USING IN-SITU TECHNIQUES TO PROBE HIGH TEMPERATURE REACTIONS: THERMOCHEMICAL CYCLES FOR THE PRODUCTION OF SYNTHETIC FUELS FROM CO\textsubscript{2} AND WATER

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ABSTRACT
Ferrites are promising materials for enabling solar-thermochemical cycles. Such cycles utilize solar-thermal energy to reduce the metal oxide, which is then re-oxidized by H\textsubscript{2}O or CO\textsubscript{2}, producing H\textsubscript{2} or CO, respectively. Mixing ferrites with zirconia or yttria-stabilized zirconia (YSZ) greatly improves their cyclability. In order to understand this system, we have studied the behavior of iron oxide/8YSZ (8 mol-% Y\textsubscript{2}O\textsubscript{3} in ZrO\textsubscript{2}) using \textit{in situ} X-ray diffraction and thermogravimetric analysis at temperatures up to 1500 °C and under controlled atmosphere. The solubility of iron oxide in 8YSZ measured by XRD at room temperature was 9.4 mol-% Fe. The solubility increased to at least 10.4 mol-% Fe when heated between 800 and 1000 °C under inert atmosphere. Furthermore iron was found to migrate in and out of the 8YSZ phase as the temperature and oxidation state of the iron changed. In samples containing > 9.4 mol-% Fe, stepwise heating to 1400 °C under helium caused reduction of Fe\textsubscript{2}O\textsubscript{3} to FeO. Exposure of the FeO-containing material to CO\textsubscript{2} at 1100 °C re-oxidized FeO to Fe\textsubscript{3}O\textsubscript{4} with evolution of CO. Thermogravimetric analysis during thermochemical cycling of materials with a range of iron contents showed that samples with mostly dissolved iron utilized a greater proportion of the iron atoms present than did samples possessing a greater fraction of un-dissolved iron oxides.

INTRODUCTION
The primary goal of this work is to lay the foundation to enable the synthesis of hydrocarbon fuels from CO\textsubscript{2} and H\textsubscript{2}O using concentrated solar power as a heat source to drive a two-step solar-thermochemical cycle. This process can be described as a way to “re-energize” CO\textsubscript{2} and H\textsubscript{2}O, which are the thermodynamically stable products of hydrocarbon combustion (Figure 1A). Once CO\textsubscript{2} and H\textsubscript{2}O have been re-energized (reduced) to CO and H\textsubscript{2}, traditional syngas chemistry can be applied to convert these products into hydrocarbon fuels.

Solar-driven two-step ferrite (e.g., Fe\textsubscript{3}O\textsubscript{4}) thermochemical cycles are promising as a method for producing H\textsubscript{2} and CO via H\textsubscript{2}O- and CO\textsubscript{2}-splitting, (Steinfeld, 2005; Kodama, 2003; Miller, 2007; Kodama \textit{et al}., 2007; Miller \textit{et al}., 2007), as illustrated in simplified form in Figure 1B. The basic cycles consist of a thermal reduction step (TR; reaction (1)) in which solar thermal energy reduces Fe\textsuperscript{III} to Fe\textsuperscript{II}, i.e., spinel transforms to wüstite, followed by a water-splitting step (WS; reaction (2)), or carbon dioxide-splitting step (CDS; reaction 3) wherein the ferrite spinel is regenerated:

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\begin{align*}
\text{Fe}_3\text{O}_4 & \rightarrow 3\text{FeO} + 0.5 \text{O}_2 \quad (1) \\
3\text{FeO} + \text{H}_2\text{O} & \rightarrow \text{Fe}_3\text{O}_4 + \text{H}_2 \quad (2) \\
3\text{FeO} + \text{CO}_2 & \rightarrow \text{Fe}_3\text{O}_4 + \text{CO} \quad (3)
\end{align*}
\]

Nakamura (1977) first proposed a two-step thermochemical cycle for hydrogen production from water using un-supported iron oxide, however, hydrogen production using the bulk iron oxides is not practical since the TR requires temperatures in excess of the melting point for significant
conversion, and the resulting fusion must be subsequently undone, e.g., by mechanical crushing or milling in order to reactivate the material for successive cycles; supporting Fe$_3$O$_4$ on zirconia or yttria-stabilized zirconia (YSZ) reduces this problem (Kodama et al., 2006; Kodama et al., 2003). Alternative ferrite redox systems using A$_x$Fe$_{3-x}$O$_4$ where $A \neq$ Fe, e.g., $A$ = Mn, Co, Ni, Zn, enable TR at reduced temperature and are now receiving considerable attention (Kodama and Gokon, 2007). The TR can occur as low as 1100 °C, although kinetics usually dictate that temperatures above 1300 °C be used, which are readily achievable using concentrated solar-thermal energy (Allendorf et al., 2008). For WS or CDS, the yields of H$_2$ and CO are maximized in the range 1080 – 1230 °C. These materials however also benefit from a comingling with YSZ. Low surface area monolithic structures of cobalt-ferrite, for example, are essentially un-reactive (Miller et al., 2007). The requirements of large temperature swings as well as spatial/temporal isolation of the TR and WS/CDS reactions to avoid energetic re-combination of O$_2$ and H$_2$/CO were addressed in the design of Sandia’s Counter-Rotating-Ring Receiver Reactor Recuperator (CR5), described in detail elsewhere (Diver et al., 2008). The work described here focuses on elucidating some of the materials fundamentals through in situ characterization as a step towards enabling efficient H$_2$ and CO production.

Significant advances have been made in the field of solar thermochemical H$_2$O- and CO$_2$-splitting technologies using metal oxides, including first-principles DFT modeling (Meredig and Wolverton, 2009); however a lack of fundamental research into the behavior of metal oxides under the high temperature conditions present in these cycles has hampered materials development. Basic questions relating to oxygen transport, surface chemistry, structural changes vs. redox reactions, materials synthesis methods, effects of thermochemical cycling on the material, and the role of supports have still to be addressed. For example, while it is known that the ad-mixing of a high temperature-stable support, such as ZrO$_2$ or YSZ to the ferrite is necessary in order for the process to be repeatedly cycled (Kodama et al., 2006), the interaction between the reactive material (e.g., ferrite) and the support is largely un-explored in the high temperature environment relevant to thermochemical processing.

The current work has probed the complex interaction between the ferrite and the support, with
particular emphasis on investigating solid solubility and phase evolution during thermal processing. The iron oxide/YSZ system was chosen for study based on a combination of its effectiveness in CDS and WS, and because an understanding of the basic $\text{Fe}_3\text{O}_4$ system can be used as a basis to understand the more complex systems such as $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ and other substituted ferrites which are currently under investigation. Fe oxide/YSZ was chosen over Fe oxide/ZrO$_2$ for several practical reasons, the foremost being that an operating thermochemical system would repeatedly cycle through the temperature range at which different ZrO$_2$ polymorphs are thermodynamically favored; the continual transformations would be expected to result in eventual mechanical failure of the active material itself. Also, it is clear from the considerable body of published work describing the physico-chemical properties of iron oxide-ZrO$_2$ (Bechta et al., 2006; Beck and Kaliba, 1990; Berry et al., 1989; Davison et al., 1988; Ghigna et al., 1999; Inwang et al., 1995; Jiang et al., 1999; Lajavardi et al., 2000; Li et al., 1994; Štefanič et al., 2000; Štefanič et al., 2001; Wyrwalski et al., 2005) that this system has a wide variation in Fe solubility ($<2$ to $>30$ mol%) that is a function of both temperature and Fe oxidation state, and also that the presence of dissolved Fe shifts the temperatures of the zirconia polymorph transitions. Hence the cycling material would be expected to perform in an inconsistent, history-dependent manner, confounding the operation of an already complex system. Fewer studies of Fe/YSZ can be found (Hartmanova et al., 1994; Raming et al., 2002; Verkerk et al., 1982; Wilhelm and Howarth, 1979; Shannon and Prewitt, 1969) but it is clear that the Fe does not destabilize the cubic polymorph. The solubility was reported, however, to vary with temperature (Raming et al., 2002). Also, it was anticipated that the oxygen mobility afforded by yttria doping could be an advantage in carrying out the redox chemistry. The temperature range for studying the behavior of iron oxide/YSZ was derived from previous results. From a thermodynamic point of view one would like to drive the thermal reduction at as high a temperature as possible, however 1500 °C is a reasonable upper limit as complications such as loss of Fe due to volatilization become important considerations at higher temperatures. Beyond the relative lack of literature data for the Fe/YSZ system, the fact that this upper temperature limit is significantly higher than has been typical for these iron/zirconia systems is an important factor motivating this work. Additionally, our work (Coker et al., 2011a; Coker et al., 2011b; Ambrosini et al., 2010) has targeted monitoring the materials in situ during simulated thermochemical cycles, as opposed to post-mortem analysis. This simply affords the greatest likelihood that the data obtained accurately reflects the properties of the material under actual high temperature operating conditions. The principal techniques employed in the current work include high-temperature X-ray diffraction (HT-XRD) and thermogravimetric analysis (TGA) under conditions simulating TR/CDS reactions, as well as conducting post mortem analysis with scanning electron microscopy (SEM) and XRD.

**EXPERIMENTAL DETAILS**

**MATERIALS SYNTHESIS**

The yttria ($\text{Y}_2\text{O}_3$) content of YSZ is defined as mol-% $\text{Y}_2\text{O}_3$ in ZrO$_2$; thus 8YSZ has the composition $(\text{ZrO}_2)_{0.92}(\text{Y}_2\text{O}_3)_{0.08}$. Iron contents are quoted as mol-% Fe, i.e., moles$_{\text{Fe}}$ / (moles$_{\text{Fe}}$ + moles$_{\text{Zr}}$ + moles$_{\text{Y}}$). Samples were prepared by either chemical synthesis (CS) or solid state synthesis (SS). For CS, iron(III) nitrate ($\text{Fe(NO}_3)_3\cdot9\text{H}_2\text{O}$, Fisher Certified ACS, 99.8%), yttrium nitrate ($\text{Y(NO}_3)_3\cdot6\text{H}_2\text{O}$, Alfa Aesar 99.9% (REO)), and zirconyl nitrate ($\text{Zr(NO}_3)_4\cdot2\cdot\text{H}_2\text{O}$, Aldrich, 35 wt.-% in dilute HNO$_3$, 99+%)) were dissolved in water at 60 °C. The quantities of reagents depended on the targeted composition, and the co-precipitation was assumed to be a
stoichiometric reaction. This solution was then added slowly to a solution of ammonium hydroxide (NH₄OH, Fisher Certified ACS Plus, 29%, 14.8N) in water also at 60 °C with stirring. The quantity of NH₄OH was such that the concentration of OH⁻ exceeded the concentration of NO₃⁻ for precipitation of the desired composition. Powder samples were mixed with an organic binder consisting of 3.5 wt.-% polyvinyl alcohol and 3.5 wt.-% polyethylene glycol dissolved in water. The powders were mixed thoroughly with the solution, dried at 60 °C, re-ground in a mortar and pestle, and then isostatically pressed into circular discs of approximately 1 g in a pellet press at 3 tons. The binder was then burned out in a vented furnace by heating in air from room temperature to 600 °C at 5 °C min⁻¹, and holding for 2 hours. Calcination involved ramping the temperature from ambient to 1350 °C at 5 °C min⁻¹, holding there for 36 hours, then ramping to 1450 °C at 5 °C min⁻¹, and holding for 4 hours. The temperature was then ramped back to ambient at 5 °C min⁻¹ (nominal). For iron oxide/8YSZ samples prepared by the SS route, Fe₂O₃ (Fisher, 99.5%) was ground with 8YSZ (Tosoh Corporation, TZ-8YS, 99.9%) in a mortar and pestle and mixed thoroughly. The addition of binder, pellet formation, binder burn-out, and calcination were identical to those described for the CS materials.

Preliminary data has indicated that fusion and volatility of iron oxides can occur at 1500 °C, (Ambrosini et al., 2010; Coker et al., 2011b) and the intermediate soak at 1350 – 1375 °C was to allow iron species to diffuse into the 8YSZ and form a solid solution prior to the final sinter at 1450 or 1500 °C. [Fe₂O₃ melting point: 1566 °C (decomp.); Fe₃O₄ melting point: 1597 °C; FeO melting point: 1377 °C] In addition, some physically mixed but un-calcined materials were investigated by HT-XRD to elucidate the changes occurring during initial calcination.

**CHARACTERIZATION**

Room temperature XRD patterns were recorded for finely-ground powders on a Siemens D500 diffractometer using Cu Kα radiation. High-temperature XRD (HT-XRD) experiments were performed using a Scintag PAD X diffractometer (Thermo Electron Inc.; Waltham, MA). This diffractometer is equipped with a sealed-tube source (Cu Kα, λ = 0.15406 nm), an incident-beam mirror optic, a peltier-cooled Ge solid-state detector, and a Buehler hot-stage with Pt/Rh heating strip and surround heater. The hot stage resides within a sealed chamber with an X-ray-transparent beryllium window, and is operable from ambient temperature to 1600 °C, and at gas pressures from 10⁻⁹ to 10³ Torr. An all-metal gas manifold was attached to the inlet of the reaction cell allowing the controlled flow of helium, air, or carbon dioxide through the cell. An oxygen getter furnace (Centorr TM 1B) was installed in the helium inlet line to remove trace levels of oxygen, and an oxygen- and moisture-specific adsorbent purifier bed was used in the CO₂ line. Figure 2 shows a schematic diagram of the HT-XRD experimental setup.

Specimens of typically 20 – 30 mg material were analyzed as thin layers (ca. 50 – 100 μm) of powder on top of single-crystal <100> 9YSZ platelets (10mm x 10mm x 0.5mm, MTI Corporation). Specimen layers were deposited from a slurry of the finely-ground sample in methanol. In situ HT-XRD experiments were conducted at atmospheric pressure, under gas flow rates of 150 sccm. Experiments investigating the solubility and phase evolution of iron oxides in 8YSZ typically involved purging the reaction chamber with He, then ramping the temperature stepwise to 1400 °C and back down to ambient. The temperature intervals were typically 200 °C (ambient to 600 °C), 100 °C (600 to 1000 °C) and 50 °C (1000 to 1400 °C) for both the up- and down-ramps. Diffraction patterns were recorded at each step during a 30 minute isothermal
hold. Heating and cooling ramp rates were set to 20 °C min⁻¹. For the study of phase transformations during TR/CDS cycling, the sample was typically heated stepwise to 1400 °C under He, held at 1400 °C under He for 2 hours, stepped down to 1100 °C under He, then exposed to CO₂ at 1100 °C for 5 hours, or until no further change in XRD pattern was observed. Using this experimental set-up, phase fractions as low as ~ 1 wt.-% could be reliably detected. The temperature calibration was performed using the thermal expansion behavior of known materials (e.g., alumina or Pt) to an accuracy of ±5 °C. Diffraction patterns were collected at 40 kV and 30 mA using fixed slits over a scan range of 20 – 80 °2θ at a step-size of 0.04 °2θ and a count time of 1 s. Subtle displacement of the stage was observed in the process of instrument calibration. The displacement effects (stage moved up upon heating) were repeatable and therefore mapped out through structure refinement of various materials under differing atmosphere conditions. An established sample displacement table as a function of temperature enabled the removal of this systematic instrumentation error from the structural results obtained on each sample.

**Figure 2.** Diagram of the layout of the high-temperature XRD apparatus. A = O₂-getter furnace; B = O₂ absorbent bed; C = X-ray source; D = Pt/Rh heated sample stage; E = solid state detector

Thermogravimetric analysis (TGA) was carried out using a Netzsch 449 F3 Jupiter, equipped with a water-cooled graphite furnace. The sample carrier used for this work was a TGA plate (Al₂O₃), which enabled large samples to be accommodated. Samples for TGA analysis were sintered discs of reactive material (approx. 12mm diameter, 2-3mm thick, weighing ~ 0.8g) placed on top of a sheet of Pt/Rh foil to prevent reaction of the sample with the Al₂O₃ plate. 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 CO₂ was passed through a purification bed (Advanced Specialty Gas Equipment) to remove traces of oxygen prior to entering the TGA. The TGA was evacuated and backfilled with argon a minimum of three times, then the system was allowed to equilibrate at ambient temperature and pressure for an hour prior to starting the measurement. Thermochemical cycling experiments were conducted under heating and cooling rates of 25 °C min⁻¹, and gas flow rates of 140 ml min⁻¹. Generally, the sample was heated under Ar to 1400 °C, held isothermally for 5 hours (TR), cooled to 1100 °C, exposed to CO₂ (120 ml min⁻¹ CO₂ with 20 ml min⁻¹ Ar) and held isothermally for 10 hours (CDS). Each sample was analyzed in the TGA at least two times, and the sample was re-weighed between runs. A baseline run was conducted under identical conditions to those described above but without a sample, and the data from the baseline run was subtracted from all samples runs, resulting in virtual absence of any buoyancy or gas-switching effects in the reported results.
RESULTS AND DISCUSSION
An estimation of the solubility limit of iron in 8YSZ at room temperature was conducted by preparing samples of varying Fe₂O₃:8YSZ mass ratios, calcining them in air at 1375 °C for 48 hrs followed by 1500 °C for 2 hrs, and measuring the lattice parameters of the resulting 8YSZ phase by XRD at ambient temperature. Since the samples were not quenched from the high temperature soak to ambient, there is likely an interplay between the thermal reduction of Fe³⁺ to Fe²⁺ in air at high temperature, and the gradual re-oxidation of some Fe²⁺ as the temperature decreased. The data presented here represents a measure of the solubility of iron at the instantaneous temperature during cool down where the transport of iron species into and out of 8YSZ became kinetically limited. The solubility of Fe³⁺ in 8YSZ is higher than that of Fe²⁺, vide infra, and the solubility discussed here reflects mostly Fe³⁺ in 8YSZ. Dissolution of Fe into 8YSZ causes a decrease in the unit cell size of the 8YSZ, and application of Vegard’s Law (Vegard, 1921) indicated that approximately 9.4 mol-% Fe (equivalent to 6.3 wt.-% Fe₂O₃) could dissolve into 8YSZ under the conditions used, as shown in Figure 3 by the intersection point of the two lines connecting datum points. Samples with iron loadings below 9.4 mol-% Fe are thus assumed to contain only dissolved iron, whereas those with higher loadings contain both dissolved iron and bulk iron oxide species. The SEM and EDS images of iron distribution for 4.5 and 14.5 mol-% Fe samples (SS synthesis) given in Figure 4 corroborate this assumption; images of materials prepared by the CS route show similar results. Prior art reported slightly lower iron solubilities from room temperature XRD analysis: an Fe₂O₃/9YSZ sample which was quenched after sintering at 1200 °C had an estimated solubility of 4.2 mol-% Fe, while slow cooling of a similar sample yielded an iron-solubility one half of that value (Verkerk et al, 1982). Using a multi-step procedure including the formation of a slurry of 8YSZ with aqueous ferric nitrate, freezing the slurry in liquid N₂, and then sintering to 1550 °C, values for iron oxide solubility in 8YSZ as high as 8.7 mol-% Fe were reported, based upon electron microprobe analysis for the detection of phase segregation (Wilhelm and Howarth, 1979). Similar analysis of Fe-doped 8YSZ prepared by firing of dry mixtures of Fe₂O₃ and 8YSZ at 1400 °C for 2 hours revealed a solubility of 7.6 mol-% Fe. Defining the extent of change of unit cell size of 8YSZ (Å) with change of iron content (mol-% Fe) as \( \alpha = \frac{\Delta}{\text{Å}} \text{(mol-% Fe)}^{-1} \), the data for iron oxide-loadings below 9.4 mol-% Fe (Figure 3) can be expressed as \( \alpha = -0.0035 \text{ Å} \text{(mol-% Fe)}^{-1} \). An earlier analysis of this type, targeting iron-doped 8YSZ for oxygen sensors, had plotted the unit cell size from XRD against concentration of iron in solid solution with 8YSZ from electron microprobe data, and reported \( \alpha = -0.0074 \text{ Å} \text{(mol-% Fe₂O₃)}^{-1} \), (Wilhelm and Howarth, 1979); equivalent to -0.0037 Å (mol-% Fe)⁻¹, i.e., in close agreement with our results.
Figure 3 (left). Variation in lattice parameter for 8YSZ with changing iron content after calcination at 1500 °C, from room temperature XRD. The vertical dashed line indicates the limit of solubility at room temperature of iron in 8YSZ.

Figure 4 (right). SEM backscatter images (A, B) and corresponding EDS elemental maps for iron (C, D) for iron oxide/8YSZ containing 4.5 mol-% Fe (A, C), and 14.5 mol-% Fe (B, D) after calcination in air at 1375 °C for 48 hrs followed by 1500 °C for 2 hrs. The scale bars in A-D represent 10 μm, 20 μm, 20 μm and 40 μm, respectively.

A more detailed investigation into iron oxide/8YSZ containing 14.5 mol-% Fe was carried out using in situ HT-XRD. To understand the initial formation of the thermochemically active material during calcination, a freshly-prepared, un-calcined physical mixture of Fe₂O₃ and 8YSZ (1:9 mass ratio, equivalent to 14.5 mol-% Fe) was heated up to 1500 °C stepwise under flowing air in the HT-XRD reaction cell. Once at 1500 °C, the sample was held isothermally for 30 min before cooling down stepwise to ambient temperature. At the beginning of the experiment, Fe₂O₃ was the only iron phase observed. Between 1000 and 1100 °C a trace of Fe₃O₄ was observed, and this phase grew at the expense of Fe₂O₃ as the temperature was raised to 1500 °C. A small amount of residual Fe₂O₃ remained in the material after cooling back to room temperature. The (111) d-spacing of 8YSZ in the iron-containing system at the outset of the experiment coincided with that of pure 8YSZ, as shown in Figure 5. Approximately linear expansion of the lattice with increasing temperature was observed for 8YSZ in the absence of iron, and the heating and cooling branches coincided within experimental error. The d-spacing of 8YSZ with Fe₂O₃ matched that of pure 8YSZ as the temperature was raised until the temperature reached 1000 °C, at which point the slope of the d-spacing versus temperature curve for the iron containing system decreased significantly. The 8YSZ lattice contracts slightly upon ingress of iron, and expands again when it is expelled, as shown in the literature (Verkerk et al., 1982). The contraction of the lattice on increasing iron content is a consequence of the smaller size of the Fe³⁺ cation than Y³⁺ or Zr⁴⁺ (ionic radii: 0.78, 1.01, and 0.84 Å, respectively) (Shannon and Prewitt, 1969). The final (111) d-spacing, recorded at 200 °C upon cooling, was almost 0.01 Å smaller than at the corresponding temperature during heat up. Upon repeating the oxidative heat treatment cycle on this same sample, very little net change in lattice parameter was measured, indicating that the Fe content in the 8YSZ was essentially the same before and after the second cycle. The d-spacing versus temperature plot was approximately linear, except for a narrow hysteresis loop between 900 and 1300 °C. The slight depression of the d-spacing at 900 °C during heating indicated that a small amount of additional iron was diffusing into the
8YSZ, vide infra. However, on reducing the temperature from 1500 °C, the Fe diffused back out of the 8YSZ such that the lattice parameters below 900 °C matched those on the up-ramp. The d(111) spacing of the twice-cycled material (2.954 Å) corresponds to an iron oxide content equivalent to ~ 7.1 mol-%, using the data from Figure 3. For comparison, a sample of un-calced 8YSZ without added iron oxide was cycled to 1500 °C under air. Significant sintering was observed at temperatures above 1150 °C as a sharpening of the initially broad diffraction peaks; however the unit cell size was the same before and after cycling, within experimental error. As a check, we also analyzed the 8YSZ (220) lattice spacings (not shown) which also varied linearly with temperature, and the heating and cooling branches of the plots of lattice spacing versus temperature coincided. Similar thermal cycling of Fe$_2$O$_3$ without 8YSZ in air to 1500 °C did not result in detectable thermal reduction to Fe$_3$O$_4$ in the timeframe of the experiment. Thermodynamics and equilibrium calculations indicate that reduction of Fe$_2$O$_3$ is possible under these conditions. The absence of reduced iron phases in the pure Fe$_2$O$_3$ sample reflects the slow kinetics of the process; in the presence of 8YSZ, the rate of reduction of the iron is enhanced.

Figure 5. Variation in 8YSZ (111) d-spacing during two consecutive heating and cooling cycles for a non thermally-treated physical mixture of Fe$_2$O$_3$ and 8YSZ (14.5 mol-% Fe) under air. The behavior of 8YSZ powder without added iron is also shown for comparison.

A specimen containing 4.5 mol-% Fe (i.e., below the solubility limit), prepared by SS synthesis, was treated to a reduction cycle under He in the HT-XRD, and a contour plot summarizing the results is shown in Figure 6A. The only diffraction peaks observed were those of iron-doped YSZ, and no iron oxide phases were detected during the thermal cycle to 1400 °C under He. Furthermore, the lattice parameters of the iron-doped YSZ were found to vary with temperature in a linear fashion, showing that iron migration in/out of 8YSZ was below detection level. Figure 6B shows a contour plot summarizing the results of a similar reduction cycle carried out on a SS-synthesized specimen containing 27.6 mol-% Fe (i.e., above the solubility limit of Figure 3). The pedigree of this sample prior to the HT-XRD measurement was calcination in air at 1350 °C (36 hours) and 1450 °C (4 hours). The initial room temperature diffraction pattern consisted of a strong 8YSZ signature and a set of weak Fe$_2$O$_3$ peaks only; the remainder of the iron species being assumed to
be in solid solution with the 8YSZ. Once the sample temperature reached 1150 °C, the Fe₂O₃ peaks began to disappear, and were no longer detected by 1200 °C. At 1200 °C the first observation of Fe₃O₄ was made. FeO was not observed during the first cycle, but was first detected during the cooling stage of the second cycle at around 1300 °C. The FeO coexisted with Fe₂O₃. The thermal reduction of iron (III) to iron (II) appears to drive the migration of iron out of 8YSZ, i.e., the latter species appears to have lower solubility in 8YSZ. Similar phenomena have been observed for the solubility of iron in ZrO₂ during crystallization of iron-zirconia co-gels at various temperatures (Inwang et al., 1995; Štefanič et al., 2000). The 8YSZ remained cubic throughout the temperature cycling.

**Figure 6.** HT-XRD intensity plots for iron oxide/8YSZ during thermal reduction cycling under He. A: 4.5 mol-% Fe (one cycle); B: 27.6 mol-% Fe (two consecutive cycles). Intensities are plotted on a square-root scale. Magenta/violet = low intensity; green/orange = high intensity.

The plot of 8YSZ unit cell volume versus temperature for 27.6 mol-% Fe was not linear, nor did the forward branch (heating) coincide with the reverse branch (cooling), as shown in Figure 7. The thin dashed line superimposed on the cycle 1 up-ramp data is a guide to the eye; it has the slope of a linear regression through the data recorded between 1200 and 50 °C during cool-down, which is assumed to represent thermal expansion only (vide infra). The decrease in slope of the forward branch for the iron-containing system around 700 °C is attributed to the migration of Fe or FeₓOᵧ from Fe₂O₃ into the 8YSZ. Taking the difference between the volume data measured at 1000 °C and that projected by the dashed line, and using the results from Figure 3, it is estimated that in the range 800 – 1000 °C the solubility of iron oxide in 8YSZ exceeded 10.4 mol-% Fe. Between 1000 and 1050 °C the unit cell volume returned to that projected by the dashed line, and at temperatures of 1100 °C and above, the volume exceeded the projected value as iron was ejected from the 8YSZ. The Fe content of the 8YSZ decreased to an estimated 8.2 mol-% Fe equivalent at 1400 °C. After heating to 1400 °C the volume versus temperature slope remained almost constant, suggesting that Fe was no longer shuttling in or out of the 8YSZ lattice. The
second cycle was essentially linear during both the up- and down-ramps, with a slight deviation above 1300 °C. Unit cell refinements carried out at room temperature before and after this experiment revealed an overall expansion of the 8YSZ lattice of ~0.01 Å. Multiple thermal reduction cycles on other Fe₂O₃/8YSZ materials showed the same phenomena. Generally, it was found that two cycles to 1400 °C in the HT-XRD resulted in a steady state composition; in a third cycle, convergence of up- and down-ramp lattice parameter data was observed.

**Figure 7.** Variation in 8YSZ unit cell volume during two heating and cooling cycles of iron oxide/8YSZ containing 27.6 mol-% Fe under helium. The thin dashed line superimposed on the cycle 1 up-ramp is provided as a guide for the eye, and has the same slope as the data measured during temperature down-ramp.

The re-oxidation of FeO to Fe₃O₄ in the 27.6 mol-% Fe material by carbon dioxide was also investigated via HT-XRD. A sample which had been previously cycled under He was used, thus the sample began the experiment with a mixture of FeO and Fe₃O₄ as the only detectable iron-containing phases. The results are shown in Figure 8. The relative intensity of the FeO peaks increased slightly during TR and remained stable at 1100 °C, but then disappeared rapidly upon exposure to CO₂. The scan time for each XRD pattern was 10 min (20 – 80 °2θ) to try to capture any transient phases; however the re-oxidation appeared to be complete within the first 10 min of CO₂ exposure. This scan rate resulted in the poor signal-to-noise level in Figure 8.

**Figure 8.** HT-XRD of a TR/CDS cycle using iron oxide/8YSZ containing 27.6 mol-% Fe as the reactive material. Symbols are identified in Figure 6.
Thermogravimetric analyses of numerous samples spanning a range of iron oxide-loadings were conducted under thermochemical cycling conditions, using argon as the inert gas under which thermal reduction occurred, and CO$_2$ to re-oxidize the reduced metal oxide. In contrast to the HT-XRD samples, these materials were analyzed as self-supporting discs of ca. 800 – 1000 mg each which had been sintered in air at 1350 °C (36 hrs) and 1450 °C (4 hrs). Representative TGA results are shown in Figure 9A for samples containing 4.5, 14.5, and 27.6 mol-% Fe, which were synthesized by the SS route. The samples lost mass during thermal reduction due to loss of oxygen, and gained mass on exposure to CO$_2$ as oxygen was extracted from the CO$_2$ to re-oxidize the metal oxide. For all samples, the extent of mass loss during the first thermal reduction (dashed lines) was greater than for the second cycle (solid lines); two subsequent cycles were measured for some samples (total: four cycles), not shown, and these were identical to cycle 2. The data presented above suggests a scenario wherein the greater mass loss during the first TR is due to the fraction of Fe$_2$O$_3$ present (see Figure 6B), which reduces to Fe$_3$O$_4$ and FeO but is not re-formed upon re-oxidation by CO$_2$ under the prevailing conditions (Figure 8); at the start of the second cycle the sample contains no measureable Fe$_2$O$_3$, but cycles from Fe$_3$O$_4$ to FeO (eq. 1) and back to Fe$_3$O$_4$ (eq. 3). Hence the second and subsequent cycles all return to a mass similar to the starting mass of the sample. While this model clearly rationalizes the behavior of the 14.5 and 27.6 mol-% Fe samples, it does not as readily explain the small difference between 1$^{st}$ and 2$^{nd}$ cycle curves for 4.5 mol-% Fe. For the high-loaded samples, a large proportion of iron is observed to exist as a separate iron oxide phase since the iron content is in excess of the solubility limit. This is not the case for the sample containing 4.5 mol-% Fe, i.e., a separate Fe$_2$O$_3$ phase is not directly observed. That the latter sample nonetheless shows a small difference between 1$^{st}$ and 2$^{nd}$ cycle behavior suggests that the distinction between “dissolved” and “bulk” iron oxides may not be truly definitive. Possible explanations for this observed behavior are that 1) the iron oxides are not completely dissolved in the 8YSZ, i.e., some portion of Fe persists in the form of Fe$_2$O$_3$ below the detection limits, and the sample may not have reached equilibrium distribution of Fe; 2) a fraction of dissolved iron oxides do not cycle between Eq. 1 and Eq. 3 as readily as the majority of the dissolved iron species, i.e., some sort of preferred equilibrium between Fe$^{3+}$ and Fe$^{2+}$ exists in the solid solution; 3) there may be an excess of surface or interstitial oxygen in each sample after initial calcination in air which is eliminated during the first thermal reduction step. Re-oxidation of a sample after TGA cycling by heating to 800 °C in air restored the sample to its original state; repeating the TGA measurement after re-oxidation resulted in data which coincided with the original 1$^{st}$ cycle TGA data.

Figure 9B plots mass-gain on re-oxidation against iron loading for the second TGA cycle for a range of CS- and SS-synthesized materials. The plateau in mass-gain once the iron oxide loading exceeded ~ 10 mol-% Fe (CS and SS) shows that the excess (un-dissolved) iron in high-loaded samples does not enhance the sample’s capacity to produce CO. The data in Figure 9B tracks with the changes seen in 8YSZ lattice parameter with iron loading (Figure 3), supporting the supposition that the solid solution is more amenable than the composite material to CO production via this route. The plateaux in CDS mass increase versus Fe-content for both CS and SS materials shows that any iron in excess of the solubility limit contributes only a minor amount to the thermochemical activity of the material under these conditions.
CONCLUSIONS

Since being investigated by Nakamura, iron oxides have been a prototypical material for two-step metal oxide-based thermochemical cycles. The thermochemical cycle undertaken here involved reducing iron oxide/8YSZ under inert atmosphere at 1400 °C, and re-oxidizing with CO\textsubscript{2} at 1100 °C. We aim to apply this understanding to improve materials that enable conversion of H\textsubscript{2}O and CO\textsubscript{2} into H\textsubscript{2} and CO (syngas) using concentrated solar power as the energy source.

*In situ* and *ex situ* XRD confirmed that a fraction of the iron in a composite system dissolved into the 8YSZ lattice. The 8YSZ lattice parameters are sensitive indicators of the migration of Fe; decreasing unit cell volume correlated with insertion of Fe into the 8YSZ lattice, while ejection of Fe resulted in unit cell expansion. Iron was found by HT-XRD to have a higher solubility in the 8YSZ matrix between approximately 800 and 1000 °C (> 10.4 mol-% Fe) than at room temperature (9.4 mol-% Fe). Iron oxides present in concentrations beyond these limits remain as a second phase distributed through the 8YSZ matrix. On heating iron oxide/8YSZ containing > 9.4 mol-% Fe under helium, the un-dissolved iron oxide (initially present as Fe\textsubscript{2}O\textsubscript{3}) reduced...
stepwise to Fe$_3$O$_4$ and then FeO. Upon exposure to CO$_2$ at 1100 °C, the FeO re-oxidized rapidly to Fe$_3$O$_4$, evolving CO. Similar thermal cycling of a sample containing less than 9.4 mol-% Fe also produced CO, but no structural changes were observed by HT-XRD; i.e., the iron species remained dissolved in the 8YSZ. Thermogravimetric analyses during thermochemical cycling of iron oxide/8YSZ containing a range of iron loadings showed that iron loadings above ca. 14 mol-% offered little improvement in reduction/re-oxidation extent. The results suggest that the iron present in solid solution with 8YSZ is more amenable to the thermochemistry of interest than the iron present as a separate, bulk phase within the 8YSZ matrix.

ACKNOWLEDGMENT
This work was supported by the Laboratory Directed Research and Development program at Sandia National Laboratories, in the form of a Grand Challenge project entitled “Reimagining Liquid Transportation Fuels: Sunshine to Petrol,” Ellen Stechel, program manager. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy’s National Nuclear Security Administration under contract DE-AC04-94AL85000. We thank James NMI Griego and Jonathan Torres for help with HT-XRD data collection and analysis.

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