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Partial oxidation of methane to syngas in $BaCe_{0.15}Fe_{0.85}O_{3-\delta}$ membrane reactors

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Dense planar $Ba_{0.15}Ce_{0.85}FeO_{3-\delta}$ (BCF1585) membrane reactors were investigated to produce syngas from methane. Firstly, the membrane itself catalytic activity to methane was investigated using a blank BCF1585 without any catalysts. Then a LiLaNi/γ-Al_2O_3 catalyst was packed on the BCF1585 membrane surface to test the synergetic effects of the membrane and catalyst. It was found that the membrane itself has a poor catalytic activity to methane. The main products are CO_2 and C_2, and methane conversion is low due to the low oxygen permeation flux. However, after the catalyst was packed on the membrane surface, both methane conversion and oxygen permeation flux were greatly improved by the synergetic effect between the membrane and catalyst. Carbon monoxide selectivity reached at 96% with methane conversion of up to 96%. The oxygen permeation flux reached at 3.0 mL/cm^2 min at 850 °C for a 1.5 mm disk membrane and can effectively be increased by reducing the thickness of the membranes. After operation for 140 h at 850 °C, the used membrane was examined with SEM and EDXS. The results revealed that the decomposition of the membrane materials could not be avoided under such conditions. Oxygen partial pressure gradient across the membranes is suggested as a critical factor to accelerate the kinetic decomposition of the materials.

KEY WORDS: oxygen permeation; membrane reactor, syngas; stability; perovskite oxides.

1. Introduction

Perovskite and perovskite-related oxides membranes have been extensively investigated [1], because they have high oxygen ionic and electronic conductivities at elevated temperatures resulting in high oxygen permeability. During the past decade, the partial oxidation of methane to syngas based on oxygen permeable membrane reactors was regarded as a potential approach to produce syngas from natural gas [1–3]. In recent years, many perovskite oxide membrane materials were employed to produce syngas from methane [4–9]. Pei *et al.* found that tubular membrane reactors made of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ broken into several pieces shortly after methane was introduced to the reactor. The authors concluded that the fracture of the membrane reactor was due to the phase transformation induced by the oxygen chemical potential gradient across the membranes [4]. While Balachandran *et al.* [5] reported a membrane reactor made of a kind of perovskite-related membrane materials $SrCo_{0.5}FeO_x$ can be steadily operated for syngas generation over 1000 h with an oxygen permeation flux of 2–4 mL/min cm^2. Tsai *et al.* [6] reported a disk perovskite $La_{0.2}Ba_{0.8}Fe_{0.8}Co_{0.2}O_{3-\delta}$ membrane reactor for partial oxidation methane to syngas. The reactor was successfully operated for 850 h, and with a destruction of the membrane surface. In our group, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ was used to constructed membrane reactor for partial oxidation of methane to syngas and the mixed reforming of gasoline to syngas [7–9]. The two reactions were also successfully operated for 500 h with oxygen permeation fluxes of 8–11 mL/cm^2 min. Unfortunately, the decomposition of the perovskite oxide was also found on the surface exposed to the syngas environment. To improve the stability of the membrane materials, ions with constant valence (Zr^{4+}, Ga^{3+}, Al^{3+}) [10–13] were used to partially substitute the reducible B-site ions (Co^{3+}, Fe^{3+}). Based on this idea, we developed Zr-doped perovskite, $BaZr_{0.2}Co_{0.4}Fe_{0.4}O_{3-\delta}$ (BZCF), which possesses a good operation stability for syngas generation [10]. The membrane reactor made of BZCF was successfully operated for 2200 h at 850 °C, and the oxygen permeation flux reached at 5.6 mL/cm^2 min. EDXS results revealed that the decomposition of the membrane surface is up to several microns in depth. To obtain oxygen permeable membrane materials with high operation stability, cobalt should be excluded from perovskite B-site and less reducible ions should be included the perovskite B-site. $La_{1-x}Sr_xGa_{1-y}Fe_yO_{3-\delta}$ is such a kind of high structural stability membrane materials. It was reported that the membrane still kept intact and no impurity was found due to the decomposition of the membrane after

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more than 1000 h of syngas generation operation [12]. However, the high cost due to the expensive gallium and low oxygen permeation flux hurdles for large scale application.

We have reported that a cobalt free material named $BaCe_{0.15}Fe_{0.85}O_{3-\delta}$ (BCF1585) possesses considerable oxygen permeability and structural stability under reducing environment [14]. In this paper, we will investigate the performance of BCF1585 membrane reactor under syngas production conditions.

2. Experimental

BCF1585 powder was prepared by an EDTA-citric acid process. The required amounts of the cation nitrates solutions were introduced into a beaker, and then EDTA and citric acid (EDTA: citric acid: total metal ions = 1:1:1) were added into the mixed solution. Ammonia was used to adjust the pH value around 6. After water was evaporated on a hot plate with stirring, a gel was formed. Then the gel was combusted to remove organic compounds to produce primary powder, which was calcined at 950 °C for 5 h to yield a homogenous composite oxide. Green membrane disks were pressed under 200–400 MPa for several minutes using a stainless steel mold, and sintered at 1300–1350 °C for 3 h in stagnant air with both a heating and a cooling rate of 1–2 °C/min. Only the membrane with relative density higher than 93% was used for oxygen permeation test and constructed membrane reactors. The catalyst $LiLaNiO/\gamma\text{-}Al_2O_3$ was prepared via the impregnation method according to the reference [15], and its performance is also shown in the reference [16].

Gold rings were used as sealant and sealed at 1040 °C. The membranes used for the partial oxidation of CH_4 were polished with 1000 mesh polishing paper to make a glabrous surface, which is favorable to the sealing of the reactor. Figure 1 shows a vertical high-temperature quartz reactor for the oxygen permeation and partial oxidation of methane to syngas. Areas of the membrane discs were controlled around 0.9–1.0 cm^2. The operation temperature was controlled by a microprocessor temperature controller (Model Al-708, Xiamen Yuguang Electronics Technology Research Institute, China) and measured through a K-type thermocouple. Dried synthesized air was controlled at a constant flow rate of 150 mL/min. High purity CH_4 diluted with He flowed on the reaction side of the membrane. The flow rates of the feed gases were controlled by mass flow controllers (Models D07-7A/ZM, Beijing Jianzhong Machine Factory, China). The effluents were analyzed by a gas chromatograph (GC, Agilent 6890) equipped with 13 X and Porapak Q columns. The GC was operated at 80 °C with He as the carried gas. The CH_4, CO_2, CO, O_2 and N_2 concentration were calculated by the external standard method. The oxygen permeation flux through the membrane was calculated based on the effluents flow rate and the oxygen-containing compounds in the effluents. CH_4 conversion (X_{CH_4}) and product selectivities (S_i) were defined as follows:

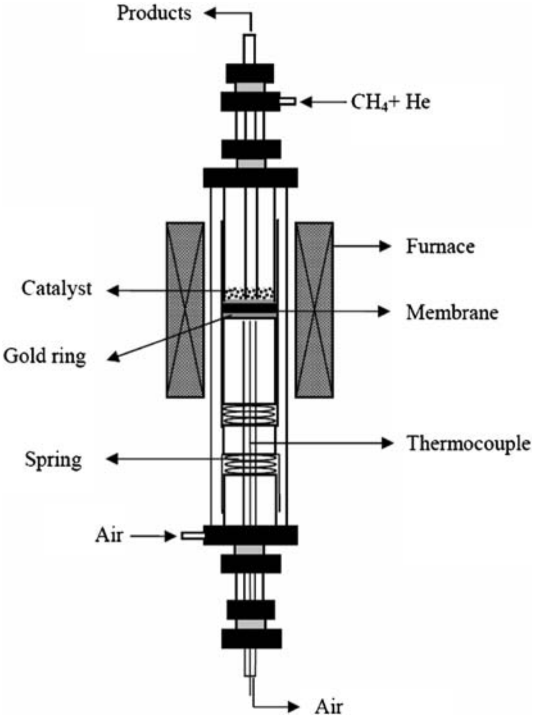

Figure 1. Membrane reactor for the partial oxidation of methane to syngas.

$$X_{CH_4} = 100 - \frac{F_{CH_4}^{out}}{F_{CH_4}^{in}} \times 100\% \tag{1}$$

$$S_i = \frac{n_i F_i}{F_{CH_4}^{in} - F_{CH_4}^{out}} \times 100\% \tag{2}$$

where n_i is the number of carbon atoms in the molecules of carbon-containing products i, F_i is the flow rate of species i.

The phase structure of the membrane materials was determined by X-ray diffraction (XRD, Rigaku D/Max-RB, Cu Kα radiation) in the 2θ range of 20–80° with a step width of 0.02°. The membrane surface morphologies before and after reaction were observed with a scanning electron microscopy (SEM, Philips XL-30). The approximate atomic composition of the membranes obtained from local areas Energy-dispersive X-ray spectra (EDXS) analysis.

3. Results and discussion

3.1. Blank membrane reactor experiment

Perovskite oxides possess high catalytic activity to many reactions, such as partial oxidation of methane, oxidation coupling of methane and oxidation dehydrogenation of ethane and so on [1]. Furthermore, oxygen permeable membrane reactors were reported for oxidations coupling of methane with high selectivity to C_2 [17–19]. So it is necessary to investigate the catalytic performance of the BCF1585 to methane.

Figure 2 shows the temperature effects on the catalytic performance to methane in the blank BCF1858 membrane reactor. The conversions of CH_4 and O_2 as well as selectivity of CO_2 and CO gradually increase with temperature. However, the selectivity of C_2 decreases with the temperature. Both CH_4 and O_2 conversions are low. These results indicate that BCF1585 itself possesses a poor catalytic activity to methane, which 1s possibly due to a lower surface area of the dense. Therefore, a suitable catalyst is needed to accelerate methane activation.

3.2. *Membrane reactor with methane partial oxidation catalyst*

The partial oxidation reaction of methane to syngas was studied in a planar membrane reactor packed with unreduced LiLaNiO/γ-Al_2O_3 catalysts. After only 20 min for activation, the CH_4 conversion reached 80% with CO selectivity of 97%. Then the CH_4 conversion increase gradually while the CO selectivity levels off. It took about 30 h to reach the steady state. Finally, the CH_4 conversion reached above 96% with CO selectivity of above 98% and oxygen permeation flux around 3.0 mL/cm^2 min for a 1.5 mm membrane. It is about 8 times higher than that of He as the sweeping gas. After the reaction reached at a steady state, the effects of temperature, CH_4 flow rate and He flow rate were deeply investigated.

Temperature has a significant effect on the membrane reaction because the oxygen permeation flux of the membrane is strongly dependent on temperatures. At a constant CH_4 flow rate, the ratio of CH_4 to O_2 can be changed by the variation of temperature, and will affect on the methane conversion and products selectivity. Furthermore, the variation of products composition will influence the oxygen partial pressure at the reaction side, which will alter the oxygen permeation flux in turn. This is a self-consistent process between oxygen permeation and catalytic partial oxidation reaction. Figure 3 shows the effects of temperature on POM performance in the BCF1585 membrane reactors. All data were collected after steady states had reached. It took about 30 min at the indicated temperatures. As shown in figure 3, the conversion of CH_4 increases rapidly with increasing temperature and reaches near 100% at 850 °C, while the selectivity of CO decreases gradually with the increase of temperature. It is because that the oxygen fluxes increased from 1.4 to 4.0 mL/cm^2 min when the temperature changed from 750 to 950 °C, at the same time, the CH_4/O_2 ratio gradually decreased.

Figure 4 shows an effect of CH_4 flow rate on the POM performance in the BCF1585 membrane reactor

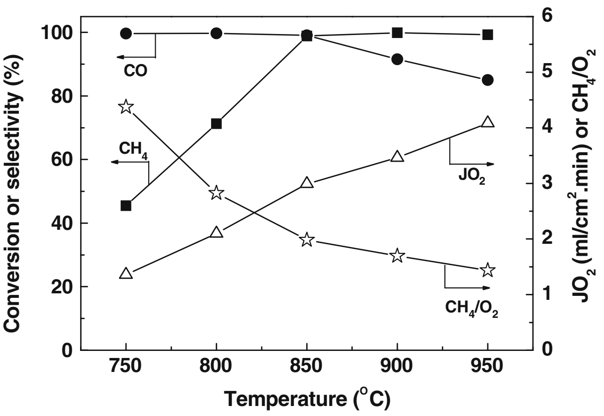

Figure 3. Effects of temperature on the catalytic reaction in the membrane reactor. Air flow rate, 150 mL/min; He flow rate, 20 mL/min; CH_4 flow rate, 6 mL/min; thickness of the membrane, 1.5 mm.

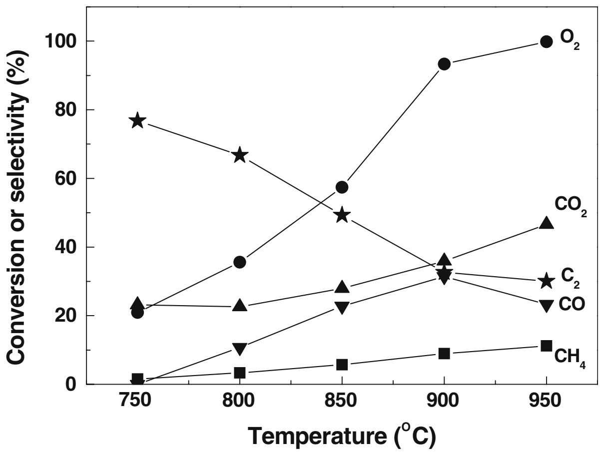

Figure 2. Effects of temperature on the blank membrane reaction. Air flow rate, 150 mL/min; He flow rate, 20 mL/min; CH_4 flow rate, 6 mL/min; thickness of the membrane, 1.5 mm.

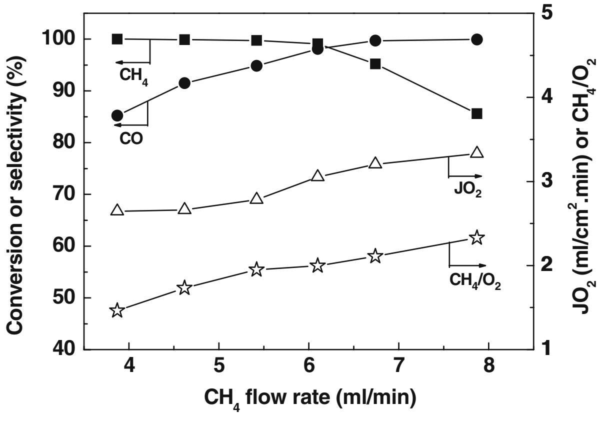

Figure 4. Effects of CH_4 flow rate on the catalytic reaction in the membrane reactor. Air flow rate, 150 mL/min; He flow rate, 20 mL/min; thickness of the membrane, 1.5 mm; temperature, 850 °C.

at 850 °C. With the increase of methane flow rate, the conversion of CH_4 decreased gradually, while the selectivity of CO increased and reached at nearly 100% when the CH_4 flow rate was 7.9 mL/min. It was also found that the oxygen permeation flux through the membrane increased from 2.6 mL/cm^2 min to 3.3 mL/cm^2 min in the range of CH_4 flow rates studied. According to the Wagner's theory, the oxygen permeation flux through a membrane is affected by the thickness of the membrane, operation temperature and oxygen partial gradient across the membrane. Figure 5 shows the relationship of oxygen permeation fluxes with oxygen partial pressure gradients under the partial oxidation of methane to syngas. The oxygen partial pressure at the reaction side was adjusted by changing the flow rate of CH_4, and can be calculated by a thermodynamic soft assuming the reaction reaches an equilibrium state under the conditions. As shown in figure 5, the oxygen permeation fluxes increase gradually with oxygen partial pressure gradient. According to the Wagner's equation, the oxygen permeation flux should increase with the oxygen partial gradient lineally at both constant operation temperature and membrane thickness when the oxygen transport through the membrane is only limited by bulk diffusion. However, we found that the oxygen permeation flux does not accord with the linear relationship under the POM conditions, because the oxygen surface exchange reaction rate and the CO_2 partial pressure in the products can also play a significant role on the oxygen permeation flux in our case [20].

For syngas generation, oxygen permeable membranes are operated under severely reducing environment. Few membranes can keep their structure in such a reducing environment. The main problem is a partial decomposition of the surface exposed to reducing atmosphere. Consequently, a fracture induced by such a decomposition of materials will happen during a long-term operation. Therefore, it is necessary to test the perovskite structural stability under POM reaction conditions. Before carrying out the membrane reaction, the stability

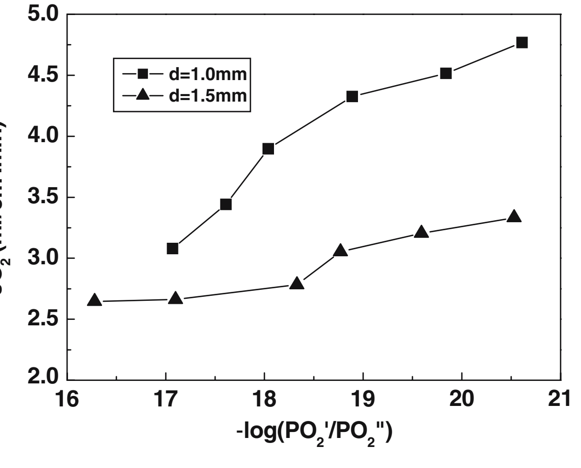

Figure 5. Relationship between oxygen permeation flux and oxygen partial pressure gradient under the partial oxidation reaction conditions. PO_2' and PO_2'' are oxygen partial pressure of air side and reaction side, respectively. The oxygen partial pressure was adjusted by changing the flow rate of CH_4 from 3.9 to 10.6 mL/min. Temperature, 850 °C; air flow rate, 150 mL/min; He flow rate, 20 mL/min.

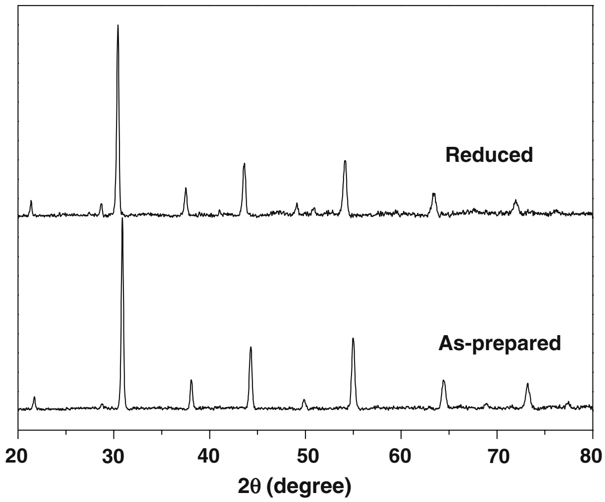

Figure 6. XRD patterns of BCF1585 membrane materials reduced under 10% H_2–Ar mixed gas at 900 °C for 1 h.

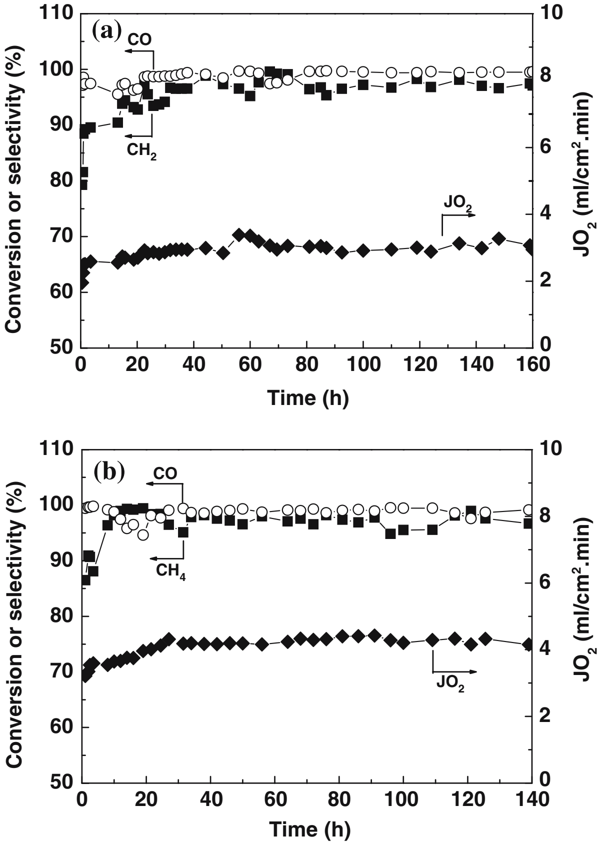

Figure 7. Stability operation of the partial oxidation methane in the membrane reactor. (a) and (b) for 1.5 mm and 1.0 mm membranes, respectively. Air flow rate, 150 mL/min; He flow rate, 20 mL/min; CH_4 flow rate, 6 mL/min for (a) and 8 mL/min for (b); temperature, 850 °C.

of the membrane materials under reducing environment was investigated. As shown in figure 6, the materials can still keep its perovskite structure although they were reduced under 10% H_2–Ar mixed gas at 900 °C for 1 h. However, the solid solution amount of cerium in the B-site reduces a little and this can be found as the increase of the intensity of the peak around 28°.

Considering the good stability of the membrane materials, we intentionally stopped the membrane reaction only after 160 and 140 h operations for 1.5 and 1.0 mm disk membrane respectively. As shown in figure 7, it took about 30 h to reach the steady state with the CH_4 conversion of $>96\%$, and CO selectivity of $>98\%$. The oxygen permeation flux through the membrane with a thickness of 1.5 mm is $\sim$3.0 mL/cm^2 min. However, the oxygen permeation flux increases to $\sim$4.2 mL/cm^2 min if the membrane thickness is reduced to 1.0 mm.

After 140 h operation for POM reaction, the used membrane was characterized with SEM and EDXS. Figure 8 shows the SEM pictures of the as-prepared and used membranes. For the as-prepared membrane, ceramic grains with clear boundaries are visible as shown in figure 8a. Although the morphologies of the used membrane surfaces exposed to syngas and air are different, they are all compact, as shown in figure 8c and e. Membranes surfaces exposed to the reaction side were often found to become porous and loose in literatures [3, 11, 21–23]. For examples, the thickness of porous layer about 60 μm was found after $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ [23] membrane reactors were operated for 100 h under syngas production; and the structural changes were found up to about 150 μm for $SrFe_{0.7}Al_{0.3}O_{3-\delta}$ after 215 h operation under CH_4 environment [13]. Although the structural changes were also found on the both surfaces of the BCF1585 membrane, as shown in figure 8d and f, they are only up to several microns in depth and not loose like other materials, such as $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$, $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, $La_{0.6}Ca_{0.4}Fe_{0.75}Co_{0.25}O_{3-\delta}$,etc., reported in literatures [3, 11, 21–23]. Table 1 shows the EDXS results of the used membrane. As shown in table 1, the composition of the membrane surfaces have changed. An enrichment of barium was found and $BaCO_3$ was the main phase detected by XRD on the membrane surface exposed to the reaction side. The elements composition of D and F are similar to that in the middle section of the

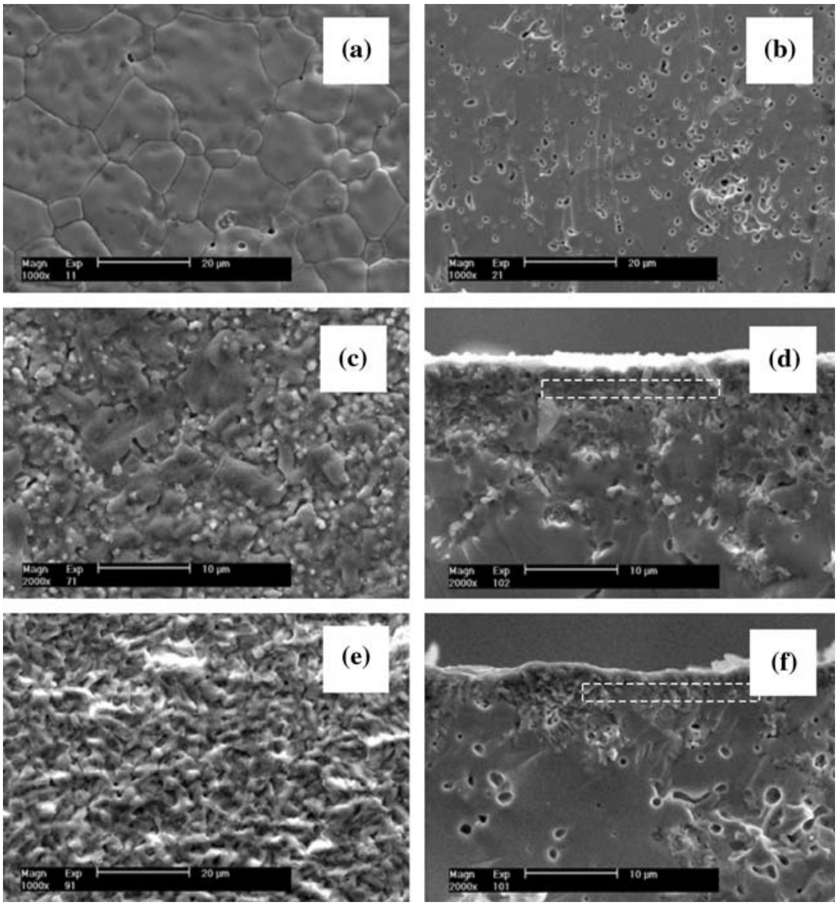

Figure 8. SEM pictures of the as-prepared and used membrane. (a) and (b) are surface and cross section of as-prepared membrane, respectively; (c) and (e) are reaction side and air side of the used membrane, respectively; (d) and (f) are cross sections of near the reaction side and near the air side of the used membrane, respectively. The white broken line frames in (d) and (f) show the areas of the EDXS analysis.

Table 1
Approximate atomic composition of the different areas obtained from local EDXS analysis of the used membrane

Zone	Depth from reaction side (μm)	Composition (Atom %)			
		Ba	Ce	Fe	O
C	0	27.61	0.40	9.21	62.78
D	2–5	25.85	3.65	18.19	52.31
Middle	~500	24.76	1.48	16.93	56.83
F	998–995	19.97	1.68	13.75	64.60
E	1000	32.02	~0	1.22	66.76

membrane. This revealed that the decomposition of this material occurs on the surface of the membrane only several microns in depth.

Although both BCF1585 and $SrFe_{0.7}Al_{0.3}O_{3-\delta}$ [13] can sustain their perovskite structure under reducing environments at elevated temperatures, the destruction of the structure cannot be avoided under long-term syngas generation operation. It seems that the different operation models have remarkable effects on the structural stability of the perovskite oxides. Materials are under an uniform atmosphere if the powders of membrane materials are exposed to reducing atmosphere. However, materials are under a high oxygen chemical potential gradient if the membrane materials are operated as membrane reactor for syngas generation. It is the gradient that accelerates the kinetic decomposition of the materials. van Doorn *et al.* [24] reported a kinetic decomposition of $La_{0.3}Sr_{0.7}CoO_{3-\delta}$ perovskite membrane if the membrane was operated under an oxygen partial pressure gradient of air/He for oxygen permeation, but no decomposition if the homogenous oxide powder was annealed in either flowing air or nitrogen for several days. In our case, the situation of BCF1585 membrane is similar to $La_{0.3}Sr_{0.7}CoO_{3-\delta}$ membrane only with a difference in the oxygen chemical potential gradient. Although CO_2 as one of by-products possibly has a remarkable effect on the decomposition of the material, the air side and reaction side are both found the decomposition of the material. Therefore, the oxygen chemical potential gradient is the main reason for the degradation. Consequently, it is important not only to improve materials' stability under reducing environments at high temperatures, but also to restrain the kinetic decomposition of materials under such asymmetric oxygen partial pressure environments.

4. Conclusions

POM was investigated in BCF1585 membrane reactors. The blank experiment reveals that the membrane itself has a poor catalytic activity to CH_4. When Ni-based catalysts were packed on the membrane surface, high CH_4 conversion and CO selectivity were achieved after the membrane catalytic reaction reached a steady state. It was found that the oxygen permeation flux of the membrane and the catalytic reaction influence each other, and it is a synergetic process. After 140 h operation under the POM condition, the SEM and EDXS analysis showed that both surfaces of the membrane were still keep compact, but the decomposition of the materials up to several microns in depth could not be avoided. This is due to the asymmetric oxygen partial pressure cross the membranes accelerates the kinetic decomposition of the materials.

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