net reaction (H_2O or CO_2 splitting) at those same condition. This relationship allows one to define two thermodynamically important temperatures. The reduction reaction is thermodynamically favorable ($\Delta G° \leq 0$) at temperatures (T) at or above T_{TR}; the oxidation

reaction is thermodynamically favorable at $T \leq T_{OX}$. T_{TR} and T_{OX} are subject to the constraint $T_{TR} \neq T_{OX}$. The theoretical maximum thermodynamic efficiency (not to say the reaction cannot be carried out under other, less efficient, conditions) is directly linked to these two temperatures and the similarly defined thermolysis temperature ($T_{thermolysis}$) for the net reaction [5]:

$$\eta_{TH} = \frac{\left[1 - \frac{298}{T_{thermolysis}}\right]}{\left[1 - \frac{T_{OX}}{T_{thermolysis}}\right]}\left[1 - \frac{T_{OX}}{T_{TR}}\right] \; (all \; temperatures \; in \; K) \tag{1}$$

Note that if T_{OX} = 298 K, then the equation reduces to a Carnot relationship. In this case, if one assumes a practical upper limit for operation of 1500 °C (i.e. considering materials of construction, potential for radiation loss, etc.), the theoretical maximum thermodynamic efficiency is η_{th}(max) = 83%. Figure 1 illustrates the theoretical efficiencies associated with other possible combinations of T_{TR} and T_{OX} for CO_2 splitting ($T_{thermolysis} \cong 3340K$). Based on the need to realize a thermal efficiency of 36%, we suggest that one should the development of materials target materials with theoretical efficiencies of at least 70%. From the figure, a minimal acceptable value of T_{TR} is thus 720 °C (i.e. at T_{OX}= 25 °C). However, as can be seen, setting TTR ≤ 1500 °C and $\eta_{th} \geq 0.7$ for CO_2 splitting sets a limit of $T_{OX} \leq 420$ °C. That is, an ideal material is defined by a relatively small thermodynamic window.
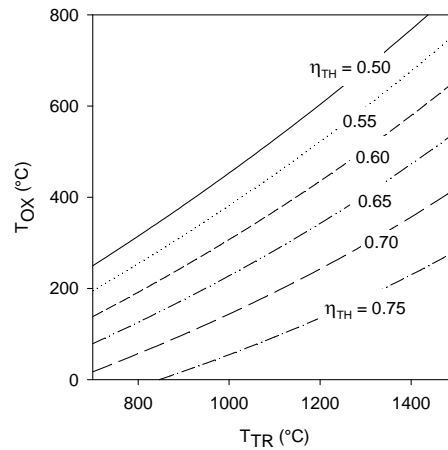

Fig. 1. Theoretical maximum efficiencies as a function of the thermodynamically defined reduction (TTR) and oxidation (TOX) temperatures for a two-step CO_2 splitting cycle ($T_{thermolysis}$ = 3067 °C)

Currently there are no materials identified that fall within the criteria defined here; nonetheless they serve as useful guideposts for materials development. Materials meeting the criteria 1500 °C ≥ TTR ≥ 720 °C should be targeted. We note however that while the lower end of this range offers potential advantages in terms of operability, materials with very low reduction temperatures will likewise require very low oxidation temperatures that will very likely be associated with very slow reaction kinetics. We believe it is more realistic to target for T_{OX} on the high end of this range to help promote the kinetics of the oxidation reaction; the reduction kinetics will also likely benefit from higher temperatures.

To conclude this section we direct the reader interested in the less ideal conditions to [2] where the effects of limited conversion, operating under conditions where the thermodynamics are not favorable, and imperfect recuperation are considered.

2.2. Reaction Kinetics

From the larger point of view, what is desired for the two-step cycle operating as described is for the net thermal flux entering the reactor to be matched to a mass flux of oxygen scaled by the enthalpy of the reduction reaction. That is, for a directly illuminated plate, for example, the following should hold true:

$$Q\left(\frac{W}{cm^2}\right) = R_{O_2}\left(\frac{moles}{s\,cm^2}\right)\Delta H°\left(\frac{J}{mole}\right) \tag{2}$$

Any mismatch in the solar and chemical energy fluxes during reduction corresponds to a loss of efficiency. However it is not only the rate of the reduction reaction that matter. The stoichiometric constraints of the cycle must be also met; the H_2 or CO yield integrated over time must be twice the integrated O_2 yield. Thus, sluggish oxidation holds the potential to create a rate-determining bottleneck. The degree to which this becomes manifest will be determined both by the magnitude of the difference in the two reaction rates, and the degree to which the overall system design allows the two reactions and (reaction time frames) to be de-coupled from one another.

In any case, the high energy fluxes available from concentrating solar power present a formidable challenge for reaction kinetics. As a simple example, a reaction enthalpy of 367 kJ/0.5mol O_2 (corresponding to T_{TR} = 1500 °C and T_{OX} = 420 °C for CO_2 splitting) corresponds to a reaction rate of 27 μmol O_2/s-cm^2 or 27 μmol O_2/s-g assuming a 0.2 cm thick loading of an oxide with a bulk density of 5 g/cm^3 and an energy flux of 20 W/cm^2. Reaction rates > 10 μmol O_2/s-cm^2 are desirable.

In considering the reaction kinetics, it is important to keep in mind that the observed rate is most always an apparent rate that results from a combination of factors including the fundamental chemical kinetics (i.e. surface reaction kinetics), external mass transport (through the gas phase to and away from the surface), internal transport (diffusion of oxygen and metal species and electrons), and thermal transport. Isolating these different effects is challenging and often requires specialized equipment and sophisticated approaches. Nonetheless, an appreciation that the physical form of the material may be as important as the chemistry itself can be highly beneficial.

2.3. Stability

Stable or at least very predictable performance over the long-term will be a necessary requirement for implementing any thermochemical cycle. Both the chemical and physical stability should be taken into account. Systems wherein the metal oxide may react to form inactive and stable phases (i.e. thermodynamic sinks) should be avoided. Thermochemical cycles require the exposure of materials to high temperatures over long periods. Under these conditions the possibility of reactions between active phases and other components generally considered to be inert (e.g. supports) must be taken into account. At the macro scale, stresses tied to thermal cycling can lead to physical degradation and breakage of monolithic type structures. As this issue is one combining reactor systems and materials issues, engineering models are invaluable designing these types of structures.

At the micro scale loss of surface area and porosity are of concern as is migration and segregation of components. As a general rule of thumb, one can expect sintering to be significant at temperature that are 40% of the melting point or higher. This metric is very unlikely to be met if T_{TR} = 1500 °C. Consequently, long-term stability can expected to be a significant challenge that designers must contend with for systems whose performance is tied to a specific microstructure. Coupled with the vaporization processes discussed in Sect. 5, these microstructural phenomena may be the ultimate limits to the longevity of any active layer material used in a thermochemical cycle.

Finally, one must consider loss of or changes in active material resulting from vaporization. At typical thermal reduction temperatures, the vapor pressure of metal species can be significant, even for refractory oxides such as ceria. Interactions with gas phase components, e.g. steam, can enhance the volatility. An upper limit to the rate of mass loss (Me) can be estimated using the Langmuir sublimation model if the vapor pressures (P, in Torr) and molecular weights (MW) of the evaporating species are known at a given temperature:

$$Me = 5.85 \times 10^{-2} \cdot P \cdot \left(\frac{MW}{T}\right)^{\frac{1}{2}} \quad \frac{g}{cm^2 \cdot s} \tag{3}$$

Applying this equation to a material of MW 175 and density 6 g/cm^3 in a system operating daily for 8 hours at temperatures of 1000-2000 ° suggests that the vapor pressure can be no greater than 3x10^{-7} Torr (4x10^{-10} atm) if material losses are to be kept to less than 100 μm/year equivalent. Vapor pressures reported for relevant metal oxides species are often more than 10,000 times higher than this metric [6]. This is mitigated somewhat by the fact that the equation strictly applies to vaporization from a plane into a vacuum. Nonetheless, the potential for significant rates of material loss should be kept in mind, and has been observed experimentally from ceria, particularly from isolated surfaces in vacuum or gas swept environments [7].

3. Paths to improvement

Until recently, work on solid metal oxide thermochemical cycles has been largely focused iron-based (ferrite) and ceria-based chemistries. (The zinc oxide system which includes vapor phase chemistry has also been intensely investigated.) CeO_2 is the most recent material of choice, largely due to the rapid kinetics it exhibits, and it spite of relatively less than ideal thermodynamics and limited reaction extents. Here we discuss pathways for developing improved materials, applying lessons learned from studies of the ferrite system as an illustration.

3.1. Modification

The limitations of the archetypical metal oxide cycle based on the reduction and oxidation of magnetite (Fe_3O_4) and wustite (FeO) are well known and documented. Namely, extensive reduction of Fe_3O_4 can only be achieve at temperatures above its melting point and the resulting low surface area oxide mass has poor reactivity. The positive effects achieved by substituting other metallic elements (e.g. Ni, Co, Mn, etc.) into the material, i.e. decreasing the reduction temperature and increasing the melting point, are likewise well documented. While these modifications favorably alter the thermodynamics of the system, they did not significantly improve the reaction kinetics or material utilization. Similar methods have been applied both experimentally and computationally to the ceria-based system in attempts to improve the materials thermodynamics (commonly apparent as limited reaction extent). In general, improvements have been modest at best [5, 8]. Modification of known materials is thus a proven low-risk strategy for materials improvement, but this strategy alone has not and probably will not yield game-changing results.

3.2. Hybridization

The discovery by Kodama et al. that ferrites supported on zirconia or yttria-stabilized zirconia (YSZ) were much more robust that ferrites alone and could be repeatedly thermochemically cycled without intermediate processing was a significant advance that helped motivate interest in the field [9]. Since that time detailed studies of the ferrite/zirconia system have revealed it to be quite dynamic and complex. Figure 2 is a schematic depiction of the understanding we have developed of the material in our laboratories. We begin on the left hand side with the depiction of large ferrite particles. Though the thermodynamics of these materials may be attractive, transport with the metal oxide is extremely limited, effectively limiting the reaction to a very small fraction of the total present as the surface. The second panel depicts the combination of Fe with YSZ up to the solubility limit (about 10 mol % Fe depending on the temperature and redox state of the Fe [10]). Oxygen transport through YSZ is quite facile. This new "hybrid material" maintains important properties of both parents; the dissolved Fe is redox active while the YSZ provides transport of oxygen into and out of the bulk solid making the Fe highly accessible for reaction. The material is highly stable; there is no iron oxide phase to sinter, and the reaction is not surface limited. While this this hybrid approach has yet to be successfully applied to other systems, it is a clear demonstration of the need to

accommodate both thermodynamics and transport in new systems and offers at least option for how that might be accomplished.
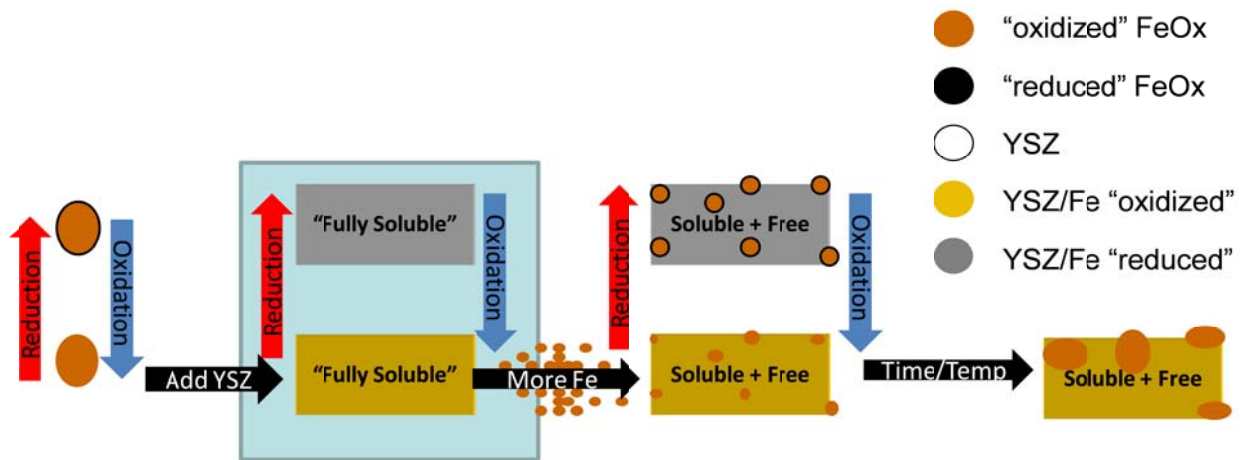

Fig. 2. Schematic depicting behavior of ferrite/YSZ thermochemical system (see text). Blue box highlights the hybrid material that facilitates indefinite redox cycling.

To complete the picture, A two phase system is formed when the solubility is exceeded. The encapsulated iron oxide particles provide very little additional reaction capacity beyond the surface (interface regions) as we conclusively demonstrated via reactive isotopic labeling [11]. The excess Fe oxide species are in fact relatively mobile within the system and over time will migrate and coalesce to effectively segregate themselves into largely unreactive particles (at right) much like those on the left of the schematic [10].

3.3. Structuring materials

A third option for improving materials is through manipulation of the physical structure. Specifically, one could match the physical size scales of materials to relevant transport dimensions, i.e. make the critical physical dimension (e.g. producing a particle of a radius or film of thickness smaller than the reaction penetration depth). Indeed, it has been observed that nanoscale ferrite films on porous zirconia substrates exhibit reaction rates and extents far in excess of more conventional materials [12]. That is, both the fundamental kinetics are thermodynamics of ferrites are highly favorable; transport is confirmed as the limited factor.
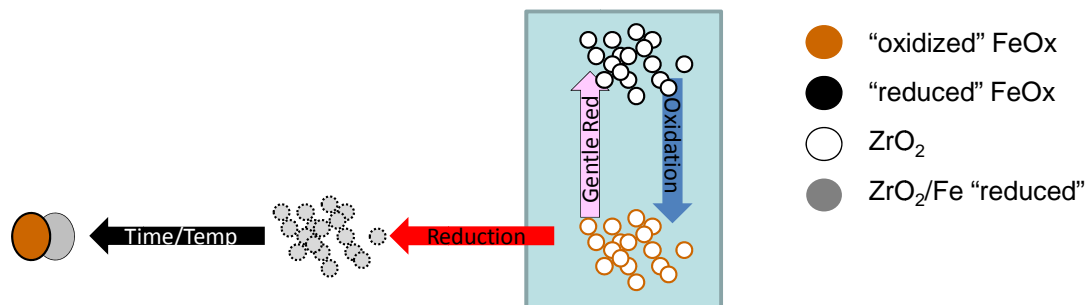

Fig. 3. Schematic depicting behavior of ferrite film/zirconia thermochemical system (see text). Blue box highlights highly reactive structures.

Unfortunately as illustrated in Figure 3, the materials must be gently reduced, e.g. by chemical means, in order to limit evolution of the solid state to a form physically and chemically resembling conventionally prepared materials, thus reinforcing the challenge identified above for microstructured materials at high temperatures. However, should a method be found to stabilize ferrite or other materials with similarly favorable kinetics and thermodynamics the consequences could be profound.

3.4. Design and discovery

A final option for materials improvement is to recognize that the palette of possible materials families and formulations has largely been unexplored, and apply the lessons learned to this point to identify promising new avenues. We are currently focusing our attention on perovskites and other mixed ionic electronic conducting materials containing redox active metals.

4. New formulation

Exciting new results for $Sr_xLa_{1-x}Mn_yAl_{1-y}O_3$ (SLMA, x = 0.4 or 0.6, y = 0.4 or 0.6) perovskites were recently reported in the literature [13]; additional information is provided in a companion paper in this forum [14]. Briefly, the capacity of these materials (reaction extent) exceeds that of ceria by at least a factor of five and exhibits superior kinetics during reduction and oxidation (with both CO_2 and H_2O) cycles. Stability was maintained through 80 complete cycles. Typical results for oxidation of several SLAM formulations in a stagnation flow reactor are shown in Figure 4. Results for ceria are included for comparison. Note not only the apparent kinetics, but also that in all cases the yield of CO or H_2 is significantly improved relative to ceria even though the ceria was reduced at 150 °C higher temperature.
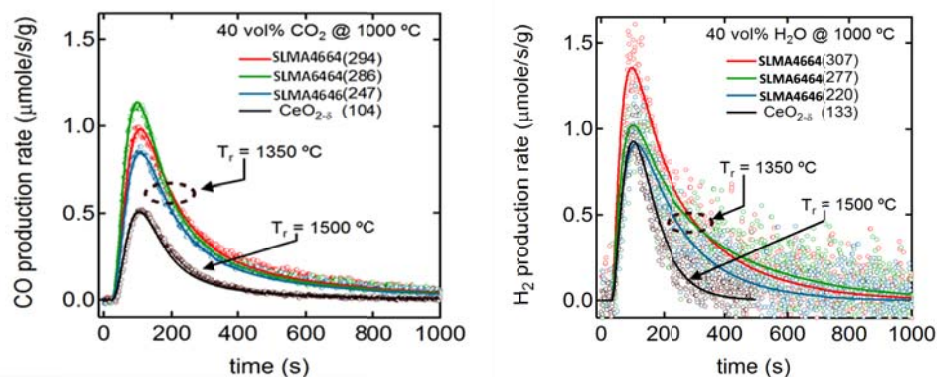

Fig. 4. CO (left) and H_2 (right) production rates at 1000 °C over various SLAM formulations thermally reduced at 1350 °C. Numbers in parentheses are the integrated totals. Ceria data included for comparison was obtained over a material thermally reduced at 1500 °C.

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