Thermochemical splitting of CO₂ using solution combustion synthesized lanthanum–strontium–manganese perovskites

Gorakshnath Takalkar a, Rahul R. Bhosale a,*, Fares AlMomani a, Suliman Rashid a, Hazim Qiblawey b, Mohammed Ali Saleh Saad a, Majeda Kharmaish S a, Gopalakrishnan Kumar b, Ram B. Gupta c, Rajesh V. Shende d

a Department of Chemical Engineering, College of Engineering, Qatar University, P. O. Box – 2713, Doha, Qatar
b Institute of Chemistry, Bioscience and Environmental Engineering, Faculty of Science and Technology, University of Stavanger, Box 8600 Forus, 4036 Stavanger, Norway
c Department of Chemical and Life Science Engineering, Virginia Commonwealth University, Richmond, VA 23284, United States
d Department of Chemical and Biological Engineering, South Dakota School of Mines and Technology, Rapid City, SD 57701-3995, United States

ARTICLE INFO

Keywords:
- LSM perovskites
- CO₂ splitting
- Solar energy
- Thermochemical cycles
- Solution combustion synthesis
- Thermogravimetric analysis

ABSTRACT

Redox reactivity of La₁₋₀.₃Srₐ₀.₇MnO₃ (LSM) perovskites towards a solar thermochemical CO₂ splitting (CS) cycle is investigated. The LSM perovskites are synthesized via a solution combustion synthesis (SCS) method using glycine as the reducing agent. Multiple analytical techniques are used for the structural characterization of the LSM perovskites. Thermogravimetric thermal reduction (TR) and CS cycles (in three sets: one, three and ten cycles) are conducted to estimate the amounts of O₂ released (nO₂) and CO produced (nCO) by each LSM perovskite. Higher nO₂ by each LSM perovskite, as compared to the nCO during the first cycle. The nO₂ is decreased, and the re-oxidation capacity of each LSM perovskite is improved from cycle one to three. In terms of the average nO₂ and nCO, from cycle 2 to cycle 10, the La₀.₆₇Sr₀.₃₃Mn₀.₆₂O₂.₉₉₃ (214.8 μmol of O₂/g-cycle) and La₀.₃₀Sr₀.₇₀Mn₀.₃₀O₂.₉₈₂ perovskites (342.1 μmol of CO/g-cycle) are observed to have the uppermost redox reactivity. The redox reactivity of all the LSM perovskites (except for La₀.₈₈Sr₀.₁₁Mn₀.₃₀O₂.₉₈₀) is recorded to be higher than that of the widely studied CeO₂ material.

1. Introduction

Meeting the ever-increasing worldwide demand for energy by using solar fuels produced via H₂O (WS)/CO₂ splitting (CS) reactions is one of the feasible approaches for harnessing the renewable and sufficiently available solar energy [1,2]. This process exploits the concentrated solar power to drive the high-temperature thermal reduction (TR) of metal oxides (MOs) [3]. Effectively, by applying this technology, the storage of solar energy in the form of chemical energy is possible [4,5]. This stored chemical energy is preferred as it can be transported and stockpiled for a long time without any degradation. Recently, Marxer et al. [6] developed a first of its kind pilot-scale set up for the production of 700 L of solar syngas via 291 stable redox cycles.

According to the studies so far, the process efficiency of the thermochemical WS/CS process heavily depends on the redox properties of the MOs [7]. The desirable characteristics of a good MO include high H₂/CO yield, faster TR and re-oxidation (RO) kinetics, lower cycle time, higher thermal stability over multiple cycles, elevated O₂ diffusion rates from the surface to the bulk of the MO, and a smaller temperature difference between the TR and RO steps. The redox materials investigated for both WS and CS reactions include volatile MOs such as zinc oxide [8-10] and tin oxide [11,12], and non-volatile MOs for instance, iron oxide [13-15], ferrites [16-19], doped ceria [20-23], and herylinate [24,25]. Among these, ceria and doped ceria appears to be a beneficial choice, as these oxides possess the anticipated material properties.

In recent years, perovskite-based oxides [26-28] were investigated for thermochemical WS/CS reactions with an assumption that they will outperform ceria. Among these perovskites, the La-Sr-Mn-based (LSM) perovskites were inspected for the production of both H₂ and CO via WS and CS cycles. For the TR temperature range of 1523 to 1923 K, the La₀.₇₀Sr₀.₃₀MnO₃ (LSM30) and La₀.₆₀Sr₀.₄₀MnO₃ (LSM40) perovskites showed higher TR yield as compared to ceria [29]. According to Yang...
et al. [30], the La$_{1-x}$Sr$_x$MnO$_3$ materials ($x = 0$ to 0.5) represented a higher TR yield as a function of an increase in the atomic concentration of Sr. Demont and Abanades [31] synthesized and tested the La$_{0.35}$Sr$_{0.65}$MnO$_3$-δ, La$_{0.45}$Sr$_{0.55}$MnO$_3$-δ, La$_{0.65}$Sr$_{0.35}$MnO$_3$-δ, and La$_{0.85}$Sr$_{0.15}$MnO$_3$-δ towards the CS reactions (in one cycle) and reported La$_{0.5}$Sr$_{0.5}$MnO$_3$-δ as the best choice for producing a maximum amount of O$_2$ ($n_{O_2} = 195$ μmol/g-cycle) and CO ($n_{CO} = 242$ μmol/g-cycle). Dey and Rao [32] studied the La$_{1-x}$Sr$_x$MnO$_3$ ($x = 0.3$, 0.4, and 0.5) towards splitting of CO$_2$ at isothermal operating conditions and observed high CO production ($n_{CO} = 134$ μmol/g-cycle) by La$_{0.25}$Sr$_{0.75}$MnO$_3$ at 1400 °C (partial pressure of O$_2$ = 10$^5$ atm and partial pressure of CO$_2$ = 1 atm). Dey and Rao [32] further reported that the La$_{0.5}$Sr$_{0.5}$MnO$_3$ was capable of producing ~three times higher CO than the CeO$_2$ at 1500 °C. As per the several studies, the rise in the Sr content was responsible for an increase in the reduction extent and decreased in the re-oxidation yield [29,31,33–38].

As per the literature review, selected LSM compositions were investigated for solar thermochemical fuel production. It is essential to find the finest combination of LSM perovskite, which is capable of producing the maximum amount of solar fuel in multiple thermochemical cycles. In this regard, this work concentrates on the exploration of the TR and RO behavior of the LSM perovskites, i.e., La$_{1-x}$Sr$_x$MnO$_3$ and La$_{1-x}$Sr$_x$MnO$_3$, towards the CS reactions (Fig. 1) and CO production (Fig. 2). Details allied with the TGA set-up were already reported elsewhere [40]. A platinum pan was placed inside the furnace (surrounded by an alumina tube) to support the reference and the sample alumina crucibles. The flowrates of the gases were monitored and controlled by using mass flow controllers, and the temperature was regulated by using a Pt–Rh type-B thermocouple. Thermogravimetric CS experiments were carried out by using approximately 50 mg of the LSM perovskite powder. The drift in the mass of the LSM perovskite during the TR and CS steps was recorded by using the Calisto software. Based on the variation in the mass during both steps and following equations, the amounts O$_2$ released ($n_{O_2}$) and CO produced ($n_{CO}$) by each LSM perovskite were estimated.

\[
\frac{n_{O_2}}{M_O \times m_{LSM}} = \frac{\Delta m_{\text{loss}}}{\Delta m_{\text{gain}}} \tag{1}
\]

\[
\frac{n_{CO}}{M_C \times m_{LSM}} = \frac{\Delta m_{\text{gain}}}{\Delta m_{\text{loss}}} \tag{2}
\]

In the above equations, the $\Delta m_{\text{loss}}$ and $\Delta m_{\text{gain}}$ represents the loss and gain in the mass of the LSM perovskites during the TR and CS steps. The molecular weights of the O and O$_2$ are represented as $M_O$ and $M_{O_2}$. Likewise, the amount of LSM perovskite used during the TGA experiments is presented as $m_{LSM}$. TGA blank runs (performed by using empty crucibles) were subtracted from the TGA actual experiments (conducted by using the LSM perovskites) to avoid the effect of the thermal buoyancy.

### Table 1

| Abbreviation | La/Sr/Mn (as-prepared) | La/Sr/Mn (from EDS) | Composition |
|--------------|------------------------|---------------------|-------------|
| LSM10        | 0.90/0.10/1.00         | 0.88/0.11/1.00      | La$_{0.8}$Sr$_{0.2}$MnO$_{1.9}$ |
| LSM20        | 0.80/0.20/1.00         | 0.81/0.21/1.01      | La$_{0.75}$Sr$_{0.25}$MnO$_{1.9}$ |
| LSM30        | 0.70/0.30/1.00         | 0.68/0.30/1.01      | La$_{0.7}$Sr$_{0.3}$MnO$_{1.9}$ |
| LSM40        | 0.60/0.40/1.00         | 0.60/0.41/0.99      | La$_{0.65}$Sr$_{0.35}$MnO$_{1.9}$ |
| LSM50        | 0.50/0.50/1.00         | 0.52/0.49/1.00      | La$_{0.6}$Sr$_{0.4}$MnO$_{1.9}$ |
| LSM60        | 0.40/0.60/1.00         | 0.41/0.59/0.98      | La$_{0.55}$Sr$_{0.45}$MnO$_{1.9}$ |
| LSM70        | 0.30/0.70/1.00         | 0.30/0.70/0.99      | La$_{0.5}$Sr$_{0.5}$MnO$_{1.9}$ |
| LSM80        | 0.20/0.80/1.00         | 0.21/0.78/1.01      | La$_{0.45}$Sr$_{0.55}$MnO$_{1.9}$ |
| LSM90        | 0.10/0.90/1.00         | 0.09/0.91/1.00      | La$_{0.4}$Sr$_{0.6}$MnO$_{1.9}$ |

Fig. 1. Schematic of LSM based solar thermochemical fuel production process.
3. Results and discussion

The phase composition of the SCS synthesized LSM perovskites were identified by performing the PXRD analysis. The PXRD peaks, presented in Fig. 3, shows nominally phase pure LSM perovskites with no evidence of any impurities such as La-, Mn-, Sr-based individual oxides, or La, Sr, Mn metals. As the crystal ionic radii of Sr (132 pm) is higher than that of La (117.2 pm), the increase in the atomic concentration of the Sr resulted in a shift in the PXRD peaks towards higher 2θ angle. This observation provided further confirmation of the successful synthesis of LSM perovskites via the SCS method. The PXRD peaks reported in Fig. 3 matched very well with the PXRD findings reported in previous studies [41]. By employing the Scherrer formula, the average crystallite size of all LSM perovskites was estimated to be in the range of 50 to 70 nm.

In addition to the PXRD, by using the SEM/EDS instrument, the elemental composition of each LSM perovskite was verified. The EDS results were observed to be consistent with the findings reported by the PXRD analysis. The EDS patterns associated with the LSM20, LSM40, LSM60, and LSM80 perovskites (exemplified) are presented in Fig. 4. Besides, the atomic concentrations of La, Sr, and Mn, and the chemical composition of each LSM perovskite identified by using the EDS patterns are reported in Table 1.

In order to examine the microstructural morphology of the LSM perovskites, SEM analysis was conducted. The representative images obtained for LSM20, LSM40, LSM60, and LSM80 perovskites are shown in Fig. 5. The drift in the La and Sr atomic concentrations had an insignificant effect on the LSM morphology. However, as the images were taken at different locations (for each LSM), we cannot wholly neglect the chances of having dissimilar/disordered images. The SEM analysis showed that all the LSM perovskites possess a porous

![Fig. 2. Experimental set-up used for the evaluation of the LSM perovskites.](image)

![Fig. 3. PXRD patterns of LSM perovskites, a) 2θ = 20° to 80° and b) 2θ = 31° to 34° (prepared via SCS and calcined at 1000 °C in the air for 4 h).](image)
morphology.

We have first tested the redox performance of the SCS synthesized LSM perovskites in one thermochemical CS cycle. In thermochemical cycles, the mass of a MO decreases during the TR step due to the release of lattice O\(_2\). In contrast, due to the gain of O\(_2\), the mass of the MO increases during the re-oxidation step. The mass of each LSM perovskite was decreased as a function of the increase in the TR temperature (\(T_{tr}\)) and the reaction time during the TR step (Fig. 6). In terms of the mass loss, the LSM50 perovskite reached its plateau after attaining the TR temperature of 1400 °C. In contrast, the remaining LSM perovskites continued to lose weight throughout the entire TR step. By considering that the TR starts at 800 °C, the kinetics was quickest for LSM90 and the slowest for the LSM10 perovskite. Furthermore, from 800 °C to 1400 °C (dwell time equal to 60 min), the %\(\Delta m_{\text{TR}}\) was highest for LSM90 perovskite (~6.8%) and lowest in the case of the LSM10 perovskite (~0.65%).

The TGA profiles obtained in case of each LSM perovskite (during the TR step) were translated into the \(n_{TR}\) by using Eq. (1). The numbers reported in Fig. 7 indicate that the \(n_{TR}\) by the LSM90 perovskite was the greatest as compared to other LSM perovskites. For instance, the \(n_{TR}\) by LSM90 perovskite (1476.6 \(\mu\)mol/g) was higher by 1298.7, 1243.5, 1003.5, 932.0, 885.9, 866.7, 828.3, and 675.0 \(\mu\)mol/g when compared to the LSM10, LSM20, LSM30, LSM40, LSM50, LSM60, LSM70, and LSM80 perovskites, respectively. The inclusion of Sr\(^+\) as a partial substitute for La\(^{3+}\) on A-site (from \(x = 0.1\) to 0.9) results into a deviation in the oxidation state of Mn from +3 to +4. Because of this drift, the LSM perovskites (with higher Sr content) seems to be favorable towards TR reaction as compared to the LSM perovskites with the lower Sr content.

The thermally decomposed LSM perovskites were further examined towards CS step at 1000 °C for 30 min. Fig. 8 represents the TGA profiles associated with the first CS step. As mentioned earlier, it was expected that the mass of the MO would rise due to the re-oxidation. As per the expectation, as shown in Fig. 8, the mass of each LSM perovskite was increased during the CS step. Close inspection of these TGA profiles indicates that the LSM70 and LSM50 perovskites exhibited the quickest RO rates. At the same time, the LSM90 perovskite showed the slowest RO kinetics. Obtained results further show that the LSM70 perovskite attained the maximum mass gain, and the LSM90 perovskite indicated the lowest increase in the mass during the first CS step. With the help of the obtained TGA profiles and Eq. (2), the calculated \(n_{CO}\) by each LSM perovskite is presented in Fig. 9. The LSM70 perovskite displayed the highest CO production (424.0 \(\mu\)mol/g), and the LSM90 displayed the lowest \(n_{CO}\) (64.7 \(\mu\)mol/g) in cycle 1. The LSM40, LSM60, and LSM80 perovskites indicated approximately identical \(n_{CO}\) in the range of 285.7 to 309.5 \(\mu\)mol/g. Likewise, the LSM20 and LSM30 perovskites produced ~162.0 \(\mu\)mol of CO/g in cycle 1. The authors would like to admit that it is difficult to know the exact reason for such results as the TGA set-up only provides the information related to the mass variations.

The overall analysis of the 1st thermochemical cycle indicate that the \(n_{CO}\) produced by the LSM perovskites were lower than the \(n_{TR}\). The probable reasons for such trends are a) all the LSM perovskites were freshly prepared and never underwent any thermal cycling before performing the first TR step, and b) all the LSM perovskites have not reached their thermal stability during cycle 1. It was highly essential to know if the LSM perovskites show a similar trend in additional cycles. Hence, these redox materials were further scrutinized by performing three consecutive cycles (Fig. 10).

Table 2 report the calculated \(n_{TR}\) and \(n_{CO}\) by each LSM perovskite during three cycles. The numbers listed shows that the \(n_{TR}\) by all LSM perovskites decreased considerably in cycle 2. For example, the \(n_{TR}\) by LSM10, LSM30, LSM50, LSM70, and LSM90 was reduced by 117.6, 292.1, 465.4, 402.5, and 1133.4 \(\mu\)mol/g in cycle 2 as compared to cycle 1. The results reported in Table 2 further shows that, except for LSM30, LSM80, and LSM90 perovskites, most of the LSM perovskites underwent a drop in the CO production capacity in cycle 2. The \(n_{CO}\) by LSM10, LSM20, LSM30, LSM50, LSM60, and LSM80 diminished by 19.1, 34.9,
17.9, 100.7, 17.9, and 61.5 μmol/g, individually in cycle 2 as compared to the first cycle. In case of the LSM60 and LSM80 perovskites, the $n_{CO}$ during cycle 2 enhanced by 40.9 and 19.2 μmol/g (as compared to cycle 1), whereas in the case of LSM50 perovskite, $n_{CO}$ remained steady during both cycles. A higher $n_{CO}/n_{O_2}$ ratio accomplished by all the LSM perovskites during cycle 2. For instance, the $n_{CO}/n_{O_2}$ ratio for LSM10, LSM20, LSM30, LSM40, LSM50, LSM60, LSM70, LSM80, and LSM90 upsurged by 0.936, 0.569, 0.783, 0.371, 1.324, 1.433, 0.821, 1.198, and 0.201 in cycle 2 when compared with the $n_{CO}/n_{O_2}$ attained in cycle 1.

Cycle 3 marked a further reduction in the TR capacity of all the LSM...
perovskites (except for LSM50). The $n_{O_2}$ decreased by 26.3%, 37.0%, 17.7%, 25.4%, 8.9%, 25.9%, 22.9%, and 42.5% in cycle 3 for LSM10, LSM20, LSM30, LSM40, LSM60, LSM70, LSM80, and LSM90, individually in comparison to the $n_{O_2}$ in cycle 2. Likewise, the CS ability of LSM10, LSM20, and LSM60 perovskites reduced by 13.3%, 6.9%, and 7.1% in cycle 3 as compared to cycle 2. In contrast, the $n_{CO}$ by LSM50, LSM70, and LSM80 perovskites remained stable and the $n_{CO}$ by LSM30, LSM40, and LSM90 perovskites increased by 17.1%, 5.0%, and 79.4%, respectively, in cycle 3, when paralleled with cycle 2. Overall, the $n_{CO}/n_{O_2}$ ratio for LSM10, LSM20, LSM30, LSM40, LSM50, LSM60, LSM70, LSM80, and LSM90 upsurged by 0.28, 0.60, 0.48, 0.36, 0.01, 0.04, 0.48, 0.43, and 0.52, respectively in 3rd cycle when matched to the $n_{CO}/n_{O_2}$ ratios reported for the 2nd cycle.

The results obtained during three consecutive cycles indicate a reduction in the $n_{O_2}$ by all the LSM perovskites. In contrast, an upsurge in the $n_{CO}/n_{O_2}$ ratio was noticed for all the LSM perovskites from cycle 1 to cycle 3. The probable reason for these results is the transformation of the redox reactivity of the selected LSM perovskites from an unstable zone (cycle 1) to a more stable zone (cycle 3). This probably happened as the LSM perovskites underwent three thermal cyclings. After the 3rd cycle, it is believed that some of the LSM perovskites have improved their thermal stability and redox reactivity towards the TR and CS reactions.

To determine the worthiest combination of the LSM perovskite, which can attain a stable production of CO for a longer duration, this study was further extended towards performing ten successive thermochemical cycles. Fig. 11 presents the TGA profiles obtained for all the LSM perovskites (Fig. 11) look organized, based on the average $n_{CO}$ from cycle 2 to cycle 10. Remaining perovskites showed varying amounts of $n_{CO}$ from cycle 2 to cycle 10. Likewise, the CS ability of LSM20, LSM50, LSM60, and LSM70 perovskites from cycle 2 to cycle 10. In terms of numbers, the average $n_{O_2}$ by each LSM perovskite can be arranged as: LSM40 ($214.8 \mu mol/g$-cycle) $>$ LSM70 ($187.9 \mu mol/g$-cycle) $>$ LSM90 ($152.6 \mu mol/g$-cycle) $>$ LSM80 ($140.5 \mu mol/g$-cycle) $>$ LSM60 ($139.4 \mu mol/g$-cycle) $>$ LSM50 ($126.9 \mu mol/g$-cycle) $>$ LSM30 ($123.7 \mu mol/g$-cycle) $>$ LSM20 ($66.6 \mu mol/g$-cycle) $>$ LSM10 ($43.4 \mu mol/g$-cycle). These results confirmed that the redox reactivity of the LSM20, LSM50, LSM60, and LSM70 was much better towards the TR step as compared to the remaining LSM perovskites.

According to the data reported in Fig. 13, the $n_{CO}$ of LSM10, LSM30, LSM40, and LSM90 perovskites reduced from cycle 2 to cycle 9, whereas the TR capacity of the LSM80 perovskite was inconsistent. In contrast, a stable $n_{O_2}$ by LSM20, LSM50, LSM60, and LSM70 perovskites from cycle 2 to cycle 10. In terms of numbers, the average $n_{O_2}$ by each LSM perovskite can be calculated by Eqs. (1) and (2).

$$E_{\text{tr}} = \frac{n_{CO}}{n_{O_2}}$$

$$E_{\text{cs}} = \frac{n_{O_2}}{n_{CO}}$$

According to Fig. 12, the $E_{\text{tr}}$ by LSM10, LSM30, LSM40, and LSM90 perovskites from cycle 2 to cycle 10, estimated by using Eqs. (1) and (2).
perovskites was the highest as compared to the other LSM perovskites. For most of the LSM perovskites (except for LSM40 and LSM90) the average $n_{\text{CO}}/n_{\text{O}_2}$ ratio was higher than 1.6. The average $n_{\text{CO}}/n_{\text{O}_2}$ ratio > 1.6 indicates that the re-oxidation capacity of the LSM perovskites is reduced, and further work needs to be done for its improvement. A possible option is to improve the ion mobility of the LSM perovskites via the inclusion of one or more suitable dopants in the crystal structure. Overall, the LSM perovskites, based on their average $n_{\text{CO}}/n_{\text{O}_2}$ ratio, can be organized as: LSM60 > LSM80 > LSM70 > LSM50 > LSM20 > LSM30 > LSM10 > LSM40 > LSM90.

Table 3 reports the comparison between the LSM perovskites and CeO$_2$ (experiments conducted at identical operating conditions). The data listed indicate that, except for LSM10 perovskite, all the LSM perovskites produced higher $n_{\text{O}_2}$ and $n_{\text{CO}}$ than CeO$_2$. In contrast, CeO$_2$ exhibited higher average $n_{\text{CO}}/n_{\text{O}_2}$ ratio than most of the LSM perovskites. The elevated average $n_{\text{CO}}/n_{\text{O}_2}$ ratio indicates that the RO
potential of CeO₂ is superior to the LSM perovskites. We believe that the CS temperature (1000 °C) and re-oxidation time (30 min) used were appropriate for the CeO₂ material to re-oxidized completely. However, the experimental conditions employed were insufficient for the LSM perovskites to regain their oxidized state.

In addition to CeO₂, the LSM perovskites investigated in this study were also compared with LSM perovskites studied by Dey and Rao [32] and Yang et al. [30]. Dey and Rao [32] tested LSM30, LSM40, and LSM50 perovskites for the thermochemical splitting of CO₂ at isothermal experimental conditions (1673 K). The amounts of O₂ released and CO produced by the LSM30, LSM40, and LSM50 perovskites investigated by us were considerably higher than the similar perovskites examined by Dey and Rao [32]. The probable reason for this lower amount of fuel production reported by Dey and Rao [32] is the lesser time (15 min) permitted for the TR step.

Yang et al. [30] examined LSM10, LSM20, LSM30, and LSM40 perovskites for the thermochemical splitting of H₂O (TR at 1400 °C and re-oxidation at 800 °C). As the aim of the presented investigation was to split the CO₂, only the results associated with the TR step (O₂ release) were compared. As the time allowed for the TR step by us and by Yang et al. [30] were comparable (especially for LSM30 and LSM40), the amount of O₂ released by LSM10, LSM20, LSM30, and LSM40 in this study was approximately identical to the TR ability of the similar perovskite reported by Yang et al. [30]. Based on the comparison with published literature, presently, we are investigating the effect of temperature and dwell time allied with both TR and CS steps to understand the long-term redox reactivity of the LSM perovskites.

4. Summary and conclusions

In this investigation, LaₓSrₓMnO₃ (where x = 0.1 to 0.9) i.e., LSM perovskites were examined towards thermochemical CS cycles. A solution combustion synthesis approach was utilized for the synthesis of LSM perovskites. Derived LSM perovskites were further characterized using PXRD, EDS, and SEM techniques. Formation of nominally phase pure LSM perovskites with no evidence of any impurities such as La₃O₅, Mn₃O₄, Sr-based individual oxides or La, Sr, Mn metals was confirmed from the PXRD and EDS analysis. The average crystallite size of all LSM perovskites was estimated to be in the range of 50 to 70 nm. The SEM analysis verified the insignificant effect of the variation in the La and Sr atomic concentrations on the porous morphology of the LSM perovskites. The CS ability of each LSM perovskite was examined by performing one, three, and ten thermochemical cycles (at a fixed T_H = 1400 °C and T_L = 1000 °C). Obtained results indicate that the rise in the Sr molar concentration is favorable to improve the TR yield of the LSM perovskites. As the number of cycles increased from two to ten, most of the LSM perovskites reached their thermal stability and produced roughly stable amounts of O₂ and CO. The long-term thermal cycling (from cycle 2 to cycle 10) shows that the LSM40 perovskite was the best choice in terms of n_o₂ = 214.8 µmol/g-cycle, whereas LSM70 showed the highest activity towards CS reaction (n_o₂ = 342.1 µmol/g-cycle). In terms of the re-oxidation ability (n_o₂/n_o3 ratio), the LSM60 was observed to be the most promising choice as it is capable of attaining the highest n_o₂/n_o3 ratio = 1.96. All the LSM perovskites (except LSM10) exhibited higher amount of O₂ release and CO production when compared with the ceria material. The improved fuel production capacity of the LSM perovskite will result into a higher solar-to-fuel-energy conversion efficiency.

CRedit authorship contribution statement

Gorakshnath Takalkar: Methodology, Investigation, Data curation. Writing - original draft. Rahul R. Bhosale: Conceptualization, Validation, Data curation, Writing - original draft, Writing - review & editing, Project administration, Funding acquisition. Fares AlMomani: Validation, Data curation, Writing - original draft, Writing - review & editing. Suliman Rashid: Methodology, Investigation. Hazim Qiblawey: Data curation, Writing - review & editing. Mohammed Ali Saleh Saad: Writing - review & editing. Majeda Khrisheh: Writing - review & editing. Gopalakrishnan Kumar: Writing - original draft. Ram B. Gupta: Writing - original draft. Rajesh V. Shende: Writing - original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

Open Access funding provided by the Qatar National Library. This publication was made possible by the NPRP grant (NPRP8-370-2-154) from the Qatar National Research Fund (a member of Qatar Foundation). The statements made herein are solely the responsibility of author(s).

References

[1] Carrillo RJ, Scheffe JR. Advances and trends in redox materials for solar thermochemical fuel production. Sol Energy 2017;156:3–20. https://doi.org/10.1016/j.solener.2017.05.032.

[2] Bhosale RR, Takalkar G, Sutar P, Kumar A, AlMomani F, Khrisheh M. A decade of ceria based solar thermochemical H₂O/CO₂ splitting cycle. Int J Hydrogen Energy 2019;54:60. https://doi.org/10.1016/j.ijhydene.2018.04.080.

[3] Dry ME. The Fischer-Tropsch process: 1950–2000. Catal. Today 2002;71:227–41. https://doi.org/10.1016/S0920-5861(01)00453-9.

[4] Bhosale R, Kumar A, Almomani F. Solar thermochemical hydrogen production via terbium oxide based redox reactions. Int J Photoenergy 2016. https://doi.org/10.1155/2016/9727895.

[5] Agrafiotis C, Roeb M, Sattler C. A review on solar thermal syngas production via redox pair-based water/carbon dioxide splitting thermochemical cycles. Renew Sustain Energy Rev 2015;42:254–85. https://doi.org/10.1016/j.rser.2014.09.039.

[6] Markz D, Furler P, Scheffé J, Geerlings H, Falter C, Batteiger V, et al. Demonstration of the entire production chain to renewable kerosene via solar thermochemical splitting of H₂O and CO₂. Energy Fuels 2015;29:3241–50. https://doi.org/10.1021/acs.energyfuels.5b00351.

[7] Koepf E, Alxneit I, Wieckert C, Meier A. A review of high temperature solar driven reactor technology: 25 years of experience in research and development at the Paul Scherrer Institute. Appl Energy 2017. https://doi.org/10.1016/j.apenergy.2016.11.088.

[8] Steinfeld A. Solar hydrogen production via a two-step water-splitting thermochemical cycle based on Zn/ZnO redox reactions. Int J Hydrogen Energy 2002;27:611–9. https://doi.org/10.1016/S0360-3199(01)00177-X.

[9] Bhosale RR. Thermodynamic efficiency analysis of zinc oxide based solar driven thermochemical H₂O splitting cycle: Effect of partial pressure of O₂, thermal reduction and H₂O splitting temperatures. Int J Hydrogen Energy 2018;43:14915–24. https://doi.org/10.1016/j.ijhydene.2018.06.074.

[10] Bhosale R, Kumar A, Almomani F, Gupta RB. Solar thermochemical ZnO/ZnS04 water splitting cycle for hydrogen production. Int J Hydrogen Energy 2017;42:23474–83. https://doi.org/10.1016/j.ijhydene.2017.02.196.

[11] Abanades S, Villafan-Vidales HH. CO₂ and H₂O conversion to solar fuels via two-step solar thermochemical looping using iron oxide redox pair. Chem Eng J 2011;175:368–75. https://doi.org/10.1016/j.cej.2011.09.124.

[12] Bhosale RR, Kumar A, Sutar P. Thermodynamic analysis of solar driven Sr₂O2/SrO based thermochemical water splitting cycle. Energy Convers Manag 2017;135:226–35. https://doi.org/10.1016/j.enconman.2016.12.067.

[13] Charvin P, Abanades S, Flament G, Lemont F. Two-step water splitting thermochemical cycle based on iron oxide redox pair for solar hydrogen production. Energy 2007;32:1124–33. https://doi.org/10.1016/j.energy.2006.07.023.

[14] Bhosale RR, Kumar A, Van Den Broeke LPJ, Gharbia S, Dardor D, Jilani M, et al. Solar hydrogen production via thermochemical iron oxide-iron sulfate water splitting cycle. Int J Hydrogen Energy 2015;40:1639–50. https://doi.org/10.1016/j.ijhydene.2014.11.118.

[15] Galvez ME, Louzhenischer PG, Hohscher I, Steinfeld A. CO₂ splitting via two-step solar thermochemical cycles with Zn/ZnO and FeO/FeO₄ redox reactions: thermodynamic analysis. Energy Fuels 2008;22:3544–50. https://doi.org/10.1021/ef800230b.

[16] Amar VS, Puzynski JA, Shende RV. H₂ generation from thermochemical water-splitting using yttria stabilized NiFe₂O₄ core-shell nanoparticles. J Renew Sustain Energy 2015;7. https://doi.org/10.1063/1.4915312.

[17] Bhosale RR, Alxneit I, Van Den Broeke LPJ, Kumar A, Jilani M, Gharbia SS, et al. Sol-gel synthesis of nanocrystalline Ni-ferrite and Co-ferrite redox materials for the rmaro mical production of solar fuels. Mater. Res. Soc. Symp. Proc. 2014;1675:203–8. https://doi.org/10.1016/j.apenergy.2014.06.023.
G. Takalkar et al.

[18] Scheffe JR, Li J, Weiner AW. A spinel ferrite/hexacite water-splitting redox cycle. Int J Hydrogen Energy 2010;35:3333–40. https://doi.org/10.1016/j.ijhydene.2010.01.140.

[19] Bhosle RR. Thermodynamic analysis of Ni-ferrite based solar thermochemical H2 O splitting cycle for H2 production. Int J Hydrogen Energy 2019;61:71. https://doi.org/10.1016/j.ijhydene.2019.03.145.

[20] Scheffe JR, Jacob R, Patzke GR, Steinfeld A. Synthesis, characterization, and thermochemical redox performance of H4Fe2+, Zr4+, and Sc3+ doped ceria for splitting CO2. J Phys Chem C 2013;117:24104–10. https://doi.org/10.1021/jp4050722.

[21] Takalkar GDD, Bhosle RRR, Kumar A, AlMomani F, Khraisheh M, Shakoor RAA, et al. Transition metal doped ceria for solar thermochemical fuel production. Sol Energy 2018. https://doi.org/10.1016/j.solener.2018.03.022.

[22] Le Gal A, Abanades S. Catalytic investigation of ceria-zirconia solid solutions for solar hydrogen production. Int J Hydrogen Energy 2011;36:4739–48. https://doi.org/10.1016/j.ijhydene.2011.01.078.

[23] Ehrhart BD, Muhich CL, Al-Shankiti I, Weimer AW. System efficiency for two-step metal oxide solar thermochemical hydrogen production – Part 1: Thermodynamic model and impact of oxidation kinetics. Int J Hydrogen Energy 2016;41:19881–93. https://doi.org/10.1016/j.ijhydene.2016.07.109.

[24] Muhich CL, Evanko BW, Weston KC, Liang X, Martinek J, et al. Efficient generation of H2 by splitting water with an isothermal redox cycle. Science (80-); 2013;341:540–2. doi: 10.1126/science.1239454.

[25] Muhich CL, Ehrhart BD, Witte VA, Miller SL, Coker EN, Musgrave CB, et al. Predicting the solar thermochemical water splitting ability and reaction mechanism of metal oxides: A case study of the hencine family of water splitting cycles. Energy Environ Sci 2015;8:3687–99. https://doi.org/10.1039/c5ee01979f.

[26] Dey S, Naidu BS, Rao CNR. Splitting of CO2 by Manganite Perovskites to Generate CO by Solar Isothermal Redox Cycling. ACS Energy Lett 2016;1:237–43. https://doi.org/10.1021/acsenergylett.6b00122.

[27] Dey S, Naidu BS, Rao CNR. Ln0.5A0.5MnO3 (Ln=–La, Sr) perovskites exhibiting remarkable performance in the thermochemical generation of CO and H2 from CO2 and H2O. Chem. A Eur J 2015;21:7077–81. doi:10.1002/chem.201500442.

[28] Demont A, Abanades S, Beche E. Investigation of perovskite structures as oxygen-exchange redox materials for hydrogen production from thermochemical two-step water-splitting cycles. J Phys Chem C 2014;118:12682–92. https://doi.org/10.1021/jp5034849.

[29] Bork AH, Povoden-Karadeniz E, Rupp JLM. Modeling Thermochemical Solar-to-Fuel Conversion: CALPHAD for Thermodynamic Assessment Studies of Perovskites, Exemplified for (La, Sr)MnO3. Adv Energy Mater 2017;7. https://doi.org/10.1002/aenm.201601086.

[30] Kuo JL, Anderson HU, Sparlin DM. Oxidation-reduction behavior of undoped and Sr-doped LaMnO3 nonstoichiometry and defect structure. J Solid State Chem 1989;83:52–60. https://doi.org/10.1016/0022-4596(89)90053-4.

[31] Mizusaki J, Mori N, Takai H, Yonemura Y, Minamiue H, Tagawa H, et al. Oxygen nonstoichiometry and defect equilibrium in the perovskite-type oxides La1–xSrxMnO3+x. Solid State Ionics 2000;129:163–77. https://doi.org/10.1016/S0167-2738(99)00233-9.

[32] Takalkar G, Bhosle R, AlMomani F. Combustion synthesized A0.5Sr0.5MnO3-s perovskites (where, A=–La, Nd, Sm, Gd, Tb, Dy, and Y) as redox materials for thermochemical splitting of CO2. Appl Surf Sci 2019;489:80–91. doi: 10.1016/j.apsusc.2019.05.284.

[33] Ashok A, Kumar A, Bhosle RR, Almomani F, Saleed Saad MAH, Sulas S, et al. Influence of fuel ratio on the performance of combustion synthesized bifunctional cobalt oxide catalysts for fuel cell application. Int J Hydrogen Energy 2019. https://doi.org/10.1016/j.ijhydene.2018.02.111.

[34] Bhosle RR, Takalkar GD. Nanostructured co-precipitated Ce0.9Ln0.1O2 (Ln=–La, Pr, Sm, Nd, Gd, Tb, Dy, or Er) for thermochemical conversion of CO2. Ceram Int 2015;41:19881–93. https://doi.org/10.1016/j.ceramint.2015.05.284.

[35] Dey S, Naidu BS, Rao CNR. Ln0.5A0.5MnO3 (Ln=–La, Sr) perovskites exhibiting remarkable performance in the thermochemical generation of CO and H2 from CO2 and H2O. Chem. A Eur J 2015;21:7077–81. doi:10.1002/chem.201500442.

[36] Bork AH, Povoden-Karadeniz E, Rupp JLM. Modeling Thermochemical Solar-to-Fuel Conversion: CALPHAD for Thermodynamic Assessment Studies of Perovskites, Exemplified for (La, Sr)MnO3. Adv Energy Mater 2017;7. https://doi.org/10.1002/aenm.201601086.

[37] Mizusaki J, Mori N, Takai H, Yonemura Y, Minamiue H, Tagawa H, et al. Oxygen nonstoichiometry and defect equilibrium in the perovskite-type oxides La1–xSrxMnO3+x. Solid State Ionics 2000;129:163–77. https://doi.org/10.1016/S0167-2738(99)00233-9.

[38] Takalkar G, Bhosle R, AlMomani F. Combustion synthesized A0.5Sr0.5MnO3-s perovskites (where, A=–La, Nd, Sm, Gd, Tb, Dy, and Y) as redox materials for thermochemical splitting of CO2. Appl Surf Sci 2019;489:80–91. doi: 10.1016/j.apsusc.2019.05.284.

[39] Ashok A, Kumar A, Bhosle RR, Almomani F, Saleed Saad MAH, Sulas S, et al. Influence of fuel ratio on the performance of combustion synthesized bifunctional cobalt oxide catalysts for fuel cell application. Int J Hydrogen Energy 2019. https://doi.org/10.1016/j.ijhydene.2018.02.111.

[40] Bhosle RR, Takalkar GD. Nanostructured co-precipitated Ce0.9Ln0.1O2 (Ln=–La, Pr, Sm, Nd, Gd, Tb, Dy, or Er) for thermochemical conversion of CO2. Ceram Int 2015;41:19881–93. https://doi.org/10.1016/j.ceramint.2015.05.284.