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Nonstoichiometric perovskite oxides for solar thermochemical H₂ and CO production

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Abstract

Perovskite oxides (ABO\textsubscript{3}) are a largely unexplored class of materials in solar fuel applications. In this paper we examine the use of nonstoichiometric perovskite-type oxides in a two-step, solar-thermochemical water or carbon dioxide splitting cycle. We find that O₂ begins to evolve during thermal reduction from a Sr- and Mn-doped LaAlO\textsubscript{3} fully 300 °C lower than that of CeO\textsubscript{2}, and that these compounds will split both H₂O and CO\textsubscript{2}. The yield of H₂ and CO is significantly greater than CeO\textsubscript{2}, a benchmark material in solar fuels research, at a thermal reduction temperature 150 °C below that commonly reported for CeO\textsubscript{2}. In addition, the perovskite redox kinetics compare favorably to CeO\textsubscript{2}, which is known for its rapid reaction rates. We also find that an Fe-doped CaTiO\textsubscript{3} is redox active and will split H₂O, though the performance of this material is similar to that of CeO\textsubscript{2}. Finally, we introduce an experimental protocol that combines an ideal stagnation-flow reactor with detailed numerical modeling to effectively deconvolve intrinsic material behavior from interference induced by physical processes occurring inside the flow reactor. This method utilizes rate information contained within the entire time domain of the oxidation reaction, and assigns rate-governing processes to the material within the context of solid-state kinetic theory.

Keywords: water splitting; carbon dioxide splitting; thermochemical cycle; perovskite oxide.

1. Introduction

Developing carbon-neutral, sustainable energy sources is necessary to mitigate the impacts of anthropogenic carbon dioxide on global populations[1], especially as the demand for energy rises world-wide[2]. One solution is to
exploit solar energy, given its abundance and accessibility. The challenge, however, is to capture and store this relatively diffuse energy in an efficient and cost-effective manner. Currently, several technologies based on photosynthesis (artificial or natural) and photoelectrolysis are under consideration. These aim to produce H₂ by water splitting (WS), CO by carbon dioxide splitting (CDS), or fungible fuels from biomass[3,4]. An additional compelling approach rapidly gaining attention is the conversion of solar energy into fuel using solar-driven thermochemical processes[5,6].

Thermochemical cycles rely on heat derived from concentrating solar thermal power (CSP) to drive endothermic gas-splitting reactions, thereby converting solar energy directly into fuel[7]. Consequently, these cycles have the potential to realize greater theoretical efficiency than methods based on photosynthesis, photoelectrolysis, or conventional electrolysis coupled to solar-electric[5,7,8]. In addition, such processes are conceptually much simpler and require no input of electrical energy, semiconductor processing, separation membranes, genetic manipulation, or elaborate molecular self-assembly[3]. An example of a WS cycle using cerium oxide is outlined in the following two reactions:

\[
\frac{1}{\delta} \text{CeO}_2 \xrightarrow{+\Delta} \frac{1}{\delta} \text{CeO}_{2-\delta} + \frac{1}{2} \text{O}_2 \tag{1}
\]

\[
\frac{1}{\delta} \text{CeO}_{2-\delta} + \text{H}_2 \text{O} \xrightarrow{-\Delta} \frac{1}{\delta} \text{CeO}_2 + \text{H}_2 \tag{2}
\]

where \( \delta \) represents the extent of oxygen nonstoichiometry in the solid. In this two-step cycle, the oxide is first reduced (equation 1) on-sun at high temperature \( (T_1 > 1500 ^\circ C) \). The oxidation reaction (equation 2) resupplies O atoms to the solid, liberates H₂, and completes the cycle. The oxidation reaction occurs off-sun, typically at \( T_2 < 1100 ^\circ C \). Substituting CO₂ for H₂O, and CO for H₂, in these equations yields the corresponding reactions for CDS.

A small number of non-volatile metal oxides have been proposed for this purpose and in general fall into three categories based on the type of solid state process that results in reduction: nonstoichiometric oxygen loss[9,10], solid solution decomposition[5,11,12], and displacement reaction[13,14]. Undoped ceria (CeO₂) is a prototypical nonstoichiometric oxide with fast redox kinetics. However, very high temperatures \( (T_1 > 1500 ^\circ C) \) are necessary to achieve the extent of oxygen deficiency required for efficient fuel production. Conversely, ferrite solid solutions undergo deep reduction at 1400 ^\circ C, but the kinetics are slow[15,16] and ferrites must be combined with an oxygen-conducting refractory ceramic to prevent sintering and maintain high redox magnitudes[12,17]. Although reactive structures formed through nano-engineering methods can dramatically increase ferrite reaction rates, nanostructural instability above 700 ^\circ C limits their usefulness[18]. Here, we describe the discovery of novel perovskite compounds that achieve much higher oxygen deficiencies than reduced ceria (CeO₂-\( \delta \)) at lower \( T_1 \), and exhibit WS and CDS kinetics similar to ceria[19].

2. Methods

2.1. Perovskite synthesis

Powders of \( \text{Sr}_x \text{La}_{1-x} \text{Mn}_y \text{Al}_{1-y} \text{O}_3 \) (SLMA, \( x = 0.4 \) or 0.6, \( y = 0.4 \) or 0.6) perovskites were synthesized using a modified Pechini method. Stoichiometric amounts of nitrate precursors, \( \text{M}^n(\text{NO}_3)_m \cdot y\text{H}_2\text{O} \), were dissolved in de-ionized water. In a separate beaker, ethylenediaminetetraacetic acid (EDTA) was dissolved in ammonium hydroxide. The solutions were combined with stirring, citric acid was added, and the pH was adjusted as necessary with additional ammonium hydroxide until the solution was transparent, and no precipitates were present. The solution was heated with stirring until a viscous gel formed. The gel was heated in a furnace at 250 ^\circ C until a black resin formed. The resulting ash was collected, ground with a mortar and pestle and calcined at 800 ^\circ C for 6 h to burn off any remaining organics or nitrates. Powdered samples used in the kinetic analysis were further calcined at 1350 ^\circ C for 24 h. Pellets used in the XRD analysis were made by adding polyvinyl butyral (PVB) binder to the powder (2 wt% equivalent) and then grinding the mixture with acetone using a mortar and pestle until dry and well-mixed. 0.6
0.8 g of this resultant mixture was uniaxially dry-pressed into pellets using a 13 mm die. The pellets were fired at 1350 °C for 24 h with a heating and cooling ramp rate of 3 °C/min to achieve the final pellet.

In addition, a solid-state reaction (SSR) method was used to synthesize CaTi$_{1-x}$Fe$_x$O$_3$ (CTF, $x = 0.0, 0.1, 0.2,$ and $0.3$). The goal here is to explore perovskite materials that can be formed from more earth-abundant elements, as well as develop methods for efficiently synthesizing a vast array of prospective formulations. Here, proper amounts of solid precursors such as carbonate and binary oxide powders were added to a plastic bottle with isopropanol as a solvent for grinding (e.g., when making CaTi$_{1-x}$Fe$_x$O$_3$, CaCO$_3$, TiO$_2$, and Fe$_2$O$_3$ were used as precursors). Small yttria-stabilized zirconia (YSZ) beads were then added to the bottle and the mixture milled at low energy for 48 h. After removing the grinding beads and drying the slurry, the resultant powder was calcined at 1350 °C for 20 h, with an intermediate interval of manual grinding in between. The solid-state reaction approach is more amenable to high-throughput synthesis because grinding can be accomplished in parallel using milling machines with multiple pods. In addition, this approach is easily scaled down to produce small amounts of materials (200-mg quantities).

Both Pechini and SSR methods produced pure crystalline material. Illustrated in figure 1 are X-ray diffraction patterns for SLMA1-3 and CTF1-4 (see Nomenclature for composition information). The patterns clearly indicate the perovskite phase was formed for each of the compositions.

2.2. Kinetic measurements

Perovskites and commercial ceria powders were reduced and oxidized in a stagnation flow reactor (SFR) equipped with a modulated effusive beam mass spectrometer and laser-based sample heater which has been described elsewhere[14,15,18]. Salient features of the experimental apparatus consist of a stainless-steel gas-handling manifold, ceramic reactor core, high-temperature furnace, and 500 W near-IR laser. In stagnation flow, the gas-phase region above the sample between centerline and reactor wall can be considered an ideal one-dimensional stagnation plane governed by diffusive transport. This is an important attribute that distinguishes the fluid dynamics of this reactor type from others typically used to characterize kinetic behavior of active materials, namely, packed bed reactors[20], flow tube reactors[21], and flow geometries common to a thermogravimetric analyzer (TGA)[22]. Approximately 100 mg of powder was placed in a loosely-packed shallow bed within the stagnation plane allowing gases to access all exposed surfaces within a well-mixed control volume. Gas compositions exiting the flow reactor were measured using a differentially pumped, modulated effusive beam mass spectrometer.

Thermal reduction (TR) was accomplished by heating the perovskite or ceria to 1320—1500 °C in a helium flow (500 sccm) until the desired extent of reduction was achieved. Water splitting (WS) and carbon dioxide splitting (CDS) were performed using 40 vol% steam or carbon dioxide in He with a total flow rate of 500 sccm for a
specified time interval at 1000 or 1100 °C. The total reactor pressure for both TR and WS or CDS was 75 Torr. Measuring redox behavior at pressures below atmospheric is convenient for our particular reactor configuration and experimental protocols, but does not imply that vacuum systems must or should be used for solar fuel production from these materials.

2.3. Computational approach

A numerical approach to analyzing the transient H₂ and CO production rates observed during WS and CDS was devised that accounts for: 1) kinetic processes occurring in the solid state; 2) the finite time required to introduce water vapor or carbon dioxide into the reacting volume; 3) detector time lag; and 4) dispersion/mixing of the H₂ or CO evolved from the solid as it is transported downstream of the reactor volume to the detector. Impacts of the aforementioned physical processes intrinsic to the experimental reactor (namely 2 – 4 listed above) are not fully addressed by researchers in this field of science even though they can lead to erroneous conclusions regarding both the nature of rate limiting processes and the energetics associated with them.

As shown in figure 2 panel (a) using WS as the example oxidation chemistry, steam is introduced into the reactor volume by way of a step-function input that initiates the solid-state chemistry. We determined the shape of this step-function using a transient, 3-D computational fluid dynamics model of our reactor inlet under various operating conditions (note the minimal dispersion and narrow temporal width of the step), as well as by gas-injection tracer studies. The ensuing chemistry is treated like a black-box that is functionally described by various kinetic models taken from solid-state kinetic theory[23] (panel (b) in figure 2), which track a single variable $\alpha(t)$ representing the extent of reaction that follows Arrhenius behavior according the following equation:

$$\frac{d\alpha}{dt} = A \cdot e^{-\frac{E}{RT}} \cdot \left[Y_{H_2O}(t)\right]^Y \cdot f(\alpha).$$

(3)
In equation 3, $A$ and $E$ are the pre-exponential factor and apparent activation energy, respectively, $Y$ is the mole fraction of steam in the inlet, and $\gamma$ is an exponent that governs the dependence on steam concentration. The output of the black-box is a waveform that describes the temporal evolution of $H_2$ resulting from the oxidation chemistry and serves as the input molar flow rate to the first in a series of ideal, continuously-stirred tank reactors (CSTR). The example given in figure 2 (labeled F2 in panel (b)) is for a second order relation of the form: $f(\alpha) = (1 - \alpha)^2$. The transient pulse-like input of $H_2$ into the CSTRs is then stretched in time due to the physical actions of dispersion and mixing (panel (c) in figure 2). Governing kinetic behavior and the associated energetics are deduced by least-squares fitting the experimental $H_2$ production rate waveforms to simulations based on sampling various solid-state kinetic models[15].

We solve a system of ordinary differential equations that describe a transient process in which $H_2$ is produced by one or two solid-state mechanisms occurring irreversibly within a perfectly mixed control volume containing the active material. This product gas is then transported through a series of CSTRs that alters the temporal characteristics of the $H_2$ signal[15]. In our analytical approach the kinetic parameters ($A$, $E$, $\gamma$) and choice for kinetic model are resolved by fitting to experimental data. We test against 14 possible mechanisms that span four distinct families of solid-state reaction phenomena, including nucleation and growth (A), geometrical contraction or shrinking core (R), diffusion (D), and reaction-order behaviors (F)[23]. In cases where a single kinetic model does not adequately describe the experimental data, two kinetic models acting in parallel are tested.

The computational tool Mathematica®[24] is used to numerically solve the system of governing equations (NDSolve), produce a value for least squares residual, and then pass this information to a numerical minimization routine (NMinimize). The fitting routine uses a Differential Evolution algorithm native to Mathematica® that stochastically solves a constrained, mixed-integer optimization problem (kinetic parameters $\in \mathbb{R}$, and model choice $\in \mathbb{N}$). Constraints take the form of inequalities and brick-wall penalty functions. Differential weighting is also applied to data points surrounding the peak in $H_2$ signal ($10 < t < 200$ s), and to a lesser extent, the tails observed at longer reaction time. We believe this analytical approach is sufficiently rigorous to effectively resolve the underlying kinetic behavior of these reactive materials, within the context of solid-state kinetic theory, from the confounding affects of the experimental artifacts as described in the next section.

3. Results and discussion

3.1. Effects of dispersion and mixing

By comparing the waveforms in panel (b) and (c) of figure 2, it is clear that they have different shapes even though they represent the same kinetic behavior. The extent to which these two curves deviate from one another is dependent on the characteristic time for reaction (kinetic rate, $k_0$) and the reactor space velocity (dispersion rate, $\tau_{ex}$). Shown in figure 3(a) are three simulated production rate curves at various space velocities for a dispersion model that includes three CSTR volumes. As expected, when the space velocity decreases (i.e., greater extent of dispersion) the curves spread out in time and the peak rates decrease in order to conserve total area under each curve. One typical method of analysis reported in this field of research is to take peak rates and cast them into an Arrhenius form such as $\ln k_0 = \ln A_0 - \frac{E_0}{RT}$, then derive the apparent activation energy from the slope of $\ln k_0$ vs. $1/T$ and the apparent pre-exponential factor from the intercept. If the experimental method is not free of dispersion or adequately accounted for, then the pre-exponential factor will be erroneous and the reported peak rates too low.

We also note that the use of solid-state kinetic theory in conjunction with a Master Plot (MP) approach[25], without fully addressing how dispersion and mixing influence the analysis, can lead to misinterpretation of the results. For example, Le Gal et al.[26] use MP to analyze CDS data obtained from a TGA. In this case, the effects of both the fluid-dynamic environment (dispersion and mixing) in the vicinity of the sample and the residence time of the gas in the TGA on the analysis are unclear. They assign “peak rates” to conditions at positive extents of reaction (i.e., $\alpha = 0.15$ in one case) which implies that at reaction extents lower than $\alpha = 0.15$ the rate is accelerating. They also assume that diffusion controlled regimes are “delayed” until $\alpha$ exceeds a certain value. In actuality, they are attributing the time it takes for CO$_2$ to enter and mix within the TGA, and therefore impart an effect on the material, to an erroneous mechanistic process like nucleation and growth.
Illustrated in figure 3(b) are the results of an MP analysis conducted on simulated H₂ production rate curves using the F2 model coupled to a dispersion model that includes three CSTR volumes. Here again, as the dispersion rate increases for a fixed reaction rate constant, the shape of the MP curves dramatically change. In fact, the simulated F2 behavior can be completely masked given a sufficiently high rate of dispersion, which would lead to a misidentification of the rate controlling mechanism. For example, the correct identification of the rate controlling mechanism (F2) over all reaction extents is only possible at infinite space velocity (the open squares fall on the long-dashed line in panel (b) of figure 3). Dispersion makes the early-time (i.e., low reaction extent) behavior look more like a nucleation model such as A2 could govern this process. In addition, once the rate controlling behavior has been identified (i.e., a known \( f(\alpha) \)), the rate constant can in principle be extracted by plotting \( \frac{d\alpha}{dt} / f(\alpha) \) vs. time as illustrated in figure 3(c). The correct value for \( k_0 \) in this example is 0.10 1/s, which can be seen at infinite space velocity after the initial input transient has abated. The other dashed lines in this figure indicate that the rate constant is variable, implying either an incorrect choice for \( f(\alpha) \) or an activation energy that is dependent on the reaction extent.

It is clear that ignoring the influence of physical processes inherent to a given experimental protocol and/or apparatus, such as the finite time it takes for gases to mix within a TGA, can lead to improper identification of rate governing mechanisms. That is why we advocate the more rigorous approach described herein that couples an idealized flow reactor with a mixing model and a material chemistry model.

### 3.2. Thermal reduction of perovskites

A critical first assessment for material viability in solar fuel applications is to determine the extent of oxygen deficiency that can be achieved under conditions of rapid heating and constant oxygen activity. The oxygen deficiency for ceria and perovskites is represented by \( (\delta) \) in the chemical formula (i.e., the subscript 2-\( \delta \) for ceria and 3-\( \delta \) for perovskite). The larger the value of \( (\delta) \) in the reduced state, the more H₂ or CO you can expect to make per a mass-normalized redox cycle. Presented in figure 4(a) is the oxygen uptake and release measured for SLMA3, CTF4, and CeO₂ exposed to a constant 0.2 mbar O₂ partial pressure in helium flow and heated at 16 °C/s to a thermal reduction temperature (T₁) of 1320 °C. Rapid heating in the SFR is accomplished by irradiation from a near-infrared laser. In this figure, a positive production rate indicates O₂ released by the solid, and a negative rate indicates O₂ incorporation. It is clear by the magnitude of the area under the SLMA3 curve (shown in parenthesis) that this perovskite is reduced to a larger extent than CeO₂ under these conditions. Fully 8× more O₂ is released and subsequently re-absorbed by SLMA3 than ceria. This depth of reduction directly equates to greater cycle capacity.
and hence potentially more efficient fuel production provided the re-oxidation reaction with water or carbon dioxide is sufficiently favored. The data in figure 4(a) also show that a perovskite formulated entirely from earth-abundant ores (i.e., containing Ca, Ti, and Fe) is found to be redox active (a novel observation because not all perovskites are redox active). The total amount of oxygen expressed by CTF4 under these conditions is similar to CeO₂, therefore, we would expect the redox cycle performance and total amount of H₂ or CO produced to also be similar.

Moreover, the onset of O₂ evolution for all three SLMA compounds under a He ambient (O₂ pressure < 10⁻³ mbar) occurs at temperatures 300 °C lower than CeO₂, shown in figure 4(b), which implies that these compounds likely possess a lower reduction enthalpy than CeO₂. The reduction enthalpy has recently been identified as an important metric for assessing the viability of candidate materials for use in fuel production via CSP. In general, the magnitude of the reduction enthalpy establishes boundaries on temperature and pressure for which WS and CDS thermodynamic favorability is expected[27]. Typical CSP conditions for CeO₂ place this compound near the upper limit making it difficult to reduce but easy to re-oxidize. We find that the SLMA compounds trend in a better direction because a solar fuel production cycle using SLMA3 will operate at T₁ temperatures well below those established for either ceria (1550 °C) or ferrite (1400 °C) without losing the ability to carry out reaction 2 at a reasonable T₂ (800 °C). From a practical point of view this has important implications for reactor design and materials of construction because at lower T₁ less exotic materials may used to build the reactor.

3.3. Gas splitting kinetics on perovskites

The evolution of H₂ or CO when exposing the reduced perovskites to H₂O or CO₂ at conditions typically used in CSP thermochemical cycles demonstrates that WS and CDS chemistries are favorable. Shown in figure 5(a) are the H₂ and CO production rates for SLMA perovskites, and in figure 5(b) the H₂ production rate for the CTF4 perovskite, all measured over previously reduced oxides. Nearly 9× more H₂ and 6× more CO are produced by the SLMA compounds as compared to CeO₂ when reduced at 1350 °C and oxidized at 1000 °C. The fuel production rates for CeO₂ reduced at 1500 °C, which is a commonly used T₁ temperature, are also shown in figure 5(a). In this case too, the SLMA compounds outperform ceria. We also note that H₂ and CO capacity of the perovskites exceeds that of YSZ-supported ferrite reduced at 1400 °C[5]. To put this discovery in perspective, prior efforts to improve the performance of ceria, which focused on destabilizing the crystal structure through doping and substitution, succeeded in marginally increasing the cycle capacity at a lower T₁ of 1400 °C (notably for Zr:CeO₂ solid solutions mixed with Y, La, or Gd)[22]. However, the reduction and oxidation reaction rates decreased significantly when
compared to unmodified ceria. The enhanced H₂ production also dropped 33% by the second cycle questioning the viability of this approach (data was presented for only 2 redox cycles making it difficult to assess long term trends).

The number of perovskite compounds that may exhibit WS and CDS activity is potentially many times larger than what can be explored by modifying the ceria fluorite structure. We show another example of H₂ production activity in a perovskite capable of WS in figure 5(b). CT F4 was synthesized entirely from earth-abundant elements and while the redox behavior of this compound is similar to CeO₂, we now have identified two families of perovskites (SrₓLa₁₋ₓMnₓAl₁₋ₓO₃ and CaTi₁₋ₓFeₓO₃) that exhibit WS and CDS activity. We feel strongly that many more perovskite formulations will show this behavior and their performance will surpass both ceria and ferrite chemistries.

Although decreasing T₁ while increasing cycle capacity is significant, fast oxidation kinetics are equally important to solar fuel production because they directly influence solar conversion efficiency and ultimately govern reactor design[7,12]. Therefore, we performed a detailed numerical analysis[15] of the H₂ and CO production rates for SLMA1-3 and CeO₂ in order to compare the intrinsic WS and CDS kinetics. As mentioned in the previous section, it is important to deconvolve the effects of dispersion, mixing, and detector time lag that are inherent to the SFR experiment from the observed H₂ or CO production rate transient in order to recover the WS or CDS rate constant. Reaction rate constants (k₀) for order- and diffusion-based processes derived from this analysis are presented in table 1. The high quality of the fits to our data with these kinetic models is evident from the solid lines in figure 5(a). Unlike CeO₂, the SLMA oxidation rates are governed by two mechanisms. The first is an order-based process (labeled F1 and F2 in table 1) that explicitly refers to the exponent of (1-α)^n in the kinetic model where n = 1 or 2, respectively. This process accounts for roughly 75% of the H₂ or CO produced. The second is a Jander[23] diffusion process (labeled D3 in table 1) that generates the long tails seen in the product decay curves in figure 5(a). Although it is beyond the scope of this proceedings to discuss why WS and CDS kinetic models differ between SLMA and CeO₂, experiments suggest ceria does not manifest a diffusion limitation in our powdered samples. The
constants listed in table 1 indicate that WS and CDS rates for SLMA compounds are comparable to CeO2 at 1000 °C and 40 vol% oxidant concentration.

Table 1. Oxidation reaction rate constants (log \( k_0 \)) extracted from fits to experimental data in figure 5(a) using a coupled kinetic and dispersion model for materials thermally reduced at 1350 °C.

<table>
<thead>
<tr>
<th>compound</th>
<th>( k_0 Y_{H_2} f(\alpha) ) [1/s]</th>
<th>( k_0 Y_{CO} f(\alpha) ) [1/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SLAM1</td>
<td>F1 = (1-( \alpha )), D3 = ( 3(1-\alpha)^{2/3} / 2(1-(1-\alpha)^{1/3}) )</td>
<td>F2 = (1-( \alpha ))^2, D3 = ( 3(1-\alpha)^{2} / 2(1-(1-\alpha)^{1/3}) )</td>
</tr>
<tr>
<td>SLAM2</td>
<td>-2.00</td>
<td>-3.92</td>
</tr>
<tr>
<td>SLAM3</td>
<td>-2.11</td>
<td>-4.18</td>
</tr>
<tr>
<td>SLAM1</td>
<td>-1.81</td>
<td>-4.52</td>
</tr>
<tr>
<td>CeO2,0</td>
<td>-1.44</td>
<td>n/a</td>
</tr>
</tbody>
</table>

\( ^a \) Function for the extent of reaction \( f(\alpha) \) used in the best-fit kinetic model (see text).

4. Conclusions

Commercial success of large-scale CSP fuel production technology is predicated upon finding materials composed of earth-abundant elements that can operate at lower reduction temperatures than current ferrite- or ceria-based systems. These materials must have sufficient activity to achieve high process efficiency (solar-to-fuel conversion efficiency > 20% on an annual average basis)[8] and be inexpensive to produce. In this study we have demonstrated that the WS and CDS activity for three Sr- and Mn-doped lanthanum aluminate are comparable to CeO2, a material known for fast redox kinetics. In addition, the SLMA perovskites produce significantly more H2 and CO at reduction temperatures well below 1500 °C than either ceria or YSZ-supported ferrite. The perovskite oxides described herein are among the most promising found thus far. Furthermore, we anticipate that the amenability of the perovskite structure to doping and substitution will open a vast composition space, within which even more effective materials can be designed that will accelerate realization of economical fuel production based on thermochemical cycles.

Nomenclature

SLMA1 Sr0.4La0.6Mn0.6Al0.4O3
SLMA2 Sr0.6La0.4Mn0.6Al0.4O3
SLMA3 Sr0.4La0.6Mn0.4Al0.6O3
CTF1 CaTiO3
CTF2 CaTi0.9Fe0.1O3
CTF3 CaTi0.8Fe0.2O3
CTF4 CaTi0.7Fe0.3O3
TR thermal reduction
WS water splitting
CDS carbon dioxide splitting

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