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Final LDRD Report: Advanced Materials for Next Generation High-Efficiency Thermochemistry

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High-Efficiency Thermochemistry

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Abstract

Despite rapid progress, solar thermochemistry remains high risk; improvements in both active materials and reactor systems are needed. This claim is supported by studies conducted both prior to and as part of this project. Materials offer a particular large opportunity space as, until recently, very little effort apart from basic thermodynamic analysis was extended towards understanding this most fundamental component of a metal oxide thermochemical cycle. Without this knowledge, system design was hampered, but more importantly, advances in these crucial materials were rare and resulted more from intuition rather than detailed insight. As a result, only two basic families of potentially viable solid materials have been widely considered, each of which has significant challenges. Recent efforts towards applying an increased level of scientific rigor to the study of thermochemical materials have provided a much needed framework and insights toward developing the next generation of highly improved thermochemically active materials. The primary goal of this project was to apply this hard-won knowledge to rapidly advance the field of thermochemistry to produce a material within 2 years that is capable of yielding CO from CO₂ at a 12.5 % reactor efficiency. Three principal approaches spanning a range of risk and potential rewards were pursued: modification of known materials, structuring known materials, and identifying/developing new materials for the application. A newly developed best-of-class material produces more fuel (9x more H₂, 6x more CO) under milder conditions than the previous state of the art. Analyses of thermochemical reactor and system efficiencies and economics were performed and a new hybrid concept was reported. The larger case for solar fuels was also further refined and documented.

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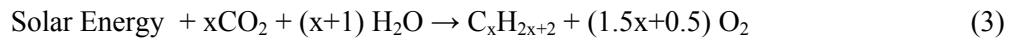
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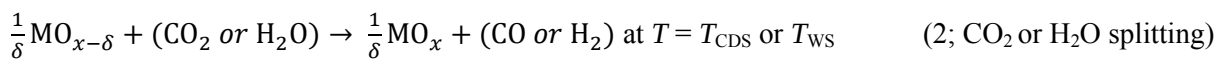
1. Background and Context

Broadly speaking, solar fuels are energy-rich compounds (typically H₂, CO, or hydrocarbons) that are produced from energy-poor compounds (e.g. H₂O and or CO₂) via reactions driven by a solar energy input. That is, solar fuels are energy carriers in which the energy of sunlight has been stored. The process can be simply represented by the following chemical reactions that form H₂, CO₂ and hydrocarbons:



With this broad view, fossil fuels can be understood to be solar fuels. However, the more common understanding and expectation of solar fuels is that they are also sustainable, i.e. solar fuels processes must produce fuel on a drastically shorter time scale relative to the fossilization process so that production rates are in line with consumption. Biomass approaches to solar fuels production have been widely pursued and the products are being integrated into the fuel market. However, the relatively low efficiency of photosynthesis poses significant challenges and raises questions as to the ultimate degree to which these approaches can meet demand. As such, interest and demonstrated promise is growing in achieving substantially higher land and energy efficiency by performing all production steps, including the initial conversion of sunlight (or other renewable energy source) to chemical energy through more traditional industrial processing means.

At Sandia we have been pursuing a two-step metal-oxide-based thermochemical approach to solar fuels. Thermochemical cycles divide the energetically unfavorable pyrolysis of water or carbon dioxide (temperatures > 3000 °C) into two or more reactions that have much more appealing thermodynamics. Many such cycles have been proposed, including hybrid sulfur, sulfur-iodine, zinc oxide, and various metal oxides. Of these, metal oxides are attractive due to typically low material cost, lack of hazardous or toxic products or intermediates, relative simplicity, and importantly, the potential to achieve high efficiency. A generic two-step metal oxide cycle is as follows:



Until very recently, only a single attribute was generally considered in the course of identifying materials for metal oxide thermochemical cycles, that being the thermodynamics of thermal reduction (TR).¹ This limited approach proved useful in identifying one- and two-metal-containing oxides for further study. The thermodynamic data, when available, can be used not only to determine whether a cycle is feasible, but to set an upper bound on the possible efficiency of the cycle. Using materials identified primarily through this most basic approach, the field of solar thermochemical cycles has gained remarkable visibility during the past several years. As prominent participants in that renaissance, we have developed a deep appreciation and understanding for the dynamic complexity of these basic materials, as well as critical knowledge regarding their application in larger-scale real solar-driven systems. The primary goal of this project was to apply this hard-won knowledge to rapidly advance the field of thermochemistry to produce next-generation materials to drive the technology towards achieving its breakthrough potential.

2. Technical Approach

This project adopted a strategy of pursuing multiple routes to improved materials that considered not only the thermodynamics, but broader principles as well. The routes were thought to span the range of risk and reward. For example, it was assumed that improvements in reaction extent (capacity) and thermodynamics (reduction temperature) were likely to be realized in existing materials through chemical modification (atomic substitution or doping), but that this approach alone might well result in a plateau inconsistent with the long-term goal (outside the scope of this effort) of providing a route to solar fuels that is more efficient and cost effective than electrolysis. Hence higher risk strategies were also pursued. The three principle approaches pursued were: 1) chemical modification of existing materials including mixed and composite systems that combine functionalities such as ion transport with a high density of redox centers; 2) structuring materials so that characteristic dimensions are matched to transport dimensions; and 3) exploring new classes of thermochemical redox systems. Also, because the metric of success must ultimately be efficiency and durability in a thermochemical reactor system and considering that the efficiency is the result of the specific combination of material and system, an analytical effort focused towards providing the necessary reactor and larger system context was undertaken. This effort produced credible system level efficiency targets and performance metrics. Results and accomplishments for each of the project areas are outlined below with references to documentation available in the open scientific literature. Detailed discussion is primarily limited to results not presented elsewhere.

3. Results and Accomplishments

3.1 Materials

Our broad understanding of materials for thermochemistry is documented in a recent publication [1]. Therein we identified and, to the extent possible, quantified important properties and targets for the rational design and implementation of metal oxide thermochemistry. We also compare established materials to these metrics.

¹ Thermodynamics of the other half cycle are defined by the combination of the TR and the fuel producing reaction.

3.1.1 Modification Strategy

Work in this area focused on two materials families that are most commonly studied for this application, iron/zirconia composites, and cerium oxides.

The composite system couples a redox center (Fe) with an oxygen conducting matrix (zirconia or yttria-stabilized zirconia (YSZ)) to alleviate some of the transport and other limitations of ferrite materials. However, the amount of iron that can be dissolved in the material is relatively low, thereby limiting the capacity of the material for each cycle. Ceria is a mixed ionic electronic conductor, i.e. transport of oxygen ions and electrons is rapid as are observed reaction rates. In the non-stoichiometric system, the redox active pair, $\text{Ce}^{3+}/\text{Ce}^{4+}$, remains in a homogenous fluorite crystal structure, where multivalency coexists. The fluorite structure is stable and able to accommodate the lattice strain induced by the formation of oxygen vacancies during thermal reduction. However, the capacity of ceria per cycle is also quite limited and the required temperatures are quite high. Therefore the goal of this subtopic was increasing the reactive capacity of the each material at reasonable temperatures while maintaining desirable kinetics and transport behavior.

3.1.1.1 Effect of yttria content in YSZ on Fe/YSZ materials

Numerous samples possessing a range of yttria and iron contents were prepared using traditional co-precipitation techniques. The as-prepared powders were mixed with organic binder, pressed into discs and sintered at 1350 °C (36 hours) and then 1450 °C (4 hours). A fragment of each disc was characterized using thermogravimetric analysis (TGA). Samples were heated to 1400 °C under inert gas flow for 5 hours to achieve thermal reduction; reduction was immediately followed by a 10 hour exposure to CO_2 at 1100 °C which re-oxidized the material. The mass increase recorded during the CO_2 re-oxidation was taken as a measure of the extent of reaction of the material.

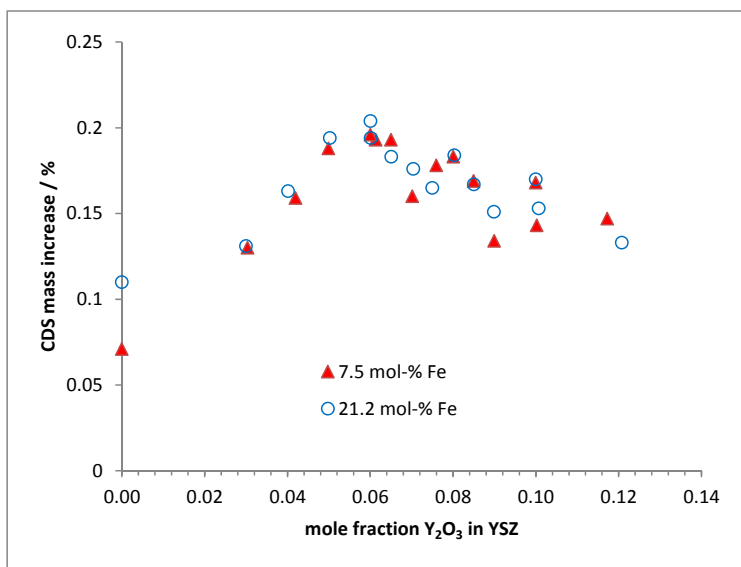


Figure 1. Effect of mole fraction of yttria in YSZ on the reactivity of ferrite/YSZ materials containing 7.5 or 21.2 mol-% Fe for carbon dioxide splitting (CDS).

Figure 1 shows the effect of varying the yttria content of ferrite/YSZ materials for two distinct ferrite loadings. There appears to be a maximum in the reaction extent at approximately 6 mol-% yttria content (expressed as mol-% of the YSZ component only, i.e. not including iron). Furthermore, there appears to be little difference in performance between the two ferrite loadings at comparable yttria levels. This may be explained by the solubility of ferrite in YSZ, where ferrite loadings above ca. 9 mol-% add little or no capacity to the system [2].

The data in Figure 2 show how the reactivity varies with ferrite content for distinct yttria levels in the YSZ. Again the 6YSZ-supported ferrites perform the best of all that were characterized, except at the very highest ferrite loading. Up to ferrite loadings of ~ 5 mol-%, all samples behave similarly, but above that loading reactivity follows the general order 6YSZ > 8YSZ > 10YSZ > 20YSZ > 0YSZ. The enhanced activity of 6YSZ could be a consequence of enhanced solubility of ferrite compared to the higher-yttria materials. This proposition is supported by the observation that the point at which the data in Figure 2 reaches a maximum increases from 10.3 to 11.7 to 13.1 mol-% Fe as the yttria content decreases from 10 to 8 to 6 mol-% yttria.

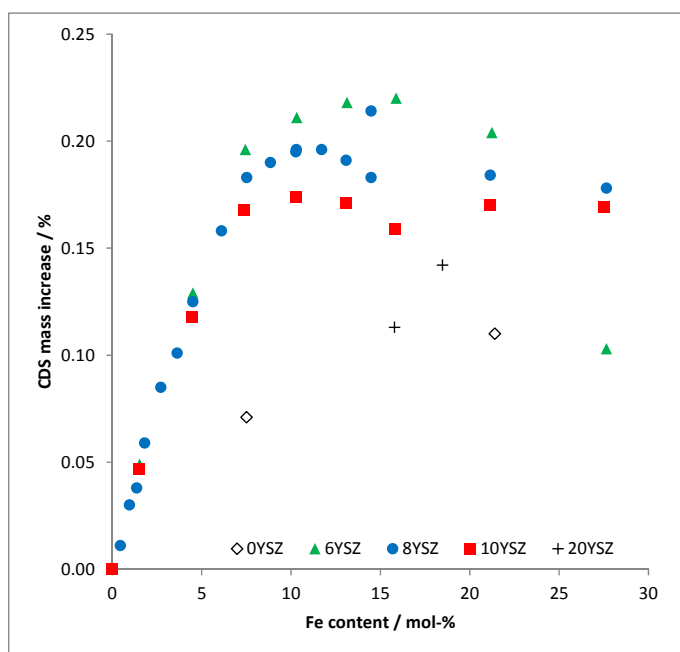


Figure 2. Effect of ferrite loading on the reactivity of ferrite/YSZ materials containing 0, 6, 8, 10, or 20 mol-% yttria.

Characterization of the as-prepared, sintered materials by X-ray diffraction (XRD) at room temperature revealed a change in structure of the zirconia phase from monoclinic at low yttria content (below 6 mol-% Y_2O_3) to cubic at higher yttria contents; Figures 3 and 4. For samples containing 21.2 mol-% Fe, undissolved hematite was observed irrespective of the yttria content (Figure 3), as should be expected for a system where the iron content exceeds the solid-state solubility limit of iron. At 7.5 mol-% Fe, only XRD peaks for zirconia were observed (Figure 4). No significant difference in solubility of iron species in YSZ as a function of yttria content was inferred from the XRD data. (Such information could be gleaned from lattice refinement, but this was not carried out).

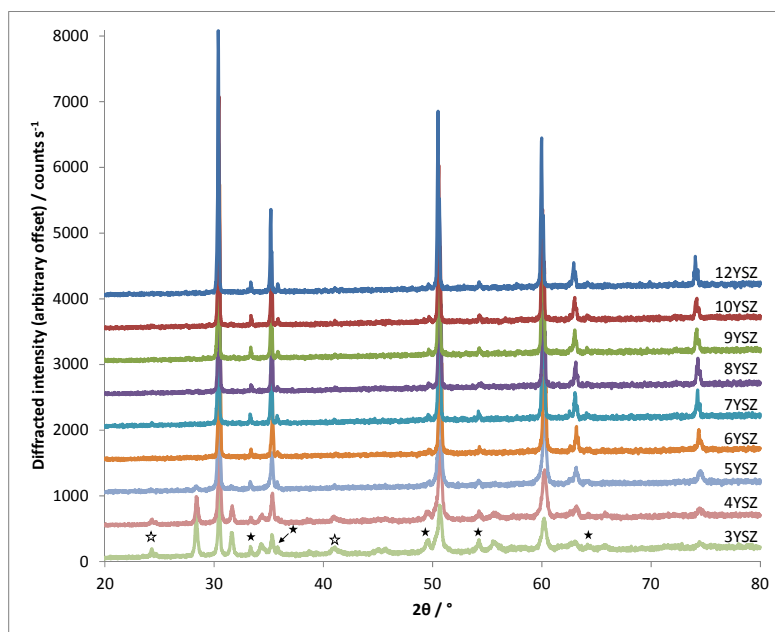


Figure 3. X-ray diffraction patterns for as-prepared specimens containing 21.2 mol-% Fe, and various yttria contents (indicated on right). Filled stars designate peaks arising mainly from un-dissolved hematite (Fe₂O₃), while the peaks with open stars have significant overlapping signals from hematite and monoclinic zirconia. Unmarked peaks are due to zirconia (monoclinic, or yttria-stabilized cubic form).

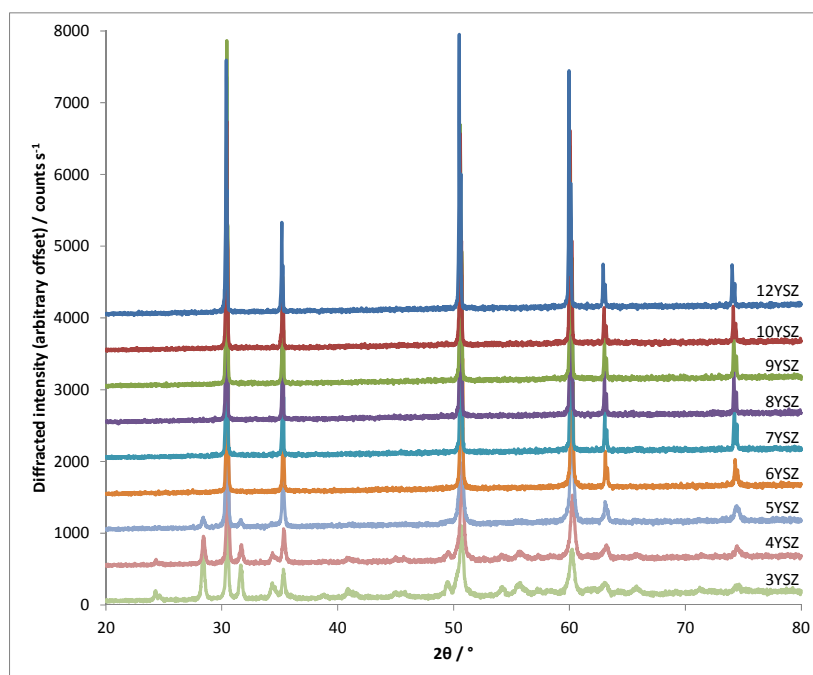


Figure 4. X-ray diffraction patterns for as-prepared specimens containing 7.5 mol-% Fe, and various yttria contents (indicated on right). Only peaks arising from zirconia or yttria-stabilized zirconia are seen.

To conclude this section, zirconia adopts a monoclinic structure at room temperature with yttria contents below 6 mol-% ; at 6 mol-% and above only the cubic structure was observed. There appears to be an optimum yttria content close to 6 mol-% (in zirconia) at which the utilization of ferrite in the ferrite/YSZ system is maximized. While no direct evidence from XRD supported changes in solubility of iron in YSZ as the yttria content was varied, the higher utilization of the 6 mol-% yttria materials infers higher solubility of iron in that system, or a higher proportion of small-grain un-dissolved iron oxide species. The iron loading at maximum utilization (i.e., maximum observed CDS mass increase) increased steadily as the yttria content in the YSZ decreased from 10 to 6 mol-% yttria.

3.1.1.2 Effect of transition metal doping on ceria

Ceria, is an intrinsic oxide ion conductor and unlike ferrites does not require a supporting matrix to remain redox active. It exhibits fast redox kinetics, maintains its cubic structure as the oxygen content varies, and is physically, chemically, and kinetically stable over multiple cycles. However, ceria presents a different set of challenges, including high reduction temperatures and limited Ce utilization. The goal therefore was to lower the thermal reduction temperature while maintaining or increasing the extent of oxygen non-stoichiometry of ceria via transition metal doping $M_x\text{Ce}_{1-x}\text{O}_{2-\delta}$, ($M = \text{Co}, \text{Fe}, \text{Ni}, \text{Mn}$).

Pure and doped ceria (10 mol-%) samples were synthesized using a modified Pechini method. Stoichiometric amounts (metals basis) of metal nitrates (Alfa Aesar) were dissolved in deionized H_2O . Citric acid was added in a 1.5:1 citric acid: metal molar ratio and the solution was heated to 90 °C with stirring until a gel formed. The gel was dried overnight at 100 °C and then ignited at 350-400 °C to decompose and burn off the nitrates and citrates. The resulting powder was ground with an agate mortar and pestle, calcined at 400 °C (1 hour) and then 850 °C (8 hours) to eliminate any remaining organic, re-ground, and calcined again at 1100 °C (24 hours). The powders were again re-ground with 2 wt% PVB binder (Butvar B-76) and uniaxially pressed (7500 lbs) into 1 cm diameter pellets. The pellets were placed in alumina crucibles, buried in a bed of sacrificial powder of the same composition, and sintered at 1400 °C (36 hours).

Room temperature XRD) was performed on a Bruker D8 Advance diffractometer in Bragg-Brentano geometry with Cu $K\alpha$ radiation and analyzed with JADE 7.0+ analysis software.² Scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS) were performed in a Zeiss scanning electron microscope at 15 kV. Samples were sputtered with a thin layer of gold-palladium before analysis to prevent charging. TGA was performed under inert (Argon flow at 1200 - 1500 °C) and CO_2 oxidizing (1000 - 1100 °C) conditions using a Netzsch 449 F3 Jupiter. Samples for TGA analysis were fragments of sintered discs weighing ~ 0.15 – 0.2 g and placed atop a sheet of Pt/Rh foil to prevent reaction of the sample with the Al_2O_3 crucible. All pipe work upstream of the TGA was stainless steel in order to minimize ingress of oxygen. Argon was passed through a heated getter furnace (SAES Getters) and CO_2 was passed through a purification bed (Advanced Specialty Gas Equipment) to remove traces of oxygen prior to entering the TGA.

A specially-designed, optically-accessible stagnation flow reactor (SFR) was used to perform redox experiments. The reactor is described elsewhere [3]. In a typical cycle, CeO_2 was oxidized with O_2 , reduced thermally at 1500 °C, reoxidized with H_2O or CO_2 , and reduced thermally again at 1500 °C. For

² 9.1 ed.; Materials Data Inc.: Livermore, CA, 2009.

thermal reductions, CeO₂ was typically heated to 1500 °C at a rate of up to 16.7 °C/sec (which closely mimics the thermal environment expected in a concentrated solar power application) and held for 4 minutes under helium flow and at 75 Torr total pressure. Oxygen evolution was monitored during this period. Heating ramp rates of 0.83 °C/sec, 1.67 °C/sec, 3.33 °C/sec, and 6.66 °C/sec to 1500 °C were also used (thermal reduction mapping). The laser which provided the high flux energy necessary to achieve the rapid ramp was then turned off, allowing the sample to cool to the static furnace temperature (650-1050 °C) under helium sweep. Subsequently, the sample was exposed to flowing oxidants (H₂O/CO₂, 20%, 30%, and 40% concentrations) during a 10 minute isothermal step at 75 Torr total pressure. Oxidation temperatures ranged from 700-1050 °C for water and from 650-1050 °C for CO₂.

XRD patterns of the as-synthesized materials, M_{0.1}Ce_{0.9}O_{2-δ} (M=Co, Ni, Mo, Fe, Mn) (Fig. 5) show that the materials are mostly single-phase. There are small impurity peaks corresponding to Fe₂O₃, NiO, and possibly Co₃O₄ in the respective sintered powders. The compound where M= Mo will not be discussed further in this report, as post-synthesis analysis shows that the Mo volatilized out of the sample during the final sinter, resulting in a material similar to pure CeO₂.

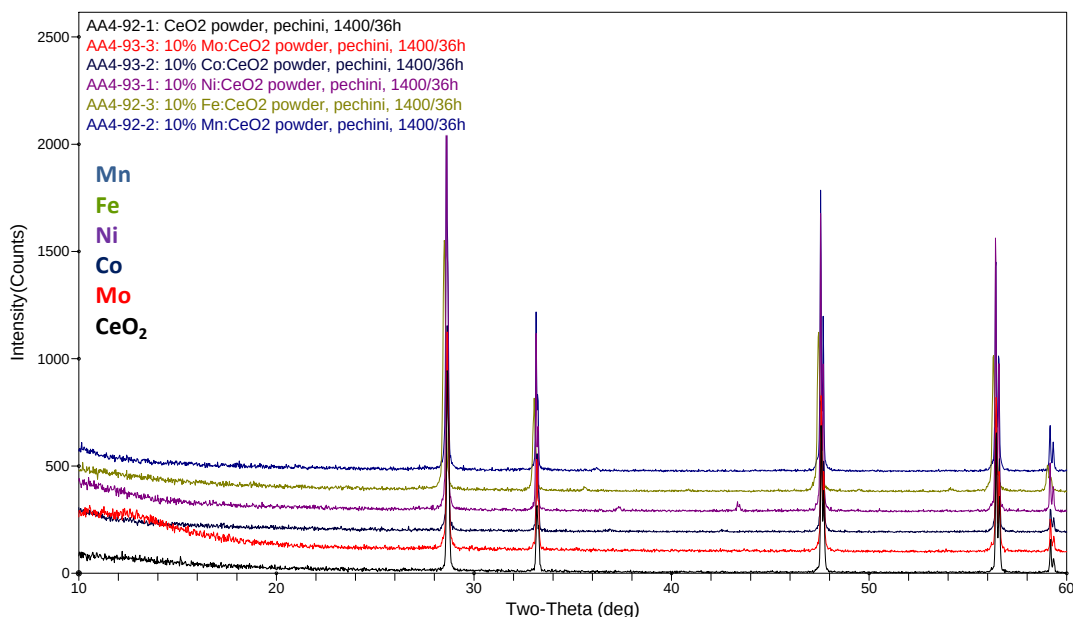


Figure 5. Powder XRD patterns of as-synthesized M_{0.1}Ce_{0.9}O_{2-δ}.

A multi-cycle TGA and an expanded portion of the TGA are shown in Figure 6. The multi-cycle TGA shows that decreasing T_{TR} decreases the reduction extent for all the materials. Most of the doped materials behave similarly to undoped ceria in kinetics and reaction extent, except for the Mn- and Fe-doped samples. These two materials show an initial increased reduction extent, but a lower-magnitude of reoxidation under CO₂. Intuitively there is some logic in this observation as materials that are easier to reduce are generally harder to reoxidize when compared to similar materials and similar conditions. Note also that the reoxidation step for the doped materials seems to occur in two kinetic phases: an initial fast oxidation, followed by a slower step, as shown in the change of slope of the curve. This behavior persists over several cycles.

In order to better elucidate the behavior of the doped materials, they were tested in the SFR. Thermal reduction mapping was performed on the doped ceria and compared to undoped ceria. All materials evolved O_2 upon reduction and demonstrated H_2O - and CO_2 -splitting upon reoxidation. During thermal reduction, $M_{0.1}Ce_{0.9}O_{2-\delta}$ ($M=Co, Ni$) performed similarly to undoped ceria in terms of O_2 evolution and kinetics. Samples where $M=Fe, Mn$ showed two O_2 peaks during thermal reductions: one that peaks at lower temperature and a second one that peaks at $1500^\circ C$. Although some of the transition metal dopants surveyed here have been studied previously [4], this phenomenon has not been reported before because the lower temperature O_2 characteristic can only be observed when the ramping rate is adequately slow. SEM and elemental analysis shows that phase segregation occurs in all of the 10% doped samples, i.e., that the transition metal dopant most likely forms a separate metal oxide phase after calcination and does not remain completely in solid solution, despite implication to the contrary by XRD. $Fe_{0.1}Ce_{0.9}O_{2-\delta}$ is shown in Figure 7 as an example. We postulate that the lower temperature reduction steps may be attributable to these secondary phases rather than from the primary ceria phase.

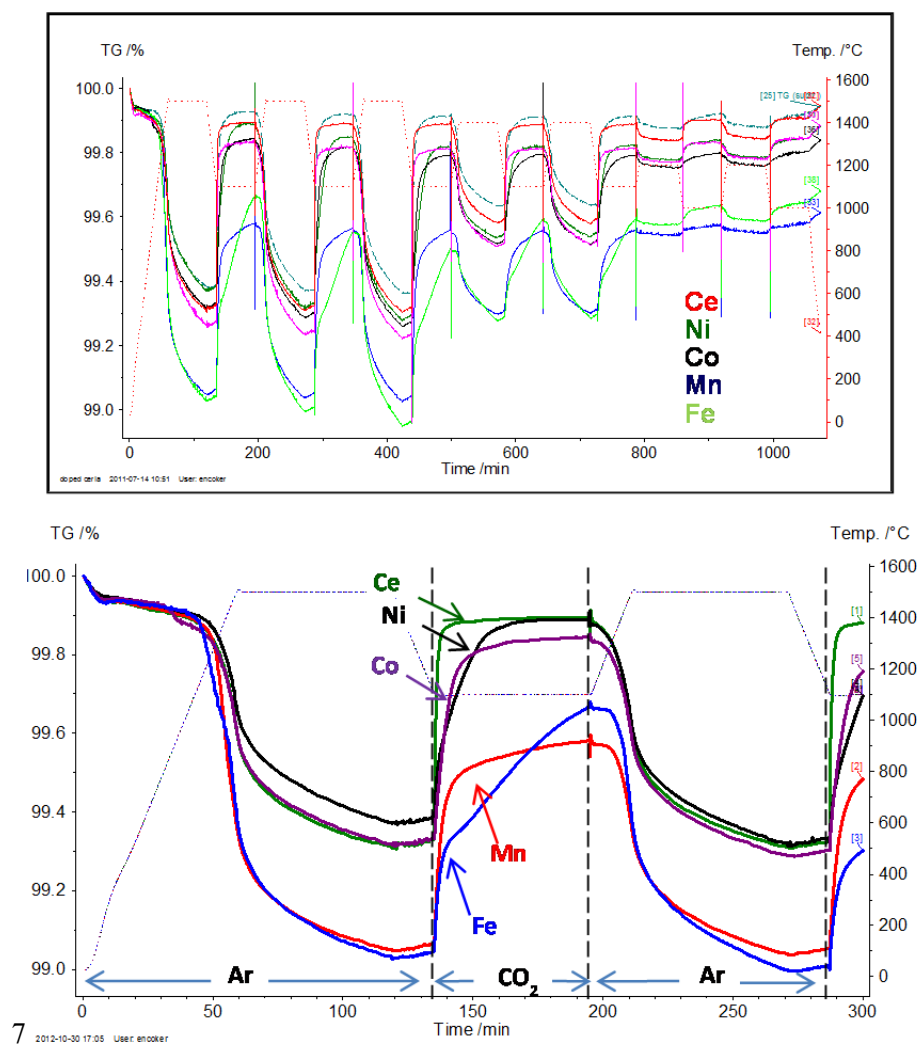


Figure 6. (Top) Multicycle TGA of $M_{0.1}Ce_{0.9}O_{2-\delta}$ under various reduction ($1500, 1400, 1200^\circ C$) and oxidation ($1100, 1000^\circ C$) temperatures. (Bottom) Detail of TGA; TR under Ar at $1500^\circ C$ and reoxidation under CO_2 at $1100^\circ C$. Note different color scheme marked in top and bottom figures.

Figure 8 shows reduction of $M_{0.1}Ce_{0.9}O_{2-\delta}$ before any reoxidation cycle (i.e. the first half of the first cycle) and after a water oxidation step has been completed (i.e. after one full cycle has been completed). The compounds $M = Co, Ni$ behave similarly before and after the water-splitting step. However, in the $M = Fe, Mn$ samples, the initial low temperature reduction step is absent after water-splitting. The low temperature O_2 thermal reduction peak for Mn- and Fe-doped samples reappears when the material is reoxidized with O_2 or air (not shown). Therefore, the reduced species formed at low temperature do not contribute the WS or CDS step; the high temperature species (presumably vacancies in the ceria phase) account for all the splitting capacity.

The low temperature O_2 evolution observed for the Mn-doped ceria sample peaks near $1300^\circ C$. Thermodynamic calculations performed with FactSage 6.2[®] suggests that the low temperature O_2 evolution can be attributed to the thermal reduction of Mn_3O_4 to form MnO . Reoxidation of MnO back to Mn_3O_4 with H_2O is thermodynamically unfavorable at $1100^\circ C$ (and at lower temperatures for that matter); therefore, this low temperature reduction peak appears only after material is oxidized with O_2 . In the case of Fe dopant, the lower temperature O_2 peak may be due to the thermal reduction of Fe_2O_3 to Fe_3O_4 . In pure materials this transition is expected to occur at higher temperatures than the Mn_3O_4 reduction. However it is observed at around $1100 - 1200^\circ C$ in high-Fe-loading Fe:YSZ composite systems under similar conditions [2].

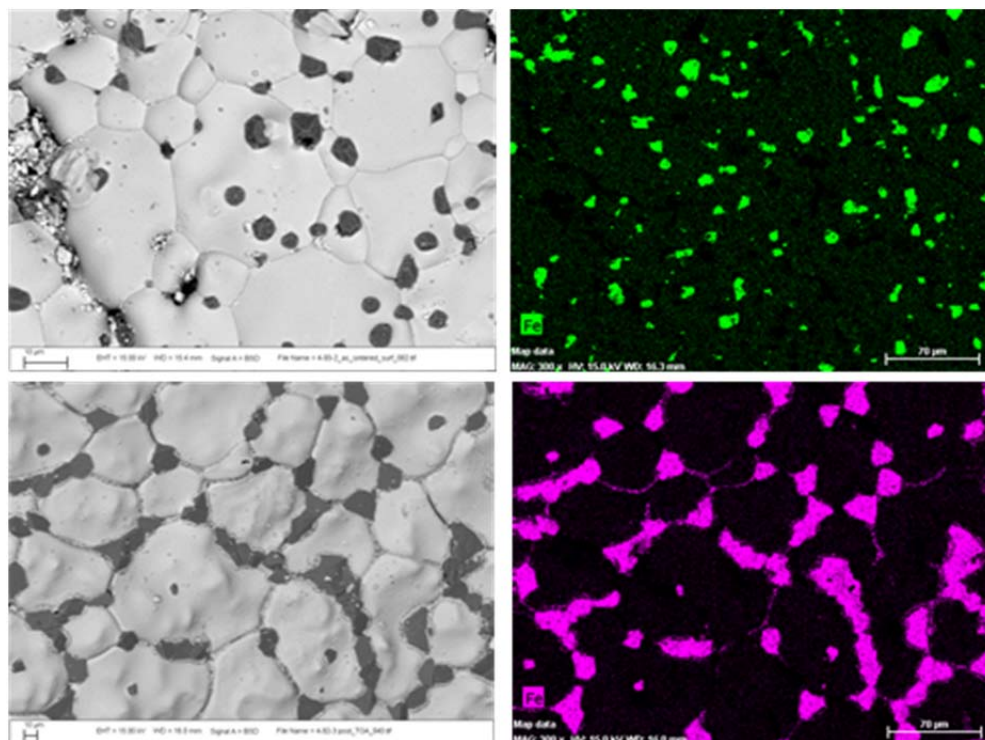


Figure 7. Backscattered SEM micrographs (left), and EDS elemental maps of Fe (right). of as-sintered (top) and post-TGA redox under Ar/CO₂ (bottom) of $Fe_{0.1}Ce_{0.9}O_{2-\delta}$.

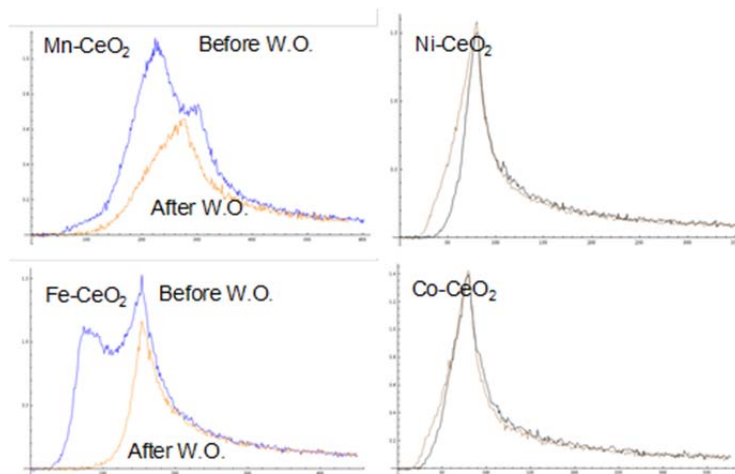


Figure 8. Oxygen production measured during thermal reduction of $M_{0.1}Ce_{0.9}O_{2-\delta}$ before and after WS step. Materials were oxidized in either 5000 ppm O_2 or 40% H_2O at 1000 °C and 75 Torr total pressure, then thermally reduced in a constant flow of He up to 1500 °C. (y-axis corresponds to O_2 concentration, x-axis corresponds to time or temperature).

The material in this case produces O_2 at an even lower temperature. In any case, Fe_3O_4 cannot be reoxidized with H_2O to form an Fe_2O_3 phase [5], O_2 is required. The SEM/EDS images in Fig. 7 show that after redox cycling, the secondary iron oxide phase aggregates at the grain boundaries of the primary sintered material; these larger particles likely provide an additional kinetic barrier to redox activity. A final potential complication in the Fe:CeO₂ system is the formation of a $FeCeO_3$ phase, which begins to appear after multiple cycles in the SFR (Fig. 9). The redox activity of this perovskite phase is unknown.

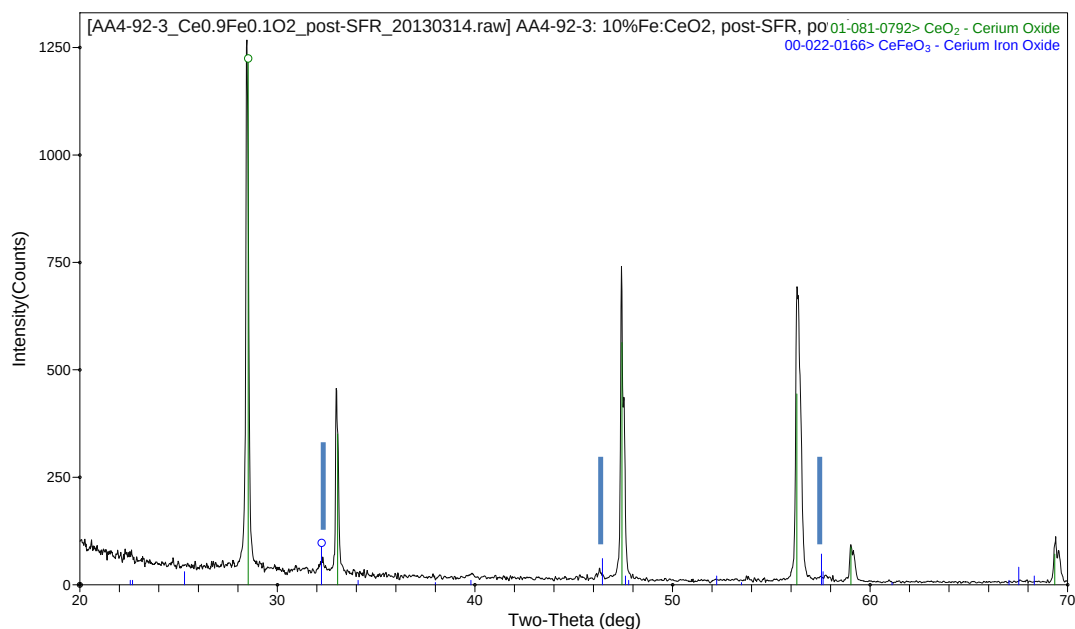


Figure 9. XRD of $Fe_{0.1}Ce_{0.9}O_{2-\delta}$ after reaction in the SFR. The blue lines denote peaks arising from the formation of a $FeCeO_3$ phase.

To conclude, improving the performance of ceria through transition metal doping had limited success. Co and Ni dopants showed little benefit in temperature and capacity, but slowed the apparent reaction rates. The reduction temperature and extent of reduction were improved somewhat with Fe and Mn, however the additional capacity was not active for WS or CDS, thus negating any benefit. The precipitation of the dopant metal oxide plus formation of secondary phases in the Fe system further limits the practicality of this line of investigation. Furthermore, the dopants qualitatively appear to enhance sintering of the material relative to undoped ceria. A thermodynamic study of doped ceria is presented in [1].

3.1.1.2 Effect of zirconium and lanthanide doping on ceria

The catalysis community has long been interested in ceria/zirconia compositions. They have been used for example in automotive exhaust after-treatment where they provide a “buffering” oxygen storage capacity (OSC) as the exhaust-gas composition rapidly cycles from oxidizing to reducing conditions. Under typical exhaust conditions, the oxygen storage and release available from un-modified ceria is limited to the surface regions which requires that small particles be used which are prone to sintering and loss of activity. Modification of ceria with zirconia renders the material easier to reduce; substitution of Ce^{4+} by isovalent Zr^{4+} lowers the reduction enthalpy. The modification also extends the OSC into the interior bulk of the particulates. Adding reducible lanthanide series cations, such as praseodymium and gadolinium, also have the potential to increase oxygen storage capacity. These properties fueled our initial interest in zirconia-modified ceria [6].

Using the SFR, we characterized the thermochemical WS behavior of ZrCe binary ($\text{Zr}_{0.1}\text{Ce}_{0.9}\text{O}_2$, $\text{Zr}_{0.15}\text{Ce}_{0.85}\text{O}_2$, $\text{Zr}_{0.25}\text{Ce}_{0.75}\text{O}_2$), and PrZrCe and GdZrCe ternary oxides ($\text{Pr}_{0.1}\text{Zr}_{0.15}\text{Ce}_{0.75}\text{O}_{2.8}$, $\text{Pr}_{0.1}\text{Zr}_{0.25}\text{Ce}_{0.65}\text{O}_{2.8}$, and $\text{Gd}_{0.1}\text{Zr}_{0.25}\text{Ce}_{0.65}\text{O}_{1.95}$) by evaluating the redox capacity of well cycled, compositionally stable materials. The materials were synthesized by co-precipitation of the requisite metallic nitrates. Appropriate amounts of the different metal (Ce, Gd, Pr, and Zr) nitrates (Alfa Aesar, Ward Hill, MA) were dissolved in distilled water. The nitrate solution was then mixed to give a mixture with the desired cation molar ratio. The pH of the mixture was then adjusted by drop wise addition of 1 M oxalic acid until precipitation is complete. The supernatant liquid was analyzed by induced coupled plasma-atomic emission spectroscopy (ICP-AES) to ensure complete precipitation of the metal cations. The precipitate was filtered, washed with distilled water, and dried in air overnight. The resulting powder was then calcined in air at 700 °C for 12 hours, and further calcined in air at 1500 °C for 16 hours.

We find that addition of Zr decreases the onset temperature for O_2 evolution during thermal reduction, and increases the capacity of the material while maintaining favorable reaction kinetics (Figure 10). The O_2 cycle (i.e. reoxidation with O_2) capacity is improved by 30%, and the H_2 production capacity by 11% (Table 1); the increase in cycle capacity is, however, independent of Zr level. We believe that high temperatures and repeated thermochemical cycling induces phase segregation/enrichment in these doped systems, and Zr levels above 10 atomic% does not yield additional benefit. In contrast to the binary ZrCe system, the ternary PrZrCe or GdZrCe systems offer no improvement in cycle capacity. In fact, the GdZrCe ternary oxide has less capacity than undoped ceria. It appears that the addition of trivalent cations, such as Pr^{3+} and Gd^{3+} , reverse the gains afforded by addition of Zr alone.

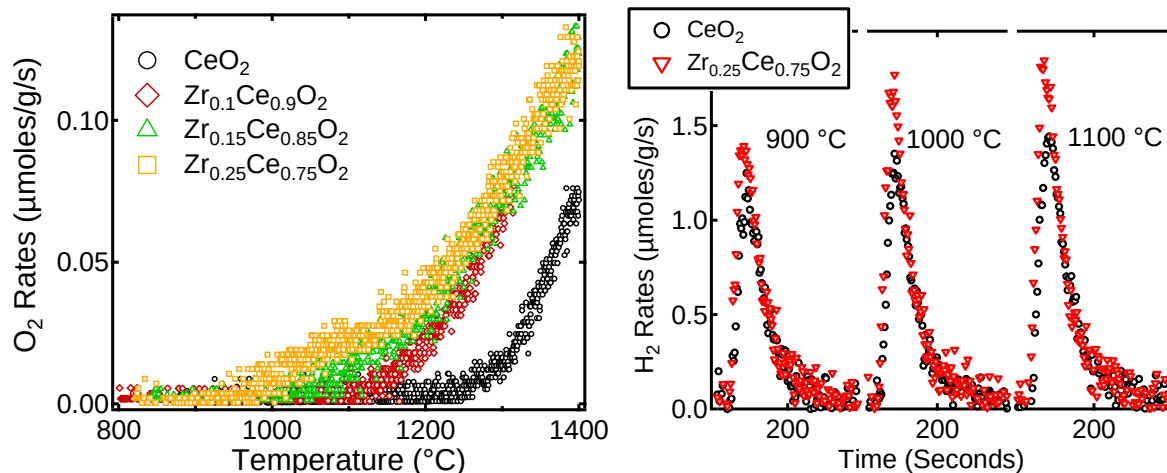


Figure 10. Comparison of ceria thermochemistry to that of zirconia-modified ceria. (Left) O₂ evolution, (Right) H₂ production. During thermal reduction, samples heated to 1500 °C at 17 °C/s while under a flow of UHP He. Sample powders were oxidized in 30 vol.-% H₂O concentration for 600 s at temperatures between 900 and 1100 °C.

Table 1. Comparison of WS capacity (30% concentration) of CeO₂ to Zr_{0.25}Ce_{0.75}O₂.

Oxidation temperature [°C]	Total H ₂ produced: CeO ₂	Total H ₂ produced: Zr _{0.25} Ce _{0.75} O ₂
900	114	139
1000	133	159
1100	145	166

3.1.2 Structured Materials Strategy

Mass and heat transport are important but perhaps underappreciated factors in metal oxide thermochemistry [1]. For example, ferrite materials have attractive thermodynamics [7], and rapid surface reactions [3], but remain unsatisfactory as an enabling material due to the inability to effectively transport oxygen into and out of the interior of a bulk sample; the reaction is surface limited. One strategy for sidestepping this hurdle is to structure the material such that the fundamental dimension of the structure is small relative to relevant dimensions for transport. In this project we explored the use of ice templating to form porous monoliths of metal oxides with narrow wall thicknesses.

A slurry of 50 wt-% CeO₂ or Fe₂O₃/8YSZ in H₂O was prepared, and 1 wt-% DARVAN 821A dispersant was added. The mixture was then ball-milled for at least 24 hours using zirconia milling media. The slurry was then poured into a silicone mold, the tip of which was then contacted with liquid nitrogen. The directional freezing, from tip upwards, caused lamellar ice crystals to form. The formation of the ice crystals resulted in rejection of the oxide particles to the inter-crystalline void spaces. The frozen mass was then de-molded while cold and immediately transferred to a pre-cooled freeze dryer set at -15 °C. The freeze dryer was evacuated, and the temperature was gradually increased to ca. -2 °C over a 36 hour period. Then the temperature was raised to a few degrees above freezing and maintained there for about 12 more hours to ensure all water had been removed. The structures thus formed were self-supporting,

but fragile (Figure 11). Sintering at temperatures between 1400 and 1600 °C increased the rigidity of the materials without causing structural loss. The SEM images in Figure 12 illustrate some of the structural forms achieved by this method, after sintering at 1400 °C.



Figure 11. An optical photograph of an ice-templated CeO_2 structure prior to sintering.

Surface area analysis (B.E.T. method) revealed surface areas of between 1 and 10 $\text{m}^2 \text{g}^{-1}$, depending on the material and precise conditions of preparation. Thermogravimetric analysis of the ice-templated structures compared to bulk (non-structured) materials verified faster reaction rates for the porous structures as compared to bulk materials (Figure 13 for CeO_2 , Figure 14 for $\text{Fe}_2\text{O}_3/8\text{YSZ}$). The results are consistent with the fact that bulk oxygen transport is rapid in ceria relative to $\text{Fe}_2\text{O}_3/8\text{YSZ}$; improvement was more pronounced in the case of the Fe-composite. Although promising, additional characterization would be required to establish the long term stability and performance of these materials as well as to optimize and integrate the structures into a given reactor concept.

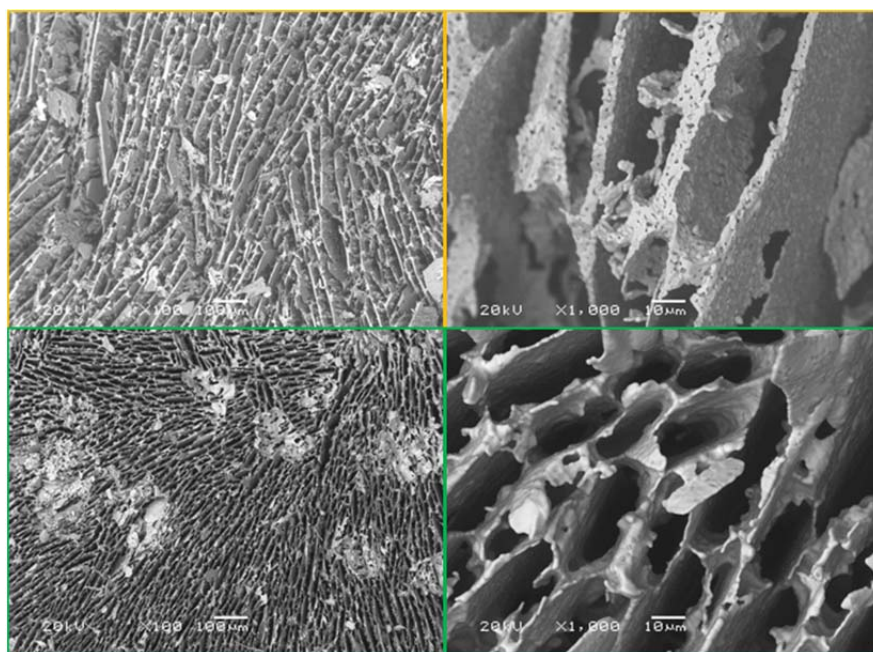


Figure 12. SEM images of CeO_2 (top) and $\text{Fe}_2\text{O}_3/8\text{YSZ}$ (bottom) structures sintered at 1400 °C for 12 hours.

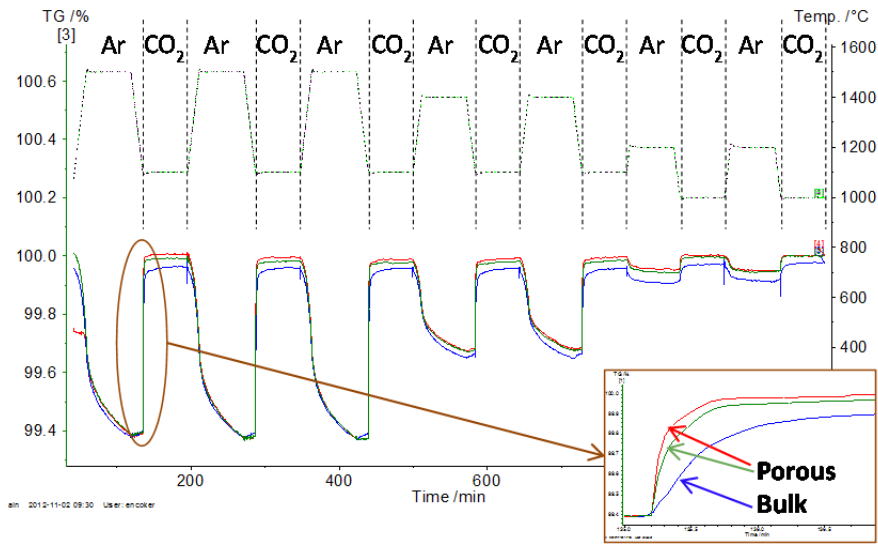


Figure 13. TGA data for CeO_2 porous structures (red, green) compared to bulk CeO_2 (blue). The solid lines show the change in mass of the specimen versus time. The dotted line shows the temperature profile, while the vertical dashed lines indicate where the gas was switched from Ar (inert) to CO_2 (oxidizing).

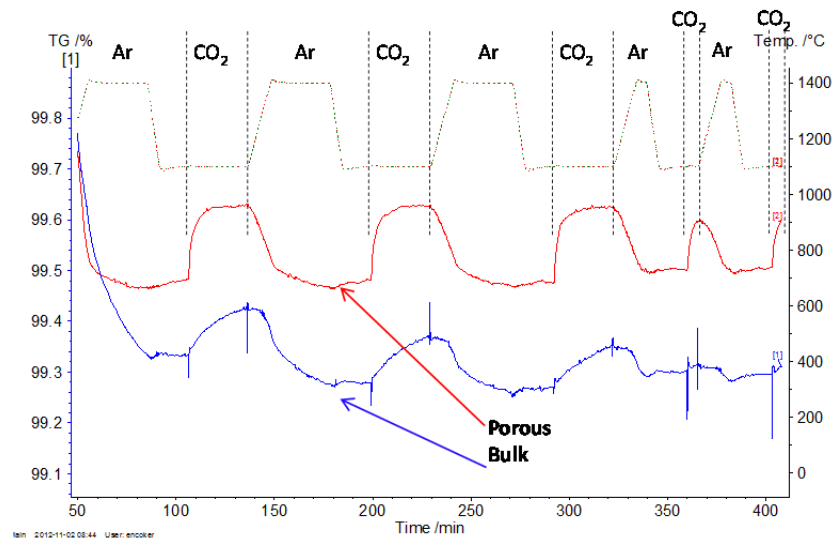


Figure 14. TGA data for a $\text{Fe}_2\text{O}_3/8\text{YSZ}$ porous structure (red) compared to bulk $\text{Fe}_2\text{O}_3/8\text{YSZ}$ (blue). The solid lines show the change in mass of the specimen versus time. The dotted line shows the temperature profile, while the vertical dashed lines indicate where the gas was switched from Ar (inert) to CO_2 (oxidizing).

3.1.2 New Thermochemical Materials Strategy

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. This strategy proved to be exceptionally fruitful. Much of our attention was focused on perovskites as these are mixed ionic electronic conducting materials that may contain redox active metals. Exciting results for were recently reported for $\text{Sr}_x\text{La}_{1-x}\text{Mn}_y\text{Al}_{1-y}\text{O}_3$ (SLMA, $x = 0.4$ or 0.6 , y

= 0.4 or 0.6) perovskites [8]. 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 CO₂ and H₂O) cycles. Stability was demonstrated through 80 complete cycles. The yield of CO or H₂ was significantly improved relative to ceria even when the SLMA was reduced at a temperature 150 °C lower than ceria. A second material system based on iron-titanium oxides was also identified that yields > 3 times the amount of CO from CO₂ at 1100 °C than does bulk ceria after a 5 hour reduction at 1400 °C albeit with slower kinetics. Investigations of this material are at an early stage and the chemistry is only partially characterized and the limits and possibilities for improvements are only poorly understood.

3.2 CeO₂ Reaction kinetics

The kinetics of water and carbon and dioxide splitting on cerium dioxide (CeO₂) were studied during the course of this LDRD. The intrinsic oxidation kinetics for undoped ceria were resolved by using an analytical approach that combines solid-state kinetic theory with an idealized flow model in order to identify rate limiting mechanisms and extract kinetic parameters via model-based data reduction [3]. This is necessary in order to decouple the material-specific behavior from experimental effects, such as gas-phase dispersion and mixing, that leave temporal imprints on the fuel production rate curve. The results of this study show that the WS process can best be described by a first-order deceleratory model ($r = k_o[1 - \alpha]$ where the rate constant k_o takes an Arrhenius form and α is a measure of the oxidation extent) with an activation energy of 29 kJ/mole. This mechanism implies that the WS reaction is a surface mediated process that will scale with surface area of CeO₂.

The CDS reaction is also a surface mediated process. However, unlike WS, complex surface phenomena such as temperature-dependent site blocking induce mechanism transitions that change the governing kinetic behavior over a narrow range of oxidation temperature. Due to these complex surface processes, multiple order-based deceleratory models are necessary to describe the CO production kinetics at different temperatures. Application of a qualitative microkinetic analysis indicates that at low oxidation temperatures (between 650 and 725 °C), the CDS reaction is limited by site blocking. Our assumption is that surface carbon is responsible for this behavior. Above 875 °C, the reaction becomes very rapid and dissociative adsorption of gaseous CO₂ becomes rate limiting. Overall, for both water and carbon dioxide splitting on undoped ceria, the kinetics are very rapid and could potentially be tailored to a specific reactor design by adjusting the gas/solid interface.

3.3 Systems, Components, Concepts

The primary focus of this LDRD was the material work discussed above. However, as indicated in Section 2, this LDRD also contributed to a secondary analytical effort focused towards providing the necessary reactor and larger system context so that credible efficiency targets and performance metrics could be established. Much of this work was accomplished in partnership with university-based collaborators.

The highest level analysis is presented in [9]. Quite simply, this paper seeks to answer the question “can technology provide a full solution by creating fuels from sunlight, water, and waste CO₂, and do so within practical resource constraints, while protecting valuable ecosystems, at a production rate that can match consumption at a level comparable and even somewhat larger than current demand, and at an acceptable cost?” That is, this paper explores the viability of solar fuels in general and presumes to be non-specific

regarding the technology. We conclude that given high enough efficiency ($>10\%$) energy conversion routes, supplanting a large fraction of global petroleum-derived liquid fuels with synthetic solar-fuels is challenging but nonetheless possible; indeed it is quite plausible but the timescale required is likely to be decades long. We emphasize the solar-to-fuel efficiency as a key metric as it drives not only the potential impact (scalability) of a technology for storing (contemporary) sunlight and sequestering carbon above ground as energy dense fuels, but also the economics. Although very specific cases may upend our expectations, the end-to-end efficiencies that we believe must be met are higher than many other technology development efforts seem to acknowledge as ultimately being necessary or are establishing as long-term targets for their labors.

The next level of detail is provided in [10]. This paper is specific to thermochemistry and considers the efficiency of a metal oxide cycle from solar energy intercepted on a collector all the way to energized chemical fuel intermediate (CO or H_2). This paper is aimed at a general audience and provides a realistic view of efficiency losses that occur in solar systems that are very often unaccounted for in the literature and discusses the implications of such. Using a generalized approach we were able to establish what we think is a credible, but challenging target for metal oxide performance. We define a new dimensionless figure of merit for thermochemistry, the utilization factor, that incorporates both materials and reactor considerations. We believe this approach will help provide a realistic metric of the potential efficiency of a reactor/material combination and help guide future efforts towards better, and better integrated, solutions.

Analysis of a specific solar fuel production configuration is provided in two additional papers [11,12]. These papers represent an expansion on previous work [13]. The first of these papers shows that in a well-designed system, sunlight, or more precisely the cost associated with the solar conversion subsystem, is a dominant factor, and the focus of this and similar development efforts should largely be on increasing the efficiency and decreasing the cost of this component. In the second paper, a life-cycle assessment is applied to evaluate environmental benefits of solar transportation fuels (subject to a specific configuration and location) relative to conventional gasoline. It is concluded that for a facility located in Victorville, California, each million vehicles running on solar gasoline yields nearly \$30M in savings in environmental impact, and displaces 335M gallons of gasoline (nearly 25.8 Mt of CO_2 -eq avoided).

A new hybrid concept for solar thermochemistry was introduced in [14]. In the solar thermal decoupled water electrolysis process a metal oxide is reduced to a lower oxidation state in air with concentrated solar energy. The reduced oxide is then used either as an anode or solute for the electrolytic production of hydrogen in either an aqueous acid or base solution. The ideal efficiencies that include radiation heat loss are as high or higher than corresponding ideal values reported in the solar thermal chemistry literature. An exploratory experimental study for the iron oxide system confirmed that the electrolytic and thermal reduction steps occur in a laboratory scale environment.

4. Project-supported Publications

The following journal and conference publications were supported in full or in part by this project.

4.1 Materials

- Anthony H. McDaniel, Elizabeth C. Miller, Darwin Arifin, Andrea Ambrosini, Eric N. Coker, Ryan O'Hayre, William C. Chueh and Jianhua Tong "Sr- and Mn-doped $\text{LaAlO}_{3-\delta}$ for solar thermochemical H_2 and CO production" *Energy Environ. Sci.*, 2013,6, 2424-2428.
- James E. Miller, Anthony H. McDaniel, Mark D. Allendorf "Considerations in the Design of Materials for Solar-Driven Fuel Production Using Metal-Oxide Thermochemical Cycles" *Advanced Energy Materials* – accepted for publication.
- James A. Ohlhausen, Eric N. Coker, Andrea Ambrosini, James E. Miller "ToF-SIMS Analysis of Iron Oxide Particle Oxidation by Isotopic and Multivariate Analysis" *Surface and Interface Analysis*, DOI:10.1002/sia.5140 (2012).
- Eric N. Coker, James A. Ohlhausen, Andrea Ambrosini, and James E. Miller "Oxygen transport and isotopic exchange in iron oxide/YSZ thermochemically-active materials via splitting of $\text{C}(^{18}\text{O})_2$ at high temperature studied by thermogravimetric analysis and secondary ion mass spectrometry" *J. Mater. Chem.*, 2012, 22, 6726. DOI:10.1039/C2JM15324F.
- Eric N. Coker, Mark A. Rodriguez, Andrea Ambrosini, James E. Miller, and Ellen B. Stechel, "Using In-situ Techniques to Probe High Temperature Reactions: Thermochemical Cycles for the Production of Synthetic Fuels from CO_2 and Water" *Powder Diffraction*, 2012, 27(02), pp. 117-125.
- James E. Miller, Andrea Ambrosini, Eric N. Coker, Anthony H. McDaniel, Mark D. Allendorf "Advancing oxide materials for thermochemical production of solar fuels" *Energy Procedia: SolarPACES 2013*, September 2013, Las Vegas, NV.
- Anthony H. McDaniel, Andrea Ambrosini, Eric N. Coker, James E. Miller, W.C. Chueh, R.O. O'Hayre, Jianhua Tong "Nonstoichiometric Perovskite Oxides for Solar Thermochemical H_2 and CO Production" *Energy Procedia: SolarPACES 2013*, September 2013, Las Vegas, NV.

4.2 Kinetics

- Scheffe, J. R.; McDaniel, A. H.; Allendorf, M. D.; Weimer, A. W. *Energy Environ. Sci.* 2013, 6, 963.

4.3 Systems, Components, Concepts

- Jiyong Kim, James E. Miller, Christos T. Maravelias, and Ellen B. Stechel "Comparative Analysis of Environmental Impact of S2P (Sunshine to Petrol) System for Transportation Fuel Production" *Applied Energy* accepted for publication.
- Ivan Ermanoski, Nathan P. Siegel and Ellen B. Stechel "A New Reactor Concept for Efficient Solar-Thermochemical Fuel Production" *J. Sol. Energy Eng.* 135(3), 2013. 031002-1

- Ellen B. Stechel and James E. Miller “Re-energizing CO₂ to fuels with the sun: Issues of efficiency, scale, and economics” *Journal of CO₂ Utilization*, 1 (2013) 28–36, DOI: 10.1016/j.jcou.2013.03.008
- Nathan P. Siegel, James E. Miller, Ivan Ermanoski, Richard B. Diver, and Ellen B. Stechel “Factors Affecting the Efficiency of Solar-Driven Metal Oxide Thermochemical Cycles” *Ind. Eng. Chem. Res.*, 2013, 52 (9), 3276–3286 DOI: 10.1021/ie400193q.
- Jiyong Kim, Terry A. Johnson, James E. Miller, Ellen B. Stechel and Christos T. Maravelias “Fuel production from CO₂ using solar-thermal energy: system level analysis” *Energy Environ. Sci.*, 2012, 5, 8417-8429. DOI: 10.1039/c2ee21798h
- R. Palumbo, C. Larson, J. Guertin, J. Schoer, M. Meyer, R. B. Diver, E. N Coker, J. E. Miller, and N. P. Siegel “Solar thermal decoupled water electrolysis process I: Proof of concept” *Chemical Engineering Science* 84 (2012) 372–380, dx.doi.org/10.1016/j.ces.2012.08.023

5. References

1. J.E. Miller, A.H. McDaniel, M.D. Allendorf “Considerations in the Design of Materials for Solar-Driven Fuel Production Using Metal-Oxide Thermochemical Cycles” *Adv. Eng. Mater.*, (2013). DOI:10.1002/aenm.201300469.
2. E.N. Coker, A. Ambrosini, M.A. Rodriguez and J.E. Miller “Ferrite-YSZ composites for solar thermochemical production of synthetic fuels: in operando characterization of CO₂ reduction” *J. Mater. Chem.* 21 (2011) 10767. DOI: 10.1039/C1JM11053E
3. J.R. Scheffe, A.H. McDaniel, M.D. Allendorf, A.W. Weimer “Kinetics and Mechanism of Solar-Thermochemical H₂ Production by Oxidation of a Cobalt Ferrite–Zirconia Composite” *Energy Environ. Sci.* 6 (2013) 963.
4. H. Kaneko, T. Miura, H. Ishihara, S. Taku, T. Yokoyama, H. Nakajima, Y. Tamaura “Reactive ceramics of CeO₂–MO_x (M=Mn, Fe, Ni, Cu) for H₂ generation by two-step water splitting using concentrated solar thermal energy” *Energy* 32 (2007) 656.
5. Christopher D. Bohn, Christoph R. Muller, Jason P. Cleeton, Allan N. Hayhurst, John F. Davidson, Stuart A. Scott, and John S. Dennis “Production of Very Pure Hydrogen with Simultaneous Capture of Carbon Dioxide using the Redox Reactions of Iron Oxides in Packed Beds” *Ind. Eng. Chem. Res.* 47 (2008) 7623.
6. J.E. Miller, M.D. Allendorf, R.B. Diver, L.R. Evans, N.P. Siegel, and J.N. Stuecker “Metal Oxide Composites and Structures for Ultra-High Temperature Solar Thermochemical Cycles” *Journal of Materials Science* 43 (2008) 4714. DOI: 10.1007/s10853-007-2354-7.
7. M.D. Allendorf, R.B. Diver Jr., N.P. Siegel, and J.E. Miller “Two-Step Water Splitting Using Mixed-Metal Ferrites: Thermodynamic Analysis and Characterization of Synthesized Materials” *Energy & Fuels* 22 (2008) 4115–4124.

8. Anthony H. McDaniel, Elizabeth C. Miller, Darwin Arifin, Andrea Ambrosini, Eric N. Coker, Ryan O'Hayre, William C. Chueh and Jianhua Tong "Sr- and Mn-doped $\text{LaAlO}_{3-\delta}$ for solar thermochemical H_2 and CO production" *Energy Environ. Sci.* 6 (2013) 2424-2428.
9. Ellen B. Stechel and James E. Miller "Re-energizing CO_2 to fuels with the sun: Issues of efficiency, scale, and economics" *Journal of CO_2 Utilization* 1 (2013) 28–36. DOI: 10.1016/j.jcou.2013.03.008
10. Nathan P. Siegel, James E. Miller, Ivan Ermanoski, Richard B. Diver, and Ellen B. Stechel "Factors Affecting the Efficiency of Solar-Driven Metal Oxide Thermochemical Cycles" *Ind. Eng. Chem. Res.*, 52 (2013) 3276–3286. DOI: 10.1021/ie400193q.
11. Jiyong Kim, James E. Miller, Christos T. Maravelias, and Ellen B. Stechel "Comparative Analysis of Environmental Impact of S2P (Sunshine to Petrol) System for Transportation Fuel Production" *Applied Energy* 111 (2013) 1089-1098. DOI: 10.1016/j.apenergy.2013.06.035
12. Jiyong Kim, Terry A. Johnson, James E. Miller, Ellen B. Stechel and Christos T. Maravelias "Fuel production from CO_2 using solar-thermal energy: system level analysis" *Energy Environ. Sci.* 5 (2012) 8417-8429. DOI: 10.1039/c2ee21798h
13. J. Kim, C.A. Henao, T.A. Johnson, D.E. Dedrick, J.E. Miller, E.B. Stechel, C.T. Maravelias "Methanol Production from CO_2 Using Solar-Thermal Energy: Process Development and Techno-Economic Analysis" *Energy Environ. Sci.* 4 (2011) 3122. DOI: 10.1039/C1EE01311D.
14. R. Palumbo, C. Larson, J. Guertin, J. Schoer, M. Meyer, R. B. Diver, E. N Coker, J. E. Miller, and N. P. Siegel "Solar thermal decoupled water electrolysis process I: Proof of concept" *Chemical Engineering Science* 84 (2012) 372–380. [dx.doi.org/10.1016/j.ces.2012.08.023](https://doi.org/10.1016/j.ces.2012.08.023)

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