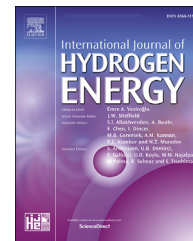


Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

ScienceDirect

journal homepage: [www.elsevier.com/locate/he](http://www.elsevier.com/locate/he)

# Application of a micro-channel reactor for process intensification in high purity syngas production via H<sub>2</sub>O/CO<sub>2</sub> co-splitting

Nonchanok Ngoenthong<sup>a</sup>, Vut Tongnan<sup>a</sup>, Thana Sornchamni<sup>b</sup>,  
Nuchanart Siri-nguan<sup>b</sup>, N. Laosiripojana<sup>c</sup>,  
Unalome Wetwatana Hartley<sup>a,c,\*</sup>

<sup>a</sup> Chemical and Process Engineering, The Sirindhorn International Thai-German Graduate School of Engineering (TGGS), King Mongkut's University of Technology North Bangkok, Bangkok, 10800, Thailand

<sup>b</sup> PTT Public Company Limited, 555 Vibhavadi Rangsit Road, Chatuchak, Bangkok, 10900, Thailand

<sup>c</sup> Joint Graduate School of Energy and Environment (JGSEE), King Mongkut's University of Technology Thonburi, Bangkok, 10140, Thailand

## H I G H L I G H T S

- Optimal reduction/oxidation temperatures for the micro-channel reactor is 700 °C.
- H<sub>2</sub>O splitting was more favored, compared to CO<sub>2</sub> splitting, in the presence of LSCF.
- Activation energy of H<sub>2</sub>O spitting and CO<sub>2</sub> splitting was estimated at 87.33 kJ/mol, and 102.85 kJ/mol.
- The pre-exponential factor of H<sub>2</sub>O splitting and CO<sub>2</sub> splitting was 595.24 s<sup>-1</sup> and 698.79 s<sup>-1</sup>, respectively.

## A R T I C L E I N F O

### Article history:

Received 27 August 2019

Received in revised form

7 November 2019

Accepted 30 November 2019

Available online xxx

### Keywords:

Thermochemical cycles

Micro-channel reactor

Perovskite

LSCF

Kinetics

## A B S T R A C T

A stainless steel micro-channel reactor was tailor-made to an in house-design for process intensification propose. The reactor was used for a two-step thermochemical cycles of H<sub>2</sub>O and CO<sub>2</sub> co-splitting reaction, in the presence of La<sub>0.3</sub>Sr<sub>0.7</sub>Co<sub>0.7</sub>Fe<sub>0.3</sub>O<sub>3</sub> (LSCF). LSCF was coated inside the reactor using wash-coat technique. Oxygen storage capacity of LSCF was determined at 4465 μmol/g, using H<sub>2</sub>-TPR technique. H<sub>2</sub>O-TPSR and CO<sub>2</sub>-TPSR results suggested that a formation of surface hydroxyl group was the cause of H<sub>2</sub>O splitting favorable behavior of LSCF. Optimal operating reduction/oxidation temperature was found at 700 °C, giving 2266 μmol/g of H<sub>2</sub>, 705 μmol/g of CO, and 67% of solid conversion, when the H<sub>2</sub>O and CO<sub>2</sub> ratio was 1 to 1, and WSHV was 186,000 mL/g.h. Activation energy of H<sub>2</sub>O spitting and CO<sub>2</sub> splitting was estimated at 87.33 kJ/mol, and 102.85 kJ/mol The pre-exponential factor of H<sub>2</sub>O splitting and CO<sub>2</sub> splitting was 595.24 s<sup>-1</sup> and 698.79 s<sup>-1</sup>, respectively.

© 2019 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

\* Corresponding author. Chemical and Process Engineering, The Sirindhorn International Thai-German Graduate School of Engineering (TGGS), King Mongkut's University of Technology North Bangkok, Bangkok, 10800, Thailand.

E-mail address: [unalome.w.cpe@tggs-bangkok.org](mailto:unalome.w.cpe@tggs-bangkok.org) (U.W. Hartley).

<https://doi.org/10.1016/j.ijhydene.2019.11.240>

0360-3199/© 2019 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

## Introduction

Thermochemical cycles of water ( $\text{H}_2\text{O}$ ) and carbon dioxide ( $\text{CO}_2$ ) co-splitting is one of the most green syngas production technologies compare to others [1–9]. It does not only require abundant, available and non-toxic  $\text{H}_2\text{O}$  as a feedstock; but also utilize  $\text{CO}_2$ , the world most concerned greenhouse gas [10]. The process consists of two separate but consecutive endothermic reduction and exothermic oxidation steps in the presence of high oxygen storage capacity (OSC) material. Main challenges for this reactions are (1) the need of the process cycling between reduction and oxidation step (2) if both reduction and oxidation steps are separately operated in one chamber of reactor, thus, a fast sophisticated feed switching system is requisition (3) because both steps have different optimal temperature (700–1700 °C for reduction step and 400 to 1200 °C for oxidation step, depending on the selected oxygen carrier material), therefore, the temperature switching is also mandatory. This leads to a loss in overall efficiency of the process, because of the time required during the temperature switching. The micro-channel reactor was designed to minimize this problem due to its well-known rapid heat and mass transfer. These characteristics also advantage in narrow product distribution according to homogeneous temperature gradient within the reactor and shorter resident time [11–16]. In terms of material development worldwide milestone, metal oxides such as  $\text{ZnO}/\text{Zn}$ ,  $\text{SnO}_2/\text{SnO}$ ,  $\text{Fe}_3\text{O}_4/\text{FeO}$ ,  $\text{CoFe}_2\text{O}_4/\text{Al}_2\text{O}_3$ , ceria, doped-ceria,  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$ ,  $\text{La}_{1-x}\text{Sr}_x\text{MnAl}_{1-y}\text{O}_{3-\delta}$ , and  $\text{La}_{1-x}\text{A}_x\text{B}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$  were studied in the past decades [17–25].

Perovskites ( $\text{ABO}_{3-\delta}$ ) are one of the most promising oxygen carriers. Its oxygen vacancies can be intrinsically formed when calcined at high temperature, offering high oxygen storage capability (OSC) and, therefore, high reducibility. A and B site in the perovskite compounds can be substituted to improve its specific properties i.e. electronic conductivity, oxygen mobility and oxygen exchange rate [26–28].  $\text{La}_{1-x}\text{Sr}_x\text{O}_3$  (LSO) perovskite family was widely researched due to its thermal stability and oxygen storage capacity [29–31]. Cobalt (Co) as a B-site substitute in LSO was found to enhance its reducibility and catalytic performance, yet allow the reaction to occur at considerable low temperature due to its weak Co–O bond.  $\text{La}_{1-x}\text{Sr}_x\text{Co}_y\text{O}_3$  (LSC) can be partially reduced/oxidized at different degree depending on the applied temperatures, where its oxidation states alter between  $\text{Co}^{2+}$ ,  $\text{Co}^{3+}$ , and  $\text{Co}^{4+}$  [29,30]. Moreover, doping Fe in the LSC was found to reduce the material's thermal expansion and increase thermal stability [31]. Amount of the A- and B- site substitution also influences the perovskite's characteristics. For  $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ , the best stoichiometric ratio between La, Sr, Co and Fe were found to be 0.3, 0.7, 0.7 and 0.3, respectively, where  $x = 0.7$  and  $y = 0.3$ .  $\text{La}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.7}\text{Fe}_{0.3}\text{O}_{3-\delta}$  (LSCF3773) showed highest stoichiometric reduction ( $\Delta\delta = 0.4$ ) amongst other perovskites in the same family such as  $\text{La}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$  (LSCF3791,  $\Delta\delta = 0.38$ ) or  $\text{La}_{0.2}\text{Sr}_{0.8}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  (LSCF2828,  $\Delta\delta = 0.35$ ) [32]. LSCF3773 could be synthesized to achieved a pure cubic structure with Goldschmidt's tolerance factor ranging from 0.9 to 1, leading to a high redox capacity [33,34]. In this work, LSCF3773 was in-house prepared using EDTA-CA-EG method [35,36]. The material was characterized

by relevant techniques i.e. XRD,  $\text{H}_2$ -TPR,  $\text{H}_2\text{O}$ -TPSR, and  $\text{CO}_2$ -TPSR. Catalytic performance of LSCF3773 towards  $\text{H}_2\text{O}$  and  $\text{CO}_2$  co-splitting was studied in a lab-designed micro-channel reactor. Both reduction and oxidation steps were operated at the same temperature, to minimize the time required for temperature switching, increase the overall efficiency, and to minimize the thermal stress of the reactor. Gas-solid reaction model was predicted. The kinetic parameters i.e. activation energy and pre-exponential factor were estimated.

## Experimental procedures

### Synthesis of LSCF powder and LSCF suspended solution

LSCF was synthesized using EDTA-CA-EG method [35,36]. The amount of relevant metal precursors were prepared from metal precursors (M), citric acid (CA), ethylenediaminetetraacetic acid (EDTA) and ethylene glycol (EG) at the mole ratio of 1:1.5:1:1, respectively. Nitrate precursors of the metals; lanthanum (III) nitrate hexahydrate ( $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , 99%, Himedia); strontium (II) nitrate ( $\text{Sr}(\text{NO}_3)_2$ , 99%, Himedia); cobalt (II) nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 99%, Ajax finechem); iron (III) nitrate nonahydrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , 98%, Ajax finechem); were dissolved in deionized water. EDTA ( $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8$ , 99.4%, Ajax finechem) was added into 2 M ammonium hydroxide solution ( $\text{NH}_4\text{OH}$ , 28%wt, J.T.Baker) and stirred until EDTA was completely dissolved. EDTA- $\text{NH}_4\text{OH}$  solution was dropped into the mixed metal nitrate solution and added CA ( $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ , 99.5%, Lobachemie) and EG ( $\text{C}_2\text{H}_6\text{O}_2$ , 99.5%, Ajax finechem) until a clear homogeneous solution was achieved. The solution's pH was maintained at 6 using  $\text{NH}_4\text{OH}$  solution, while heated to 90 °C and stirred until becoming gel. The gel was dried at 180 °C overnight, then crushed, and calcined in air at the best calcination temperature function studied, shown in Section [Effect of calcination temperature profile on the physical properties of LSCF](#). The resulting LSCF was sieved to less than 38  $\mu\text{m}$  particle size. The LSCF sieved particles were then suspended in a mixture of water, polyvinyl alcohol and acetic acid at the ratio of 10–84: 5: 1 by weight. Polyvinyl alcohol ( $(\text{C}_2\text{H}_4\text{O})_x$ , Chem-supply) was dissolved in deionized water while stirred at 65 °C for 3 h. The solution was left overnight before the catalyst and acetic acid were added into. The obtained suspension was stirred at 65 °C for 3 h before cooled down to room temperature and stirred continuously for 72 h.

### Surface pre-treatment and catalyst coating process

Micro-structured stainless-steel (grade 316L) plates were fabricated to lab-designed, shown in [Fig. 1](#), by Thai German Institute (TGI, Thailand). The substrates were cleaned with 20% v/v of citric acid in the ultrasonic bath for 30 min. They were annealed at 800 °C with 1 °C/min of heating rate for 2 h, to form mixed-oxides layer on the stainless steel surface for the better adhesion ability. The prepared LSCF suspension solution was then wash-coated on the micro-channels inside each plate. The coated plates were left at room temperature until dried. The substrates were heated up to 120 °C in an oven overnight and calcined at 500 °C for 3 h at 1 °C/min of heating

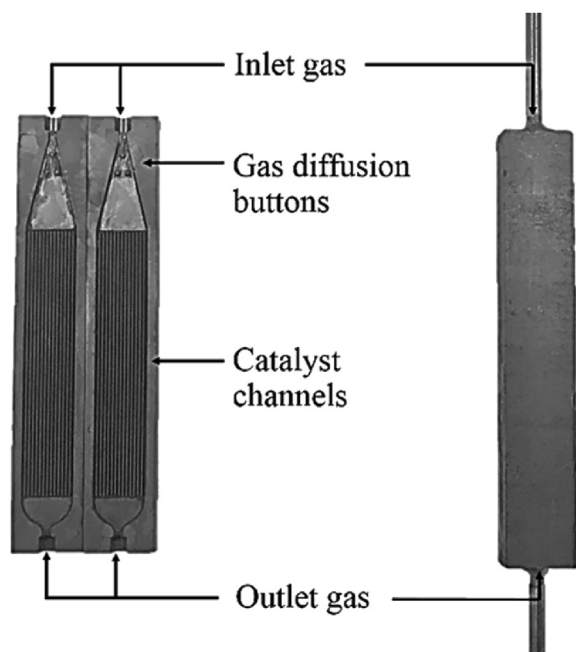


**Fig. 1 – Micro-channel plates with 14 channels with 300  $\mu\text{m}$  depth, 370  $\mu\text{m}$  width, and 50 mm length (left) and the laser-welded micro-channel reactor (right).**

rate. The two coated substrates were laser-welded together as shown. 1/8-inch stainless steel tubing (Swagelok) was as well welded to the top and bottom of the reactor and used for gaseous inlet and outlet.

### Characterizations

#### Physical properties of LSCF

The catalyst's crystal structure was observed using XRD (Rigaku TTRAX III model) with  $\text{CuK}\alpha$  as x-ray source and wavelength 1.5418 Å, the angle range 5–80°, and rate 5°/min.

#### Transient experiments

Fig. 2 shows the rig that used for both transient and steady-state experiments. Transient experiments were carried out in a quartz tube packed-bed reactor (i.d. = 10 mm, o.d. = 13 mm, length = 25 cm), to characterize catalytic behaviors of LSCF while the steady-state experiments were performed in a micro-channel reactor, to determine optimal operating conditions and kinetic parameters. An electrical furnace (Inconel, heating zone = 20 cm) was used as an external heat supply for all the experiments. Hydrogen temperature programmed reduction ( $\text{H}_2$ -TPR),  $\text{H}_2\text{O}$  temperature programmed surface reaction ( $\text{H}_2\text{O}$ -TPSR), and  $\text{CO}_2$  temperature programmed surface reaction ( $\text{CO}_2$ -TPSR) were carried out separately to investigate the oxygen release behavior versus time, the oxygen uptake behavior by  $\text{H}_2\text{O}$  and  $\text{CO}_2$  on the LSCF surface, respectively. Feed molar ratio was fixed at 1 to 1. Ar, as a make-up gas, was used to control the total flow rate at 200 mL/min. Steam was produced using a combination of a peristaltic pump and an evaporator before introduced into

the system via 170 °C trace-heated piping system. For the transient experiments, the weight of the catalyst was maintained at 0.5 g for all experiments. During the  $\text{H}_2$ -TPR, 10%  $\text{H}_2/\text{Ar}$  was passed through the catalyst's bed in the reactor. The temperature was then increased from room temperature to 950 °C and hold for 30 min. For TPSR, LSCF was reduced by 10%  $\text{H}_2/\text{Ar}$  at 700 °C for 30 min before each experiment. The corresponding reactant, either  $\text{H}_2\text{O}$  or  $\text{CO}_2$  was fed through the reactor while the temperature increased from room temperature to 950 °C at 5 °C/min of heating rate. The gaseous products were analyzed using on-line mass spectrometer (MS, GSD 320 O1, OmniStar gas analysis) for all experiments.

### Steady-state experiments

All steady-state experiments were carried out in a micro-channel reactor as mentioned in the previous section, although using the same rig, shown in Fig. 2. Before each experiment, the system was purged by Ar using a mass flow controller at room temperature for 1 h. The catalyst was reduced at either 500, 600 or 700 °C for 30 min before the oxidation step was carried out at 500, 600, 650, and 700 °C for 15 min. Ar was purged through the system between each step every time. The gaseous products were intervally collected every single minute using gas bags and analyzed by a gas chromatography (Shimadzu GC-2014ATF, Thermal Conductivity Detector (TCD)). Solid conversion was calculated using the following equation;

$$X(t) = \frac{n_{\text{O}_2, \text{reacted}}}{n_{\text{O}_2, \text{available}}} = \frac{\int_0^t n_{\text{H}_2, \text{CO}} dt}{n_{\text{O}_2, T_{\text{red}}}} \quad (1)$$

where  $X(t)$  is the solid conversion,  $n_{\text{O}_2, \text{reacted}}$  is the amount of  $\text{H}_2$  and  $\text{CO}$  production and  $n_{\text{O}_2, \text{available}}$  is the amount of released oxygen of LSCF at the selected reduction temperature, received from the  $\text{H}_2$ -TPR result.

### Kinetics analysis

The kinetic parameters were estimated using Arrhenius equation, shown in Eq. (2);

$$\frac{dX}{dt} = k(T) \cdot f(x) \quad (2)$$

$f(x)$  is a solid conversion model which was applied from Boltzmann model [37] as following;

$$X(t) = X_u - \frac{X_u}{1 + \exp\left[\frac{(t-t_0)k'}{X_u}\right]} \quad (3)$$

where  $X_u$  is the ultimate conversion,  $k'$  is the reaction rate constant ( $\text{s}^{-1}$ ),  $t$  is time at conversion and  $t_0$  is time at 0.5 $X_u$

$$k(T) = k_0 \cdot e^{\frac{-E_a}{RT}} \quad (4)$$

The equation was rearranged as;

$$\ln k(T) = \ln k_0 - \frac{E_a}{RT} \quad (5)$$

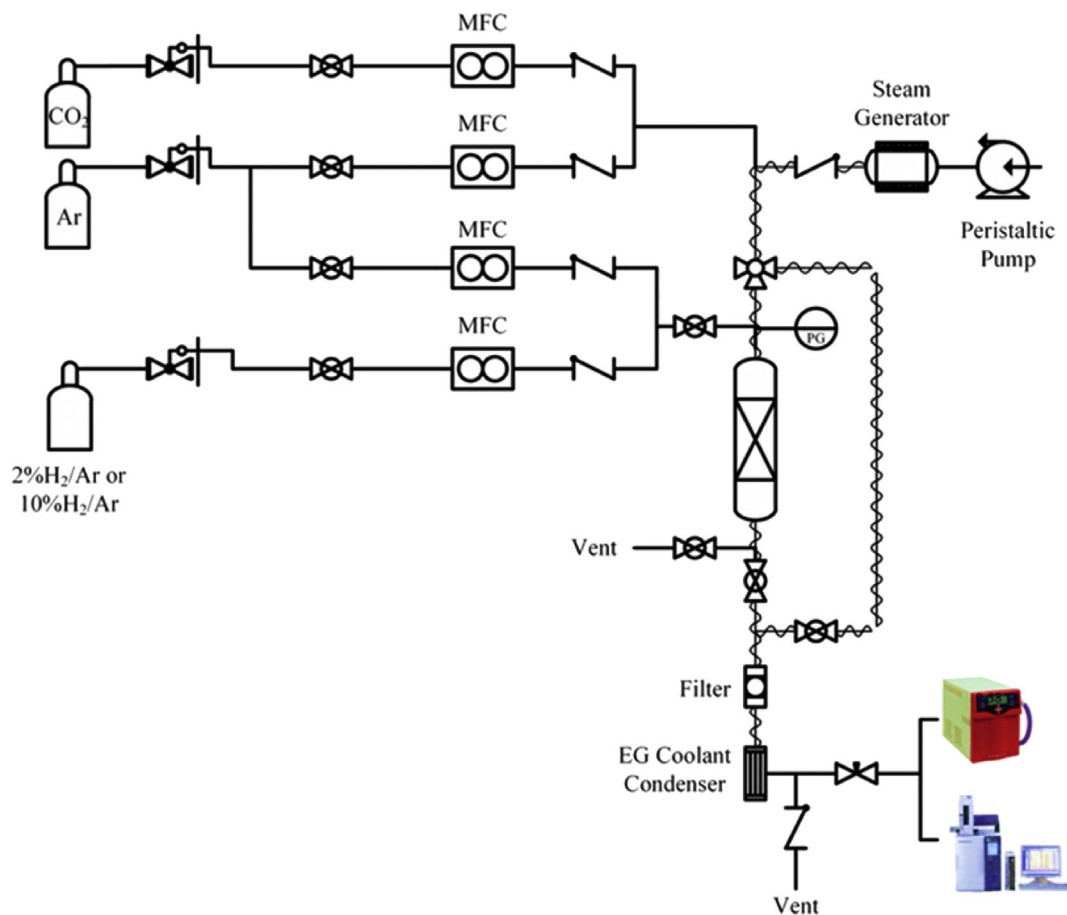


Fig. 2 – Rig schematic diagram for transient and steady-state experiments.

The activation energy ( $E_a$ ) and the pre-exponential factor ( $k_0$ ) were achieved by plotting  $\ln k$  versus  $1/T$ .

## Result and discussion

### Effect of calcination temperature profile on the physical properties of LSCF

From Fig. 3, it can be seen that LSCF formed a pure cubic structure when temperature profile (2) was applied. Temperature profile (2) consisted of 4 stepped temperatures; which were 325, 400, 600 and 900 °C; at 2 °C/min of heating whereas profile (1) had 2 stepped temperatures at 600, and 900 °C with a much higher heating rate at 10 °C/min. Both LSCF calcined using either calcination profile (1) or (2) showed cubic structure, corresponding to the atomic plane {012}, {110}, {202}, {024}, {214}, {208} and {128}. The result was agreeable with previous reports [32,38]. The cubic structure perovskites were well-known to have larger unit cell compared to other structures, leading to a wider space and resulting in a faster oxygen transfer rate [39,40]. LSCF which calcined using temperature profile (1) was found to form an incomplete/contaminated cubic structure. This was possibly due to its fast heating rate, leading the residuals contamination. Slow heating rate during the calcination process was found to enhance the purity of the material.

### Transient experiments

#### H<sub>2</sub>-TPR

H<sub>2</sub>-TPR was carried out to investigate reduction behavior of LSCF. Fig. 4 shows reduction profile of LSCF when the temperature ramped from 100 to 950 °C. The first reduction peak occurred at 345 °C where  $\text{Co}^{3+}$  was reduced to  $\text{Co}^{2+}$ , giving H<sub>2</sub> consumption at 1265  $\mu\text{mol/g}$  (presumably equivalent to oxygen atom release). The second peak was presented at 575 °C where there was the reduction of  $\text{Fe}^{4+}$  to  $\text{Fe}^{3+}$  and  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ . This peak contributed to 2030  $\mu\text{mol/g}$  of H<sub>2</sub> consumption.  $\text{Co}^{2+}$  was reduced to Co at 700 °C, giving H<sub>2</sub> consumption of 1170  $\mu\text{mol/g}$ . The reduction peaks occurred at 815 and 920 °C, giving overall H<sub>2</sub> consumption of 1655  $\mu\text{mol/g}$ , were corresponded to partial reduction of  $\text{Fe}^{2+}$  to Fe. The result was agreed with other works, reporting the change of B-site's oxidation state [41–45].

#### H<sub>2</sub>O-TPSR and CO<sub>2</sub>-TPSR

Temperature programmed surface reaction of H<sub>2</sub>O splitting (H<sub>2</sub>O-TPSR), and CO<sub>2</sub> splitting (CO<sub>2</sub>-TPSR) were separately carried out over LSCF. H<sub>2</sub>O-TPSR profile, shown in Fig. 5(a), illustrated 4266  $\mu\text{mol/g}$  of H<sub>2</sub> production at 725 °C, estimated at 95% of solid conversion. CO<sub>2</sub>-TPSR profile was shown in Fig. 5(b), where it represented 725  $\mu\text{mol/g}$  of CO production at 805 °C, equivalent to 16% of solid conversion. From the result,

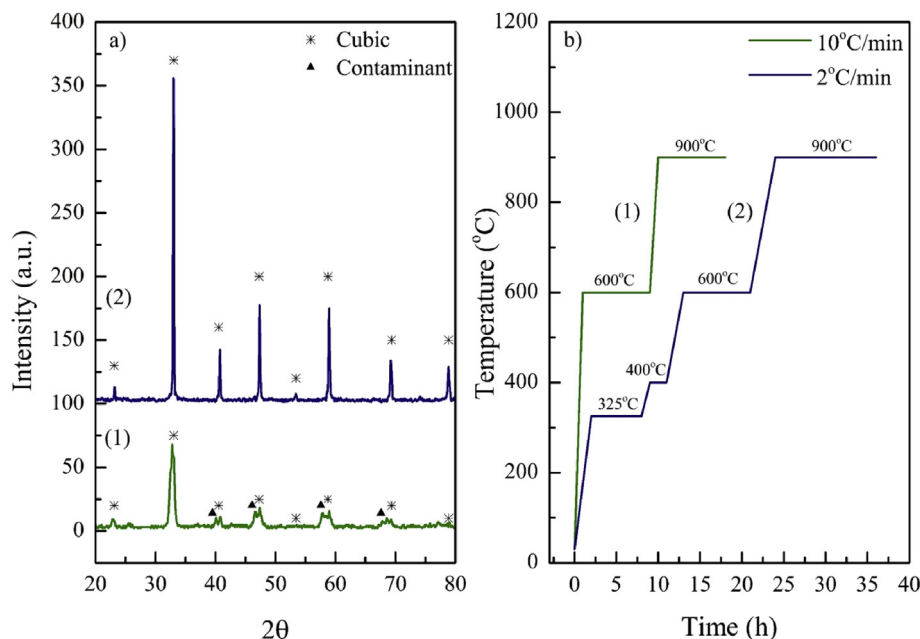


**Fig. 3 – The effect of calcination temperature profile on phase structure of LSCF; (a) diffractograms of LSCF calcined under calcination profile illustrated in (b) where profile (1) represented in green and (2) represented in blue (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article).**

it can be concluded that the majority of  $\text{H}_2\text{O}$  splitting and  $\text{CO}_2$  splitting occurred at similar temperature range (600–850 °C), although  $\text{CO}_2$  splitting started to occur at slight higher temperature (600 °C) than  $\text{H}_2\text{O}$  splitting (520 °C) (see Fig. 6).

#### LSCF activity on micro-channel reactor

##### The effect of reduction temperature on oxygen vacancy concentration and syngas productivity

The reduction temperature was varied at 500, 600, and 700 °C while the oxidation temperature was fixed at 700 °C, to study

the effect of reduction temperature on the oxygen release (during reduction step) and syngas productivity (during the oxidation step). Total flow rate was adjusted to 200 mL/min, and  $\text{H}_2$  to  $\text{CO}_2$  ratio was kept at 1 to 1, for all experiments.

The result showed that when the reduction temperature was higher, the oxygen vacancy concentration was increased, leading to the better performance during the oxidation step. However, the syngas productivity was remained similar when the reduction temperature increased from 600 to 700 °C, due to the thermodynamic limitation during the oxidation step, meaning that the higher syngas productivity would be higher if

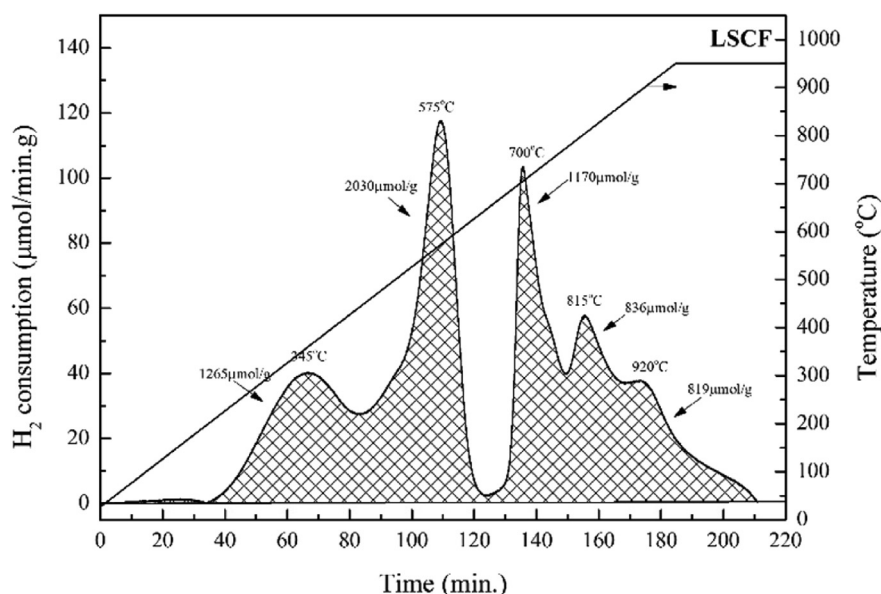


**Fig. 4 –  $\text{H}_2$ -TPR profile of LSCF.**

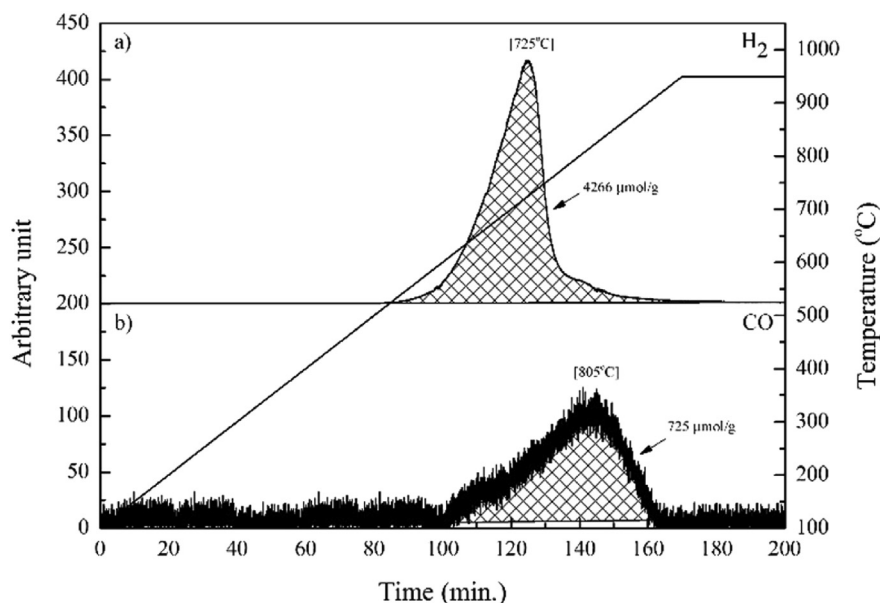


Fig. 5 – H<sub>2</sub>O-TPSR (a) and CO<sub>2</sub>-TPSR (b) profile of LSCF.

the oxidation temperature is higher than 700 °C. H<sub>2</sub>O was favored over CO<sub>2</sub> splitting on LSCF for all temperatures. The result agreed with H<sub>2</sub>O-TPSR and CO<sub>2</sub>-TPSR result from the previous section.

*The effect of oxidation temperature on the syngas productivity*  
The result from Fig. 7 showed that syngas productivity was increased when the oxidation temperature increased for all temperature range. The result suggested that the optimal oxidation temperature, where it offers the maximum syngas productivity, could be higher than 700 °C. At such temperature, all the oxygen vacancies are supposed to be used up for either H<sub>2</sub>O and/or CO<sub>2</sub> splitting, although it is like to be CO<sub>2</sub> splitting rather than H<sub>2</sub>O splitting due to its higher activation energy, evidenced in Fig. 5. However, since the reactor was made of stainless steel (316L), thus, would not be able to tolerate temperature higher than 700 °C due to the thermal

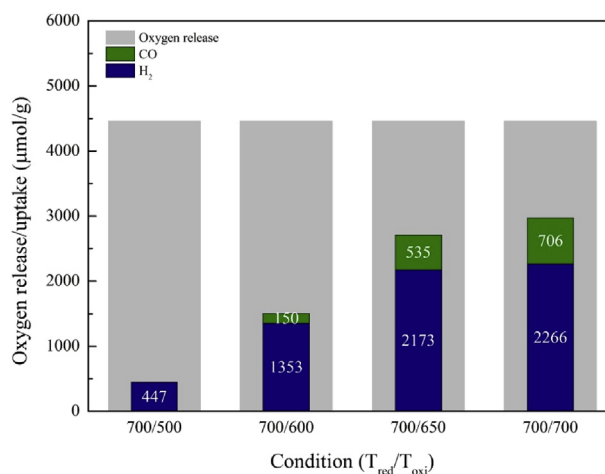


Fig. 7 – The effect of oxidation temperature on syngas productivity. The reduction temperature was 700 C for all experiments.

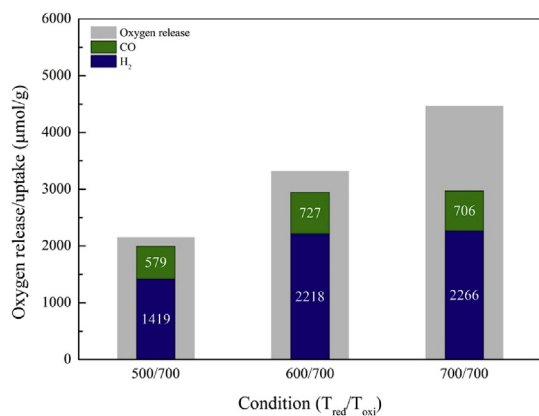


Fig. 6 – The effect of reduction temperature on oxygen vacancy concentration and syngas productivity during reduction and oxidation step, respectively.

limitation of the reactor. In addition, CO production was not detected at 500 °C, and only slightly found at 600 °C. The result was also corresponded with H<sub>2</sub>O-TPSR and CO<sub>2</sub>-TPSR mentioned in the previous section.

*Oxygen vacancy concentration and syngas production when the same reduction and oxidation temperatures were paired and applied at 500/500, 600/600 and 700/700 °C*

The same reduction and oxidation temperature were selected at 500/500, 600/600 and 700/700 °C, to reduce the time required for switching reduction temperature to oxidation temperature. This approach aimed to increase the overall efficiency of the redox process and decreased the thermal stress of the reactor. Fig. 8 showed that the highest syngas productivity was achieved at 700/700 °C.

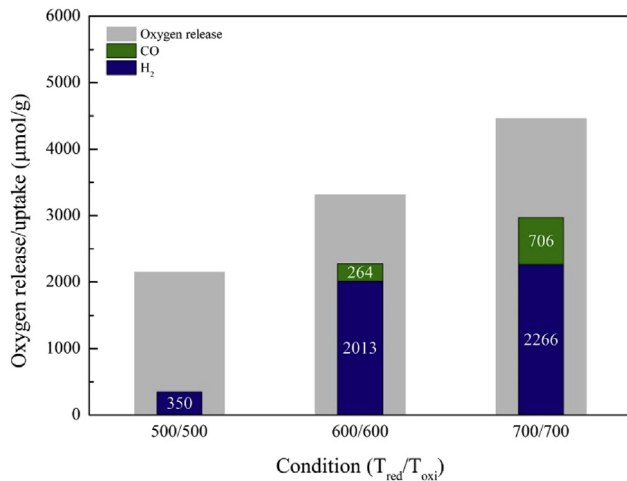


**Fig. 8 – Syngas productivity by setting the same reduction/oxidation temperature at 500/500, 600/600 and 700/700 °C.**

### Kinetics study

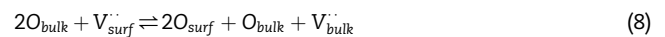
Activation energy and pre-exponential factor were estimated using Boltzmann equation. Fig. 9 showed the solid conversion of LSCF at any time during the oxidation step while H<sub>2</sub>O/CO<sub>2</sub> was co-fed. From Fig. 9, both H<sub>2</sub>O and CO<sub>2</sub> splitting were found to be favored at higher temperature. All the results from each experiment showed the same trend where the reaction control regime took place after the diffusion control regime was overcome, at around minute 8th to 10th. The solid conversion of LSCF oxidation using H<sub>2</sub>O was found to be much higher than that using CO<sub>2</sub> at all temperatures. Thus, LSCF was more selective to H<sub>2</sub>O splitting than CO<sub>2</sub> splitting.

Fig. 10 illustrated kinetic prediction using Arrhenius plot. The activation energy of H<sub>2</sub>O and CO<sub>2</sub> splitting over LSCF was estimated at 87.33 and 102.85 kJ/mol, respectively. The pre-exponential factor was determined at 595.24 s<sup>-1</sup> of H<sub>2</sub>O and 698.79 s<sup>-1</sup> of CO<sub>2</sub>.

### Mechanism of H<sub>2</sub>O/CO<sub>2</sub> thermochemical cycles via LSCF

The mechanism of LSCF reduction using H<sub>2</sub> were proposed as shown in Eqs. (6)–(8). H<sub>2</sub> started to be adsorbed on lattice

oxygen on LSCF's surface (O<sub>surf</sub>), creating surface hydroxyl radical (OH<sub>surf</sub><sup>•</sup>). The hydroxyl radicals donate electrons to the surface lattice oxygen and the bulk lattice oxygen (O<sub>bulk</sub>), creating surface vacancy (V<sub>surf</sub><sup>••</sup>) via the charge transfer process [46]. An active low electron charge (O<sub>surf</sub>) is then formed via Eq. (7), giving surface H<sub>2</sub>O as a product in which it is desorbed afterwards. While the concentration of surface lattice oxygen becomes lower, the concentration of the bulk lattice oxygen (O<sub>bulk</sub>) is still relative high and therefore solid-state diffuses to fill the surface oxygen vacancy (V<sub>surf</sub><sup>••</sup>), creating V<sub>bulk</sub><sup>••</sup> and the low electron charge O<sub>bulk</sub>, shown in Eq. (8). The high electron charge O<sub>surf</sub> then receives the electron, recycling back to Eq. (6).



where O<sub>surf</sub> and O<sub>bulk</sub> represents low charge site (electron donor) on LSCF's surface and bulk, respectively. O<sub>surf</sub> and O<sub>bulk</sub> stands for high charge site (electron acceptor) on LSCF's surface and bulk, respectively. V<sub>surf</sub><sup>••</sup> and V<sub>bulk</sub><sup>••</sup> is a charged oxygen vacancy on LSCF's surface and bulk, respectively, while OH<sub>surf</sub><sup>•</sup> is a hydroxyl radical on an oxygen surface site. The oxidation step of LSCF in the presence of H<sub>2</sub>O and CO<sub>2</sub> is modeled using a two-step mechanism [47], shown as Eqs. 9–12. The bulk oxygen formation (O<sub>bulk</sub>) is formed via the surface-to-bulk transport of the oxygen vacancy defect. The oxidation reaction of LSCF by H<sub>2</sub>O was presumably favored according to the results from other parts. The H<sub>2</sub>O is then adsorbed and dissociated on the oxygen vacancy active sites and incorporated with low electron charge lattice oxygen. The gaseous H<sub>2</sub> is then desorbed from the hydroxyl radical (OH<sub>surf</sub><sup>•</sup>). CO<sub>2</sub> is also adsorbed on the LSCF's surface, resulted in a surface carbonate (CO<sub>3surf</sub><sup>••</sup>) formation. However, CO<sub>2</sub> splitting and CO desorption is merely occurred at this range of operating temperature, according to the results in previous section. The charge exchange is then occurred between the subsequent charge-transfer of hydroxyl radical (OH<sub>surf</sub><sup>•</sup>) and/or carbonate surface adsorbate (CO<sub>3surf</sub><sup>••</sup>), followed by the association and desorption of H<sub>2</sub> and/or CO in Eq. (10) and Eq. (12). The lattice

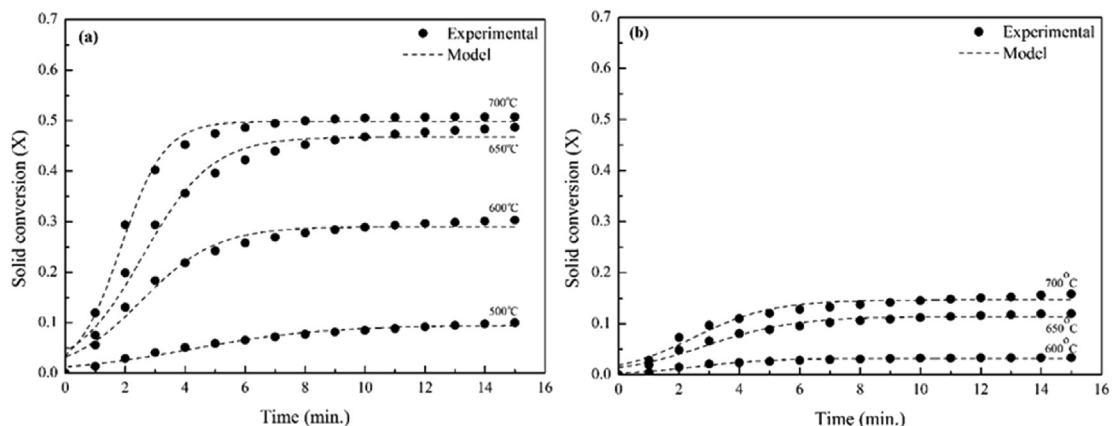


**Fig. 9 – Comparison of experimental and solid conversion model of LSCF for H<sub>2</sub> (a) and CO (b) production at 500, 600, 650, and 700 °C.**

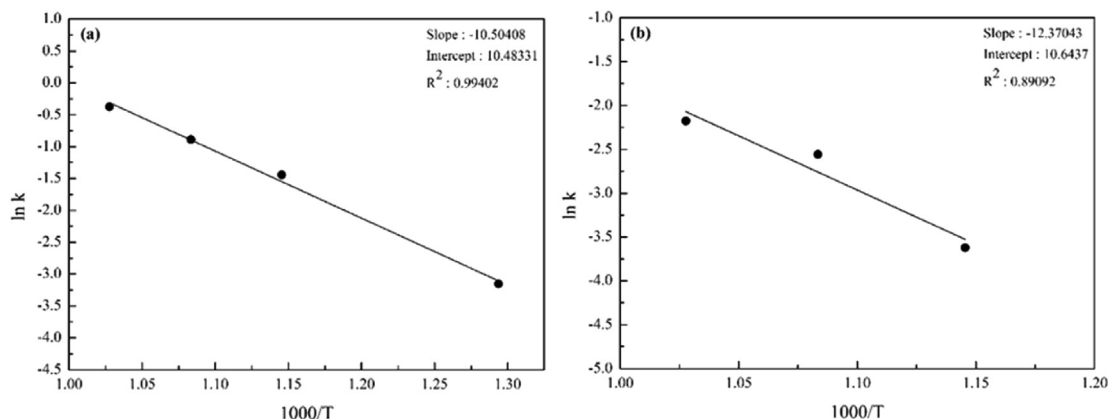
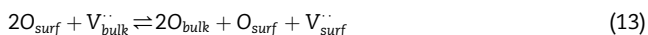


Fig. 10 – Arrhenius equation graph of LSCF for H<sub>2</sub> (a) and CO (b) production at 500, 600, 650, and 700 °C.

oxygen will diffuse from surface to bulk, shown in Eq. (13) until reaching its equilibrium.



## Conclusions

La<sub>0.3</sub>Sr<sub>0.7</sub>Co<sub>0.7</sub>Fe<sub>0.3</sub>O<sub>3</sub> (LSCF) was successfully synthesized using EDTA-CA-EG method. A pure cubic structure; known to possess high oxygen mobility, oxygen exchange rate at low temperature; was achieved when calcined at 2 °C/min of heating rate where the temperature was increased from room temperature to 325, 400, 600 and 900 °C. In terms of B-site substitute oxidation state, Co<sup>3+</sup> was (evidenced by H<sub>2</sub>-TPR) reduced to Co<sup>2+</sup> at 345 °C, then the Co<sup>2+</sup> was further reduced to Co at 700 °C. Whereas the reduction of Fe<sup>4+</sup> to Fe<sup>3+</sup> and that of Fe<sup>3+</sup> to Fe<sup>2+</sup> occurred at 575 °C. The Fe<sup>2+</sup> was found to be further reduced to Fe at 815 and 920 °C. The two-step thermochemical cycles of H<sub>2</sub>O and CO<sub>2</sub> co-splitting was successfully carried out in a lab-designed micro-channel reactor. H<sub>2</sub>O splitting was favored over CO<sub>2</sub> splitting when using LSCF as an oxygen carrier material. CO<sub>2</sub> splitting was not traced at 500 °C due to its thermodynamic limitation, although it was likely to compete H<sub>2</sub>O splitting at higher temperature. Both H<sub>2</sub>O and CO<sub>2</sub> splitting were favored by the risen temperature. The oxidation temperature had a stronger influence on syngas production compared to the reduction temperature, during the studied temperatures, ranging from 500 to 700 °C. Reduction and oxidation temperature was paired at the same temperature, to increase the overall efficiency and reduce the thermal stress of reactor. The result showed that the syngas productivity reached maximum at 700/700 °C of reduction/

oxidation temperature. The experimental results were well validated by the computational results. Activation energy of H<sub>2</sub>O and CO<sub>2</sub> splitting over LSCF was estimated at 87.33 and 102.85 kJ/mol, respectively. The pre-exponential factor was determined at 595.24 s<sup>-1</sup> of H<sub>2</sub>O and 698.79 s<sup>-1</sup> of CO<sub>2</sub>.

## Acknowledgement

This work was financially supported by the Thailand Research Fund (RSA6180061), National Research Council of Thailand (KMUTNB-GOV-59-43, KMUTNB-GOV-60-55), KMUTNB-61-GOV-03-44 and KMUTNB-61-GOV-C1-46), PTT Public Company Limited, King Mongkut's University of Technology North Bangkok (KMUTNB-GEN-57-49, KMUTNB-GEN 59-65) and NUI-RC for student sponsorship through Nonchanok.

## REFERENCES

- [1] Chibane L, Djellouli B. Methane steam reforming reaction behaviour in a packed bed membrane reactor. *Int J Chem Eng Appl* 2013;2:147–56. <https://doi.org/10.7763/ijcea.2011.v2.93>.
- [2] Zhu Q, Zhao X, Deng Y. *Advances in the partial oxidation of methane to synthesis gas* 2004;13:191–203.
- [3] Couto N, Rouboa A, Silva V, Monteiro E, Bouziane K. Influence of the biomass gasification processes on the final composition of syngas. *Energy Procedia* 2013;36:596–606. <https://doi.org/10.1016/j.egypro.2013.07.068>.
- [4] Detchusananard T, Ponpesh P, Saebea D, Authayanun S, Arpornwihanop A. Modeling and analysis of sorption enhanced chemical looping biomass gasification. *Chem Eng Trans* 2017;57:103–8. <https://doi.org/10.3303/CET1757018>.
- [5] ezzahra Chakik F, Kaddami M, Mikou M. Effect of operating parameters on hydrogen production by electrolysis of water. *Int J Hydrogen Energy* 2017;42:25550–7. <https://doi.org/10.1016/j.ijhydene.2017.07.015>.
- [6] Lange M, Roeb M, Sattler C, Pitz-Paal R. Efficiency assessment of a two-step thermochemical water-splitting process based on a dynamic process model. *Int J Hydrogen Energy* 2015;40:12108–19. <https://doi.org/10.1016/j.ijhydene.2015.07.056>.
- [7] Kniaginicheva E, Pismenskaya N, Melnikov S, Belashova E, Sistat P, Cretin M, et al. Water splitting at an anion-exchange

- membrane as studied by impedance spectroscopy. *J Membr Sci* 2015;496:78–83. <https://doi.org/10.1016/j.memsci.2015.07.050>.
- [8] Ganzoury MA, Fateen SEK, El Sheltawy ST, Radwan AM, Allam NK. Thermodynamic and efficiency analysis of solar thermochemical water splitting using Ce-Zr mixtures. *Sol Energy* 2016;135:154–62. <https://doi.org/10.1016/j.solener.2016.05.053>.
  - [9] Rao CNR, Dey S. Generation of H<sub>2</sub> and CO by solar thermochemical splitting of H<sub>2</sub>O and CO<sub>2</sub> by employing metal oxides. *J Solid State Chem* 2016;242:107–15. <https://doi.org/10.1016/j.jssc.2015.12.018>.
  - [10] Abanades S, Villafan-Vidales HI. CO<sub>2</sub> and H<sub>2</sub>O 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>.
  - [11] Cai W, Wang F, van Veen A, Descorme C, Schuurman Y, Shen W, et al. Hydrogen production from ethanol steam reforming in a micro-channel reactor. *Int J Hydrogen Energy* 2010;35:1152–9. <https://doi.org/10.1016/j.ijhydene.2009.11.104>.
  - [12] Du X, Shen Y, Yang L, Shi Y, Yang Y. Experiments on hydrogen production from methanol steam reforming in the microchannel reactor. *Int J Hydrogen Energy* 2012;37:12271–80. <https://doi.org/10.1016/j.ijhydene.2012.06.027>.
  - [13] Izquierdo U, Barrio VL, Cambra JF, Requies J, Güemez MB, Arias PL, et al. Hydrogen production from methane and natural gas steam reforming in conventional and microreactor reaction systems. *Int J Hydrogen Energy* 2012;37:7026–33. <https://doi.org/10.1016/j.ijhydene.2011.11.048>.
  - [14] Chiuta S, Everson RC, Neomagus HWJP, Bessarabov DG. Experimental performance evaluation of an ammonia-fuelled microchannel reformer for hydrogen generation. *Int J Hydrogen Energy* 2014;39:7225–35. <https://doi.org/10.1016/j.ijhydene.2014.02.176>.
  - [15] Chiuta S, Everson RC, Neomagus HWJP, Bessarabov DG. Performance evaluation of a high-throughput microchannel reactor for ammonia decomposition over a commercial Ru-based catalyst. *Int J Hydrogen Energy* 2015;40:2921–6. <https://doi.org/10.1016/j.ijhydene.2015.01.003>.
  - [16] Cheng Y, Zhai X, Cheng Y, Zhang Z, Jin Y. Steam reforming of methane over Ni catalyst in micro-channel reactor. *Int J Hydrogen Energy* 2011;36:7105–13. <https://doi.org/10.1016/j.ijhydene.2011.03.065>.
  - [17] 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](https://doi.org/10.1016/S0360-3199(01)00177-X).
  - [18] Popa SG, Ungureanu BS, Gheonea IA, Mitrea A, Ardeleanu CM, Ghilusi MC, et al. Experimental study of SnO<sub>2</sub>/SnO/Sn thermochemical systems for solar production of hydrogen. *Rom J Morphol Embryol* 2015;56:1495–502. <https://doi.org/10.1002/aic>.
  - [19] Charvin P, Abanades S, Flamant G, Lemort 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>.
  - [20] Scheffe JR, Li J, Weimer AW. A spinel ferrite/hercynite water-splitting redox cycle. *Int J Hydrogen Energy* 2010;35:3333–40. <https://doi.org/10.1016/j.ijhydene.2010.01.140>.
  - [21] Furler P, Scheffe J, Gorbar M, Moes L, Vogt U, Steinfeld A. Solar thermochemical CO<sub>2</sub> splitting utilizing a reticulated porous ceria redox system. *Energy Fuels* 2012;26:7051–9. <https://doi.org/10.1021/ef3013757>.
  - [22] Meng QL, Lee C II, Ishihara T, Kaneko H, Tamaura Y. Reactivity of CeO<sub>2</sub>-based ceramics for solar hydrogen production via a two-step water-splitting cycle with concentrated solar energy. *Int J Hydrogen Energy* 2011;36:13435–41. <https://doi.org/10.1016/j.ijhydene.2011.07.089>.
  - [23] Scheffe JR, Weibel D, Steinfeld A. Lanthanum-strontium-manganese perovskites as redox materials for solar thermochemical splitting of H<sub>2</sub>O and CO<sub>2</sub>. *Energy Fuels* 2013;27:4250–7. <https://doi.org/10.1021/ef301923h>.
  - [24] McDaniel Anthony H, Miller Elizabeth C, Arifin Darwin, Ambrosini Andrea, Coker Eric N. Ryan O'Hayre WCC and JT. Sr- and Mn-doped LaAlO<sub>3</sub>-d for solar thermochemical H<sub>2</sub> and CO production. *Energy Environ Sci* 2013;6:2424–8.
  - [25] Jiang Q, Tong J, Zhou G, Jiang Z, Li Z, Li C. Thermochemical CO<sub>2</sub>splitting reaction with supported La<sub>0.8</sub>A<sub>0.2</sub>B<sub>1-y</sub>O<sub>3</sub>(A=Sr, Ce, B=Co, Mn; 0≤x, y≤1) perovskite oxides. *Sol Energy* 2014;103:425–37. <https://doi.org/10.1016/j.solener.2014.02.033>.
  - [26] Tanasescu S, Yang Z, Martynczuk J, Varazashvili V, Maxim F, Teodorescu F, et al. Effects of A-site composition and oxygen nonstoichiometry on the thermodynamic stability of compounds in the Ba-Sr-Co-Fe-O system. *J Solid State Chem* 2013;200:354–62. <https://doi.org/10.1016/j.jssc.2013.01.030>.
  - [27] Mehmood S, Ali Z, Khan I, Ahmad I. Effects of cobalt substitution on the physical properties of the perovskite strontium ferrite. *Mater Chem Phys* 2017;196:222–8. <https://doi.org/10.1016/j.matchemphys.2017.04.065>.
  - [28] Demont A, Beche E. Investigation of perovskite structures as oxygen-exchange redox materials for hydrogen production from thermochemical two-step water-splitting cycles. 2014. <https://doi.org/10.1021/jp5034849>.
  - [29] Mineshige A, Inaba M, Yao T, Ogumi Z. Crystal structure and metal-insulator transition of La<sub>1-x</sub>Sr<sub>x</sub>CoO<sub>3</sub>. *J Solid State Chem* 1996;429:423–9.
  - [30] Mizusaki J, Mima Y, Yamauchi S, Fueki K. Nonstoichiometry of the perovskite-type oxides La<sub>1-x</sub>Sr<sub>x</sub>CoO<sub>3</sub>. *J Solid State Chem* 1989;80:102–11. <https://doi.org/10.1007/s11075-015-0051-1>.
  - [31] Kim S, Ryu J, Lee H. Degradation behaviours of Fe-doped La<sub>0.8</sub>Sr<sub>0.2</sub>CoO<sub>3-δ</sub> by thermal stress. *Adv Appl Ceram* 2018;117:155–60. <https://doi.org/10.1080/17436753.2017.1386426>.
  - [32] Babiniec SM, Coker EN, Ambrosini A, Miller JE. ABO<sub>3</sub>(A = La, Ba, Sr, K; B = Co, Mn, Fe) perovskites for thermochemical energy storage. *AIP Conf Proc* 2016;1734. <https://doi.org/10.1063/1.4949104>.
  - [33] Park J-S, Yang M, Zhu K, Li Z, Wei S-H, Berry JJ. Stabilizing perovskite structures by tuning tolerance factor: formation of formamidinium and cesium lead iodide solid-state alloys. *Chem Mater* 2015;28:284–92. <https://doi.org/10.1021/acs.chemmater.5b04107>.
  - [34] Babiniec SM, Coker EN, Miller JE, Ambrosini A. Investigation of La<sub>0.8</sub>Sr<sub>0.2</sub>CoO<sub>3-δ</sub> (M=Mn, Fe) perovskite materials as thermochemical energy storage media. *Sol Energy* 2015;118:451–9. <https://doi.org/10.1016/j.solener.2015.05.040>.
  - [35] Snytnikov PV, Popova MM, Men Y, Rebrov EV, Kolb G, Hessel V, et al. Preferential CO oxidation over a copper-cerium oxide catalyst in a microchannel reactor. *Appl Catal A Gen* 2008;350:53–62. <https://doi.org/10.1016/j.apcata.2008.07.036>.
  - [36] Abdullah NA, Hasan S, Osman N. Role of CA-EDTA on the synthesizing process of cerate-zirconate ceramics electrolyte. *J Chem* 2013;2013. <https://doi.org/10.1155/2013/908340>.
  - [37] Tongnan V, Sornchamni T, Laosiripojana N, Hartley UW. Study of crystal growth and kinetic parameters of Zn/ZnO oxidation in the presence of H<sub>2</sub>O and CO<sub>2</sub>. *React Kinet Mech Catal* 2018;125:99–110. <https://doi.org/10.1007/s11144-018-1411-3>.

- [38] Hartley UW, Tongnan V, Laosiripojana N, Kim-Lohsoontorn P, Li K. Nitrous oxide decomposition over  $\text{La}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.7}\text{Fe}_{0.3}\text{O}_{3-\delta}$  catalyst. *React Kinet Mech Catal* 2018;85–97. <https://doi.org/10.1007/s11144-018-1398-9>.
- [39] Johnsson M, Lemmens P. Crystallography and chemistry of perovskites. *Handb Magn Adv Magn Mater* 2007;1–11. <https://doi.org/10.1002/9780470022184.hmm411>.
- [40] Nb F. Investigation of the functional characteristics of perovskites  $\text{SrCo}_{0.8-x}\text{Fe}_{0.2}\text{Nb}_x\text{O}_{3-z}$  2010;18:649–55.
- [41] Zhao Z, Wang L, Ma J, Feng Y, Cao X, Zhan W. Deoxygenation of coal bed methane on  $\text{LaCoO}_3$  perovskite catalyst: the structure evolution and catalytic performance. 2017. p. 15211–21. <https://doi.org/10.1039/c6ra28339j>.
- [42] Nemati A, Khodadadi AA, Mortazavi Y, Alinezhadchamazketi A.  $\text{Pd/La}_x\text{Sr}_{1-x}\text{FeO}_3$  perovskite nanocatalysts for selective catalytic reduction of  $\text{NO}_x$  by hydrogen. *Sci Iran C* 2015;22:2341–9.
- [43] Tarjomannejad Ali, Farzi Ali, José Illán Gómez María, Niaei1 Aligholi, Dariush Salari3 VA-F. Catalytic reduction of  $\text{NO}$  by  $\text{CO}$  over  $\text{LaMn}_{1-x}\text{Fe}_x\text{O}_3$  and  $\text{La}_{0.8}\text{A}_{0.2}\text{Mn}_{0.3}\text{Fe}_{0.7}\text{O}_3$  ( $\text{A} = \text{Sr, Cs, Ba, Ce}$ ) perovskite catalysts. *Catal Lett* 2016;146:2330–40.
- [44] Al B, Fossmark Ø, Gurauskis J, Nhut T, Einarsrud M, Grande T, et al. Effect of B-site substitution on the stability of  $\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.8}\text{B}_{0.2}\text{O}_{3-\delta}$ ,  $\text{B} = \text{Al, Ga, Cr, Ti, Ta, Nb}$ . *Solid State Ion* 2011;3–6.
- [45] Zhu J, Li H, Zhong L, Xiao P, Xu X, Yang X, et al. Perovskite Oxides : preparation , characterizations , and applications in heterogeneous catalysis. <https://doi.org/10.1021/cs500606g>; 2014.
- [46] Zhao Z, Uddi M, Tsvetkov N, Yildiz B, Ghoniem AF. Redox kinetics study of fuel reduced ceria for chemical-looping water splitting. *J Phys Chem C* 2016;120:16271–89. <https://doi.org/10.1021/acs.jpcc.6b01847>.
- [47] Zhao Z, Uddi M, Tsvetkov N, Yildiz B, Ghoniem AF. Enhanced intermediate erature  $\text{CO}_2$  splitting using nonstoichiometric ceria and ceria-zirconia. *Phys Chem Chem Phys* 2017;19:25774–85. <https://doi.org/10.1039/c7cp04789d>.