Enhanced Thermochemical H₂ Production on Ca-Doped Lanthanum Manganite Perovskites Through Optimizing the Dopant Level and Re-oxidation Temperature

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Abstract

Perovskite material is one of the promising classes of redox catalysts for hydrogen production through two-step thermochemical H₂O splitting. Herein, an analogue of La_{1-x}Ca_xMnO₃ perovskite was systematically investigated as a catalyst for thermochemical H₂ evolution. The Ca doping level ($x = 0.2, 0.4, 0.6, 0.8$) and re-oxidation temperature were comprehensively optimized for the improvement of catalytic performance. According to our experimental results, La_{0.6}Ca_{0.4}MnO₃ perovskite displayed the highest yield of H₂ at the re-oxidation temperature of 900 °C and the obtained H₂ production was ~ 10 times higher than that of the benchmark ceria catalyst under the same experimental condition. More importantly, La_{0.6}Ca_{0.4}MnO₃ perovskite catalyst exhibited impressive cyclic stability in repetitive O₂ and H₂ test.

Keywords Thermochemical water splitting · Hydrogen production · Perovskite oxides · Dopant level · Re-oxidation temperature

1 Introduction

The increasing environmental deterioration and global warming that associated with the emission of greenhouse gases have resulted in serious attention toward

development of alternative renewable, clean carbon-neutral energy sources [1–4]. Hydrogen (H₂) has long been considered as an ideal fuel with high energy density and zero carbon emission [5–7]. Recently, clean solar energy-based H₂ generation routes such as photochemical and electrolytic processes have attracted widespread interests [8–10] due to their environmental friendliness. Among them, the solar-driven thermochemical H₂O splitting method is exclusively promising due to the high energy conversion efficiency over the entire solar spectrum [11–13].

During the past several decades, tremendous efforts have been devoted in searching efficient catalysts for solar-driven thermochemical H₂O splitting. Numerous promising candidates such as Fe₃O₄ [14–16], ZnO [17–19], SnO₂ [20, 21], CeO₂ [22–24], ferrites [25–27], hercynites [28–30] and transition metal ions doped CeO₂ [31–33] have been reported. Currently, non-stoichiometric CeO₂ has been regarded as the state-of-the-art catalyst due to its high stability and desired reaction thermodynamics and kinetics during thermochemical cycles [34]. However, the small oxygen exchange capacity and high thermal reduction temperature (≥ 1500 °C) limit its large-scale application. On this regard, the search for new catalyst

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candidates with high oxygen exchange capacity and low thermal reduction temperature becomes imperative.

Recently, perovskite oxides with ABO_3 structure emerged as promising alternative materials for thermochemical solar fuel production [35–39]. As shown in Fig. 1, owing to the high tolerance factor, ABO_3 structured perovskite can keep the stable perovskite crystal structure even after losing a mass of lattice oxygen atoms (Eq. (1)). As a result, a highly non-stoichiometric perovskite structure ($ABO_{3-\delta}$) can be achieved via a thermal reduction process without compromising the crystal structure [40]. Thereafter, the thermally reduced $ABO_{3-\delta}$ structure can be recovered through the introduction of H_2O vapor, resulting in overall water splitting and production of molecular H_2 (Eq. (2)).

It is generally acknowledged that the catalytic properties of perovskites depend extensively on their atomic structures which can be easily tuned through material engineering. For instance, Scheffe et al. [41] first investigated the $La_{1-x}Sr_xMnO_3$ ($x = 0.3, 0.35, 0.4$) for two-step thermochemical H_2O splitting. Compared to CeO_2 , higher O_2 exchange capacity and theoretical energy conversion efficiency were achieved by the investigated perovskites. Later, Yang et al. [42] carried out a detailed quantitative assessment on the $La_{1-x}Sr_xMnO_3$ ($x = 0.1\text{--}0.4$) perovskites from both thermodynamic and kinetic aspects. A remarkable H_2 production performance (9 mL/g) was achieved using $La_{0.6}Sr_{0.4}MnO_3$ at a thermochemical H_2O splitting cycle between 1400 and 800 °C. Some other perovskites including Sr- and Mn-doped $LaAlO_3$ [43], $La_{0.6}Sr_{0.4}Cr_{0.8}Co_{0.2}O_3$ [44], $Y_{0.5}Sr_{0.5}MnO_3$ [45] and $La_{0.6}Sr_{0.4}Mn_{0.95}Sc_{0.05}O_3$ [46] were also studied as promising thermochemical H_2O splitting catalysts.

Another similar perovskite analogue, Ca-doped lanthanum manganite ($La_{1-x}Ca_xMnO_3$) perovskites were also reported to be an effective class of catalysts for a thermochemical CO_2 splitting process to produce CO [47–49]. To date, however, the investigation of such catalysts for two-step thermochemical H_2O splitting is quite rare. To the best of our knowledge, the only report was published by Dey et al. [49] who investigated $La_{0.5}Ca_{0.5}MnO_3$ perovskite as a catalyst for thermochemical H_2O splitting at relatively higher operational temperatures (1400 °C for thermal reduction process and 1000 °C for water splitting process, respectively). Therefore, the Ca doping level and the two-step thermochemical H_2O splitting operational conditions deserve further optimization to improve the catalytic performance of $La_{1-x}Ca_xMnO_3$ catalysts.

Herein, we report $La_{1-x}Ca_xMnO_3$ (LCMO) perovskites as highly efficient and durable catalysts for two-step thermochemical H_2O splitting at low thermal reduction temperature (1300 °C). To find out the optimal composition, a series of LCMO perovskites with a wide range of Ca doping levels (0.2–0.8) have been studied. Taking the optimal perovskite composition as a reference point, further optimization on the thermochemical operational condition (e.g., re-oxidation temperatures) was also conducted.

2 Experimental

2.1 Chemicals

$La(NO_3)_3 \cdot 6H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$, $Mn(NO_3)_2 \cdot xH_2O$, ceria, citric acid and ethylene glycol were purchased from Sigma-Aldrich. All chemicals were used as received without any further purification.

2.2 Catalyst Synthesis

All the perovskite oxides were synthesized by a modified Pechini method [50]. In brief, stoichiometric amounts of metal nitrate precursors were dissolved in deionized (DI) water and heated at 70 °C with continuous stirring. Citric acid was then added to the solution with a molar ratio of 1.5:1 with respect to the metal cations. After 10 min, ethylene glycol (ethylene glycol/citric acid molar ratio = 1:1) was added to the mixture and heated at 90 °C until a brownish gel was obtained. The resulting gel was transferred to an electric oven and kept for 12 h at 120 °C to obtain a resin. The resin was then collected and ground with mortar and pestle. The final perovskite oxide powder was prepared by calcining the resin at 1300 °C for 6 h to remove any remaining organics or nitrates.

Fig. 1 Schematic illustration of two-step thermochemical H_2O splitting cycle showing the thermal reduction of ABO_3 to $ABO_{3-\delta}$ via a high-temperature treatment generating (Step 1) and re-oxidation of oxygen deficient $ABO_{3-\delta}$ to ABO_3 in water splitting to produce H_2 (Step 2)

2.3 Characterizations

The X-ray diffraction (XRD) patterns of the samples were collected using a Bruker D8 X-ray diffractometer operated at 40 kV with the current of 25 mA using a Cu $K\alpha$ radiation. The measurements of 2θ symmetrical scans were taken in the range of 20° – 80° with a step size of 0.02° and a scanning rate of $2^\circ/\text{min}$, respectively. Phase identification was conducted by comparing with the standard Inorganic Crystal Structure Database (ICSD). Scanning electron microscopy (SEM, JSM-7100), energy-dispersive X-ray (EDX, JSM-7100) mapping and transmission electron microscopy (TEM, Tecnai F20) techniques were also employed to characterize the surface morphology and element distribution within the samples. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface area (SBET) using nitrogen adsorption–desorption isotherms, while pore size distribution was calculated using the Barrett, Joyner and Halenda (BJH) method in Quantachrome Autosorb-1 equipment [51]. Both BET and BJH analyses were conducted for the best sample (LCMO-0.4) before and after the cyclic stability test.

2.4 Thermochemical H₂O Splitting Test

The two-step thermochemical H₂O splitting activity was investigated at a laboratory-scale fix-bed reactor, as shown in Fig. 2. To facilitate the effective testing, the freshly prepared perovskite samples (~ 0.5 g) were transferred into a solid porous monolith structure by mixing with a proper amount of isopropanol and fired at 1300°C for 6 h in the air [52, 53]. Then the prepared redox sample was packed at the center of alumina tubular reactor coupled within a high-temperature programmable electric furnace (MTI, KSL-1800X-S60). Ar (ultra-high purity $\sim 99.99\%$)

was used as a carrier gas, and the flow rate was controlled by a mass flow controller (Alicat Scientific). Thermal reduction step was carried out by heating the perovskite sample to 1300°C and held for 1 h under an Ar flow rate of 200 sccm. (The oxygen partial pressure was around 20 ppm.) Then the temperature was allowed to decrease to a fixed value (700 – 1100°C) for H₂O splitting. Both the temperature increase and decrease rates were fixed at $10^\circ\text{C}/\text{min}$. The water was introduced into the chamber by a water pump (Easypump, BT100 N) and then vaporized and mixed with Ar gas. (The volume ratio of vapor in the mixture gas was around 40%.) The whole H₂O splitting process was kept for 1 h to complete the re-oxidation process. During the thermal reduction and H₂O splitting process, the produced O₂ and H₂ were detected by the mass spectrometer (MS, Omni Star GSD 320). For quantitative measurement of evolved gas, the ion current signal of MS result was calibrated by the standard O₂ and H₂ gases. Furthermore, the energy requirement during the cycling test was roughly calculated based on the following equation reported elsewhere [54].

$$q = hA(T_{\text{Process}} - T_{\text{Environment}}),$$

where q and h stand for heat transfer rate (flux) and average gas–solid heat transfer coefficient from the reactor to the surrounding air ($30\text{ W}/\text{m}^2/\text{K}$), respectively. A is the area of the tube with the internal diameter of 1 cm. T_{Process} and $T_{\text{Environment}}$ refer to the processing (1300°C) and surrounding air temperature (25°C).

Fig. 2 Experimental setup for two-step thermochemical H₂O splitting test

3 Results and Discussion

3.1 Structural Characteristics

A series of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ (LCMO) perovskites ($x = 0.2, 0.4, 0.6, 0.8$; labeled as LCMO-0.2, LCMO-0.4, LCMO-0.6, LCMO-0.8, respectively) were synthesized for the thermochemical water splitting measurements. As shown in Fig. 3a, the XRD pattern of the as-synthesized perovskites (take LCMO-0.4 as the representative one and the rest XRD results refer to Fig. S1 in supplementary material) can be indexed as an orthorhombic crystal structure (ICSD# 89-8086). With the increase in Ca doping level, the main Bragg peaks of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ perovskites were found to be shifted to a higher angle (Fig. S2 in supplementary material) due to the relatively smaller ionic radius of Ca (1.34 Å) when compared to that of La (1.36 Å), meaning a successful incorporation of Ca ions into the perovskite crystal structure.

Figure 3b shows a typical SEM image of LCMO-0.4, revealing an irregular porous structure with nano-sized particles (~ 90 nm, see inset of Fig. 3b). From the SEM images of the other samples (Fig. S3 in supplementary

material), it has been confirmed that Ca doping level slightly affects the surface nanostructures of the perovskites. The TEM image (Fig. 3c) further confirms the particle size of ~ 90 nm with an irregular porous structure of LCMO-0.4 sample. The high-resolution transmission electron microscopic (HRTEM) image (inset of Fig. 3c (top right)) shows a lattice spacing of 0.28 nm corresponding to the (121) plane of the orthorhombic-structured LCMO-0.4 perovskite, which is consistent with the XRD result (Fig. 3a). Furthermore, EDX mapping was also performed to analyze the cationic distributions in the perovskites. As EDX mapping images shown in Fig. 3d, a homogeneous distribution of the corresponding La, Ca and Mn elements in LCMO-0.4 sample is observed. Based on the XRD, SEM, HRTEM and EDX analyses, it can be conferred that a series of LCMO perovskites with different Ca doping levels were successfully synthesized.

3.2 Effect of Ca Doping Level

For perovskites, their properties and catalytic activities have a close relation with their chemical compositions [55]. The recent density functional theory (DFT)

Fig. 3 **a** XRD pattern, **b** SEM image (insert shows the high magnification), **c** TEM image and HRTEM image (top insets), **d** EDX mapping of La, Ca and Mn distribution of the LCMO-0.4 perovskite sample

calculations by Deml et al. revealed that the oxygen vacancy formation energies (EV) and reduction enthalpy (ΔH_{red}) of perovskites are strongly dependent on metal dopant level, which further exerts a critical effect on their thermochemical performances [56, 57]. Thus, a catalyst design strategy needs to be developed based on the optimization of EV and ΔH_{red} through tuning the perovskite compositions. Furthermore, the dopant content in the perovskites was also experimentally demonstrated to be an important factor which can greatly influence the overall performances of the catalysts in two-step thermochemical H₂O splitting cycles [46, 49, 52]. For example, Yang et al. reported that the H₂ yield increased monotonically with the increase in Sr doping level for the La_{1-x}Sr_xMnO₃ perovskites, while the H₂O splitting reaction kinetics favored the opposite trend [52]. Therefore, a detailed investigation on the Ca doping level in LCMO perovskites could be interesting. It is also worthwhile to mention that LCMO perovskites can retain their perovskite structure over the entire doping range ($0 \leq x \leq 1$) [58]. This special feature of LCMO perovskites enabled us to choose a wide range of Ca doping level from 0.2 to 0.8 to systematically investigate the effect of Ca doping content on the two-step thermochemical H₂O splitting performances in this study.

As evident from Fig. 4a, the temperature required to initiate the O₂ evolution significantly decreased and the O₂ releasing rate increased rapidly with the increase in Ca doping level. Also, the peak maxima were shifted to lower temperature with the increase in Ca doping level. This linear relationship resulted in higher O₂ evolution (402 $\mu\text{mol/g}$) by LCMO-0.8 compared to LCMO-0.6 (224 $\mu\text{mol/g}$), LCMO-0.4 (167 $\mu\text{mol/g}$) and LCMO-0.2 (94 $\mu\text{mol/g}$). However, the H₂ production performances recorded by using LCMO perovskite at 900 °C were not in full accordance with the O₂ evolution trend. As shown in

Fig. 4b, the H₂ production rate was found to be improved with the increase in Ca doping level from 0.2 to 0.4 and then decreased rapidly. As a result, the H₂ production achieved by LCMO-0.4 (314 $\mu\text{mol/g}$) is significantly higher than those achieved by the rest LCMO perovskites, e.g., LCMO-0.2 (187 $\mu\text{mol/g}$), LCMO-0.6 (243 $\mu\text{mol/g}$) and LCMO-0.8 (162 $\mu\text{mol/g}$).

The variations of O₂ and H₂ production tendencies as a function of Ca doping level can be pictorially presented in Fig. 5a. It is quite obvious that the ratio of H₂ and O₂ production remains close to the theoretical ratio of 2:1 up to Ca doping level of 0.4. However, the ratio decreases significantly at the higher Ca doping level, which indicates undesired reaction pathways for H₂ production. To gain further insight of this anomalous behavior, we have calculated the re-oxidation yield (in percentage) of each perovskite based on the recovery extent of O₂ after an intact thermochemical cycle. As shown in Fig. 5b, with the increase in Ca doping level, the re-oxidation yield decreases rapidly, especially when Ca doping level is beyond 0.4. For LCMO-0.2 and LCMO-0.4, the O₂ released during the thermal reduction process can be almost fully recovered after H₂O splitting reaction. However, only around 20% of the O₂ was recorded to be recovered for LCMO-0.8, further justifying the importance of an optimal level of Ca dopant in LCMO perovskites. Based on the Ca doping level investigation, LCMO-0.4 is confirmed to be the optimized composition among the investigated LCMO perovskites for two-step thermochemical H₂O splitting. From the aforementioned discussion, it is quite clear that the optimization of perovskite composition is as an efficient way to enhance the thermochemical catalytic performance.

Fig. 4 **a** O₂, **b** H₂ production curves for La_{1-x}Ca_xMnO₃ perovskites series with the Ca doping level from 0.2 to 0.8 in a two-step thermochemical H₂O splitting cycle carried out between 1300 and 900 °C

Fig. 5 **a** O₂ and H₂ production amounts, **b** re-oxidation yield of La_{1-x}Ca_xMnO₃ perovskites with the Ca doping level from 0.2 to 0.8 in a two-step thermochemical H₂O splitting cycle conducted between 1300 and 900 °C

3.3 Effect of Re-oxidation Temperature

After optimizing Ca doping level in LCMO perovskites, the re-oxidation temperature was further optimized for LCMO-0.4 sample. From the thermodynamic point of view, the re-oxidation temperature needs to be at least 200 °C lower than the thermal reduction temperature to favor the overall H₂O splitting performance of the catalyst [59]. However, the water splitting reaction cannot occur at very low re-oxidation temperature due to the limitation of reaction kinetics [60]. Herein, a re-oxidation temperature ranging from 700 to 1100 °C was investigated. Figure 6a, b shows the H₂ production curves and total gas production amounts using LCMO-0.4 as the catalyst. Clearly, with the increase in re-oxidation temperature, the H₂ production trend showed a typical convex parabolic shape (Fig. 6b). A maximum H₂ production amount with a steeper rate was

observed at the re-oxidation temperature of 900 °C. Thus, we can conclude that 900 °C is the most suitable re-oxidation temperature for LCMO-0.4 to carry out the water splitting.

3.4 Comparative H₂ Production Performance

Since CeO₂ is recognized as the benchmark material for two-step thermochemical H₂O splitting, the performance of our catalyst (LCMO-0.4) was rationally compared with CeO₂ under same experimental conditions. Figure 7a shows the O₂ releasing curves for LCMO-0.4 and CeO₂. It is evident that for both cases, thermal reduction is completed within 1 h at 1300 °C. Unlike CeO₂, LCMO-0.4 started to release O₂ at the onset temperature of ~ 900 °C, which is ~ 300 °C lower than that of CeO₂ (1200 °C). Also, the amount of evolved O₂ by LCMO-0.4 was larger

Fig. 6 **a** H₂ production curves, **b** summarized H₂ production amounts of LCMO-0.4 sample at different re-oxidation temperatures

Fig. 7 **a** O₂, **b** H₂ evolution curves of CeO₂ and LCMO-0.4 in the two-step thermochemical H₂O splitting cycle carried out between 1300 and 900 °C

than that by CeO₂. This observation justifies the utility of perovskite catalysts with superior O₂ releasing capacity over CeO₂ at relatively lower temperature in the thermochemical reduction process.

The H₂ production curves of the catalysts via the H₂O splitting at 900 °C are also presented in Fig. 7b. As evident, the H₂ production rate of LCMO-0.4 is significantly higher than that of CeO₂, consistent with the O₂ releasing performances (Fig. 7a). Also, the LCMO-0.4 sample can deliver O₂ and H₂ productions of 167 and 314 μmol/g, respectively (Fig. S4 in supplementary material), which are about 10 times higher than those of CeO₂ (17 and 34 μmol/g). Moreover, we also investigated the thermochemical performance of Sr-doped LMO (LSMO-0.4) with the same doping level under the same experimental condition as LCMO-0.4. As shown in Fig. S5 in supplementary material, both the O₂ and H₂ productions estimated by LSMO-0.4 (126 and 234 μmol/g, respectively) are significantly lower than those of LCMO-0.4. In addition, the performances of our optimally prepared perovskite (LCMO-0.4) catalyst are comparable with best results reported for La_{0.6}Sr_{0.4}MnO₃ [52], La_{0.6}Ca_{0.4}Mn_{0.8}Ga_{0.2}O₃ [61], La_{0.6}Ca_{0.4}Mn_{0.6}Al_{0.4}O₃ [62] and La_{0.6}Sr_{0.4}Mn_{0.6}Al_{0.4}O₃ [63] perovskites.

3.5 Cyclic Stability Test

Further, we checked the catalytic stability of LCMO-0.4 sample by running a total of six consecutive thermochemical H₂O splitting cycles between 1300 and 900 °C. As shown in Fig. 8a, relatively stable O₂ and H₂ production behaviors were observed during the entire cycling test. According to the O₂ releasing profile at thermal reduction step, the highest O₂ release rate was 0.111 μmol/g/s in the first cycle (Fig. 8a) and was found to be almost similar for

the remaining cycles. Also, the average time interval required to complete the O₂ production in each cycle was ~ 83 min. On the other hand, the H₂ evolution in the water splitting step occurred at a highest average rate of 0.364 μmol/g/s with the total average time of ~ 60 min. The summarized O₂ and H₂ production amounts for each cycle are also presented in Fig. 8b. It demonstrates that the H₂-to-O₂ production ratio of LCMO-0.4 is close to the theoretical value of 2. Therefore, all the oxygen vacancies generated during the high-temperature thermal reduction process have been successfully recovered during H₂O splitting process. Furthermore, we have roughly estimated the energy requirement during the entire cycling test which was calculated to be 0.06 kW h. After six consecutive thermochemical H₂O splitting cycles, the sample was characterized by XRD, SEM and BET-BJH [64] measurements. The XRD result suggests no significant change in the crystal structure (Fig. S6 in supplementary material), confirming that a stable perovskite structure of LCMO-0.4 sample is preserved after the redox reactions. On the other hand, only a negligible change on surface morphology (Fig. S7 in supplementary material) was observed without any serious sintering or aggregation, referring a stable porous structural property. To further justify the XRD and SEM results of LCMO-0.4 after cyclic stability test, we performed BET-BJH analysis to realize the change in surface area and porosity distribution. According to the comparative BET isotherm results, a decrease in the BET surface area from 14.2 to 11.5 m²/g was observed (Fig. S8a in supplementary material), while a slight change in the pore size distribution of LCMO-0.4 (sample after 6 cycles test) was also witnessed (Fig. S8b in supplementary material) after 6 cycles of thermochemical test. Therefore, LCMO-0.4 can be referred as a stable catalyst possessing

Fig. 8 **a** Six consecutive O₂, H₂ production profiles and **b** O₂ and H₂ yields and their corresponding ratio as a function of cycle number

the potentials for long-term thermochemical solar H₂ production applications.

4 Conclusion

Ca-doped lanthanum manganite perovskites (La_{1-x}Ca_xMnO₃) were systematically investigated at low thermal reduction temperature (1300 °C) by choosing a wide range of Ca doping level. An optimized composition of La_{1-x}Ca_xMnO₃ perovskite (La_{0.6}Ca_{0.4}MnO₃) was found to deliver an outstanding O₂ evolution and H₂ production performance in the two-step thermochemical H₂O splitting. In addition, the re-oxidation temperature of 900 °C was demonstrated to be the optimal one for the La_{0.6}Ca_{0.4}MnO₃ catalyst. More importantly, under the same experimental conditions, a maximum H₂ production of 314 μmol/g was achieved using La_{0.6}Ca_{0.4}MnO₃ as a catalyst which is about 10 times higher than that produced by the current benchmark CeO₂ catalyst. Besides, La_{0.6}Ca_{0.4}MnO₃ also exhibits superb stability during the cycling test with stable O₂ and H₂ production. We, therefore, believe that the optimization of doping level and operational condition in the perovskites is of paramount importance to achieve much enhanced thermochemical water splitting performance, which can also be essential for the molecular design of catalysts for other thermochemical applications, e.g., CO₂ splitting.

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