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Mixed reforming of simulated gasoline to hydrogen in a BSCFO membrane reactor

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Abstract

Currently, fuel cells are receiving more and more attention as the most promising new power generation technology, and fuel processing by the mixed reforming of liquid hydrocarbons (MRL) with water and oxygen is regarded as a desirable way for fuel cells. In this paper, we developed a new mixed reforming method for hydrogen production by combining a dense ceramic membrane $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$(BSCFO) with a catalyst LiLaNiO/γ-Al_2O_3 in a membrane reactor and reforming a simulated gasoline. During a 500-h long-term test at optimized reaction conditions, all the components in the simulated gasoline converted completely, and around 90% selectivity of CO, around 95% selectivity of H_2 and around 8.0 mL cm^{-2} min^{-1} oxygen permeation flux were achieved. This provides a new optional way of hydrogen production for fuel cells.

Keywords: Membrane reactor; Mixed reforming; Simulated gasoline; Hydrogen production

1. Introduction

Traditionally, hydrogen was mainly produced from natural gas by steam reforming, partial oxidation or autothermal reforming (mixed reforming) [1–6]. Currently, there is considerable interest in reforming liquid hydrocarbons to hydrogen for on-board and on-site fuel cells, such as naphtha, gasoline, or diesel for their higher heat value, larger hydrogen content and available infrastructure all over the world [7–12]. Up to now, all researching work has been performed in a fixed-bed reactor and has used air or pure oxygen as an oxidant. However, pure oxygen is very expensive. Though air is cheap, its products contain about 50% N_2, which consumes considerable heat and dilutes the concentration of hydrogen [13]. In GTL conversion, there is interest in developing a dense ceramic membrane to supply pure oxygen from air directly for syngas production from natural gas. Since 30% of the potential capital cost could be saved with this technology [14], the potential economic benefits are very promising. Now, we tried to use this technology for hydrogen production, and hope it could be an optional procedure for a small stationary reformer for fuel cells.

In our group, the catalyst LiLaNiO/γ-Al_2O_3 was developed, and even at high space velocity (2.7×10^5 L kg^{-1} h^{-1}), it was excellent to convert methane to syngas [15]. Furthermore, a dense ceramic BSCFO membrane was also previously exploited for oxygen production from the air. During the test of partial oxidation of methane (POM), oxygen permeation flux of BSCFO membrane reached 11.5 mL cm^{-2} min^{-1} (J_{O_2}) [16].

This work is to study the hydrogen production by combining BSCFO dense ceramic membrane with LiLaNiO/γ-Al_2O_3 catalyst in a membrane reactor and reforming liquid hydrocarbons to hydrogen. Parts of the relevant results had been published previously [17,18], but they were mainly the results of heptane which was used as a typical component of liquid hydrocarbons. The life test of the simulated gasoline was also performed at the optimized reaction conditions of heptane, but it was short, only 75 h. The reaction condition of heptane was not very suitable to the simulated gasoline, because, besides heptane, there was 34 vol.% toluene, which very easily forms carbon-deposition, and proved difficult to remain in the membrane reactions for long time. Therefore, it is necessary to investigate the optimized reaction conditions of mixed reforming reactions with simulated gasoline as the feedstock. In this paper, we show the studies in detail.

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2. Experimental

Fig. 1 shows the oxygen permeable membrane reactor configuration. The membrane BSCFO was prepared as described in the literature [16], and the catalyst LiLaNiO/γ-Al_2O_3 was prepared by the usual impregnation method. The membrane reactor was assembled with a dense ceramic membrane, quartz tubes and gold ring for sealing. The gold ring was put between the membrane and the quartz tube, and at high temperature, around 1070 °C, it became soft and contacted closely with the membrane and quartz tubes under the pressure by spring. When the membrane reactions proceeded, one side of the membrane was exposed to air, while another side was exposed to reactants. The thickness of the disk membrane was 1.4 mm and its effective area exposed to the reactants was 1.00 cm^2. Before the membrane reaction, LiLaNiO/γ-Al_2O_3 catalyst particles (800 mg) were packed on the top of the membrane at 850 °C.

A mixture of heptane 40 vol.%, cyclohexane 14 vol.%, toluene 34 vol.% and hexane 12 vol.% simulated the gasoline, which was fed by a pump at a constant rate; steam was brought by helium, which was also used to adjust the partial pressure of the reactants. The steam quantum was controlled by the helium flow and the temperature of the water tin. A small quantity of oxygen (0.5 mL min^{-1}) was also added into the reactants to keep the thermal cracking of the simulated gasoline within limits. After being vaporized and mixed symmetrically in the evaporator, the mixture of the simulated gasoline, steam, oxygen and helium was fed into the membrane reactor and reacted with the oxygen supplied by the dense ceramic membrane from the airside. Firstly the products condensed, and then they were analyzed by an on-line HP4890 GC with a TCD detector. When the reaction was finished, the temperature of the reactor dropped rapidly to room temperature in a helium atmosphere. The X-ray diffraction technique and SEM were used to characterize the membrane.

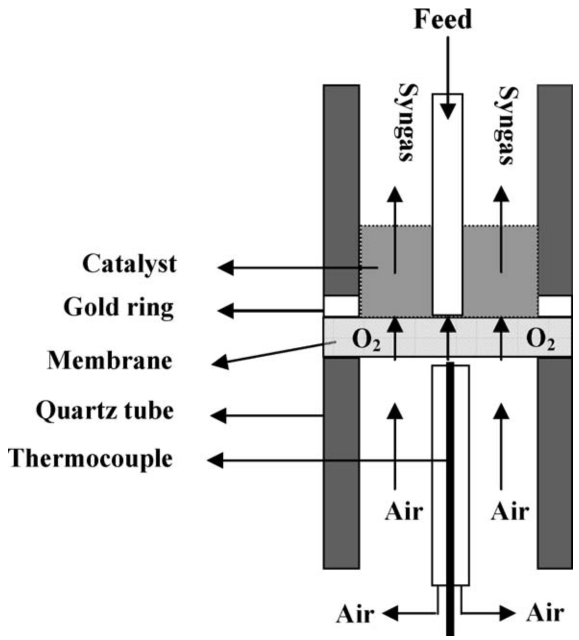

Fig. 1. The oxygen permeable membrane reactor configuration.

3. Results and discussion

Firstly, the effect of the temperature on the mixed reforming reaction of the simulated gasoline was investigated, and the results are shown in Fig. 2. With the increase of temperature from 800 to 950 °C, all the components of the simulated gasoline converted completely at the high reaction temperatures, and the oxygen permeation flux gradually increased from 5.9 to 13.6 mL cm^{-2} min^{-1}; Simultaneously, the CO selectivity decreased rapidly; on the contrary, the selectivity of CO_2 increased with the temperature. The observed phenomenon is due to the increased oxygen flux supplied by the membrane from the air, which is a function of the temperature. At a lower temperature (<850 °C), C_2H_4 and C_2H_6 were observed in the products (not shown in the figure), for the oxygen supplied by the membrane was not sufficient to completely convert all the C_2H_6 and C_2H_4 into CO and H_2. As the oxygen flux increased with the temperature, the C_2 in the products decreased and disappeared at 850 °C, while, the oxygen permeating through the membrane not only converted all of the C_2 to CO and H_2, but also produced some CO_2. Thus, CO selectivity decreased with the rise of CO_2 selectivity. Fig. 2 also shows that the selectivity of H_2 was about 100% at 950 °C. But the higher temperatures mean lower energy efficiency, and more expensive reactor materials, which are able to withstand high temperatures. Above all, it is difficult to seal the membrane reactor at higher temperature. Therefore, we selected 850 °C, not 950 °C as the reaction temperature. At this temperature, the BSCFO membrane has a high oxygen permeation flux and good stability.

In our other work, the BSCFO membrane showed high oxygen permeation (around 11.5 mL cm^{-2} min^{-1}) with heptane or methane as feeds [16–18]. However, during the mixed reforming of the simulated gasoline, the oxygen permeation flux of the membrane is less (around 8.0 mL cm^{-2} min^{-1} at 850 °C). The difference is due to toluene in the simulated gasoline. Since toluene very easily forms a carbon deposit on the catalyst, which, to some extent, prevents the reaction of oxygen with reactants during the membrane reaction, and thus

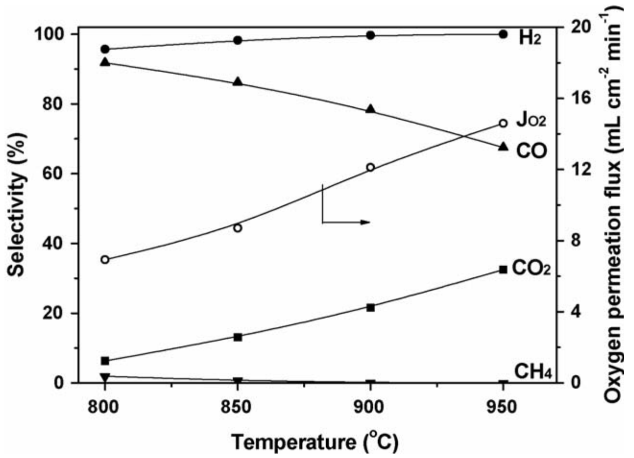

Fig. 2. The effect of reaction temperature on the selectivity of products and the oxygen permeation flux of the membrane. Reaction conditions: V_{He} = 35 mL min^{-1}; V_{air} = 200 mL min^{-1}; W/C = 0.40.

leads to increased oxygen partial pressure in the reaction side, namely a decreased concentration gradient of oxygen between the two sides of the membrane, which is the driving force of the oxygen permeation. Therefore, the oxygen permeation flux decreased with the appearance of toluene in the simulated gasoline.

Fig. 3 shows the influence of the airflow rate on the mixed reforming reaction of the simulated gasoline at 850 °C. Obviously, at the beginning, the membrane reaction changed and, subsequently, kept stable with the increase of the airflow rate. When the airflow rate increased from 50 to 200 mL min^{-1}, the oxygen permeation flux increased from 4.6 to 8.2 mL cm^{-2} min^{-1}; however, when the airflow rate was higher than 200 mL min^{-1}, the oxygen permeation flux stayed constant, around 8.0 mL cm^{-2} min^{-1}. This showed that, at the membrane temperature of 850 °C, when the airflow rate was below 200 mL min^{-1}, the exchange of oxygen on the air side of membrane was the controlling step of the oxygen permeation. Hence, the oxygen permeation flux increases with an increase in the airflow rate; while the airflow rate was above 200 mL min^{-1}, its influence on the membrane reaction was negligible. Therefore, at the reaction temperature of 850 °C, the airflow rate was fixed at 200 mL min^{-1}.

Fig. 4 shows the effect of W/C (defined as molecular ratio of H_2O/carbon) at a range of 0.26–0.54 on the mixed reforming of the simulated gasoline in the membrane reactor. When W/C was 0.26, the oxygen permeation flux was 7.5 mL cm^{-2} min^{-1} and some C_2H_4 were detected in the products (not shown in the figure). In this case, the water was insufficient and cannot react with the reactants or intermediate products in time. Thus some carbon deposit on the surface of the catalyst, which did not favor the consumption of oxygen on the near surface of the membrane, also caused high oxygen partial pressure. So the oxygen permeation flux is low. Consequently, there was not enough oxygen reacted with the reactants and C_2 was detected in the products.

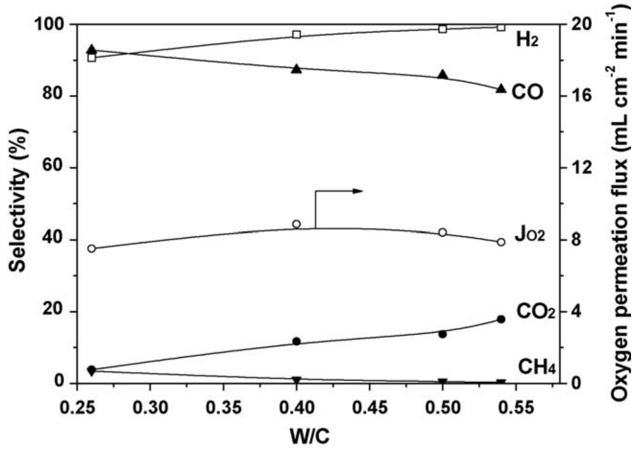

Fig. 4. The effect of W/C on the selectivity of products and the oxygen permeation flux of the membrane. Reaction conditions: $T = 850$ °C; $V_{He} = 35$ mL min^{-1}; $V_{air} = 200$ mL min^{-1}.

With the increase of W/C, more water was added to the reaction and consumed the intermediate products in time, so the oxygen permeation flux went up. However, the further increase of the W/C ratio also resulted in the decrease of oxygen permeation flux, for the concentrations of the reactants were diluted by water and did not favor oxygen consumption. Therefore, the oxygen permeation flux has a maximum (8.8 mL cm^{-2} min^{-1}) at the W/C ratio of 0.4. Because of the water shift reaction, more CO reacted with H_2O with the increase of W/C, and accordingly, the selectivity of CO_2 increased with the fall of CO selectivity. Over the whole range of W/C, H_2 selectivity increased continuously.

Helium was used as a diluent to adjust the partial pressure of the reactants. Fig. 5 shows the results of He/C (defined as the molecular ratio of Helium/carbon) on the membrane reaction. During the above investigation of W/C on the membrane reaction, the oxygen permeation flux dropped with the increase of W/C, for the water dilutes the reactants. However, the oxygen permeation flux went up with the increase of He/C, helium also being a diluent. The reason is that, though helium dilutes the

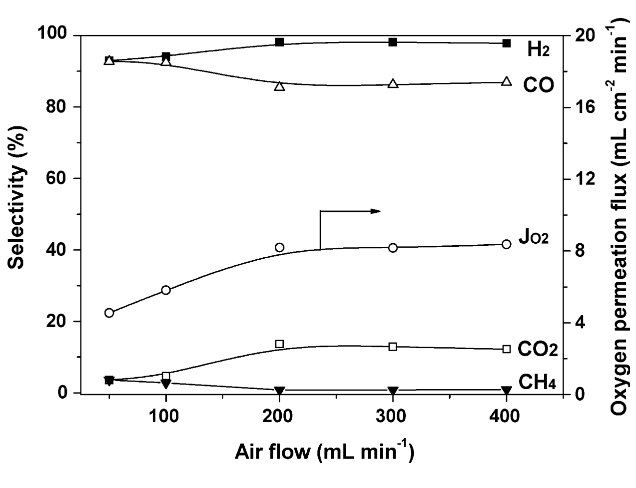

Fig. 3. The effect of airflow rate on the selectivity of products and the oxygen permeation flux of the membrane. Reaction conditions: $T = 850$ °C; $V_{He} = 35$ mL min^{-1}; W/C = 0.40.

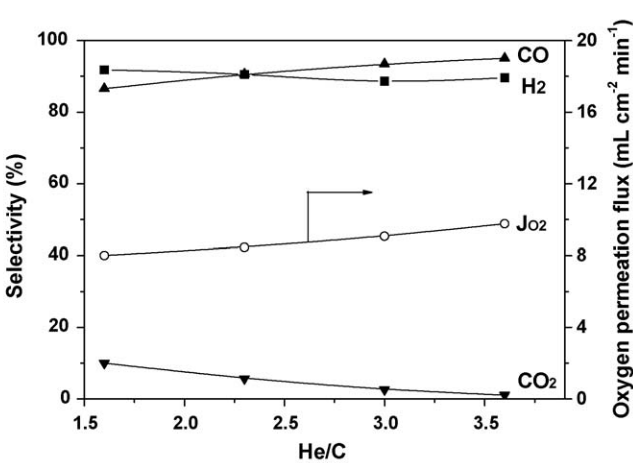

Fig. 5. The effect of He/C on the selectivity of products and the oxygen permeation flux of the membrane. Reaction conditions: $T = 850$ °C; $V_{air} = 200$ mL min^{-1}; W/C = 0.4.

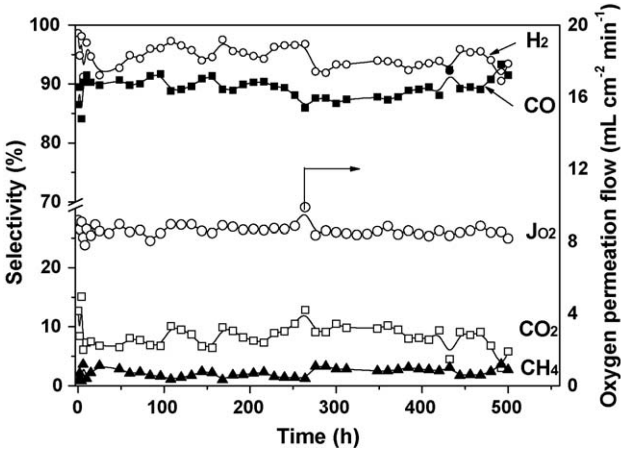

Fig. 6. Five hundred-hour long-term test of the mixed reforming of the simulated gasoline in the BSCFO oxygen permeable membrane reactor. Reaction conditions: $T = 850\ ^{\circ}\mathrm{C}$; $V_{\mathrm{He}} = 35\ \mathrm{mL\ min^{-1}}$; $V_{\mathrm{air}} = 200\ \mathrm{mL\ min^{-1}}$; W/C = 0.40.

reactants, overfull helium blown across the membrane surface intensively decreased the oxygen partial pressure on the reaction side of the membrane. Therefore, the oxygen permeation flux was augmented with He/C. Furthermore, as will be seen in the other parts of this paper, the increase of oxygen permeation flux means the rise of CO_2 selectivity and the fall of the CO selectivity. However, with the increase of He/C from 1.6 to 3.6, the selectivity of CO also went up with the rise of the oxygen permeation flux; on the contrary, CO_2 selectivity decreased. This phenomenon is due to CO_2 being the product of the CO with O_2 in the membrane reaction. At a high He/C, CO did not have enough opportunity to be absorbed on the catalyst and to react with oxygen to product CO_2, so as the oxygen permeation flux increased, CO selectivity went up gradually.

Fig. 6 shows the stability of the mixed reforming reaction of the simulated gasoline in the BSCFO membrane reactor. During 500 h of running, the performance of the reaction was stable. At the optimized reaction condition, all components in the simulated gasoline converted completely at 850 °C, W/C ratio of 0.40, and airflow rate of 200 mL min^{-1}. The selectivity of CO and H_2 was around 90% and 95% respectively during 500-h test. The oxygen permeation flux kept constant around 8.0 mL $\mathrm{cm}^{-2}\ \mathrm{min}^{-1}$.

Fig. 7 is the SEM micrographs of the used membrane. From Fig. 7(a), it can be seen that the cubic perovskite structure on the reaction side of membrane was destroyed. Compared with the fresh membrane, XRD patterns (Fig. 8(b)) of the destroyed surface show the loss of perovskite structure and the presence of $SrCO_3$ and $BaCO_3$. But if the destroyed top layer was cleared, the XRD patterns of membrane below it (shown in Fig. 8(c)) still kept a perovskite structure. SEM micrographs of the cross-section view (Fig. 7(b)) also displayed the unchanged membrane below the destructed layer. Since the air side of the membrane was in the oxidative atmosphere of oxygen, the membrane did not get any destruction and still kept a perovskite structure after 500 h, as is shown by the XRD pattern in

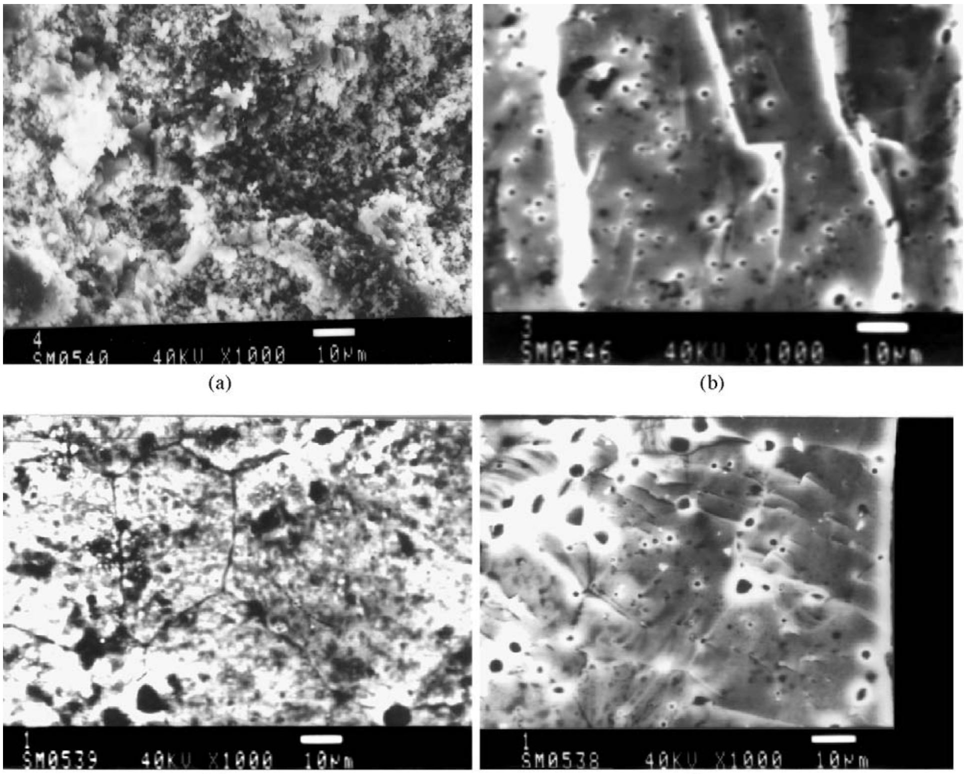

Fig. 7. The SEM micrographs of top view and cross-section of the used membrane after 500 h: (a) top view of used membrane after 500 h (reaction side); (b) cross-section view of used membrane; (c) top view of used membrane (air side); (d) cross-section view of used membrane (air side).

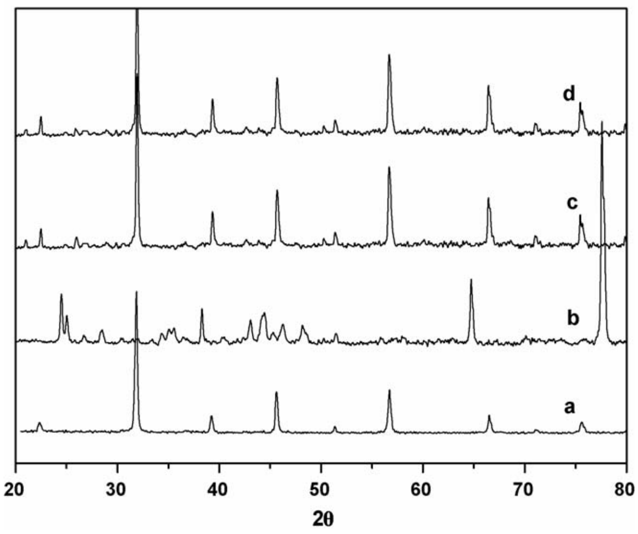

Fig. 8. XRD patterns of the used membrane after 500-h test: (a) fresh membrane; (b) reaction side of the used membrane; (c) the bulk of the used membrane; (d) air side of the used membrane.

Fig. 8(d). From the SEM micrographs of the air side (Fig. 7(c, d)), the boundary of the grains in the membrane was still clear.

As is known, stability is a key for a successful membrane, but membrane reactions (POM, OCM, MRL) always occur on the permeation/reaction side of the membrane in a reducing atmosphere, and, partial reduction is almost unavoidable. So far, in the reaction condition the redox reversibility of the membrane material is critically important. In our previous work [19], we found BSCFO material possessed a good reversibility performance. Namely the reduced oxides can be re-oxidized by the continuously transported oxygen from the air side in time and stabilize the phase structure of the BSCFO near the surface layer of the membrane. Therefore, even after 500-h running, only the top layer of the membrane was destroyed and the main body still kept a perovskite structure, which ensured the membrane reactions proceeded stably with a high oxygen permeation flux.

4. Conclusion

At the optimized reaction conditions with the presence of the mixed reforming catalyst LiLaNiO/γ-Al_2O_3, all the components in the simulated gasoline converted completely during a 500-h long-term test at a temperature of 850 °C, W/C ratio of 0.40, and airflow rate of 200 mL min^{-1}. The selectivity of CO and H_2 was around 90% and 95%, respectively. The oxygen permeation flux kept constant around 8.0 mL cm^{-2} min^{-1}. From the XRD patterns and SEM micrographs of the used membrane after 500-h running, it can be seen that, only the top layer of the membrane was destroyed, the main body of the BSCFO membrane still kept a perovskite structure. The phase stability of the BSCFO membrane is good.

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