

Synthesis and experimental study of improved double perovskite-type $\text{PrBaCo}_2\text{O}_{5+\delta}$ materials to produce oxygen-enriched CO_2 for oxyfuel combustion application

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Perovskite oxides are promising oxygen carrier materials to produce O_2/CO_2 gas for oxyfuel combustion application. In this study, $\text{PrBaCo}_2\text{O}_{5+\delta}$ double perovskite oxide was prepared by the EDTA sol-gel method and first applied as oxygen carrier for oxygen production. The oxygen adsorption/desorption performance of $\text{PrBaCo}_2\text{O}_{5+\delta}$ perovskite was carried out in a fixed-bed set-up. The operating factors of oxygen releasing performance were investigated in detail including adsorption temperature, desorption temperature, CO_2 volumetric flow rate, and CO_2 partial pressure. Due to the kinetic effects of gas-solid reactions, it is found that the adsorption and desorption temperature has greatly influence on the oxygen production performance. The surface morphology was observed by scanning electron microscope (SEM). In addition, the cyclic performance of $\text{PrBaCo}_2\text{O}_{5+\delta}$ under the optimal operating condition was examined. The oxygen production amount was reduced slightly from 110.9 mg/g perovskite to 99.2 mg/g after 8 cycles' test. Therefore, the results indicated that $\text{PrBaCo}_2\text{O}_{5+\delta}$ has good stability and reactivity for cyclic use.

Keywords: Double-Perovskite, $\text{PrBaCo}_2\text{O}_{5+\delta}$, Oxygen desorption, Oxyfuel combustion.

Introduction

Billion tons of CO_2 was let off into the air each year, which in part cause global warming and climate changes [1, 2]. New ways to reduce CO_2 emissions need to be urgently developed to meet industrial demand. Oxyfuel combustion is also known as O_2/CO_2 cycle combustion, which uses the mixture of pure oxygen obtained from air separation and part of boiler exhaust gas, instead of air as oxidant in fossil fuel combustion [3]. In this way, the concentration of CO_2 in the flue gas generated by boiler combustion can be up to 90%. Therefore, most of the CO_2 in flue gas can be directly liquefied and recycled without separation. This can not only effectively reduce greenhouse gas emissions, but also effectively reduce reduce the emission of NO_x and SO_2 at the same time. Therefore, oxyfuel combustion technology is an effective way to reduce CO_2 emission [4].

This combustion technology requires a high concentration of oxygen. At present, cryogenic process is the only commercial operation mode that can provide large-scale oxygen production [5]. However, the large investment and high energy consumption are the main

bottle-necks for this technology. Perovskite-type materials as high temperature oxygen carriers are envisaged to produce oxygen for oxyfuel combustion application [6]. This new technology can reduce 35% cost on oxygen production which can also cut the energy penalty by 50% when applied in an oxyfuel power plant [2].

Perovskite-type oxides can absorb oxygen from air at high temperature, which can be used as the oxygen carrier for oxyfuel combustion [7]. Our group has reported a procedure which used perovskite oxides as oxygen carriers to directly produce O_2/CO_2 mixed gas at high temperature [2]. This O_2/CO_2 production process consists of two steps, as shown in Fig. 1.

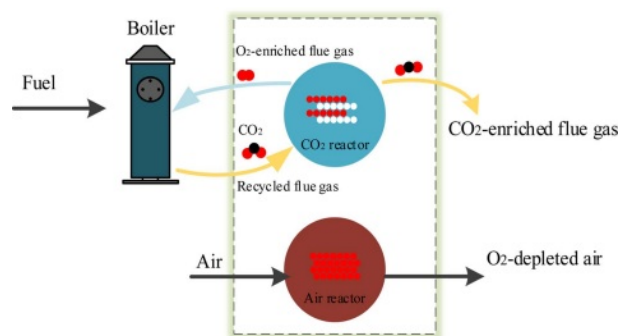


Fig. 1. Schematic diagram of producing O_2/CO_2 by perovskite-type oxides.

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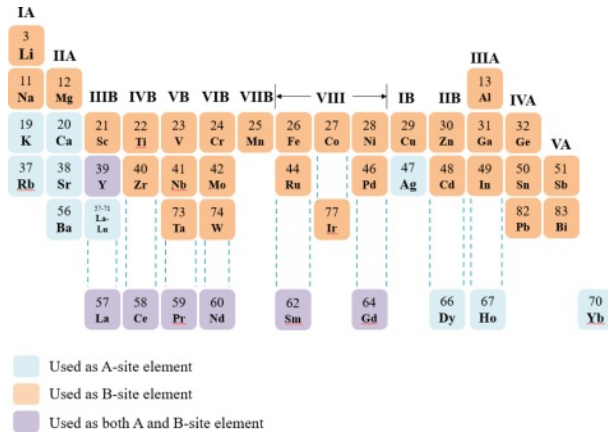


Fig. 2. Common elements in the ABO_3 -type perovskite oxides.

For a ideal cubic structure perovskite oxide, the value of t is about 1. The A-site is generally a rare earth or alkaline earth element ion, while the B-site is a transition element ion (Fig. 2). To form the perovskite structure, the radii of the A-site and B-site ions need to satisfy the formula.

$$t = (r_A + r_q) / \sqrt{2}(r_B + r_q) \quad (1)$$

where t is tolerance factor ($0.77 < t < 1.1$)

r_A is the ion radii of the A-site cation

r_B is the ion radii of the B-site cation

r_q is the ion radii of the oxygen anion

The A and B positions can be radius similar metal ions which are partially substituted to keep their crystal structure basically unchanged, so it is theoretically an ideal sample for studying the catalyst surface and catalytic performance [8]. Because of the unique crystal structure, perovskite-type oxides can be used in many fields such as solid fuel cell, solid electrolyte, sensor, high temperature heating material and solid resistor [9-11].

In the past decade, double perovskite materials with a formula of $AA'B_2O_{5+\delta}$ (A as the rare earth element, A' as the alkaline earth element, B as the transition metal element) have attracted much more attention (Fig. 3) [12]. When the B-site transition metal ions of double perovskite are replaced, oxygen vacancies or defects will be formed due to the change of transition metal oxidation price state. Therefore, the adsorption and desorption properties of oxygen can be changed. Double perovskite $PrBaCo_2O_{5+\delta}$ (PBCO) has attracted much attention as potential cathodes for SOFCs thanks to its superior oxygen-ion transport capability [13, 14]. Due to its special crystal structure, $PrBaCo_2O_{5+\delta}$ have been also found to exhibit a large capacity for reversible oxygen absorption and desorption [15]. Thus double perovskite is a promising material for the O_2 -enriched CO_2 gas production for oxyfuel combustion.

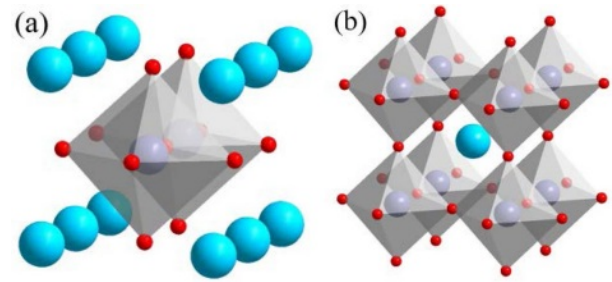


Fig. 3. Schematic diagram of double perovskite $A_2B_2O_{5+\delta}$ cell: (a) monolayer cell (b) bilayer cell.

However, there are limited studies about $PrBaCo_2O_{5+\delta}$ (PBCO) used as potential oxygen carrier for oxyfuel combustion application. The objective of this study is to evaluate the oxygen adsorption/desorption performance of PBCO double perovskite. Especially, a thorough study of the effects of the reaction conditions on the oxygen production properties of synthesized PBCO double perovskite are investigated.

Experimental

PBCO synthesis

PBCO was prepared by EDTA sol-gel method as shown in Fig. 4. Metal nitrates, $Ba(NO_3)_2$ (AR, Aladdin), $Pr(NO_3)_3$ (AR, Aladdin) and $Co(NO_3)_2 \cdot 6H_2O$ (AR, Aladdin) were used as the raw materials and all were of analytical purity. Metal nitrate, citric acid and EDTA are added to the beaker at a ratio of 1:1.5:1. The specific preparation steps are shown in details in our previous study [2, 3].

Oxygen production experiments

The oxygen adsorption/desorption experimental process have been presented in details in the previous works (Fig. 5) [1, 2]. 1 g of sample is tightly rolled with quartz cotton and placed in the center of the quartz tube so that it can fully contact with the gas.

In the oxygen adsorption process, the perovskite is heated to a given adsorption temperature. Air and nitrogen were adopted as the feed and purge gas, respectively. In the desorption stage, the sample was exposed under a flow of CO_2 . After a adsorption/

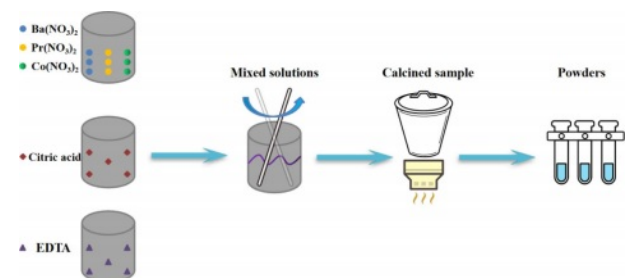


Fig. 4. Flow diagram of the preparing process of PBCO powders.

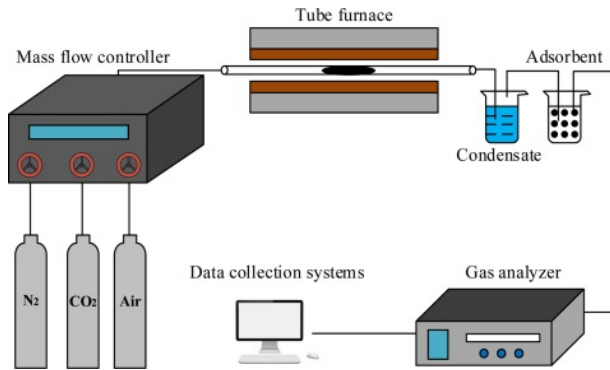


Fig. 5. Experimental system diagram.

desorption experiment is completed, the tube furnace is adjusted to the preset temperature of the adsorption step for the following cyclic test.

The oxygen concentration of the outlet gas was recorded during the experiment, and the oxygen release quantities was calculated according to the formula:

$$M_{O_2} = \frac{\sum C_{O_2} \times f \times m_{O_2}}{60 \times 22.4 \times m} \quad (3)$$

where M_{O_2} : Oxygen release amount
 $\sum C_{O_2}$: Sum of oxygen concentration measured by gas analyzer
 f : Flow rate of desorption gas CO_2
 m_{O_2} : Molar mass of oxygen molecules
 m : Sample quality to be placed in a tubular furnace

Through the formula, the amount of released oxygen can be calculated for 1 g of the test sample, which is convenient for comparison of different perovskite properties.

Characterization

Particle morphology of the sample was observed by scanning electron microscopy (SEM, SUPRA 55 SAPPHERE).

Results and Discussion

Adsorption temperature

Fig. 6(a) and 6(b) present the comparison of oxygen release performance by PBCO at different adsorption temperatures (650 °C, 750 °C, 850 °C, 950 °C), respectively. The remaining operating conditions are determined as follows according to our previous study [1]. The performance of oxygen desorption PBCO is improved with the increase of temperature, reaching a relatively ideal value at 850 °C and then decreasing. It can be clearly seen that the PBCO produced 110.9 mg/g of oxygen when the adsorption temperatures is 850 °C. This is because the adsorption capacity of PBCO to oxygen in the adsorption phase is influenced by

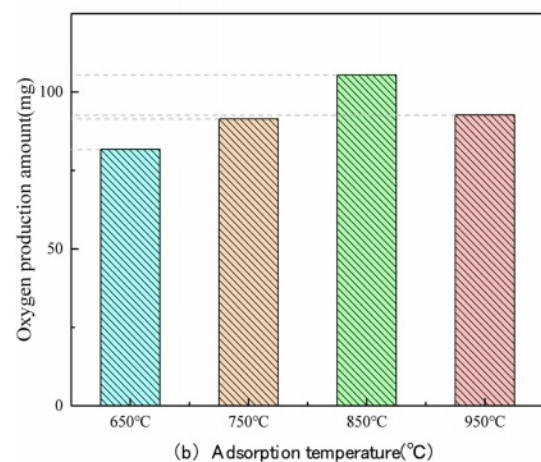
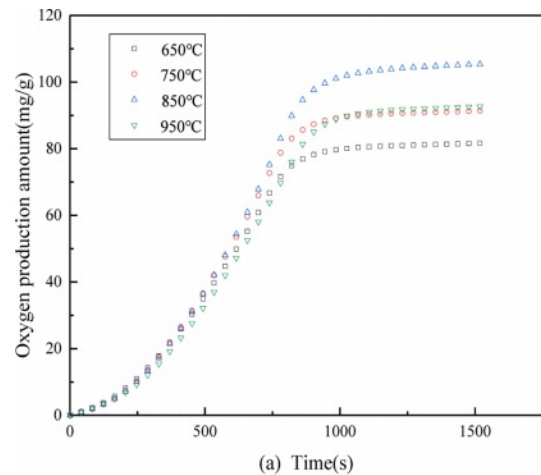


Fig. 6. Oxygen release performance of PBCO at different adsorption temperature: (a) Penetration curve. (b) Oxygen production diagram.

kinetics below 850 °C. With the increase of the adsorption temperature of PBCO, the quality of the provided oxygen production increased remarkably. Due to thermodynamic constraints, the adsorption process is regarded as exothermic at temperatures above 850 °C and high temperature will lead to the sintering of perovskite, which affect the oxygen desorption performance [4]. Oxygen cannot be adsorbed at high temperatures, thus 850 °C has been determined as the optimal adsorption temperature.

Desorption temperature

It can be seen from the Fig. 7 that the oxygen production of PBCO will increase with the increase of the desorption temperature. Oxygen production rates and amount reach a minimum of 650 °C. Then temperature rises to 850 °C, the reaction rate was increased significantly. The production of oxygen was improved nearly double. The results further indicated that the PBCO desorption reaction time was 2min30s. The oxygen desorption reaction of PBCO is a gas-solid reaction. Due to the kinetic effects of gas-solid reactions,

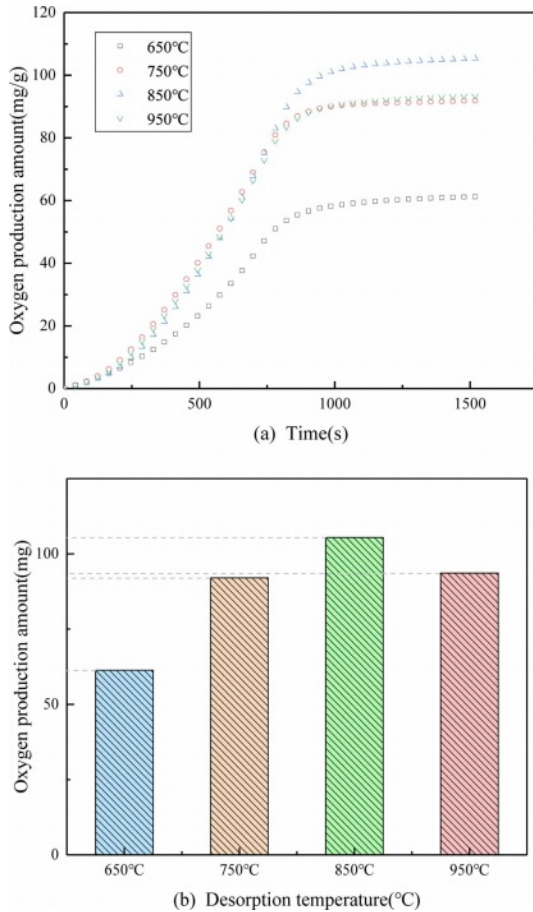


Fig. 7. Oxygen production amount of PBCO at different desorption temperature: (a) penetration curves, (b) oxygen production quality diagram.

oxygen desorption reactions are associated with temperature [7]. However, when the temperature increases to 950 °C, the amount of O₂ production is declined. Thus 850 °C was used as the optimal desorption temperature for PBCO in the following experiments.

CO₂ volumetric flow rate

The comparison of oxygen release performance at different CO₂ volumetric flow rate conditions can be seen in Fig. 8. The oxygen production amount values are also displayed in Fig. 8. As a general trend, with the increase of CO₂ flow rate, the desorption rate of PBCO increases. The results show that the production of oxygen was increased when the rate of CO₂ gas increases from 150 ml/min to 200 ml/min. The desorption time of the sample is about 17 mins at 150 ml/min, while it is only 8 mins at 300 ml/min. The oxygen production reached at the highest at 200 ml/min and the final oxygen production amount was 110 mg. When the CO₂ flow rates was increased to 300 ml/min, the PBCO did not react adequately due to the excessive flow. Thus it can be concluded that the optimal CO₂ volumetric flow rate is 200 ml/min.

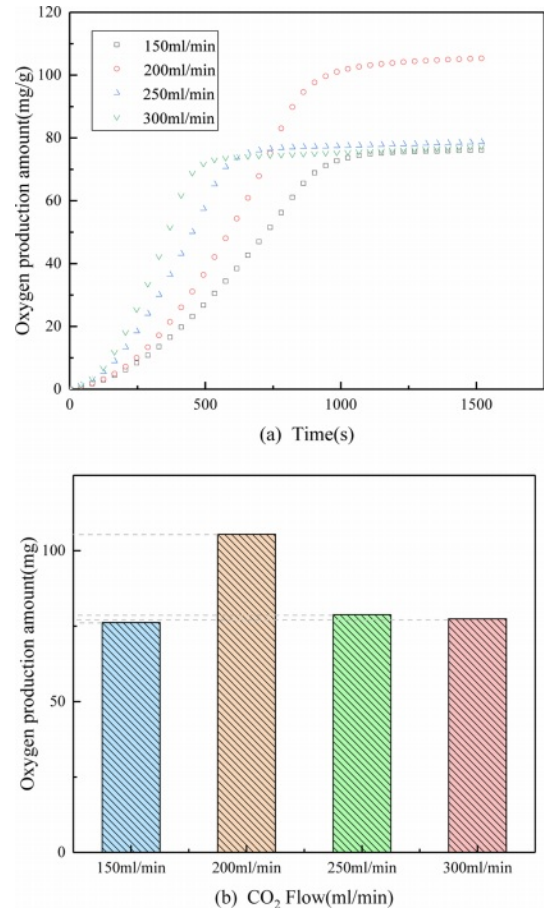


Fig. 8. Oxygen production amount of PBCO at different CO₂ flow rate: (a) penetration curves, (b) oxygen production quality diagram.

CO₂ partial pressure

The partial pressure of carbon dioxide has an important influence on the carbonation reaction between perovskite and CO₂. The oxygen desorption performance of PBCO can be seen in the Fig. 9 (the partial pressures of N₂ and CO₂ are 10:0, 6:4, 2:8 and 0:10, respectively). As can be seen from Fig. 9(a), the fluctuation of oxygen desorption performance is very small in the reaction time of 1500 s. With the increase of CO₂ volume, the production of oxygen increases gradually. When the ratio of N₂/CO₂ increases from 6:4 to 10:0, the production of oxygen increases significantly. This is because perovskite reacts with CO₂ to produce more oxygen than desorbed oxygen in low oxygen and high nitrogen atmosphere. Therefore, the higher the partial pressure of carbon dioxide, the more oxygen is produced.

Cycle capacity of novel PBCO

PBCO is used as an oxygen carrier to provide a stable mixture of gases for oxyfuel combustion, so it should have excellent cycling characteristics. The oxygen desorption amounts for continuous 8 cycles

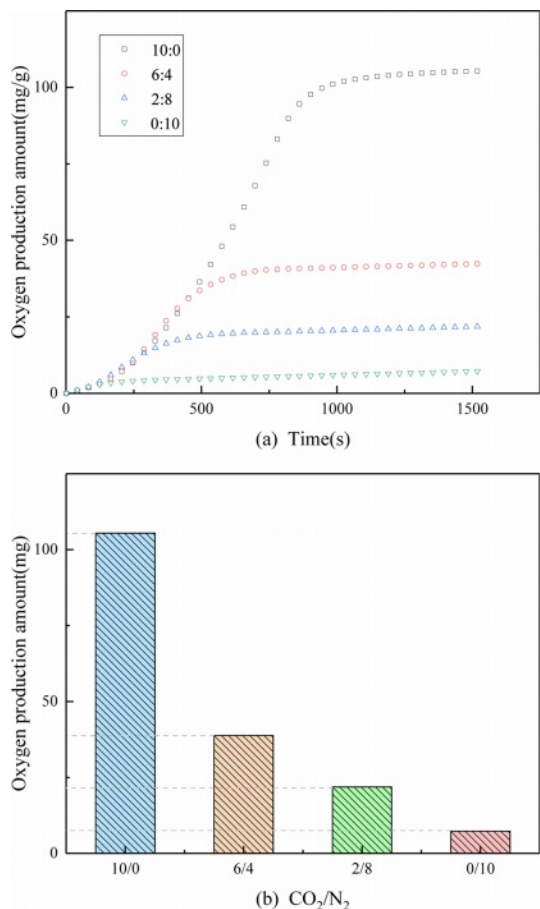


Fig. 9. Oxygen production amount of PBCO in different CO₂ partial pressure: (a) oxygen concentration curves. (b) oxygen production amount.

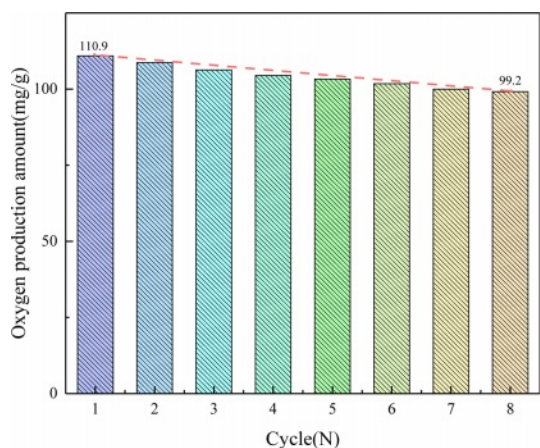


Fig. 10. Cyclic tests of PBCO.

demonstrated in Fig. 10 were obtained from Eq. (3). As can be seen in Fig. 10, the PBCO sample still has excellent oxygen release capability after cyclic experiments. The amount of oxygen released was stabilized at 99.2 mg/g after cyclic testing. Although the oxygen desorption performance of PBCO decreased with the increase of cycle times, the decreasing trend of

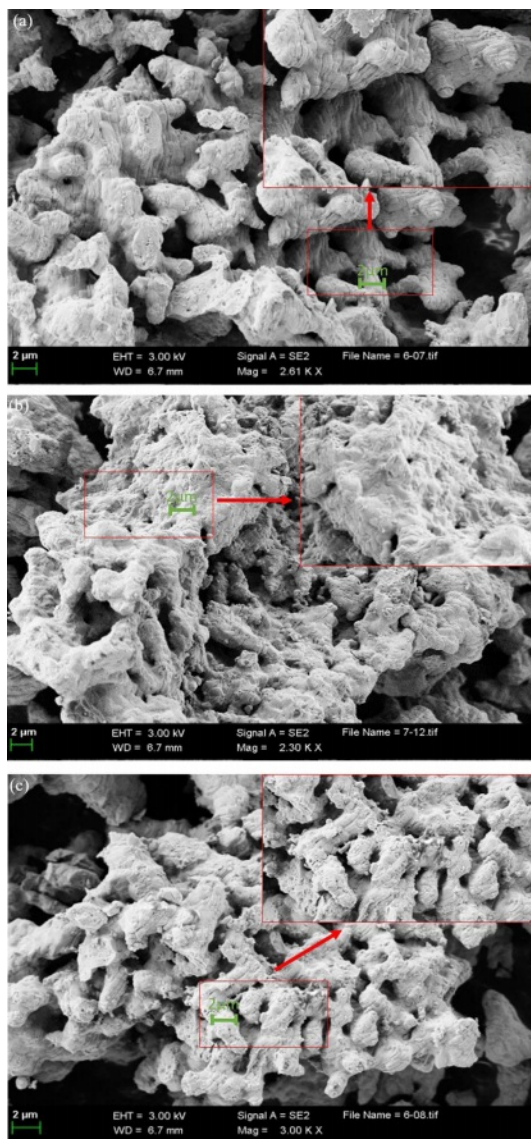


Fig. 11. SEM images of PBCO powders: (a) fresh sample. (b) after 8 cycles' reacted sample. (c) reverted sample after 8 cycles.

oxygen release was smoothed. Compared with single perovskite BaCo_{0.6}Ni_{0.4}O_{3-δ}, the oxygen desorption capacity of PBCO perovskite is significantly improved [7]. It is concluded that PBCO has excellent cycling performance and is an excellent oxygen carrier to provide stable circulating gas for oxyfuel combustion.

SEM analysis

Fig. 11 displays the SEM images of the fresh PBCO samples, the samples after 8 cycles' reacted and the reverted products of PBCO after 8 cycles. It can be seen from the fresh sample that the morphology of PBCO is porous and rough. The fresh PBCO presents a fluffy porous network structure. As shown in the Fig. 11b, the structure of PBCO becomes massive and irregular. This is because after 8 adsorption and desorption cycles of perovskite, the structure of

perovskite disappears and becomes massive. It can be seen from the Fig. 11c that PBCO restores porous and sparse components. After recycling, the appearance of perovskite hardly changes and returns to porous structure. Therefore, perovskite is expected to have strong recycling capacity.

Conclusions

In this study, the double perovskite $\text{PrBaCo}_2\text{O}_{5+\delta}$ with excellent performance was prepared by the EDTA sol-gel synthesis method and firstly applied to produce oxygen for oxyfuel combustion application. The oxygen production properties of the $\text{PrBaCo}_2\text{O}_{5+\delta}$ were investigated in a fixed-bed system. The optimal operation conditions for $\text{PrBaCo}_2\text{O}_{5+\delta}$ were studied in-depth. The main conclusions are as follows:

1. The experimental results show that the adsorption/desorption temperature has the greatest influence on the oxygen desorption performance of perovskite. The optimal reaction conditions of $\text{PrBaCo}_2\text{O}_{5+\delta}$ to oxygen production are as below: adsorption temperature was 850 °C; desorption temperature was 850 °C; the volume proportion of CO_2 and N_2 was determined to be 10:0; CO_2 volumetric flow rate was confirmed 200 ml/min.
2. The higher the partial pressure of carbon dioxide, the more oxygen is produced. This is because perovskite reacts with CO_2 to produce more oxygen than desorbed oxygen in low oxygen and high nitrogen atmosphere.
3. The proposed novel double perovskite $\text{PrBaCo}_2\text{O}_{5+\delta}$ provided excellent performance, the O_2 production of $\text{PrBaCo}_2\text{O}_{5+\delta}$ can still reach 99.2 mg/g after 8 cycles. SEM results show that after 8 cycles, after recycling, the appearance of perovskite hardly changes and returns to porous structure.
4. In summary, the synthesized PBCO powders shows excellent O_2 production performance which may be a potential oxygen carrier material for oxyfuel application. Moreover, this simple synthetic method can be extended to other double perovskite oxide systems for more applications.

Acknowledgments

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Conflicts of Interest

The authors declare no conflict of interest.

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