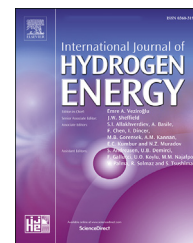


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Mechanisms of synthesis gas production via thermochemical cycles over $\text{La}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.7}\text{Fe}_{0.3}\text{O}_3$

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HIGHLIGHTS

- Activation energy of CO_2 splitting is higher than H_2O splitting.
- CO_2 adsorption causes the catalyst's active site blockage.
- LSCF is keen on H_2O splitting rather than H_2O splitting.
- Oxygen storage capacity of the LSCF is estimated at $4072 \mu\text{mol/g}_{\text{cat}}$.

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ABSTRACT

$\text{La}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.7}\text{Fe}_{0.3}\text{O}_3$ (LSCF3773) was chosen as an oxygen carrier material for synthesis gas production and synthesized using ethylene-diamine-tetra-acetic acid (EDTA) citrate-complexing method. LSCF exhibited a pure cubic structure where 110 and 100 plane diffractions were active for CO_2 splitting, while 111 was more favored by H_2O splitting. Overall oxygen storage capacity (OSC) of LSCF was $4072 \mu\text{mol/g}_{\text{cat}}$. During the reduction process, regular cations (Co^{4+} , Fe^{4+}), polaron cations (Co^{3+} , Fe^{3+}) and localized cations (Co^{2+} , Fe^{2+}) were achieved when the LSCF was reduced at 500, 700 and 900 °C, respectively. The strength of the active sites depended on reduction temperatures. An increase in oxidation temperature enhanced H_2 production at temperature ranging from 500 °C to 700 °C while effected CO production at 900 °C. H_2O and CO_2 was competitively split during the oxidation step, especially at 700 °C. The activation energy of each reaction was ordered as; CO_2 splitting > H_2O splitting > CO_2 adsorption, supporting the above evidence where H_2 and CO production were found to increase when the operating temperature was increased.

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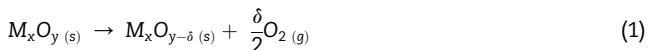
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Introduction

CO₂, as the world most well-known greenhouse gas, can be utilized to many kinds of valuable energy and chemicals. The most interesting CO₂ utilization processes amongst many are ones that used abundant, available and toxic-free co-feedstock, yet reactive with CO₂, thus, in most cases, the energy requirement of such processes is considered main challenge. One of the non-toxic and available co-feedstocks for CO₂ utilization is water (H₂O). CO₂ can be reacted with H₂O directly, although the external energy requisition for the process is extremely high (>2500 °C). Moreover, the process requires a sophisticated and expensive separation unit. The two-step thermochemical cycles process has been applied for H₂O and CO₂ splitting reaction to minimize such problems, and has been studied intensively during the past decades. The two-step process consists of an endothermic reduction and an exothermic oxidation step of an oxygen carrier materials. During the reduction step, the oxygen carrier is reduced by either thermal or chemical process (using reducing gaseous agents i.e. CH₄). Afterwards, the reduced material is oxidized by CO₂ and H₂O, giving high purity syngas as a product, while the oxygen carrier is recycled back into its original form.

Step 1: During the reduction step, the active oxygen vacancies are created in the material's lattice. The gaseous oxygen is released as a by-product.

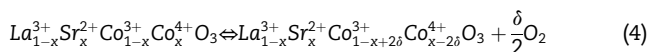


Step 2: During the oxidation step, CO₂ and H₂O are decomposed on the material's surface, giving syngas as a product, while regenerating the material.



The optimal operating temperatures for the two steps depend on many factors (such as type of the selected oxygen carrier, oxygen partial pressure in the system and the chosen reducing agents) and are independent from each other and. The productivity of syngas thus can be maximized by choosing the most suitable operating temperature on each step. However, this results in the loss of the process's overall efficiency due to the temperature swing while operating the 2 steps. Unsurprisingly, the highest theoretical efficiency of the process was reported at only 13–22% [1]. Therefore, maximization of the overall efficiency by minimizing the difference of temperatures between the reduction and oxidation step while maintaining the industrially acceptable yield during each step is one of the key challenges. The selected materials are also playing significant role for the process efficiency and productivity. The material screening for such reaction has been researched widely worldwide. Volatile and stoichiometric redox materials such as ZnO/Zn, CdO/Cd, and SnO/Sn were the first set of materials studied [2–4]. These materials give high yield of synthesis gas but require a complicated fluidized bed reactor and quenching system as it involves material's phase change. Non-volatile metal oxide materials, such as Fe₃O₄ [5], Fe₃O₄/m-ZrO₂ [6], CoFe₂O₄ [7], MFe₂O₄ [8], Fe₂O₃/8YSZ

[9], NiFe₂O₄, NiFe₂O₄/m-ZrO₂, NiFe₂O₄/c-YSZ [10], offer low operating temperature range and have been recently applied in the reaction. The most attractive candidates among the non-volatile compounds are perovskites (ABO₃) which are well researched in many applications depending on its various features such as membrane oxygen separation [11–13], solid oxide fuel cells (SOFC) [14–16] and catalysis [16,17]. Substitution of A and/or B atoms in the perovskites can lead to designed specific chemical properties [18] such as thermal stability and oxygen vacancy concentration [13,18–23]. The effect of substitution of cobalt (Co) and iron (Fe), in some perovskites, on redox capacity and stability have also been studied especially in applications in the thermochemical cycles, semiconductor and energy storage [24]. Co and Fe possess various oxidation states, therefore, have different degree of reductions and oxidations where the depletion and uptake of oxygen lattice can occur partially. Small content of La substitution on A-site was reported to establish a cubic structure, providing a higher reducibility compared to other structures [24]. The redox ability could as well be enhanced by a substitution of bivalent A-site cation atom, such as Sr, to create tetravalent Co [25,26], into the based perovskite, shown in Eq. (4).



The redox ability of La_xA_{1-x}Fe_yB_{1-y}O₃ (A = Sr, Ce, B = Co, Mn; 0 ≤ x, y ≤ 1) was compared to each other [27]. 58 μmol/g_{perovskite} of the oxygen lattice in LaFeO₃ was released at 1210 °C while 527 μmol/g_{perovskite} of that in LaCoO₃ was found to release at lower temperature, 800 °C. It was concluded that the reduction of Co₃O₄ to CoO has lower activation energy compared to that of Fe₃O₄ to FeO. The effect of A-site cation substitution was also investigated [27]. For the B-site substitution, it was reported that when La³⁺ was partially substituted by Sr²⁺, the O₂ was released at lower temperature, reducing from 1230 (pure La³⁺) to 970 °C (La³⁺ substituted by Sr²⁺). Its maximum oxygen evolution was 2 times larger than Ce⁴⁺ substitution. In addition, O₂ evolution activity was found to increase when the Co content increased. Thus, La_xSr_{1-x}Fe_yCo_{1-y}O₃ (LSCF) became one of the most promising oxygen carriers due to its high oxygen concentration, distinctive reducibility. It was reported that the suitable stoichiometry of La:Sr:Fe:Co was 3:7:7:3 as it showed the highest degree of oxygen deficiency (Δδ = 0.4) amongst LaFeO_{3-δ} based perovskites [27–33]. La_{0.3}Sr_{0.7}Fe_{0.7}Co_{0.3}O₃ (LSCF3773) was reported to have a cubic structure, in which it allows oxygen mobility, leading to high oxygen exchange rate at high stability. Not many published literatures have specifically studied technoeconomic of perovskites or LSCF3773 on synthesis gas production via thermochemical splitting of H₂O and CO₂, however, it was believed to be only feasible when coupled with affordable/renewable energy such as solar thermal technology. This work studied catalytic performance of LSCF3773 towards thermochemical cycles of H₂O/CO₂ co-splitting in a packed-bed reactor. The gas-solid reduction/oxidation mechanisms and optimal temperatures were predicted using transient experiments i.e. H₂-temperature programmed reduction (H₂-TPR), temperature programmed oxidation

(TPO), temperature programmed on single reactant (either H₂O or CO₂) splitting and CO₂ temperature programmed desorption (CO₂-TPD). Optimal reduction/oxidation temperature conditions were carried out by co-feeding H₂O/CO₂ under isothermal experiments.

Methodology

Catalyst preparation and characterization

A modified Pechini type reaction called ethylene-diamine-tetra-acetic acid (EDTA) citrate complexing method [34], was selected for LSCF3773. The molar ratio of total metal cations to EDTA to citric acid was 2:2:3. EDTA-NH₃·H₂O solution was prepared by adding EDTA (0.05 M) into 100 mL of NH₃·H₂O (1 M) solution. Nitrate salts of the relevant metals which are La(NO₃)₃·6H₂O (≥99.00%, Himedia), Sr(NO₃)₂ (≥98.00%, Himedia), Co(NO₃)₂·6H₂O (≥99.00%, Carlo Erba Reagents) and Fe(NO₃)₃·9H₂O (≥99.00%, Ajax Finechem), were dissolved into EDTA-NH₃·H₂O solution correspondingly to the desired stoichiometry. The solution was kept at 80 °C while stirred continuously until well-mixed. 0.07 mol of citric acid was then applied into the solution where its pH was adjusted to 6 approximately by using NH₄OH. The solution was evaporated until dark purple gel was obtained. The gel was then dried in an oven at 180 °C for 48 h. The dried gel was ground to powder before being calcined. During the calcination process, the temperature was raised at 10 °C/min to 500 °C and hold for 5 h. Once reaching 5 h, the temperature was raised again at the same heating rate to then 1100 °C. The material's crystallinity was characterized using X-ray diffraction (XRD, Bruker AXS, Diffractometer D8) equipment using CuK- α radiation, with $\lambda = 1.5418 \text{ \AA}$, as a radiation source at 40 kV and 30 mA with a scanning speed of 0.02 ° sec⁻¹, in the range of 10° < 2 θ < 80°.

Experimental procedure

Reactor set-up

Thermochemical cycles of H₂O/CO₂ splitting were carried out in a lab-scaled packed-bed reactor system, shown in Fig. 1. LSCF3773 with particle sizes of 180–212 μm was packed into a quartz tubular reactor (i.d. = 13 mm). The sieved catalyst was placed in the middle of a 20 cm heating-zone of electric furnace (Inconel, Suan-luang Engineering). K-type thermocouple was inserted to where the bed was placed. Gaseous reactants involved in any single experiment i.e. 40% O₂/Ar (99.9%, BIG), CO₂ (99.9%, BIG), Ar (99.95%, BIG) and 10% H₂ in Ar (BIG), were introduced into the system using mass flow controllers (New Flow-TLFC-00-A-1-W-2). Steam was generated by combining a peristaltic pump (BT100 M) with an evaporator (Suan-luang Engineering). The evaporator's temperature was set at 130 °C. The gaseous outlet stream was passed through a condenser unit before analyzed by an on-line mass spectrometer (OMNI Star, Pfeiffer vacuum).

Temperature program reduction (H₂-TPR)

Transient H₂-TPR was carried out to observe reduction behavior of the LSCF3773. 50 mL min⁻¹ of 10% H₂/Ar was introduced through 1 g of LSCF bed. Total flow rate was

maintained at 100 mL min⁻¹ using Ar as a make-up gas. Temperature of the system was increased at the rate of 5 °C·min⁻¹ from room temperature to 950 °C, then hold for 30 min. The amount of H₂ consumption, in which it's related to the amount of oxygen released was measure on-line.

Temperature program oxidation (TPO)

Before performing the TPO experiment, 1 g of the sample was reduced using 100 mL min⁻¹ of 10% H₂/Ar at 500, 700 and 900 °C for 30 min. The system was then cooled down to room temperature and stabilized using pure Ar at the total flow rate of 300 mL min⁻¹. During the TPO, 5 mL min⁻¹ of 40% O₂/Ar was introduced into the system. The total flow rate was 100 mL min⁻¹ using the make-up Ar. The temperature was increased from room temperature to 950 °C at 5 °C·min⁻¹, then hold for 30 min. The O₂ consumption was measured/calculated using the on-line mass spectrometer.

Transient experiments on single reactant (either H₂O or CO₂) splitting

Gas-solid mechanism of both H₂O splitting and CO₂ splitting were investigated separately using transient experimental method. 1 g of LSCF was reduced by 10% H₂/Ar, at either 500, 700 or 900 °C before stabilized at room temperature using 300 mL min⁻¹ of Ar. For the H₂O splitting, 0.07 mL min⁻¹ of water from the syringe pump was introduced into the steam generator where 100 mL min⁻¹ of Ar was used as a carrier gas. For the CO₂ splitting, 87 mL min⁻¹ of CO₂ was applied while Ar was used as the make-up gas to the total flow rate of 100 mL min⁻¹. For both reactions, the temperature was increased from room temperature to 950 °C at 5 °C·min⁻¹ of heating rate, then hold for 30 min. The gaseous products were analyzed using the on-line mass spectrometer.

Temperature program –CO₂ adsorption/desorption (CO₂-TPD)

Temperature programmed CO₂ adsorption/desorption were carried out to investigate gas-solid interaction between CO₂ and the surface of LSCF. 1 g of LSCF was reduced in 10% H₂/Ar at 500, 700 or 900 °C for 30 min before each test. As usual, the catalyst was stabilized in 300 mL min⁻¹ of Ar for 30 min 100 mL min⁻¹ of 87%CO₂/Ar was introduced into the system while the temperature was cooled down from either 500, 700, or 900 °C to room temperature. The CO₂ desorption was afterwards performed by flowing pure Ar through the system while increasing the temperature from room temperature to 950 °C at 5 °C·min⁻¹ of heating rate. The amount of CO₂ desorption was measured and plotted against time and temperature.

Optimum operating temperature

To achieve the optimal operating temperature, feed molar ratio of H₂O to CO₂ was fixed at 1 to 1 for all experiments. During the reduction step, the reactor was heated up to 500, 700 and 900 °C at 10 °C·min⁻¹. Pure Ar was afterwards purged through the system to eliminate any possible physical adsorptions and stabilize the sample for 30 min at 300 mL min⁻¹. During the oxidation step, 0.07 mL min⁻¹ of water was fed through evaporator using Ar as a carrier gas. The trace heat was applied throughout the inlet piping line at 130 °C, to prevent water condensation. 87 mL min⁻¹ of CO₂ was co-fed to

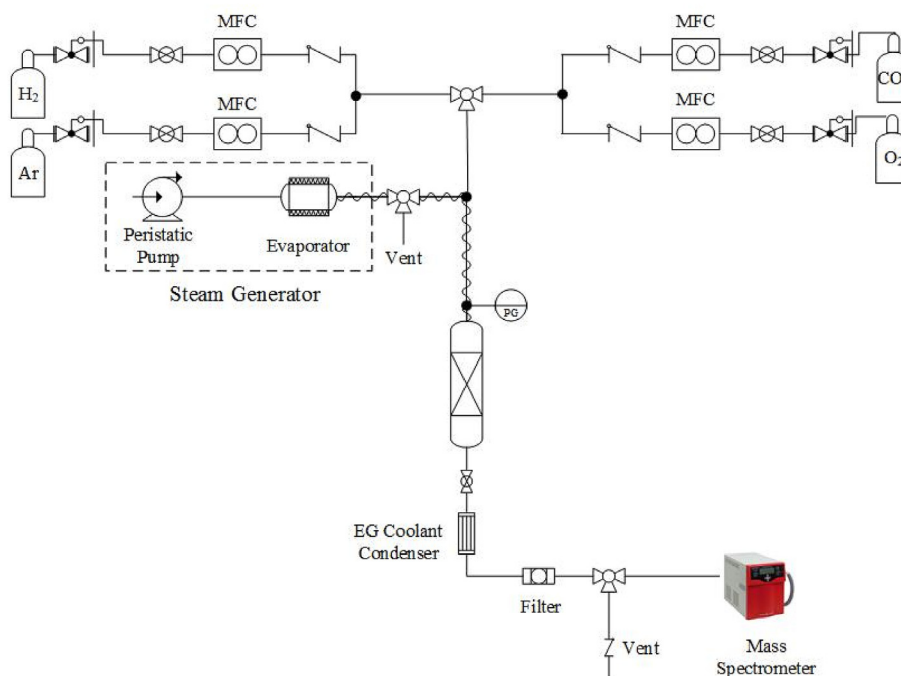


Fig. 1 – Rig's diagram.

the system. Total flow rate was fixed at 200 mL min^{-1} using pure Ar as a make-up gas. The oxidation temperature was kept at the same temperature as the reduction temperature at 500, 700 or 900 °C. The reaction time was 60 min for all experiments. Gaseous products were detected on-line using the mass spectrometer. H_2 and CO production yield were calculated.

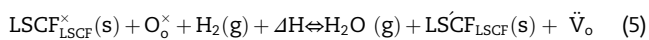
Result and discussion

Catalyst characterization

From the XRD result, it showed that LSCF3773 was successfully synthesized via EDTA citrate-complexing method. The material's diffraction peaks were seen at 23.28, 33.08 40.84, 47.46, 59.02, 69.32 and 78.86°, shown in Fig. 2. Average crystalline size was calculated at 31.90 nm using Scherrer equation [35]. The prepared material had perovskite phase and an ideal cubic structure.

Reducibility and mechanism

Fig. 3 shows H_2 -TPR of LSCF3773. Three main peaks of reduction were seen in 3 different temperature ranges; (1) below 530 °C, (2) from 530 to 750 °C and, (3) above 750 °C. Oxygen storage capacity (OSC) of LSCF3773 was calculated using Eqs. (4) and (5). The overall OSC received from 3 regions of temperature was $4072 \text{ } \mu\text{mol/g.cat}$.



where $\text{LSCF}_{\text{LSCF}}^{\times}$ stands for regular LSCF before reduction, $\text{O}_{\text{o}}^{\times}$ is

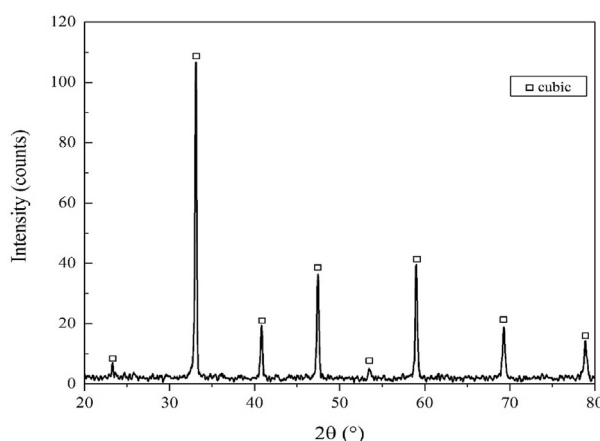


Fig. 2 – Diffractogram of the prepared LSCF3773 after calcination at 1100 °C.

an oxygen ion in lattice of LSCF, $\text{LSCF}_{\text{LSCF}}$ is a localized electron $\text{Co}^{3+}/\text{Co}^{2+}$, $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\ddot{\text{V}}_{\text{o}}$ is oxygen vacancy.

$$\text{OSC} = \frac{\int_0^{t_f} n_{\text{H}_2}}{m_{\text{LSCF}}} \quad (6)$$

From eq. (5), OSC stands for oxygen storage capacity, n_{H_2} is the amount of H_2 consumption in mole and m_{LSCF} is the total weight of LSCF. At temperature lower than 530 °C, the amount of the oxygen release was $1871 \text{ } \mu\text{mol/g}$, requiring relatively lowest external energy compared to other regions, to adopt oxygen vacancies. There were 2 reduction bands were found at temperature 346 °C and 462 °C which were corresponded to partial transformation of Co^{4+} to Co^{3+} and Fe^{4+} to Fe^{3+} , respectively [36–38]. Thus, the non-stoichiometric LSCF3773

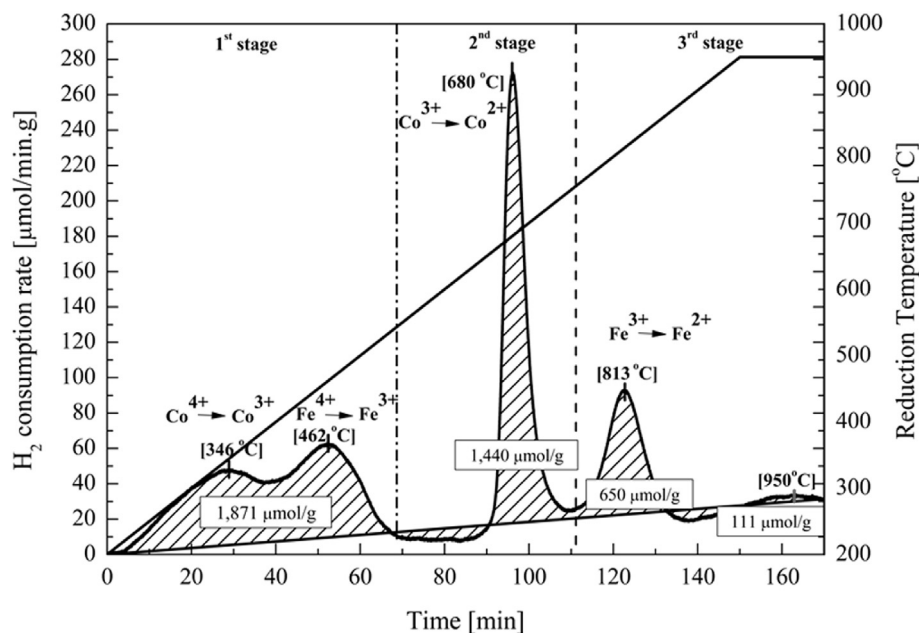


Fig. 3 – H₂-TPR profile represents H₂ consumption rate and calculated oxygen release over LSCF3773.

was partially reduced and the reactive material was transformed from $\text{La}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.49}\text{Fe}_{0.21}^{4+}\text{Fe}_{0.09}^{3+}\text{O}_{3-\delta 1}$ to $\text{La}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.49}\text{Fe}_{0.21}^{4+}\text{Fe}_{0.09}^{3+}\text{O}_{3-\delta 1}$ and then $\text{La}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.49}\text{Fe}_{0.21}^{3+}\text{Fe}_{0.09}^{3+}\text{O}_{3-\delta 2}$. This partially reduced LSCF was proven to be active for associated reactions with relatively low activation energy such as CO₂ adsorption and H₂O splitting, reported in later section.

During the second stage, a reduction band was found at 680 °C with 1440 μmol/g of oxygen release. Co³⁺ in $\text{La}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.49}\text{Fe}_{0.21}^{3+}\text{Fe}_{0.09}^{3+}\text{O}_{3-\delta 2}$ was converted to a localized electron Co²⁺ and becoming $\text{La}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.49}\text{Fe}_{0.21}^{2+}\text{Fe}_{0.09}^{3+}\text{O}_{3-\delta 3}$ in which it was found to be active for moderate activation energy reactions such as H₂O splitting and a part of CO₂ splitting.

At temperature higher than 750 °C, the valence of transition metal of iron altered from Fe³⁺ to a localized electron Fe²⁺ where $\text{La}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.49}\text{Fe}_{0.21}^{2+}\text{Fe}_{0.09}^{3+}\text{O}_{3-\delta 3}$ was changed to $\text{La}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.49}\text{Fe}_{0.21}^{2+}\text{Fe}_{0.09}^{2+}\text{O}_{3-\delta 4}$, leaving it in the most excited stage and active for the high activation energy reactions such as CO₂ splitting. This can be concluded that the OSC received from different reduction stage has different degree of activity and selectivity towards the H₂O and/or CO₂ splitting.

O₂ adsorption/oxidation

Temperature programmed oxidation was conducted after the LSCF was reduced at 500, 700 and 900 °C, shown as Fig. 4a, b and 4c, where the O₂ consumption was calculated at 581, at 2512 and at 2846 μmol/g_{cat}, respectively. From the results, O₂ consumption was seen to increase when the reduction temperature was increased. This means that the higher reduction temperature rendered the better O₂ consumption, contributing to the better OSC. When compared the O₂ consumption from Fig. 4c (reduced at 900 °C) with overall OSC from TPR result from the previous section, it can be seen that the O₂ consumption of 2846 μmol/g_{cat} which equaled to O atom consumption of 5692 μmol/g_{cat} was higher than OSC obtained

from TPR result, at 4072 μmol/g_{cat}. Therefore, approximately 1620 μmol/g_{cat} of O atoms were presumably adsorbed on the surface of LSCF. OSC estimated from TPO was found to be slightly higher than that obtained from TPR, especially at temperature lower than 550 °C, due to involvement of O₂ adsorption in the TPO.

Mechanism survey and optimum temperature

Fig. 5 showed productivities of H₂ and CO when the reduction/oxidation temperatures were paired at 500/500 °C, 700/700 °C and 900/900 °C. The feed ratio of H₂O to CO₂ was fixed constant at 1 to 1. From the result, the total productivity was risen when the operating temperature increased from 500/500 to 700/700 °C (from 340 to 2364 μmol/g). However, when the temperature was increased from 700/700 to 900/900 °C, the total productivity remained nearly unchanged (from 2364 to 2415 μmol/g). This implies that the full surface coverage was achieved at this temperature range and upon. Fig. 6 represented temperature programmed reaction of CO₂ splitting over LSCF, which was reduced at a) Tred 500 °C, b) Tred 700 °C and c) Tred 900 °C. From the results, it can be seen that CO production was untraceable during the oxidation step when the catalyst was reduced at 500 °C. The result also agreed with result achieved from Fig. 5 where CO production significantly occurred in the presence of the catalyst which was reduced at 700 °C. The amount of CO production was only slightly increased when the reduction temperature increased from 700 to 900 °C. Fig. 7 showed temperature programmed reaction of H₂O splitting over LSCF, which was reduced at a) Tred 500 °C, b) Tred 700 °C and c) Tred 900 °C, respectively. The result from Fig. 7 represented the similar trend as result from Fig. 5, where H₂ production was increased when the catalyst was reduced at higher temperatures. However, only small amount of H₂ production was risen when the reduction temperature increased from 700 to 900 °C. Fig. 8 showed CO₂

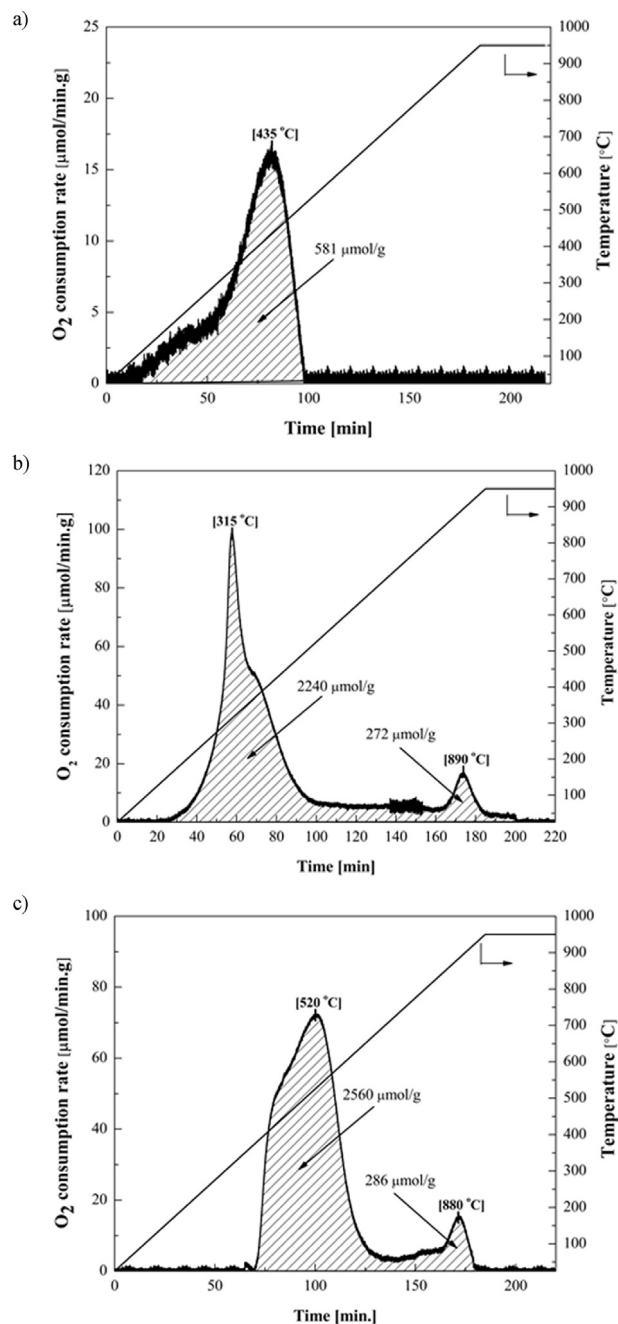


Fig. 4 – Transient O₂-TPO illustrator, showing the amount of O₂ oxidation/chemisorption over reduced LSCF at a) 500 °C, b) 700 °C and c) 900 °C.

desorption. The desorbed CO₂ over the LSCF reduced at 700 °C was much higher than that reduced at 500 °C. However, the amount of CO₂ desorption remained more or less similar when using LSCF reduced at 700 and 900 °C.

The CO₂ adsorption was also evidenced in Fig. 5. Both H₂O and CO₂ splitting were suppressed by the blockage of CO₂ adsorption on the active sites for all temperature range. Thus, the H₂ and CO production during the isothermal experiments (Fig. 5) were less than what they could be without the influence of CO₂ adsorption (Figs. 6–8). It can be seen from Fig. 5 that the H₂O splitting was flavored over the CO₂ splitting at

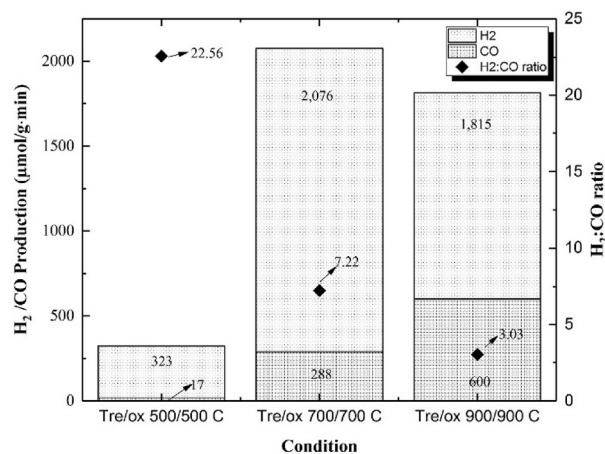


Fig. 5 – Total gas production via isothermal H₂O/CO₂ co-splitting over LSCF3773.

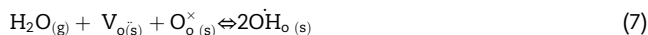
700/700 °C, but inhibited by the CO₂ splitting at 900/900 °C. These results implied that the Ea order of all the reactions could be; CO₂ splitting > H₂O splitting > CO₂ adsorption. It can be concluded that;

- (1) When operated at 500/500 °C, H₂O splitting and CO₂ adsorption were involved (Figs. 5, 7 and 8). CO₂ splitting could not occur at this temperature as there was no CO production found (Fig. 6). The H₂ production at this temperature was presented at its lowest amount compared to other operating temperatures due to the fact that the LSCF which was reduced at such low temperature (500 °C) has low OSC and therefore low-strength active sites (regular cation Co³⁺, Fe³⁺).
- (2) At 700/700 °C; H₂O splitting, CO₂ splitting and CO₂ adsorption were occurred over the active sites which were the localized electrons of cobalt (II) ion Co²⁺. The LSCF which was reduced at this temperature range has higher OSC compared to the previous stage (evidenced in higher total productivity) and has higher-strength active sites.
- (3) The majority of CO₂ splitting occurred at 900/900 °C, giving the highest amount of CO among all temperature ranges (Figs. 5 and 6). While H₂O splitting as well occurred at this temperature (Fig. 7), however, it was suppressed by the CO₂ splitting (Fig. 5). CO₂ adsorption was also found at this temperature range (Fig. 8). It is possible that the H₂O splitting and CO₂ splitting were competitively split on the same active site, Fe²⁺.

Gas-solid surface reactions

H₂O splitting was occurred via below mechanism:

Adsorption:



where O_{o(s)}[×] is an active site and OH_{o(s)} is a hydroxyl ion group on an oxygen anion site, and V_{o(s)} stands for doubly charge of

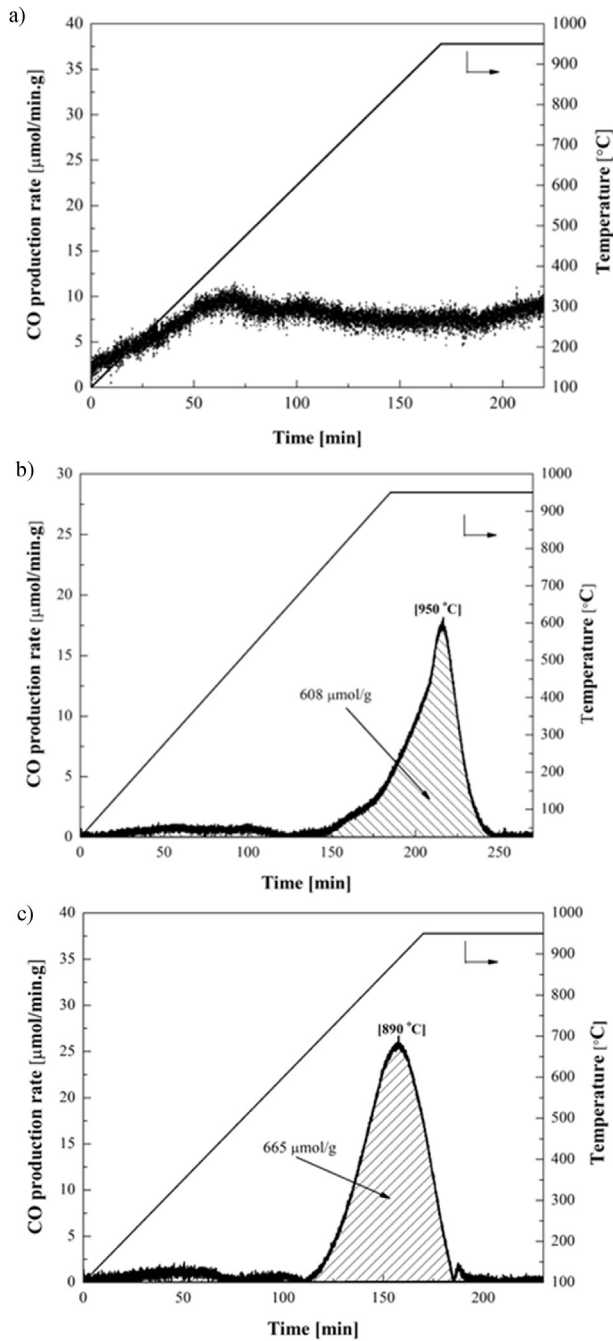


Fig. 6 – CO production/desorption via temperature programmed CO₂ splitting over LSCF reduced at a) T_{red} 500 °C, b) T_{red} 700 °C and c) T_{red} 900 °C.

oxygen vacancy site. H₂O from the enrich bulk stream diffused to the surface of available active site and then dissociated to form a hydroxyl ion group on an oxygen anion site.

Surface reaction:

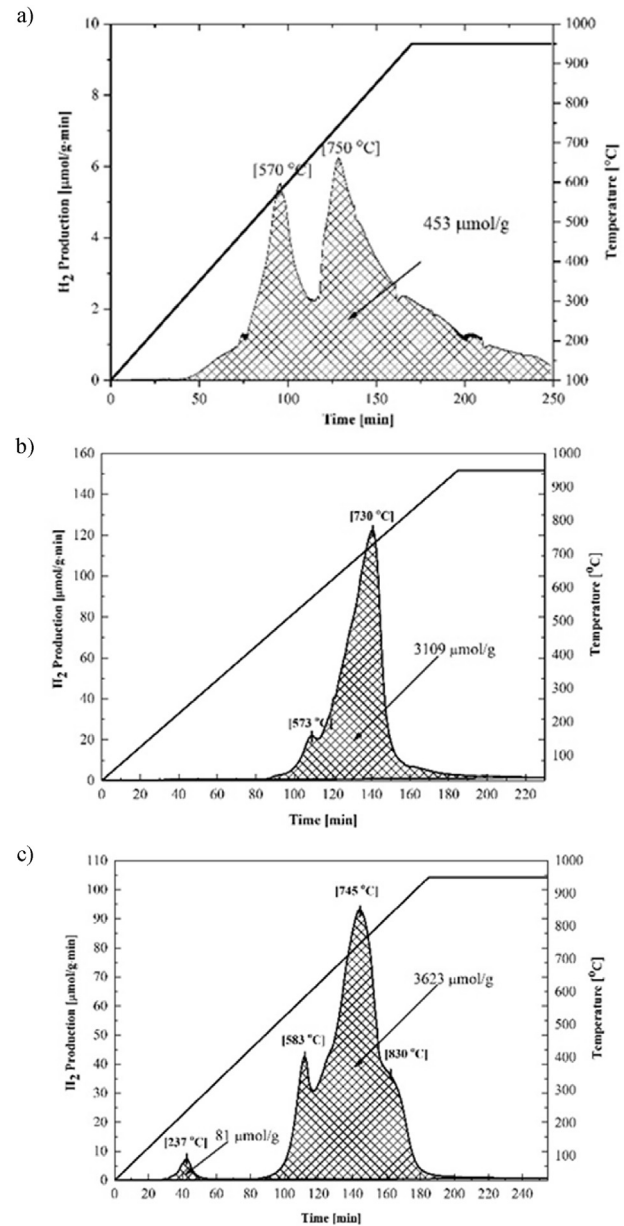
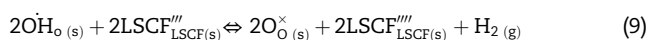
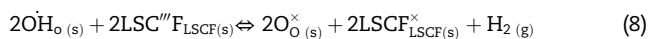
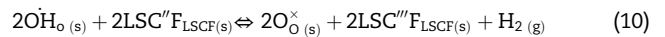


Fig. 7 – H₂ production/desorption via temperature programmed H₂O splitting over LSCF reduced at a) T_{red} 500 °C, b) T_{red} 700 °C and c) T_{red} 900 °C.



where $\text{LSCF}^{\text{X}}_{\text{LSCF}(\text{s})}$ denotes the regular LSCF, $\text{LSCF}^{\text{III}}\text{F}_{\text{LSCF}(\text{s})}$ is a polaron cation of Co^{3+} , $\text{LSCF}^{\text{III}}_{\text{LSCF}(\text{s})}$ is a polaron cation of Fe^{3+} , $\text{LSCF}^{\text{X}}_{\text{LSCF}(\text{s})}$ is a localized electron of Co^{2+} , and $\text{LSCF}^{\text{III}}_{\text{LSCF}(\text{s})}$ is a localized electron of Fe^{2+} . During the H₂O splitting. A hydroxyl ion group is able to incorporate with the excited localized (Co^{2+} , Fe^{2+}) electrons of LSCF to form gaseous hydrogen and revert to extra proton for B-site cation to be a regular (Co^{3+} , Fe^{3+}) cation and return the available active site on the surface. The H₂O splitting pathways were showed on Fig. 9.

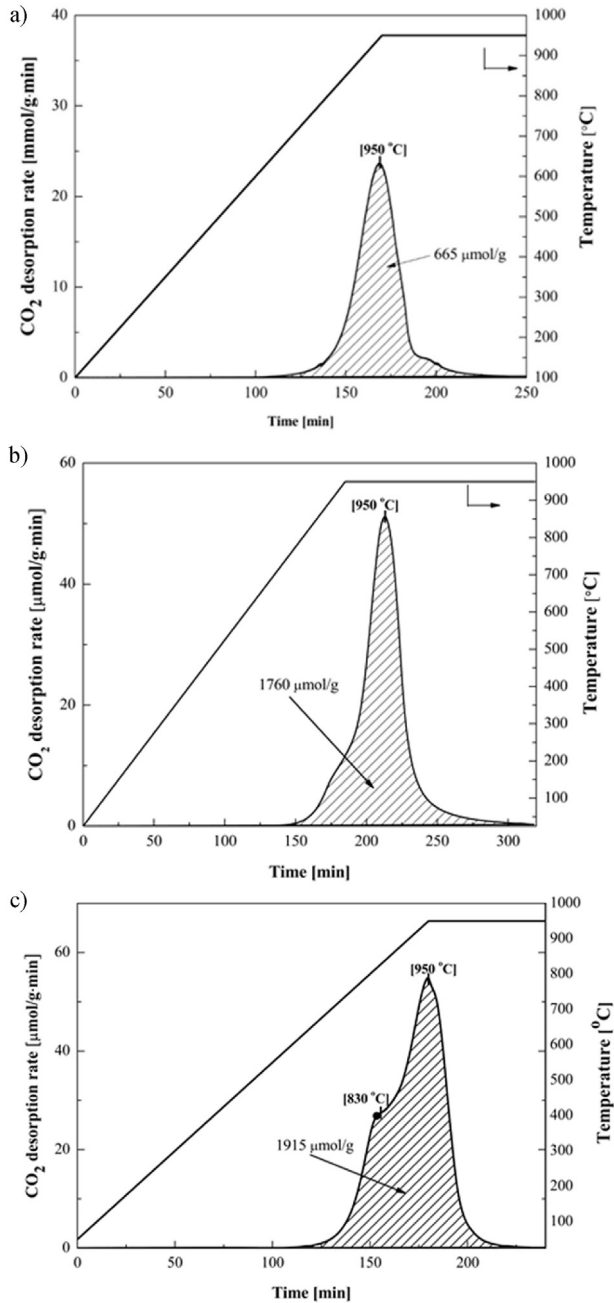


Fig. 8 – CO₂ desorption via temperature programmed over LSCF3773 reduced at a) T_{red} 500 °C, b) T_{red} 700 °C and c) T_{red} 900 °C.

Carbon dioxide splitting mechanism was also predicted as shown below:

Adsorption of CO₂ species:



Thus, the surface reactions were proposed:

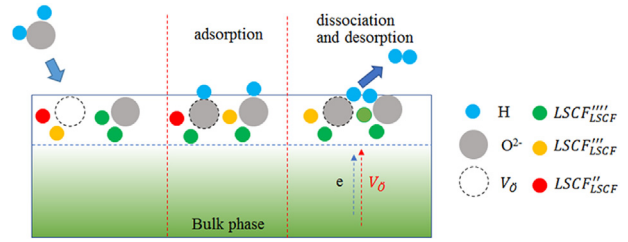
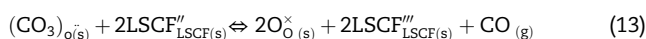
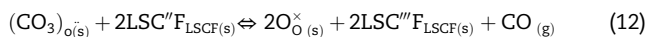


Fig. 9 – Schematics of H₂O splitting possible pathways.

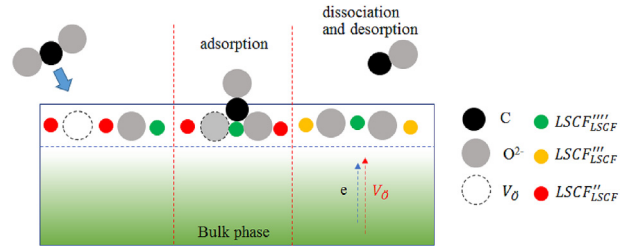
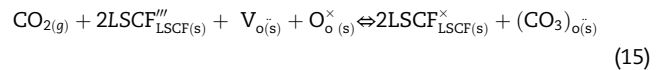
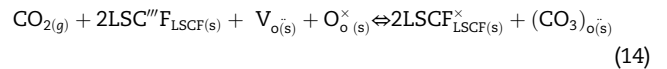


Fig. 10 – Schematics of CO₂ splitting possible pathways.

where $(\text{CO}_3)_{\text{O}(s)}$ is an adsorbed carbonyl ion group, which would be reacted further during the surface reaction step, shown in Fig. 10. In addition, 110, 100 plane diffractions were found to be active for CO₂ splitting, while 111 plane diffraction was more favored by H₂O splitting [39]. Besides, the carbonyl ion was believed to be competing with hydroxyl ion during the surface adsorption process on localized Co²⁺, Fe²⁺ of the LSCF3773.

Carbon dioxide adsorption:



Eqs. (14) and (15) expressed the mechanism pathway of surface CO₂, also illustrated in Fig. 10. CO₂ molecules diffused from the bulk steam to the available active site on the surface of LSCF and incorporate with the lowest stage of polaron cation (Co³⁺, Fe³⁺) with O²⁻ ion. The carbonyl ion (CO₃²⁻) was generated and adsorbed on the surface, blocking the surface to react with H₂O and CO₂. The proposed mechanism was well agreed with other works [40,41] reporting that high amount of alkaline earth metals (such as Ba or Sr), as an A site substitution in perovskite (ABO₃), tended to incorporate with carbonyl ions, creating a layer of such compound and covering the surface of the perovskite. In conclusion, the CO₂ adsorption could poison the catalyst and lower the productivity of syngas.

Conclusion

LSCF3773 was successfully synthesized by EDTA-citrate complex method. The prepared material had pure cubic

structure with average crystalline size of 31.90 nm. The reduction behavior was observed by a transient H_2 -TPR experiment carried from room temperature to 950 °C. Oxygen storage capacity of the LSCF3773 was estimated at 4072 $\mu\text{mol/g}_{\text{cat}}$. Oxygen vacancy concentration can be enhanced by increasing the reduction temperature, causing B-site cation's oxidation stage change. The substitution of A-site and B-site cation also contribute to the change of oxidation stage, as shown in H_2 -TPR where the regular cations (Co^{4+} , Fe^{4+}), polaron cations (Co^{3+} , Fe^{3+}) and localized cations (Co^{2+} , Fe^{2+}) were discussed. CO_2 adsorption occurred throughout the studied temperature range. The activation energy of the relevant reactions ordered from high to low was CO_2 splitting > H_2O splitting > CO_2 adsorption. H_2O splitting could split since T_{red} at 500 °C and gave a good performance since T_{red} at 700 °C and no significantly different when T_{red} was at 900 °C, in vice versa CO_2 splitting gave the best performance when T_{red} was at 900 °C and hardly to split when T_{red} at 500 °C.

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REFERENCES

- [1] Scheffe JR, Weibel D, Steinfeld A. Lanthanum-Strontium-Manganese perovskites as redox materials for solar thermochemical splitting of H_2O and CO_2 . *Energy Fuels* 2013;27(8):4250–7.
- [2] Abanades S, et al. Novel two-step SnO_2/SnO water-splitting cycle for solar thermochemical production of hydrogen. *Int J Hydrogen Energy* 2008;33(21):6021–30.
- [3] Kromer M, et al. Support for cost analyses on solar-driven high temperature thermochemical water-splitting cycles. 2011 [Massachusetts].
- [4] Stamatiou A, Loutzenhiser PG, Steinfeld A. Solar syngas production via $\text{H}_2\text{O}/\text{CO}_2$ -splitting thermochemical cycles with Zn/ZnO and $\text{FeO}/\text{Fe}_3\text{O}_4$ redox reactions. *Chem Mater* 2010;22(3):851–9.
- [5] Charvin P, et al. Two-step water splitting thermochemical cycle based on iron oxide redox pair for solar hydrogen production. *Energy* 2007;32(7):1124–33.
- [6] Gokon N, et al. Monoclinic zirconia-supported Fe_3O_4 for the two-step water-splitting thermochemical cycle at high thermal reduction temperatures of 1400–1600°C. *Int J Hydrogen Energy* 2009;34(3):1208–17.
- [7] Scheffe JR, Li J, Weimer AW. A spinel ferrite/hercynite water-splitting redox cycle. *Int J Hydrogen Energy* 2010;35(8):3333–40.
- [8] Muhich Christopher L, E BW, Weston Kayla C, Lichty Paul, Liang Xinhua, Martinek Janna, Musgrave Charles B, Weimer Alan W. Efficient generation of H_2 by splitting water with an isothermal redox cycle. *Science* 2013;341(6145):540–2.
- [9] Coker EN, et al. Ferrite-YSZ composites for solar thermochemical production of synthetic fuels: in operando characterization of CO_2 reduction. *J Mater Chem* 2011;21(29).
- [10] Gokon N, Sagawa S, Kodama T. Comparative study of activity of cerium oxide at thermal reduction temperatures of 1300–1550 °C for solar thermochemical two-step water-splitting cycle. *Int J Hydrogen Energy* 2013;38(34):14402–14.
- [11] Chi Y, et al. Morphology, performance and stability of multi-bore capillary $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ oxygen transport membranes. *J Membr Sci* 2017;529:224–33.
- [12] Luo H, et al. Novel cobalt-free, noble metal-free oxygen-permeable $40\text{Pr}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}-60\text{Ce}_{0.9}\text{Pr}_{0.1}\text{O}_{2-\delta}$ dual-phase membrane. *Chem Mater* 2012;24(11):2148–54.
- [13] Yang F, et al. Structure and oxygen permeability of $\text{BaCo}_{0.7}\text{Fe}_{0.3}-x\text{InxO}_{3-\delta}$ ceramic membranes. *J Membr Sci* 2015;492:559–67.
- [14] Ding X, et al. Electrode redox properties of $\text{Ba}_{1-x}\text{La}_x\text{FeO}_{3-\delta}$ as cobalt free cathode materials for intermediate-temperature SOFCs. *Int J Hydrogen Energy* 2014;39(23):12092–100.
- [15] Ko HJ, et al. Synthesis and evaluation of $(\text{La}_{0.6}\text{Sr}_{0.4})(\text{Co}_{0.2}\text{Fe}_{0.8})\text{O}_3$ (LSCF)– $\text{Y}_{0.08}\text{Zr}_{0.92}\text{O}_{1.96}$ (YSZ)– $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ (GDC) dual composite SOFC cathodes for high performance and durability. *Int J Hydrogen Energy* 2012;37(22):17209–16.
- [16] Zhang L, Chuang SSC. Perovskites and related mixed oxides for SOFC applications. Wiley-VCH Verlag GmbH & Co. KGaA; 2016. p. 863–79.
- [17] Asma HA, Medkhali KN, Basahel Sulaiman N, Mokhtar Mohamed. Divalent transition metals substituted LaFeO_3 perovskite catalyst for nitrous oxide decomposition. *J Membr Sep Technol* 2014;3:206–12.
- [18] Pena MA, Fierro JLG. Chemical structures and performance of perovskite oxides. *Chem Rev* 2001;101(7):1981–2017.
- [19] Luo HX, et al. Novel cobalt-free, noble metal-free oxygen-permeable $40\text{Pr}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}-60\text{Ce}_{0.9}\text{Pr}_{0.1}\text{O}_{2-\delta}$, dual-phase membrane. *Chem Mater* 2012;24(11):2148–54.
- [20] Lu Y, et al. Novel cobalt-free $\text{BaFe}_{1-x}\text{Gd}_x\text{O}_{3-\delta}$ perovskite membranes for oxygen separation. *J Mater Chem* 2016;4(27):10454–66.
- [21] Zeng Q, et al. CO_2 -tolerant oxygen separation membranes targeting CO_2 capture application. *J Membr Sci* 2009;335(1–2):140–4.
- [22] Gupta S, et al. Processing and electrochemical performance of manganese-doped lanthanum-strontium chromite in oxidizing and reducing atmospheres. *Int J Hydrogen Energy* 2015;40(39):13479–89.
- [23] Zhu XF, Wang HH, Yang WS. Structural stability and oxygen permeability of cerium lightly doped $\text{BaFeO}_{3-\delta}$ ceramic membranes. *Solid State Ion* 2006;177(33–34):2917–21.
- [24] Babiniec SM, et al. Investigation of $\text{La Sr}_{1-\text{Co}} \text{M}_{1-\text{O}3-\text{M}}$ ($\text{M} = \text{Mn, Fe}$) perovskite materials as thermochemical energy storage media. *Sol Energy* 2015;118:451–9.
- [25] Tanaka H, Misono M. Advances in designing perovskite catalysts. *Curr Opin Solid State Mater Sci* 2001;5(5):381–7.
- [26] Zhu J, et al. Perovskite oxides: preparation, characterizations, and applications in heterogeneous catalysis. *ACS Catal* 2014;4(9):2917–40.
- [27] Jiang Q, et al. Thermochemical CO_2 splitting reaction with supported $\text{La}_{x-1}\text{Fe}_y\text{B}_{1-y}\text{O}_3$ ($\text{A}=\text{Sr, Ce, B}=\text{Co, Mn; } 0\leq x, y\leq 1$) perovskite oxides. *Sol Energy* 2014;103:425–37.
- [28] Schlehuber D, et al. Long-term operation of a $\text{La}_{0.58}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ membrane for oxygen separation. *J Membr Sci* 2010;351(1–2):16–20.

- [29] Norton TT, Ortiz-Landeros J, Lin YS. Stability of La–Sr–Co–Fe oxide–carbonate dual-phase membranes for carbon dioxide separation at high temperatures. *Ind Eng Chem Res* 2014;53(6):2432–40.
- [30] Sean M, Babiniec ENC, Ambrosini Andrea, Miller James E. ABO₃ (A = La, Ba, Sr, K; B = Co, Mn, Fe) Perovskites for thermochemical energy storage. In: AIP Conference Proceedings. 1734; 2016. p. 1–8. 050006.
- [31] Tan X, Pang Z, Li K. Oxygen production using La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3- α} (LSCF) perovskite hollow fibre membrane modules. *J Membr Sci* 2008;310(1–2):550–6.
- [32] Wang Zhigang, Y N, Meng Bo, Tan Xiaoyao, Li K. Preparation and oxygen permeation properties of highly asymmetric La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3- α} perovskite hollow-fiber membranes. *Ind Eng Chem Res* 2009;48(1):510–6.
- [33] L.a. MHR, t Elshof JE. Thermodynamic quantities and defect structure of La_{0.6}Sr_{0.4}Co_{1-y}Fe_yO_{3- δ} (y=0–0.6) from high-temperature coulometric titration experiments. *J Solid State Chem* 1997;130:302–310.
- [34] Ding XF, et al. Synthesis and characterization of doped LaCrO₃ perovskite prepared by EDTA-citrate complexing method. *J Alloy Comp* 2008;458(1–2):346–50.
- [35] Scherrer P. Bestimmung der Grösse und der inneren Struktur von Kolloidteilchen mittels Röntgenstrahlen. *Nachr. Ges. Wiss. Göttingen* 1918;26:98–100.
- [36] Orlovskaya N, Browning N, editors. Mixed ionic electronic conducting perovskites for advanced energy systems. Springer Science & Business Media; 2012.
- [37] Sunarso J, et al. Mixed ionic–electronic conducting (MIEC) ceramic-based membranes for oxygen separation. *J Membr Sci* 2008;320(1–2):13–41.
- [38] Wu Y, et al. Stoichiometric and non-stoichiometric perovskite-based catalysts: consequences on surface properties and on catalytic performances in the decomposition of N₂O from nitric acid plants. *Appl Catal B Environ* 2012;125:149–57.
- [39] Zhao Z, et al. Enhanced intermediate-temperature CO₂ splitting using nonstoichiometric ceria and ceria-zirconia. *Phys Chem Chem Phys* 2017;19(37):25774–85.
- [40] Tan Xiaoyao, L N, Meng Bo, Sunarso Jaka, Zhang Kun, Liu Shaomin. Oxygen permeation behavior of La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O₃ hollow fibre membranes with highly concentrated CO₂ exposure. *J Membr Sci* 2012;216–22.
- [41] Yi Jianxin, S M, Weirich Thomas, Mayer Joachim. Behavior of Ba(Co, Fe, Nb)O_{3- δ} perovskite in CO₂-containing atmospheres: degradation mechanism and materials design. *Chem Mater* 2010;6246–53.