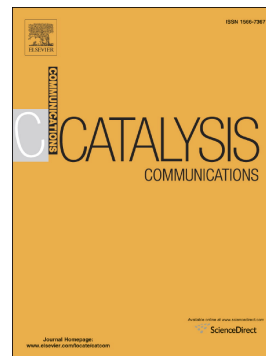


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Effect of La and Gd Substitution in $\text{BaFeO}_{3-\delta}$ Perovskite Structure on Its Catalytic Performance for Thermochemical Water Splitting

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Abstract

High-purity hydrogen production via water splitting over $\text{BaFeO}_{3-\delta}$ (BF)-based perovskites was studied, where reduction/oxidation temperatures were paired at 500/500, 700/700 and 900/900 °C. $\text{Ba}_{0.95}\text{La}_{0.05}\text{FeO}_{3-\delta}$ (BLF) yielded the highest H_2 production, ca. 1,310 $\mu\text{mol/g}$ at 900 °C. Adding either La or Gd into BF established a cubic phase structure, allowing a higher concentration of oxygen deficiency. Sintering was observed over all catalysts, which became more obvious when the oxidation temperature and number of cycles were increased. The apparent activation energy and pre-exponential factor for BLF oxidation in the presence of H_2O were estimated to be 47.4 kJ/mole and 0.18 s^{-1} , respectively.

Keywords: Water splitting, hydrogen production, thermochemical cycles, oxygen carriers, perovskites.

1. Introduction

Conventional hydrogen production via hydrocarbon steam reforming releases large amounts of carbon dioxide [1,2]. Hydrogen production from a two-step thermochemical water-splitting process affords an alternative and cleaner method. This process consists of two steps: reduction and oxidation of a metal oxide, which serves as an oxygen carrier within the process. The endothermic reduction step normally occurs at high temperatures, ranging from 800 to 1,700 °C [3,4], releasing oxygen atoms, and creating oxygen vacancies. The exothermic oxidation step occurs at relatively lower temperatures, ranging from 400 to 1,100 °C [3,4], generating hydrogen, and refilling oxygen vacancies in the material lattice. When cycling between the

reduction and oxidation step, temperature switching contributes to the thermal stress in the reactor system, and to a decrease in the overall efficiency of the process.

It has been reported that CeO_2 and CeO_2 - ZrO_2 were successfully used for the splitting of CO_2 and co-splitting of $\text{H}_2\text{O}/\text{CO}_2$ by thermochemical cycling, when the operating temperatures of the reduction and oxidation steps were kept the same, ca. 700/700 °C and 900/900 °C [5,6]. The results showed that, in the presence of CeO_2 , productivities ranging from 555 to 1,026 $\mu\text{mol/g}$ were achieved depending on the operating temperature and morphology of the CeO_2 . On the other hand, the productivities for CeO_2 - ZrO_2 were found to be 168 to 1,013 $\mu\text{mol/g}$ depending on the operating temperature.

In this work, the reduction and oxidation steps were operated at 500/500, 700/700 and 900/900 °C, with the aim of reducing the thermal stress in the system and increasing the overall efficiency of the process. The oxygen storage release/uptake was considered as the oxygen storage capacity (OSC), which depends on the reduction temperature, the environment gas, i.e., reducing gas or inert gas, and the partial pressure of the atmospheric oxygen[3]. In addition, a low concentration of reducing gas can be retrieved from the waste gaseous streams of some industries, e.g. waste CH_4 from biomass processes or waste H_2 from gas separation plants, and chlor-alkali plants can be utilized in the reduction steps.

A perovskite is a type of mixed metal oxide compound that has been widely applied for reactions due to its high OSC and reducibility. Barium ferrite oxide ($\text{BaFeO}_{3-\delta}$ or BF) was chosen in this work as the base perovskite because it possesses good chemical and thermal stability under severe conditions [7]. BF has been widely synthesized using the sol-gel method and applied in many applications, such as solid oxide fuel cells (SOFCs), photocatalytic processes, methane oxidation, or membrane separation[8–11]. The Pechini complex (PC) method is another catalyst preparation method that has been commonly used for perovskite synthesis[12]. However, BF has been reported to be suitable for only a limited range of operating temperatures[13,14].

In this work, ethylene glycol (EG) was used to assist the Pechini complex (PC) method, as EG has been reported to help decrease the calcination temperature of some perovskites, leading to the formation of a complete perovskite phase with operation at lower temperature [15]. Partial substitution of A and/or B sites into BF-based perovskites was reported to enhance the stability by forming a cubic phase as the major crystalline phase, and to improve the oxygen mobility at a lower operating temperature[7,11,16]. The cubic structure was reported to be established by the addition of smaller A-site or larger B-site cations into materials[16], resulting in an increase in the lattice free volume [16]. Due to the different atomic sizes of the A and/or B substitutes, the size of the unit cell volume is, therefore, changed, leading to a different distance of the critical radius bottleneck for oxygen migration [16]. In this work, La

(smaller A-site compared to Ba) and Gd (larger B-site compared to Fe) were chosen as the A- and B-site substitutes, respectively. The ionic radii of Ba^{2+} , Fe^{3+} , La^{3+} and Gd^{3+} have been reported to range from 1.350-1.610, 0.490-0.780, 1.032-1.360 and, 0.938-1.107 Å [17]. La and Gd were added into the BF-based perovskites for comparison purposes. The physical and chemical characteristics and catalytic performance of each catalyst towards the thermochemical cycles of H_2O splitting were observed. The kinetic parameters of this reaction for the best catalysts among all the prepared catalysts were determined.

2. Methodology

2.1 Catalyst preparation and characterization

An ethylene diamine tetra acetic acid (EDTA)-citrate complexing sol-gel method was utilized for catalyst preparation [18]. Relevant precursors, such as $\text{Ba}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{La}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and $\text{Gd}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, were dissolved and stirred in deionized water before adding EDTA at a molar ratio of total nitrates, EDTA, and citric acid of 1:1:1.5. The pH of solution was adjusted to 7 by dropwise addition of NH_4OH . The solution became a transparent gel after evaporation of the water, which then was placed in an oven at 180 °C, followed by calcination in air. During calcination, the temperature was increased at the rate of 3 °C min^{-1} from room temperature to 325 °C. After holding at 325 °C for 6 h, the temperature was then increased to 400 °C for 3 h, 600 °C for 10 h, and 1,000 °C for 1 h at the same heating rate.

The resulting perovskite was characterized using X-ray diffraction (XRD, Bruker D8 ADVANCE) with $\text{CuK}\alpha$ ($\lambda=1.5418$ Å) radiation at a scanning speed of 0.02°/s for 2θ ranging from 20° to 80°. The morphology of the fresh and spent materials was examined using a field emission scanning electron microscope (FE-SEM, SU-8230 Hitachi, Japan), operated at 10 kV. Hydrogen temperature programmed reduction (H_2 -TPR) was carried out afterwards to determine the optimal reduction temperature of each catalyst by introducing 10% H_2/Ar (BIG Company) and pure Ar through the sample bed at the rates of 5 and 195 mL/min using mass flow controllers. Prior to running H_2 -TPR, the sample was packed into a quartz tubular reactor, pretreated in 40% O_2/Ar (BIG Company) at 950 °C for 1 h and then cooled to room temperature while being purged with pure Ar (99.99%, BIG Company) throughout the process. During the H_2 -TPR, the temperature was increased at the rate of 5 °C/min from 25 °C to 950 °C. The gaseous product was analyzed using a quadrupole mass spectrometer (MS, GSD 320 O1, Balzers).

2.2 Experimental set-up

All the powder catalysts were pelletized and sieved to the selected particle size, ranging from 75 to 180 microns. Then, 0.5 g of the sieved catalyst was packed into the same quartz tube reactor used for H_2 -TPR. During the reduction and oxidation steps, the catalyst was reduced in 10% H_2/Ar at 100 mL/min and oxidized in 30% $\text{H}_2\text{O}/\text{Ar}$ at 200 mL/min at the paired temperatures of 500/500, 700/700, and 900/900 °C for 30 min for each step. The gaseous product stream was analyzed in realtime by MS.

3. Results and discussion

3.1 Catalysts characterization

Fig. 1 illustrates that the BF perovskite has a mixed phase structure consisting of hexagonal (PDF card no. 01-089-4618), rhombohedral (PDF card no. 01-078-5233) and cubic structures (PDF card no. 00-050-1844), based on ICDD (International Centre for Diffraction Data). This agrees with other works that reported that BF perovskites are commonly found to exhibit hexagonal and rhombohedral structures [19]. In contrast, the diffractograms for $\text{Ba}_{0.95}\text{La}_{0.05}\text{FeO}_{3-\delta}$ (BLF) and $\text{BaFe}_{0.975}\text{Gd}_{0.025}\text{O}_{3-\delta}$ (BFG) showed that cubic structures were achieved. The results are in agreement with previous works[11,20]. The latter studies reported that the substitution of A and B sites into BF-based perovskites establishes a desirable cubic structure, which provides a high oxygen deficiency concentration. The crystallite sizes of BF, BLF and BFG were calculated to be 58.7, 42.6, and 54.1 nm, respectively, using the Scherrer equation[21]. The sizes of the unit cells were calculated from the peak positions (2θ) and atomic planes of cubic phase, using least squares refinement, based on Bragg's equation via UNITCELL software[22].

The peak positions and planes for the BF solids (Fig. 1) were found at 22.161 (1 0 0), 31.550 (1 1 0), 38.116 (1 1 1), 45.234 (2 0 0), 50.921 (2 1 0), 56.178 (2 1 1), 65.853 (2 2 0), 70.435 (2 2 1), 74.894 (3 1 0), and 79.210 (3 1 1). Those values for BLF were identified at 22.264 (1 0 0), 31.693 (1 1 0), 39.057 (1 1 1), 45.418 (2 0 0), 51.146 (2 1 0), 56.444 (2 1 1), 66.364 (2 2 0), 70.782 (3 0 0), 75.241 (3 1 0), and 79.619 (3 1 1), and those for BFG at 22.182 (1 0 0), 31.591 (1 1 0), 38.934 (1 1 1), 45.234 (2 0 0), 50.962 (2 1 0), 56.219 (2 1 1), 65.955 (2 2 0), 70.925 (2 2 1), 74.894 (3 1 0), and 79.291 (3 1 1). The lattice constants of BF, BLF and BFG were determined to be 4.0102, 3.9890 and 4.0010 Å, while their cell volumes were estimated to be 64.493, 63.475 and 64.048 Å³, respectively. The BF unit cell and crystallite size were found to be the highest among all the catalysts, followed by BLF, and, surprisingly, BFG, where the latter was expected to be larger than that of BF because the atomic radius of Gd^{3+} is larger than that of Fe^{3+} . It is suggested that the smaller BFG unit cell was achieved because of the orthorhombic BaCO_3 , which is formed as an impurity minor phase, found in both BLF and BFG solid compositions. These results agree with previous works[19,20], where it has been reported that the impurity phase in perovskite oxides are responsible for shifting the peak positions of the major phase to slightly higher values[20], which results in a decrease in the lattice constant and cell volume for the materials. In this work, the peak positions for BaCO_3 (PDF card no. 00-005-0378) were detected at 24.299, 27.725, 33.719, 41.989 and 46.789[23].

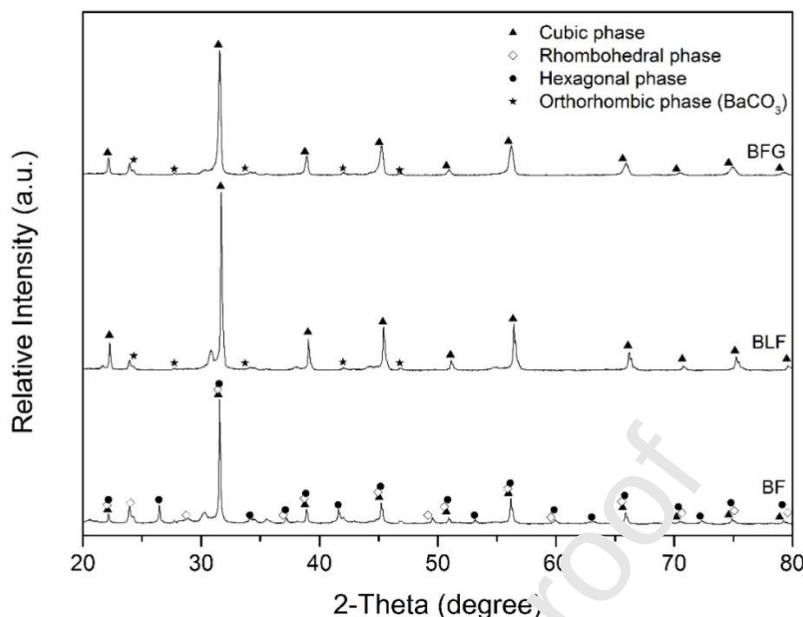


Fig. 1. XRD patterns for fresh BF, BLF, and BFG perovskite solids prepared using the EDTA citrate complexing sol-gel method.

H₂-TPR was carried out to determine the reducibility of the perovskites. H₂ consumption was plotted versus temperature for BF, BLF and BFG, as shown in Fig. 2. The TPR traces consist of three peaks for all the materials, which occur at 450-468 °C (reduction of Fe⁴⁺ to Fe³⁺), 800-879 °C (Fe³⁺ to Fe²⁺), and 950 °C (Fe³⁺ to Fe²⁺ and partially Fe²⁺ to Fe⁰[18,24]). The total amount of H₂ consumption over BF, BLF and BFG was estimated to be 1,448 1554, and 1282 μmol/g, respectively. In addition, at temperatures higher than 800 °C, BF was found to show the highest H₂ consumption (560.1 μmol/g) compared to BLF (236 μmol/g) and BFG (215.7 μmol/g), since BF exists as a mixed-phase structure at temperatures lower than 800 °C, and becomes a purely cubic structure at temperatures higher than 800 °C[20,25]. Thus, it could be concluded that addition of La³⁺ and Gd³⁺ can enhance the reducibility of such materials at temperatures lower than 800 °C. These results agree with the powder XRD diffractograms discussed in the previous section, where it was clearly shown that only BF has a mixed structural phase, while BLF and BFG have the cubic structure as the major crystalline phase. Correspondingly, La³⁺ addition (A-site substitution) decreased the perovskite crystallite size[7,26,27]. In contrast, Gd³⁺ addition (B-site substitution) was found to have the opposite effect on oxygen mobility due to the strong Gd-O chemical bonding. Upon comparing the bonding energy of Gd-O with that of Fe-O, it was found that the bonding energy of Gd-O is 719 kJ/mol, while that of Fe-O is only 390.4 kJ/mol[11]. Therefore, the addition of La³⁺ has a greater advantage for the BF-based perovskite than the addition of Gd³⁺ with respect to oxygen mobility.

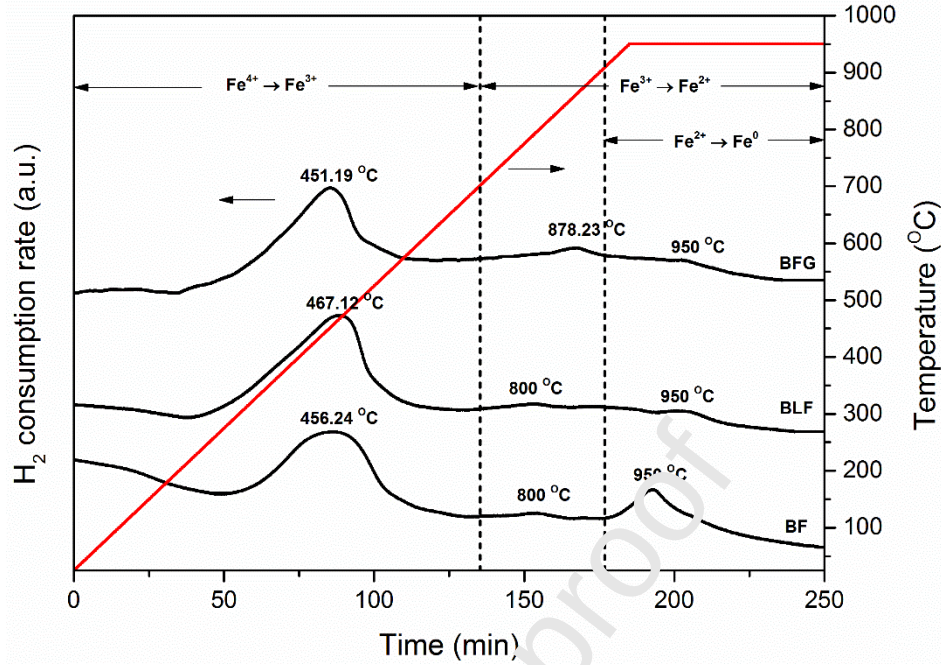


Fig. 2. H₂-TPR traces for the prepared BF, BLF and BFG perovskites in the range 25 - 950 °C.

3.2 Performance test for the thermochemical cycles of H₂O splitting

Fig. 3 shows 9 cycles of H₂ production (μmol/g) via thermochemical H₂O splitting in the presence of BF, BLF and BFG at T_{red}/T_{ox} = 500/500, 700/700 and 900/900 °C. The H₂ production was determined using the cumulative quantity of hydrogen produced per gram of solid as expressed by the following Eq. (1).

$$\text{H}_2 \text{ production } (\mu\text{mol/g}) = \frac{\int_0^t n \text{H}_2(t) dt}{g_{\text{solid}}} \quad (1)$$

For all the catalysts, it can be seen that when the temperature is increased, the H₂ productivity is also increased. Thus, the maximum H₂ production was achieved at 900/900 °C. At 900/900 °C, BLF showed the best performance among all the perovskites, yielding an average H₂ production of ~1,310 μmol/g, which is higher than that achieved through the use of BF, ~1,282 μmol/g. Thus, the addition of La³⁺ enhanced the oxygen mobility [7,26,27] due to its smaller cationic size compared to that of Ba²⁺. On the other hand, BFG showed poorer performance compared to BF, as evidenced in Fig. 3, where BFG yields a H₂ production of 852.5 μmol/g. This result agrees with the explanation given in the previous section, i.e., that the Gd-O bond is stronger than the F-O bond [11] and requires more energy to break. However, at T_{red}/T_{ox} of 500/500 and 700/700 °C, BF yielded the lowest H₂ productivity among the perovskites because BF contains a mixed crystal structure, consisting of hexagonal, rhombohedral and cubic phases, as shown in Fig. 1 and discussed above. In this temperature

range, BLF still showed the best performance for the same reason mentioned earlier.

In addition, catalyst sintering was suggested to occur based on the decrease in H_2 productivity observed when the number of cycles was increased. It is common for sintering to occur despite solid's calcination pre-treatment if the surrounding gas atmosphere is changed. In this case, the calcination gas composition changed from air to the reactant gas, H_2O , which can result in a different mechanism pathway due to the change in the surface energy [28,29]. In fact, the sintering was also due to the consecutive reduction and oxidation of the materials during repeated redox cycles.

The SEM technique was carried out to define the morphology of BLF before and after reaction in order to determine whether sintering was involved when the number of cycles and the operating temperature were increased.

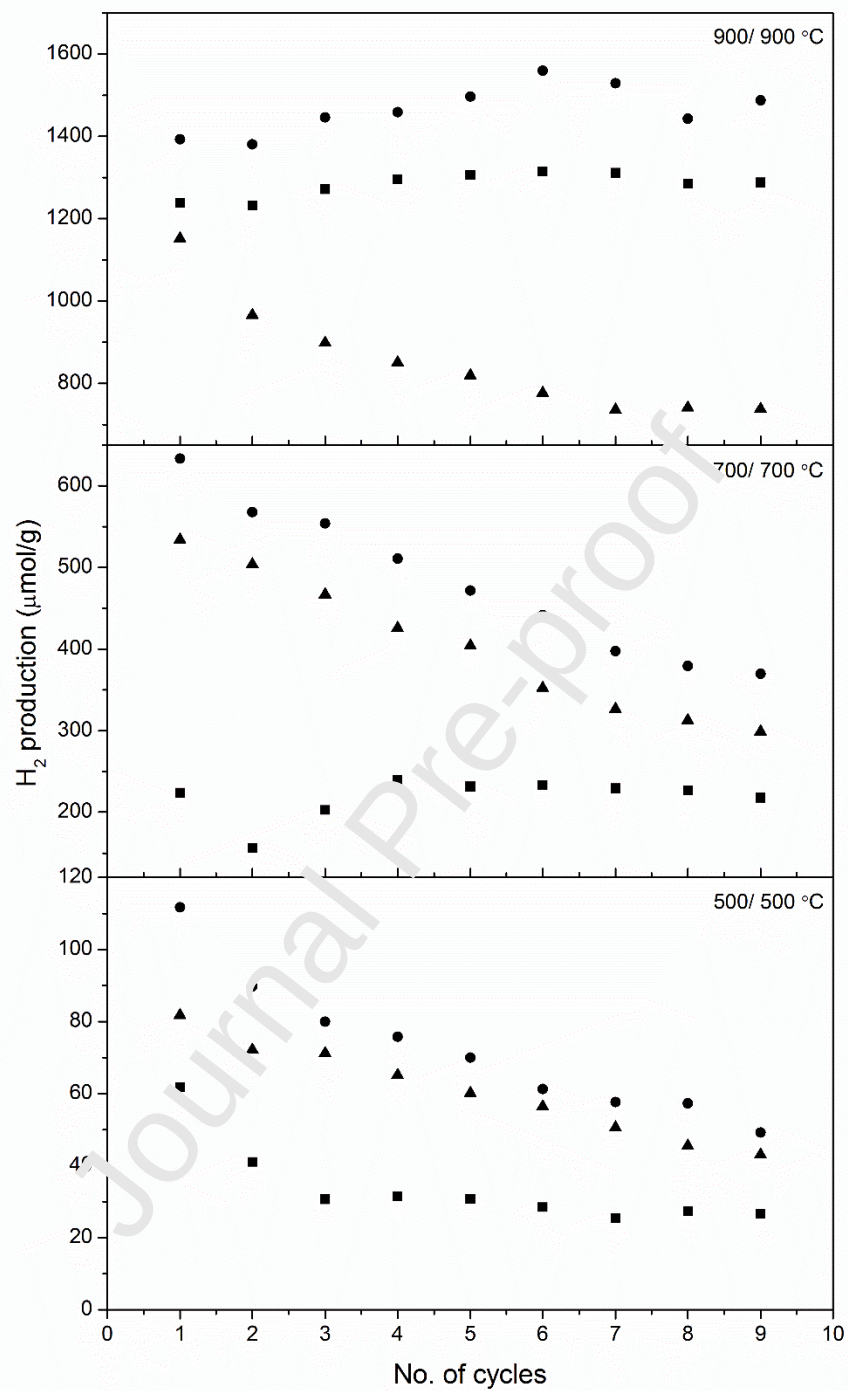


Fig. 3. Nine cycles of H_2 production via thermochemical H_2O splitting in the presence of BF (■), BLF (●), and BFG (▲) at 500/500 °C, 700/700 °C and 900/900 °C.

3.3 Morphology of the BLF pre- and post-exposure

Fig. 4 shows SEM images of the fresh BLF before the reaction (top left), BLF after 9 cycles of reaction at 500/500 °C (top right), BLF after 9 cycles of reaction at 700/700 °C (middle left), BLF after 9 cycles of reaction at 900/900 °C (middle right), BLF after the 1st reduction step cycle at 900 °C (bottom left), and BLF after the 1st oxidation step cycle at 900 °C (bottom right). It can be seen that sintering occurs in BLF at all temperatures after 9 cycles. The degree of sintering was obviously increased with increasing operating temperature. Sintering was also found after the 1st reduction cycle (bottom left). However, after the 1st oxidation cycle, the size of the grains became slightly smaller. The observed change in the surface was due to the reoxidation process, in which the oxygen in H₂O refilled the surface oxygen vacancies.

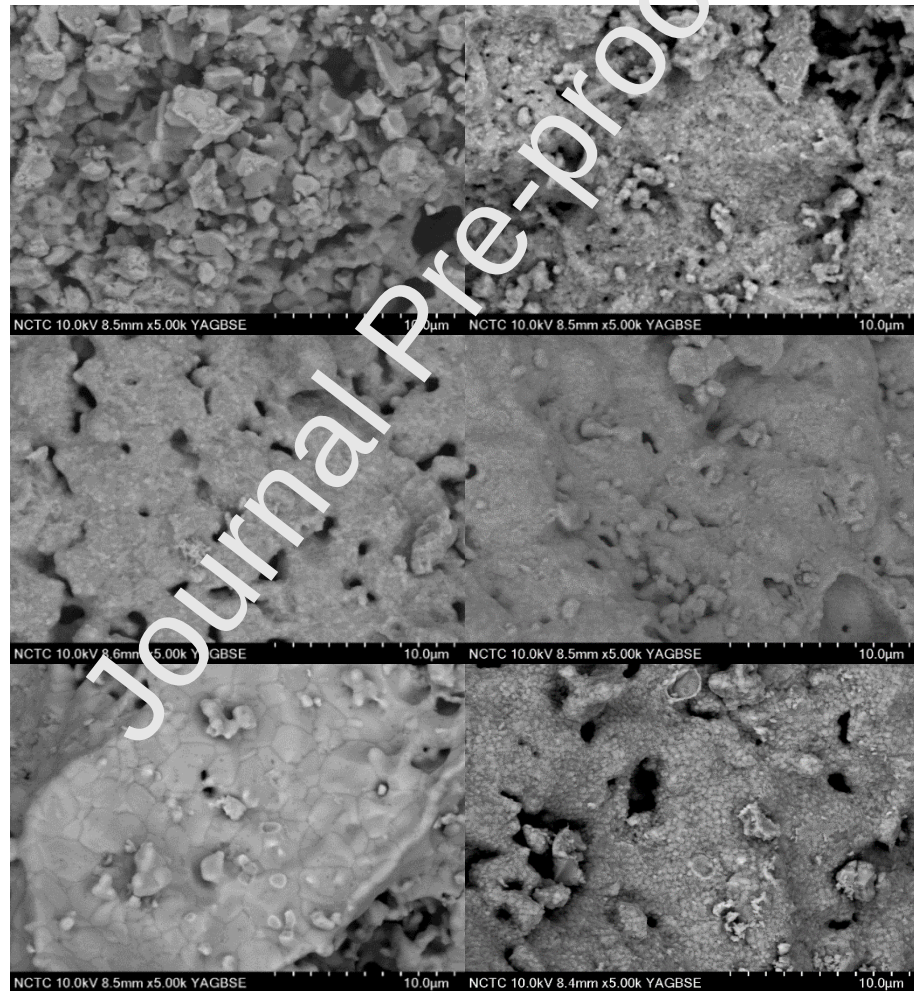


Fig. 4. Morphology of fresh BLF (top left) before reaction, BLF after 9 cycles of reaction at 500/500 °C (top right), BLF after 9 cycles of reaction at 700/700 °C (middle left), BLF after 9 cycles of reaction at 900/900 °C (middle right), BLF after the 1st reduction step cycle at 900 °C (bottom left), and BLF after the 1st oxidation step cycle at 900 °C (bottom right).

3.4 The adverse effect of the presence of other gases in waste gas

A mixed gas of $\text{CH}_4:\text{CO}_2:\text{H}_2$ at a ratio of 6:3:1 was used as a model H_2 -containing waste gas and applied as a reducing gas. This experiment was carried out to study the effect of the presence of other gases that might have an influence on H_2 productivity during the oxidation step. Fig. 5 compares the H_2 production rates achieved during the oxidation step when using 10% H_2/Ar and the model waste gas during the reduction step.

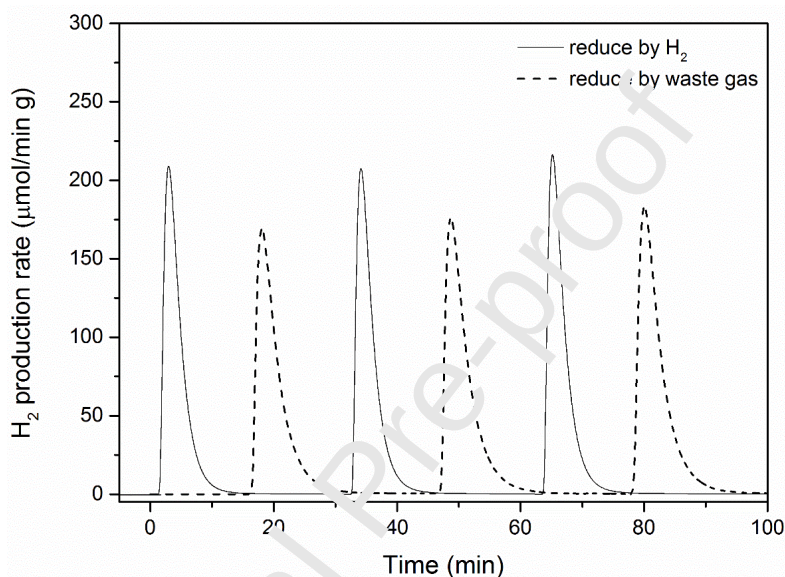


Fig.5. Effect of the type of reducing gas on H_2 production rate during 3 oxidation step cycles performed at 900/900 °C in the presence of BLF catalyst.

As shown in Fig. 5, the transient production rates are compared over 3 cycles of H_2O splitting in the presence of BLF when using H_2 and waste gas as a reducing gas. It was found that the average amount of H_2 production when using H_2 and waste gas as a reducing gas is 1,405 and 1,240 $\mu\text{mol/g}$, respectively. This result shows that H_2 production is lower when using the waste gas as a reducing gas, although the H_2 level in both reducing gases is the same (10 vol%). It might then be concluded that the other gases contained in the waste gas (CH_4 , CO_2) have a negative influence on the solid-gas reaction during the reduction process. One process step that could inhibit the reduction process performance is CO_2 adsorption, where CO_2 is adsorbed onto the surface of BLF, resulting in the blockage of active sites. However, since the waste gas only offers 11.8% less productivity than the H_2 reducing gas, it could be well utilized in this process.

3.4 Kinetic analysis

The kinetic parameters for BLF oxidation in the presence of H_2O were estimated. The solid conversions achieved under isothermal operation at 500, 700 and 900 °C were calculated using the following Eq. (2):

$$X(t) = \frac{n_0 \text{ reacted } (t)}{n_0 \text{ available}} = \frac{\int_0^t n H_2(t) dt}{n_{\text{reactive oxygen}}} \quad (2)$$

where, n represents the amount (mols) of reactive oxygen.

According to the gas-solid kinetics model, the reaction rate can be expressed in terms of solid conversion as a function of time, $dX(t)/dt$:

$$\frac{dX(t)}{dt} = k f(X) \quad (3)$$

where $f(X)$ is a function of the kinetic model to be described that represents the dependence of the reaction rate on the solid conversion. The functional forms for $f(X)$ were taken from several mathematical models for various rate-limiting mechanisms, namely [30]: model I: nucleation model ($nX^{(n-1)/n}$), model II: progressive conversion or order based model ($(1-X)^n$), model III: diffusion model ($1/2X$), and model IV: geometrical contraction model ($n(1-X)^{1/n}$). After fitting all the mentioned models with the present experimental data, it was found that the order-based model II showed the best fit, when a 1st-order reaction ($n = 1$) was assumed. The result agreed with previous work reported by K.S. Go et al. [37], where such equation was applied for reduction and oxidation of metal oxides for hydrogen production. Eq. (4) was therefore obtained and further applied, together with the Arrhenius relationship to estimate the activation energy (E_a) and pre-exponential factor (k_0) for oxidation water splitting reaction over the reduced BLF catalyst.

$$\frac{dX(t)}{dt} = k (1-X(t))^n, n=1 \quad (4)$$

In addition, the order-based model (model II) is only applicable to porous materials [36], where gaseous reactants can constantly penetrate through the solid phase with no mass transfer limitation. However, since sintering was found in BLF over the entire temperature range, the material then became nonporous sintered BLF. Since model II best fit the experimental data, the following can be concluded: (i) There were plenty of surface oxygen vacancies available for reaction with the gaseous H_2O ; therefore, the location of the oxygen vacancies (inside or outside the pore) became insignificant; (ii) The reaction rate of H_2O splitting was slower than the rate of oxygen solid diffusion (from the surface to the bulk); (iii) When the driving force for solid oxygen diffusion became small (the concentration of oxygen vacancies between the surface and bulk became similar), the reaction rate decreased and slightly deviated from that of model II. The apparent activation energy (E_a) and pre-exponential factor (k_0) were determined to be 47.4 kJ/mol and 0.18 s^{-1} , respectively. It should be noted that the E_a value for BLF was found to be lower compared to that reported for other catalysts [31–33].

4. Conclusions

BLF was successfully synthesized using the EDTA-citrate complexing sol-gel method. BLF and

BFG were found to contain a major-phase cubic structure, which has been reported to support the best oxygen transport channels with a high level of oxygen vacancy disorder, leading to a high oxygen storage capacity and a high oxygen exchange rate. These results agree with the thermochemical water splitting catalytic performance tests, which showed that BLF has the best performance among all the catalysts, with BFG showing the second best performance for temperatures ranging from 500 to 700 °C; however, BF showed the second best performance at 900 °C. This difference in performance was because the BF phase structure changes from rhombohedral/hexagonal/cubic to a pure cubic structure at temperatures higher than 800 °C; thus, BF was the least effective material at temperatures ranging from 500 to 700 °C. On the other hand, BFG was the least effective at 900 °C because, at this temperature, BF has a pure cubic structure.

From the catalytic performance results, the addition of La^{3+} was found to have a more positive effect on BF-based perovskites than the addition of Gd^{3+} . This was presumably because La^{3+} has a smaller ionic radius compared to Ba^{2+} , which is thus likely to lead to a larger lattice free volume for oxygen transport. The addition of Gd^{3+} has the opposite effect, as the strength of the Gd-O bond is greater than that of the Fe-O bond. In addition, the ionic radius of Gd^{3+} is larger than that of Fe^{3+} . A larger B-site substitute has also been reported to establish larger lattice parameters. In contradiction, the present XRD results showed the opposite behavior, as Gd^{3+} addition resulted in a smaller-sized BFG unit cell. At the same time, Fe^{3+} (B site) was also partly replaced by Gd^{3+} , resulting in similar lattice constants for BF and BFG, which were calculated to be 4.0010 and 4.0102 Å, respectively. The apparent activation energy and pre-exponential factor for the oxidation water splitting over BLF were determined to be 47.4 kJ/mol and 0.18 s^{-1} , respectively. The E_a for BLF was found to be lower than those found for catalysts recently developed by others.

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Declaration of interests

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.

Author Contribution

A. Ngoensawat: Writing-Original Draft, Investigation **V. Tongnan:** Visualization, Data curation, Methodology **N. Laosiripojana:** Resources, validation **P. Kim-Lohsoontorn:** Formal analysis **U.W. Hartley:** Supervision, Writing-Review&Editing, conceptualization, funding acquisition

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Graphical abstract:

Highlights:

- Three BaFeO_{3-δ} (BF) based perovskites towards hydrogen production were studied.

- Addition of lanthanum and gadolinium into the BF based perovskite were observed.
- BLF showed the best performance during temperature ranging from 500 to 900 °C.
- All the catalysts showed their best performance at 900 °C.
- E_a and k_0 of the BLF oxidation using water was 47.39 kJ/mole and 0.18 s^{-1} .