Oxygen Exchange in Dual-Phase La$_{0.65}$Sr$_{0.35}$MnO$_3$–CeO$_2$ Composites for Solar Thermochemical Fuel Production

Alexander H. Bork, Alfonso J. Carrillo, Zachary D. Hood, Bilge Yildiz,* and Jennifer L. M. Rupp*

ABSTRACT: Increasing the capacity and kinetics of oxygen exchange in solid oxides is important to improve the performance of numerous energy-related materials, especially those for the solar-to-fuel technology. Dual-phase metal oxide composites of La$_{0.65}$Sr$_{0.35}$MnO$_3$–$x$%CeO$_2$, with $x = 0$, 5, 10, 20, 50, and 100, have been experimentally investigated for oxygen exchange and CO$_2$ splitting via thermochemical redox reactions. The prepared metal oxide powders were tested in a temperature range from 1000 to 1400 °C under isothermal and two-step cycling conditions relevant for solar thermochemical fuel production. We reveal synergetic oxygen exchange of the dual-phase composite La$_{0.65}$Sr$_{0.35}$MnO$_3$–CeO$_2$ compared to its individual components. The enhanced oxygen exchange in the composite has a beneficial effect on the rate of oxygen release and the total CO produced by CO$_2$ splitting, while it has an adverse effect on the maximum rate of CO evolution. Ex situ Raman and XRD analyses are used to shed light on the relative oxygen content during thermochemical cycling. Based on the relative oxygen content in both phases, we discuss possible mechanisms that can explain the observed behavior. Overall, the presented findings highlight the beneficial effects of dual-phase composites in enhancing the oxygen exchange capacity of redox materials for renewable fuel production.

KEYWORDS: dual-phase composite, synergy, oxygen exchange, thermochemical CO$_2$ splitting, ceria, lanthanum strontium manganite, solar-to-fuel

1. INTRODUCTION

Two-step solar thermochemical fuel production is an auspicious technology to directly convert solar thermal energy into renewable fuels. The technology has the potential to reduce greenhouse gas emissions, while providing a sustainable supply of energy for transportation and industry. We introduce the principle of a two-step solar thermochemical cycle for a metal oxide powder. In the first step, reduction according to eq 1 is carried out at high temperatures (1200–1500 °C) under an inert atmosphere (pO$_2$ below 10$^{-3}$ atm), in a concentrated solar radiation reactor. In a second low-temperature step at 800–1000 °C, the nonstoichiometric metal oxide is oxidized in the presence of H$_2$O and CO$_2$ producing syngas (H$_2$ and CO), see eq 2.

M$_{1-x}$O$_y$ $\rightarrow$ M$_2$O$_{y-δ}$ + δ/2O$_2$(g)  

M$_{1-x}$O$_{y-δ}$ + (δ − γ)H$_2$O(g) + γCO$_2$(g)

$\rightarrow$ M$_2$O$_y$ + (δ − γ)H$_2$(g) + γCO(g)  

Undoped ceria (CeO$_2$) is widely considered as the state-of-the-art material for solar-to-fuel conversion, owing to its fast redox kinetics and phase stability over a wide temperature window. A conversion efficiency from carbon monoxide and water to syngas has been recorded at 5.25%. Indeed, the first experimental demonstration of “solar jet fuel” produced via thermochemical splitting of H$_2$O/CO$_2$ with simulated solar radiation was achieved using CeO$_2$. However, the main drawback is the relatively low fuel productivity per unit mass of metal oxide which is limited by its oxygen exchange capacity and high reduction temperature.

Perovskites have gained significant interest as an additional material class besides binary oxides over the past few years for solar-driven thermochemical cycles; see also the recent review on perovskites by Kubicek et al. The advantage of perovskites is their large oxygen exchange capacity and the ability of the perovskite structure to accommodate a large number of different cations altering the redox properties. Among the recently studied perovskites, lanthanum manganite is one of the materials that has been studied in most detail for solar-to-fuel conversion. For example,
Recently, alternative materials with high yields for thermochemical water splitting that require lower steam excess concentrations have been reported. For example, Zhai et al. introduced a new material class of poly-cation oxides (FeMgCoNi)O₆, which showed favorable higher H₂ yields compared to ceria for different concentrations of excess steam. They confirmed that ceria is invariant to the H₂O/H₂ ratio because of a high thermodynamic driving force for oxidation in the presence of H₂O. The poly-cation oxide displayed a decline in H₂ production when the steam excess concentration was reduced, but the yield was still higher than the one observed for ceria before the steam excess was reduced to H₂O/H₂ = 100:1 for 5 h of oxidation. In addition, Barcellos et al. have reported a promising new perovskite-type oxide, namely, BaCe₀.₅₂₎₂Mn₀.₇₅Oₓ₋₀₆, which retained a higher H₂ yield compared to ceria and the poly-cation oxides for H₂O/H₂ = 285:1. However, the authors note that 10 h on steam are required to produce a comparatively higher yield of H₂ for all tested conditions. Interestingly, the authors found the presence of an unintentional secondary phase (less than 5%) of ceria in their sample. They scale the H₂ productivity linearly with the amount of the ceria phase present in the sample and conclude that it is responsible for less than 1% of the total H₂ production. The progress made for these metal oxides is encouraging for the discovery of new efficient materials. Yet, the challenge remains to find a material, which is crystallographically stable and shows both high fuel production and fast kinetics.

The scope of this work is to investigate a dual-phase composite of a perovskite, namely, La₀.₆₅Sr₀.₃₅MnO₃, and ceria for the solar-to-fuel technology. The idea is to benefit from the large oxygen exchange capacity of the perovskite and purposefully utilize ceria, both as an active oxygen exchange promoter and as a catalyst for metal oxides employed as an oxygen exchange material. For instance, dual-phase composites such as CeO₂–CuMnO₂ displayed improved oxygen release rates for an optimized CeO₂ content when it was tested as an oxygen storage material. With 5 wt % CeO₂, the oxygen storage capacity reached a maximum at ca. 6 wt % for the composite CuMnO₂–5 wt %CeO₂ compared to 4.5 wt % for CuMnO₂ alone at 600 °C. Here, the authors use the term “oxygen diffusion channel” to describe the observed synergistic phenomena, where CeO₂ enhances the reduction of the bulk CuMnO₂ phase. For the same application, Machida et al. studied the relative oxygen content of CeO₂- and CeO₂-grafted Fe₂O₃ by in situ Raman spectroscopy. Under reducing conditions, the oxygen content of the pristine CeO₂ phase decreases, while the CeO₂ phase in contact with Fe₂O₃ had higher oxygen content. The authors ascribed this observation to lattice oxygen transport from Fe₂O₃ to CeO₂ and hypothesized that this exchange could explain the observed synergy.

2. EXPERIMENTAL METHODS

2.1. Materials Preparation

La₀.₆₅Sr₀.₃₅MnO₃–xCeO₂ composites were prepared from powders of LSM (Sigma-Aldrich, particle size 0.6–1.2 μm, catalog number 704261) and CeO₂ (Sigma-Aldrich, nanopowder < 50 nm, 99.95% purity) weighed in appropriate amounts (x = 0, 5, 10, 20, 50, and 100 wt %), mixed in deionized water, and sonicated for 15 min. The aqueous solution was then heated to 90 °C under constant magnetic stirring until the water was evaporated. The resulting powder was dried in an oven for 24 h at 80 °C and the powders were subsequently placed in Al₂O₃ crucibles for annealing in a box furnace (Nabertherm) at 1500 °C for 5 h in air with a heating and cooling rate of 5 °C min⁻¹. All samples were
Samples used for the ex situ structural analysis were placed in an alumina tube and exposed to an identical temperature and atmosphere conditions as in the thermochemical cycling experiments and quenched with a cooling rate of 150 °C min⁻¹ inside an IR Furnace, ULVAC VHT-E44 controlled with a S-type thermocouple.

2.2. Materials Physicochemical Characterization. Structures of all samples were collected by X-ray powder diffraction (XRD) on a PANalytical X’Pert PRO MPD diffractometer. Cu Kα radiation (Ge monochromator) produced with an extraction voltage of 45 kV at 30 mA current was used to scan the samples in a Bragg–Brentano geometry in the range of 2θ = 20° < 2θ < 90° with a spinning speed of 60 rpm, a step width of 0.008°, and irradiation time of 1 s. Unit cell parameters were calculated by full profile Rietveld refinement with PANalytical XPert Highscore Plus software. Scanning electron microscopy (SEM) was completed on a Zeiss Merlin high-resolutionSEM with an acceleration voltage of 5–10 kV. Energy-dispersive X-ray spectroscopy (EDS) elemental mapping was completed with an acceleration voltage of 15.0 kV. Raman spectra were acquired on a confocal WITec Alpha300 R Raman microscope instrument (WITec Germany) equipped with a 457 nm laser, using the 100-fold magnification objective and laser power of 1 mW, together with a spectral resolution of 0.54 cm⁻¹. The collected spectra consisted of six accumulations with an integration time of 30 s.

2.3. Thermochemical Cycling. The experimental setup to determine the oxygen evolution and CO₂ splitting properties of the dual-composite is described elsewhere, ref 1, 5, and a short description is included in Supporting Information S1 for completeness. A temperature program was designed to assess the CO₂ splitting performance of each material at different oxidation temperatures with a cycling program consisting of eight reduction/oxidation cycles. The first three cycles evaluated the CO₂ splitting behavior at three isothermal temperatures (1200, 1300, and 1400 °C) and cycles four to seven were performed under a temperature-swing scheme. Finally, the material was subjected to one more isothermal cycle at 1400 °C. Reduction was carried out at 1400 °C for 20 min, after which the temperature was cooled down to the desired value for the CO₂ splitting. All reactions were performed at atmospheric pressure and the oxygen partial pressure was pO₂ = 5 × 10⁻¹⁵ atm (50 ppm) during reduction in a flow of 300 mL min⁻¹ Ar, as measured by our gas analyzer.

After reaching the programmed temperatures (1000, 1100, 1200, and 1300 °C), CO₂ was injected at a concentration of pCO₂ = 0.5 atm for 20 min. All heating ramps were set to 50 °C min⁻¹. Cooling ramps were set to 50 °C min⁻¹ but were slower in practice because of thermal inertia of the electric furnace, for example, cooling from 1400 to 1000 °C took 18 min, instead of the set time of 8 min. For ex situ structural analysis of the thermochemical cycles, rapid heating and cooling rates were carried out with an infrared furnace with heating rates set at 150 °C min⁻¹. The samples were placed in an alumina tube and the gas atmosphere was controlled by Voetglin mass flow controllers with identical flows as in the thermochemical cycling experiments. A cooling ramp was set to match the 18 min for the cooling before exposure to CO₂.

### 3. RESULTS

3.1. Structural Characterization of LSM−x%CeO₂ Dual-Phase Composites. All prepared dual-phase composite materials are summarized in Table 1. The composites are based on commercially available CeO₂ and La₀.₆₅Sr₀.₃₅MnO₃, which are acquired in the available particle size for ceria (average particle size < 50 nm) and LSM (average particle size 0.6–1.2 μm) to enable mixing on the smallest scale possible. The powders were mixed in deionized water, sonicated for 15 min, and annealed at 1500 °C for 5 h with heating and cooling rates of 5 °C min⁻¹. Here, the high temperature during preparation was chosen to induce possible structural changes before thermochemical cycling experiments.

To investigate the microstructure of the as-prepared perovskite–fluorite composites, we turn to SEM in Figure 1. The constituent end-member materials, that is, LSM and CeO₂, display signs of sintering, in Figure 1a.f. For example, sintering is evident by grain growth and neck formation between neighboring grains of the perovskite and fluorite phases. The composites, as shown in Figure 1b–e, display finer...
grains, where the two phases are in contact, with some observable neck formation between the neighboring grains. The grain size distribution, determined by the SEM image analysis, is shown as an example for x = 50 wt % in Figure 1g. The composite LSMM−50%CeO2 has a grain size average of 0.6 ± 0.2 μm Figure 1g, which is smaller than either LSM or CeO2, with a grain size of 6.5 ± 3.6 and 2.2 ± 0.9 μm, respectively, as shown in Figure 1h. Decreased grain growth suggests that diffusion and sintering was impeded for the dual-phase composites. A similar observation of decreased grain growth was made for a composite of a well-mixed dual-phase composite of Gd-doped ceria and LSM obtained by ball milling and sintering.40,41 The finer structure, that is, grain size and porosity, of the composite materials could suggest enhanced kinetics may be observed for these materials because of a higher specific surface area. However, it is worth noting that for most relevant conditions for solar thermochemical fuel production, that is, temperatures above 1000 °C, the thermodynamics of the oxygen exchange reaction overrules the effects of grain size and porosity.19,27

X-ray powder diffraction patterns of as-prepared La0.65Sr0.35MnO3−x%CeO2 (where x corresponds to weight percent, x = 0 to 100%) composites are presented in Figure 2.

Figure 2. Powder X-ray diffraction patterns of the as-prepared La0.65Sr0.35MnO3−x%CeO2 composites with x = 0, 5, 10, 20, 50, and 100 wt % in figures (a–f), respectively. In the XRD pattern of the LSM−50%CeO2, (e) all peaks are indexed by the constituent phases La0.65Sr0.35MnO3 and CeO2, with the rhombohedral structure (R3̅m space group) for the perovskite and the cubic structure (Fm̅3m space group) for ceria. Subfigure on the right is a zoom of the two peaks at a 2θ range of 44−50° corresponding to the (024) plane of the perovskite and (022) plane of the ceria structure.

The pattern of the commercial La0.65Sr0.35MnO3 (LSM) and CeO2 powders can be indexed to a pure rhombohedral structure and the cubic fluorite structure, respectively, in agreement with the literature.37,40 For the powder composites of La0.65Sr0.35MnO3−x%CeO2, all peaks may be identified according to their constituents La0.65Sr0.35MnO3 and CeO2 and no impurity phases are detectable. An exemplified Rietveld refinement fit of the LSM−50%CeO2 is shown in Supporting Information Figure S1, confirming the phase composition of La0.65Sr0.35MnO3 and CeO2.

Raman spectroscopy reveals insights on the vibrational bonds of the composite and oxygen nonstoichiometry.41 In Figure 3, pure ceria is compared to the LSM−50%CeO2 sample: the characteristic symmetric stretching mode observed at 464 cm−1, for the as-prepared CeO2 sample is attributed to the F2g Raman mode which can be viewed as a breathing mode of O atoms around the cerium cation,42−45 see also the recent review for ceria near-order spectroscopy details.46 In the spectra acquired of the composite, x = 50 wt %, the broad Raman bands typically observed at 400−800 cm−1 for the LSM perovskite are not distinguishable because of a strong signal of a distinct peak at 461 cm−1. This latter peak is ascribed to the F2g peak of CeO2 shifted to a lower wavenumber accompanied by peak broadening with a change in full width half maximum (fwhm) from 7 to 13 cm−1. Both Mn and La are present in the perovskite, and small doping concentrations of Mn or La in CeO2 can result in a peak shift to lower wavenumbers and peak broadening,44,47 which is ascribed to lattice expansion. However, the two weak shoulders at the higher wavenumbers (532 and 589 cm−1) are commonly observed only for lanthanum-doped ceria44 and +3 dopants substituting Ce, which introduces defect vibrational bands.48 According to a systematic Raman study of rare earth (La, Pr, Nd, Eu, Gd, and Tb) doping in ceria by McBride et al.44 and a recent review by Schmitt et al.,46 La-doping results in a gradual shift of the F2g peak to lower wavenumbers and an increase in the relative height of the shoulder with respect to the F2g peak. Based on the observed shift of Δ = 2.4 cm−1 for the F2g peak and the available literature, we estimate that ceria in the composite has a small doping concentration of La between 1 and 5 atomic % after processing (via sintering of the ceramic).

In summary, the structural analysis, XRD, SEM, and Raman spectroscopy confirm a dual-phase composite that remains in two distinct phases, which are intermixed at the micron scale. Indications of a low doping concentration of La in the ceria phase can be observed, that is lower than 5 atomic % based on a conservative estimate by the Raman spectroscopic analysis. We now turn to thermochemical cycling experiments to test how the dual-phase composites perform under conditions relevant for solar-to-fuel conversion.

3.2. Oxygen Release and CO2 Splitting of LSM−x% CeO2 Dual-Phase Composites. Solar thermochemical cycling properties of the composite LSM−x%CeO2 is assessed by their O2 evolution and CO2 splitting 1000−1400 °C, as shown in Figure 4. The reaction times for reduction and oxidation of 20 min are chosen to match earlier reports and provide an assessment within a window of efficient operation.
of future solar thermochemical reactors. For details and results of the entire temperature-screening program, including splitting in isothermal cycles and conventional two-step cycles, see Figure S2. Oxygen release of the composites during heating from 1000 to 1400 °C is presented in Figure 4a. Introducing 5 wt % of CeO2 in the dual-phase composite improves the O2 peak evolution by 92% to a value of 0.24 mL g⁻¹ min⁻¹ compared to LSM. The dual-phase composites display further synergistic oxygen release kinetics for increased CeO2 content, reaching a maximum among the tested materials of 0.31 mL g⁻¹ min⁻¹ for CeO2, x = 0, 5, 10, 20, 50, and 100% for heating from 1000 to 1400 °C with a heating rate of 50 °C min⁻¹. (b) CO evolution of LSM–xCeO2, x = 0, 5, 10, 20, 50, and 100% for CO2 splitting at 1400 °C. The fluorite–perovskite composite trends were zoomed in the inset for the sake of clarity.

Figure 4. O2 and CO evolution of La0.65Sr0.35MnO3–xCeO2 during a thermochemical cycle 1000–1400 °C. (a) O2 evolution of LSM–xCeO2, x = 0, 5, 10, 20, 50, and 100% for heating from 1000 to 1400 °C with a heating rate of 50 °C min⁻¹. (b) CO evolution of LSM–xCeO2, x = 0, 5, 10, 20, 50, and 100% for CO2 splitting at 1400 °C. The fluorite–perovskite composite trends were zoomed in the inset for the sake of clarity.

The CO evolution is plotted for all tested materials in Figure 4b for CO2 splitting at 1000 °C. The maximum CO evolution rate improves gradually to 0.9 mL g⁻¹ min⁻¹ for x = 50 wt %, which is ca. 4-fold higher than that of LSM with a peak rate of 0.2 mL g⁻¹ min⁻¹. For comparison, state-of-the-art CeO2 displays a peak rate of 10.6 mL g⁻¹ min⁻¹ in Figure 4b. Evidently, the constituents of the composite illustrated in Figure 4 display an intimate interaction in terms of CO evolution. We note that at higher temperatures (1200 °C and above) CO2 splitting results in simultaneous production of O2. This is ascribed to the thermolysis of CO2 (CO2 → CO + 1/2 O2) which is in agreement with earlier observations and discussed in detail in our previous work.

To further probe the interaction between CeO2 and LSM in the composite, the accumulated CO production is plotted as a function of time for the same conditions for LSM–50%CeO2 in Figure 5. The higher oxygen release of the composite has a beneficial effect on the accumulated CO evolution. For 20 min CO2 splitting, the total evolved CO is 2.7 mL g⁻¹ for the composite, which is 17 and 19% higher than 2.3 and 2.1 mL g⁻¹ of the distinct components LSM and CeO2 respectively. The total evolved CO of LSM after 20 min is lower than some values reported in the literature because these works exposed LSM to CO2 for a longer time of 40 min or more.

In summary, the interaction between the two phases has an adverse effect on the maximum fuel rate, whereas it has a synergistic effect on the peak O2 evolution rate and total produced CO fuel.

3.3. Structural Analysis of Composites after Thermochemical Cycling. To study the microstructural and crystal structure evolution of the dual-phase composite after thermochemical cycling, we turn to SEM, EDS, and XRD analyses. Comparing the SEM image before and after thermochemical cycling, as shown in Figures 2e and 6a, respectively, the composites display grain growth after thermochemical cycling. Changes in the grain size are discussed in detail in our previous work.

Figure 5. Cumulative CO production evolution of composite La0.65Sr0.35MnO3–50%CeO2, x = 50%, compared to the constituent phases La0.65Sr0.35MnO3 and CeO2. CO2 splitting was performed at 1000 °C with a CO2 concentration of 50 vol % and after reduction at 1400 °C in an Ar atmosphere.
CeO₂ changes grain size from 0.6 ± 0.2 to 1 ± 0.4 μm, albeit, it is still smaller than ceria which displays a stable grain size before and after cycling of 2.2 ± 0.9 and 2.0 ± 0.9 μm. One could anticipate the kinetics of the composite to decrease during thermochemical cycling because the microstructure of the cycled materials has coarsened. On the contrary, comparing Cycle 3 and Cycle 8, that is, isothermal CO₂ splitting at 1400 °C, there is no measurable difference in the kinetics of the fuel production peak. Lastly, distribution of metal cations captured in the EDS linescan, as shown in Figure 6d, of the composite material indicate clear and distinct CeO₂ and LSM grains. The gradient of the metal cation concentration in the grain boundary may be interpreted as interdiffusion of metal cations from each phase or a tilt of the grain boundary with respect to the electron beam.

XRD patterns of LSM–50%CeO₂ and that of the composite after thermochemical cycling (1000–1400 °C) as well as 20 isothermal CO₂ splitting cycles at 1400 °C are presented in Figure S2. No structural changes were observed upon the cycling of the composite material with 50 wt %CeO₂, on comparing Figure S3a-c. Two peaks arising at 2θ = 26 and 35°, as shown in Figure S3c, are ascribed to the sample powder bed made of Al₂O₃ used for holding the composites in the fixed-bed reactor, which were mixed when extracting the sample from the reactor tube. Furthermore, we probe the stability of the best performing dual-phase composite by measuring the CO evolution for 20 isothermal cycles at 1400 °C, as shown in Figure S4. Here, the peak CO evolution displays no changes over the tested cycles, which is a positive indicator for the longevity of the dual-phase composite.

Thus, SEM, EDS, and XRD after thermochemical cycling and durability test of 20 cycles collectively confirm a dual-phase composite that remains in two distinct phases with no measurable additional phases besides the fluorite and perovskite structure.

3.4. Ex Situ Structural Analysis of Dual-Phase Composites through Thermochemical Cycling. To gain further insights into the intimate and synergic interaction between the constituent phases of the composite, we investigate the structural changes upon reduction and oxidation during the thermochemical cycling experiments by ex situ Raman spectroscopy and powder X-ray diffraction.

Figure 7a shows the thermochemical programs applied to imitate the conditions during the thermochemical experiments, where a rapid cooling rate of 150 °C min⁻¹ is utilized to “quench” the extent of reduction at important points during the thermochemical experiment for the ensuing ex situ Raman spectroscopy. The F₂g Raman peak signature for ceria of the dual-phase composite is plotted in Figure 7b, while the fitted peak position, and (d) fwhm of F₂g mode of ceria in composite for four different thermochemical programs. (1) As-prepared, (2) reduced for 60 min at 1400 °C, (3,4) represent reduction at 1400 °C followed by cooling with rate of 20 °C min⁻¹ to 1000 °C before and after exposure to 50 vol % CO₂ for 20 min. Error bars reflect standard deviation of the fitted parameter to Raman spectra in different spots on the same sample.
oxygen nonstoichiometry of both phases in the dual-phase composite.

Figure 8 displays results of an \textit{ex situ} X-ray diffraction analysis of the dual-phase composite, with the thermochemical programs, similar to the \textit{ex situ} Raman study, as shown in Figure 8a. Full Rietveld refinement has been carried out for all four samples, as shown in Figures S1 and S5–S7. We exemplify the changes in the crystal structure by highlighting a narrow 2\(\theta\) range to show the shift of the (111) peak of CeO\(_2\), as shown in Figure 8b, in the dual-phase composite as a function of the program it has been exposed to. In the course of heating to 1400 °C, the peak shifts to lower angles, while a shift to higher angles is observed during cooling and after exposure to CO\(_2\). We quantify those changes by the determination of the unit cell volume of ceria and the LSM phase in the composite by full Rietveld refinement, as shown in Figure 8c,d, respectively. As expected, there is an inverse proportionality between the (111) peak of ceria and the unit cell volume, as shown in Figure 8b,c. An increase in the unit cell volume from 159.68 to 159.86 Å\(^3\), that is, removal of oxygen, of ceria is reported in the course of reduction to 1400 °C, as displayed in Figure 8c and Table S1, which is in agreement with the literature.\(^{52}\) For further discussions of origin of lattice expansion in CeO\(_2\) upon reduction see Marrocchelli et al.\(^{52}\) and Muhich.\(^{53}\) During cooling, the unit cell volume of the ceria phase decreases, that is, due to incorporation of oxygen, to 159.82 Å\(^3\) which is consistent with our results from Raman spectroscopy and earlier findings in spectroscopy.\(^{54}\) The LSM phase also displays lattice expansion after reduction at 1400 °C, apparent by a unit cell volume increase from 349.87 to 354.05 Å\(^3\), as shown in Figure 8d. Lattice expansion upon introduction of O vacancies in the LaMnO\(_{3-\delta}\) phase has likewise been reported in the literature.\(^{54}\) Interestingly, the lattice slightly expands, indicative of oxygen removal, during cooling to 354.16 Å\(^3\) contrary to the CeO\(_2\) phase. After exposure to CO\(_2\), both phases display a decrease in the unit cell volume corresponding to the oxygen uptake.

In summary, the \textit{ex situ} analysis confirms that the introduction of oxygen vacancies in the CeO\(_2\) and LSM result in lattice expansion of both crystal structures when tested for the solar-to-fuel conversion temperature range of 1000 to 1400 °C. Most notably, the CeO\(_2\) phase is oxidized while cooling to 1000 °C as displayed by two independent techniques, based on bond vibrational Raman spectroscopy and XRD, whereas the perovskite phase is slightly reduced during this step of the thermochemical cycle.

3.5. Observed Synergetic Interaction of Components in the Dual-Phase Composite. Having established that dual-phase composites of the fluorite and perovskite structure display synergetic oxygen exchange under conditions relevant for solar thermochemical fuel production between 1000 and 1400 °C, we now evaluate different hypotheses to explain the observed oxygen exchange behavior.

Three mechanisms are evaluated qualitatively, based on the literature, to provide a possible mechanism for the synergetic O\(_2\) evolution, total CO production, and the adverse low value of the maximum CO evolution rate observed for the dual-phase composites. The first explanation (i) is through doping, either Ce-doping in the LSM phase or La-doping in the ceria phase; the second (ii) is through reversible CeO\(_2\) reduction followed by Ce\(^{4+}\) incorporation in the perovskite lattice during reduction/oxidation with the release/uptake of gaseous oxygen; the third (iii) is by ceria acting as an oxygen diffusion channel between the perovskite phase and the surrounding atmosphere.

First, we consider the literature on doping of the perovskite and ceria phase tested for solar thermochemical cycling and assess qualitatively whether doping can explain the observed trends. Jiang et al.\(^{55}\) investigated the substitution of Sr by Ce on the A-site of the La\(_{0.7}\)A\(_{0.3}\)FeO\(_3\) perovskite. For La\(_{0.7}\)Ce\(_{0.3}\)FeO\(_3\), the maximum oxygen release rate was 10% higher, while the maximum CO evolution rate was three times higher. The authors remark a “tiny” impurity concentration of the CeO\(_2\) phase in their synthesized perovskite, presumably due to the different ionic radii of strontium and cerium. Based on related studies of A-site substitution in perovskites, we expect that a lower content of Ce in a solid solution of La\(_{0.7}\)Sr\(_{0.3}\)Fe\(_3\)O\(_y\) would have oxygen release characteristics that lie in between its endmembers La\(_{0.7}\)Sr\(_{0.3}\)FeO\(_3\) and La\(_{0.7}\)Ce\(_{0.3}\)FeO\(_3\).\(^{18}\) In other words, a small doping concentration of cerium in the perovskite would result in a maximum oxygen release rate that is between 0 and 10% higher than La\(_{0.7}\)Sr\(_{0.3}\)FeO\(_3\). In our experiment, we show that a composite with a nominal 5 wt %CeO\(_2\) (\textit{i.e.}, LSM=5%CeO\(_2\)) results in a 92% increase in the maximum oxygen release rate. This result is significantly higher than the 10% observed for La\(_{0.7}\)Ce\(_{0.3}\)FeO\(_3\), which includes a trace amount of the CeO\(_2\) phase. From this qualitative analysis, we reason that a small doping amount of cerium in LSM of the dual-phase composite would not be responsible for the significant increase in the maximum oxygen release rate. Furthermore, LSM=50%CeO\(_2\) displays a 5-fold decrease in the maximum CO evolution rate compared to the weighted average which does not match with

![Figure 8](https://dx.doi.org/10.1021/acsami.0c04276)
the trend observed for the reference case of La0.7Ce0.3FeO3 showing a higher rate.

Recently, Haeussler et al.36 reviewed the literature on various dopants in CeO2 and its performance for solar thermochemical cycles. According to this review, pure ceria and lanthanum-doped CeO2 have similar performance. Specifically, Jiang et al.57 have shown that the CO rate generation profile of La0.12Ce0.88O2 is similar to undoped CeO2. This result is far from the trends in our experiments considering the CO evolution curve of the LSM–50%CeO2 composite, as shown in Figure 4b. Here, the peak CO evolution rate is 0.9 mL g⁻¹ min⁻¹, which is more than 5 times lower compared to a weighted average of 5.4 mL g⁻¹ min⁻¹ for the two individual phases LSM and CeO2. For the high temperatures relevant for solar thermochemical cycles, it has been established that the oxygen release profiles or thermochemical splitting profiles scale proportionally with the doping or substitution content.18 Because our analyses show that the two phases are doped by low contents and based on the available literature we reason that the effect of doping would be too small to be the dominant mechanism for the observed trends. Instead, there must be another mechanism responsible for the significant changes observed here.

Turning to the second hypothesis (ii), where CeO2 is reduced to metallic cerium and then being incorporated reversibly in the perovskite phase during the high-temperature step and oxidized back to the cerium oxide phase during the oxidation step. The lower peak fuel rate observed for the 50 wt % dual-phase composite, as shown in Figure 4, could be explained by Ce³⁺ ions being dissolved slowly from the perovskite phase and forming CeO2. This change would imply that the amount of the ceria phase in the composite should decrease during reduction and increase reversibly to 50 wt % during oxidation. Ex situ XRD results reveal that the wt % of ceria in the composite is almost invariant to the temperature change, as shown in Table S1.

Lastly, we consider mechanism (iii) which relies on ceria functioning as an “oxygen diffusion channel” or “gateway” for lattice oxygen in the bulk of the perovskite phase to the surrounding gas phase. This description is similar to the terminology used by Huang et al.29 and Machida et al.34 to describe, the synergetic oxygen release in dual-phase composites of CeO2 and CuMnO2, or Fe2O3 tested below 1000 °C as oxygen storage materials. The low maximum peak CO rate observed during CO2 splitting of the composite arises because ceria is oxidized (by oxygen from the perovskite) during cooling from 1400 to 1000 °C, which matches with our ex situ Raman spectroscopy and ex situ powder X-ray diffraction results. When the ceria phase is oxidized its capacity for CO production thus decreases. The oxygen change based on mechanism (iii) with preferential oxidation of the ceria phase is highlighted in Figure 9.

Preferential oxidation of ceria compared to the perovskite phase may be explained from a thermodynamic perspective considering the difference in the Gibbs free energy change oxidation of the respective metal oxides, ΔGoxidation. We investigate this hypothesis further, as shown in Figure 10, where it can be observed that the Gibbs free energy change of oxidation in the presence of oxygen is more negative for the CeO2 phase compared to the perovskite phase below 1200 °C, that is, ΔGoxidation,CeO2 < ΔGoxidation,LSM.

In other words, oxygen gains more energy by oxidizing ceria compared to the perovskite. This analysis indicates that, during reduction, CeO2 may function as a fast oxygen diffusion channel that facilitates faster overall reduction of the perovskite phase, due to ceria acting as a preferential intermediate host for oxygen from the perovskite phase. However, this mechanism still warrants further experimental work to prove unequivocally.

4. CONCLUSIONS

In this work, we show enhanced oxygen exchange in the La0.65Sr0.35MnO3–xCeO2 composite system for solar thermochemical cycling compared to pure ceria and the pure perovskite. The dual-phase composites were successfully fabricated via co-sintering, evident by two distinct phases mixed at the micron scale. This is the first work testing the oxygen exchange for solar thermochemical fuel production using a dual-phase composite based on nonvolatile non-stoichiometric metal oxides, compared to earlier composites relying on volatile or nonvolatile stoichiometric metal oxides.
With the La_{0.65}Sr_{0.35}MnO_3−50%CeO_2 dual-phase composite, we report a synergistic effect for the solar-to-fuel process in terms of higher oxygen release and higher CO conversion yield in the syngas production. Conversely, the fast oxygen exchange had an adverse effect on the peak CO evolution rate for solar-to-fuel production. The peak O_2 evolution rate is 0.31 mL g\(^{-1}\) min\(^{-1}\) in the course of heating to 1400 °C for the La_{0.65}Sr_{0.35}MnO_3−50%CeO_2 dual-phase oxide, which is 45 and 100% higher than CeO_2 and LSM, respectively.

Structural analyses by XRD, Raman spectroscopy, SEM, and EDS confirm a dual-phase composite that remains in two distinctive phases during thermochemical cycling. We report that there is an indication of minor cation interdiffusion leading to a small doping concentration of less than 5 mol% of La in the ceria phase after processing. Ex situ Raman and XRD analyses provide understanding to the synergistic oxygen exchange via a qualitative determination of the extent of reduction at relevant stages during thermochemical cycling. During the cooling step, that is, from 1400 to 1000 °C, it is shown that the perovskite phase is reduced, while ceria oxidizes. A likely mechanism to explain this behavior is the transport of oxygen from the perovskite acting as an oxygen reservoir at temperatures above 1000 °C, showing that the perovskite phase is oxidized. A likely mechanism to explain this behavior is the transport of oxygen from the perovskite to ceria. This effect can be explained further from a thermodynamics perspective, showing that the oxidation of ceria is thermodynamically favorable over the oxidation of the perovskite phase. A similar argument applies to the reduction step, where ceria can facilitate fast reduction of the perovskite phase. Thus, we describe how ceria can act as a “gateway” or “oxygen diffusion channel” for fast oxygen exchange from the perovskite acting as an oxygen reservoir at temperatures above 1000 °C. This observation, however, warrants more work to probe and prove the underlying mechanism.

The solar-to-fuel technology is facing a tremendous challenge in finding optimized materials that enhance the kinetics and increase the oxygen exchange capacity to improve the overall cycle efficiency. Dual-phase composites based on perovskites and cerium dioxide define a new strategy to undertake that challenge and are feasible for processing via co-sintering. This work is the proof of concept for the solar-to-fuel technology using ceria to enable a higher and faster utilization of the large oxygen exchange capacity of a perovskite model material La_{0.65}Sr_{0.35}MnO_3. Owing to the ability of perovskites to host a wide variety of different elements in the crystal structure, it is possible to design perovskite materials that are even more efficient in combination with ceria. This potential should promote further studies to explore the underlying mechanism for the observed synergy in detail.

**ASSOCIATED CONTENT**

**Supporting Information**
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c04276.

Description of fixed-bed reactor setup, Rietveld refinement fits, thermochemical program with O_2 and CO evolution profiles for all tested materials, that is, La_{0.65}Sr_{0.35}MnO_3−x%CeO_2, x = 0, 5, 10, 20, 50, 100, XRD patterns of La_{0.65}Sr_{0.35}MnO_3−50%CeO_2 as-prepared, cycled and after 20 cycles, thermochemical durability test, and table of lattice volume and LSM wt% determined by Rietveld refinement (PDF).

**AUTHOR INFORMATION**

*Corresponding Authors*

Bilge Yildiz — Laboratory for Electrochemical Interfaces, Department of Materials Science & Engineering and Laboratory for Electrochemical Interfaces, Department of Nuclear Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States; orcid.org/0000-0002-2688-5666; Email: byildiz@mit.edu

Jennifer L. M. Rupp — Electrochemical Materials Laboratory, Department of Materials Science and Engineering and Electrochemical Materials Laboratory, Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States; orcid.org/0000-0001-7160-0108; Email: jrupp@mit.edu

**Authors**

Alexander H. Bork — Electrochemical Materials Laboratory, Department of Materials Science and Engineering and Laboratory for Electrochemical Interfaces, Department of Materials Science & Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States; orcid.org/0000-0003-4513-9682

Alfonso J. Carrillo — Electrochemical Materials Laboratory, Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States; orcid.org/0000-0002-5576-9277

Zachary D. Hood — Electrochemical Materials Laboratory, Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States; orcid.org/0000-0002-5720-4392

Complete contact information is available at: https://pubs.acs.org/10.1021/acsami.0c04276
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REFERENCES


