Hydrogen Production by Catalytic Partial Oxidation of Coke Oven Gas in BaCo$_{0.7}$Fe$_{0.3-x}$Zr$_x$O$_{3-\delta}$ Ceramic Membrane Reactors

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Abstract. The BaCo$_{0.7}$Fe$_{0.3-x}$Zr$_x$O$_{3-\delta}$ (BCFZ, x = 0.04–0.12) mixed ionic–electronic conducting (MIEC) membranes were synthesized with a sol–gel method and evaluated as potential membrane reactor materials for the partial oxidation of coke oven gas (COG). The effect of zirconium content on the phase structure, microstructure and performance of the BCFZ membrane under He or COG atmosphere were systemically investigated. The BaCo$_{0.7}$Fe$_{0.24}$Zr$_{0.06}$O$_{3-\delta}$ membrane exhibited the best oxygen permeability and good operation stability, which could be a potential candidate of the membrane materials for hydrogen production through the partial oxidation of COG.

1 Introduction

Hydrogen is regarded as the most effective solution to the increasingly serious problems of environmental pollution and depleting energy sources in the 21st century. Currently, hydrogen is mainly produced from fossil fuels and chemical by–products [1, 2]. Of these methods, coke oven gas (COG), a by–product generated during the production of coke from coal, has attracted much interest as one of the most promising high quality sources of hydrogen [3, 4]. The separation of oxygen from air and catalytic partial oxidation of methane (POM) in COG has been achieved in a mixed ionic–electronic conducting (MIEC) membrane reactor, which significantly reduces the energy consumption and cost of hydrogen production compared to the conventional processes [5].The COG exhibits strong reducibility because its main components are 54–59% H$_2$, 24–31% CH$_4$, and 5.5–7% CO [6]. Therefore, structural stability under a reductive atmosphere and high oxygen permeability are expected for a MIEC membrane to meet the requirements of practical applications. The

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perovskite–type materials of ABO3 composition have attracted much interest due to their excellent oxygen permeability.

In this work, a series of $BaCo_{0.7}Fe_{0.3-x}Zr_xO_{3-\delta}$(BCFZ, x = 0.04–0.12) MIEC membranes were synthesized with a sol–gel method. Their phase structure, microstructure and performance under He or COG atmosphere were systematically investigated.

2 Materials and Methods

The $BaCo_{0.7}Fe_{0.3-x}Zr_xO_{3-\delta}$ (x = 0.04–0.12) powders were synthesized with a sol–gel method as described in our previous work [7]. The primary powders were calcined at 900 °C for 5 h to obtain the powder with the aforementioned final composition. The green disks were prepared under a hydraulic pressure of 150–200 MPa and then sintered at 1110 °C for 8 h in ambient air.

The $Ni/MgAl_2O_4$ catalyst was prepared with urea-template and impregnation method. Stoichiometric amounts of $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ were dissolved in deionized water, followed by the introduction of a defined amount of urea. The mole ratio of urea:total nitrate was 3:1. A certain amount of the triblock copolymer P123, which was to act as a template, was dissolved in deionized water in another vessel with vigorous stirring. The $P123:MgAl_2O_4$ mass ratio was about 3:2. After the urea and P123 were completely dissolved, the solutions in the two vessels were mixed together. The obtained mixture was then stirred vigorously for 24 h, dried at 110 °C overnight, and then calcined at 850 °C for 5 h in air to form a white powder composed of $MgAl_2O_4$. The $MgAl_2O_4$ support was impregnated into a nickel nitrate solution made from $Ni (NO_3)_2 \cdot 6H_2O$ and left overnight at room temperature, followed by drying at 110 °C and calcination at 850 °C for 2 h in air. The Ni mass fraction in the $Ni/MgAl_2O_4$ catalyst was 10 wt%. The $Ni/MgAl_2O_4$ catalyst powder was pressed into a bulk material in a stainless steel mold under a hydraulic pressure of 40 MPa. The bulk catalyst was subsequently broken down into 20–40 mesh granules for later use.

The phase structure of the synthesized BCFZ membranes was examined in a Bruker-AXS D8 ADVANCE diffractometer, with Cu radiation (40 kV, 40 mA). The cross−section morphology of the fresh BCFZ membranes was studied with a field emission scanning electron microscope (JEOL JSM–6700F) at an excitation voltage of 15 kV. The performance of the disk–shaped membranes under He or COG atmosphere was measured using a home-made equipment as described in our previous work [8].

3 Results and Discussion

The XRD patterns of the as–synthesized $BaCo_{0.7}Fe_{0.3-x}Zr_xO_{3-\delta}$ (x = 0.04–0.12) membranes are shown in Fig. 1(a). All of the BCFZ membranes exhibit a pure cubic perovskite structure, except for x = 0.12 with traces of a $BaZrO_3$ phase. Fig. 1(e)-(f) present the microstructure of the fresh BCFZ membranes. All the sintered membranes show a dense ceramic structure with a small amount of enclosed pores. Therefore, these synthesized BCFZ membrane can be used for the oxygen separation.
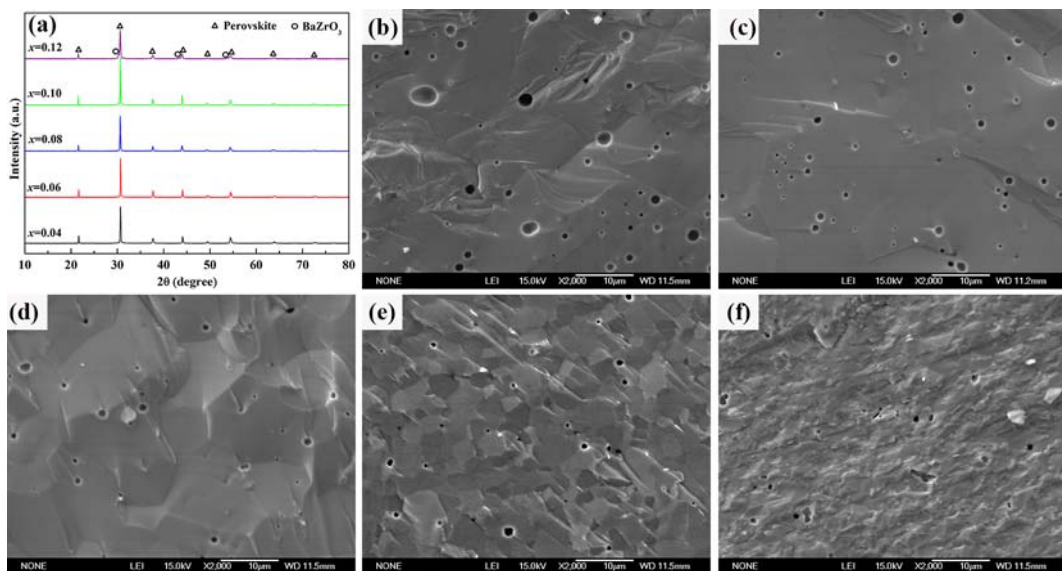
Fig. 1 – (a) The XRD patterns of the fresh BCFZ membranes; the cross section SEM images of the fresh BaCo0.7Fe0.3-xZrxO3-δ membranes: (b) x = 0.04, (c) x = 0.06, (d) x = 0.08, (e)x = 0.10, (f) *x* = 0.12.

The time dependence of oxygen permeation flux through the BCFZ membranes under pure He atmosphere at different temperature is shown in Fig. 2(a). The oxygen permeation fluxes of all the samples increase with temperatures because of the increased diffusion, surface exchange reaction rate [9]. At the low temperature (<800 °C), the oxygen permeation fluxes of all the membranes drops gradually with the prolongation of time, which may be caused by the phase transformation [10]. Of all the samples, the highest average oxygen permeation flux of 2.72 ml·min^{-1}·cm^{-2} at 925 °C under pure He atmosphere was achieved by the *x* = 0.06 BCFZ membrane.

In order to study the potential application of BCFZ membranes in the production of hydrogen from COG, the performance of the membranes under a COG atmosphere was investigated. The catalytic partial oxidation of methane in COG was conducted in the BCFZ membrane reactor packed with a Ni/MgAl$_2$O$_4$ catalyst on the permeation side.
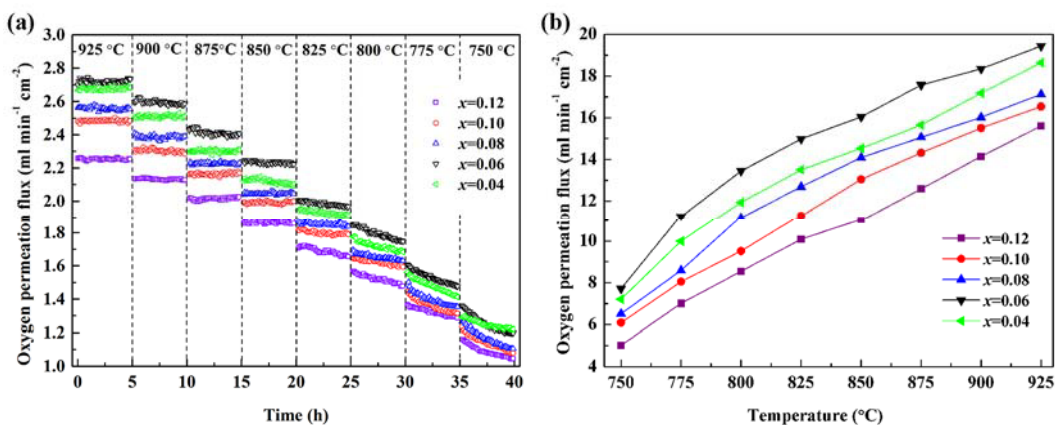

Fig.2 – (a) The time dependence of the oxygen permeation flux through BCFZ membranes under an air/pure He gradient and (b) The temperature dependence of the oxygen permeation flux through BCFZ membranes an air/COG gradient: membrane thickness = 1.0 mm; air = 300 ml min-1; pure He = 300 ml min-1; COG = 100 ml·min-1.
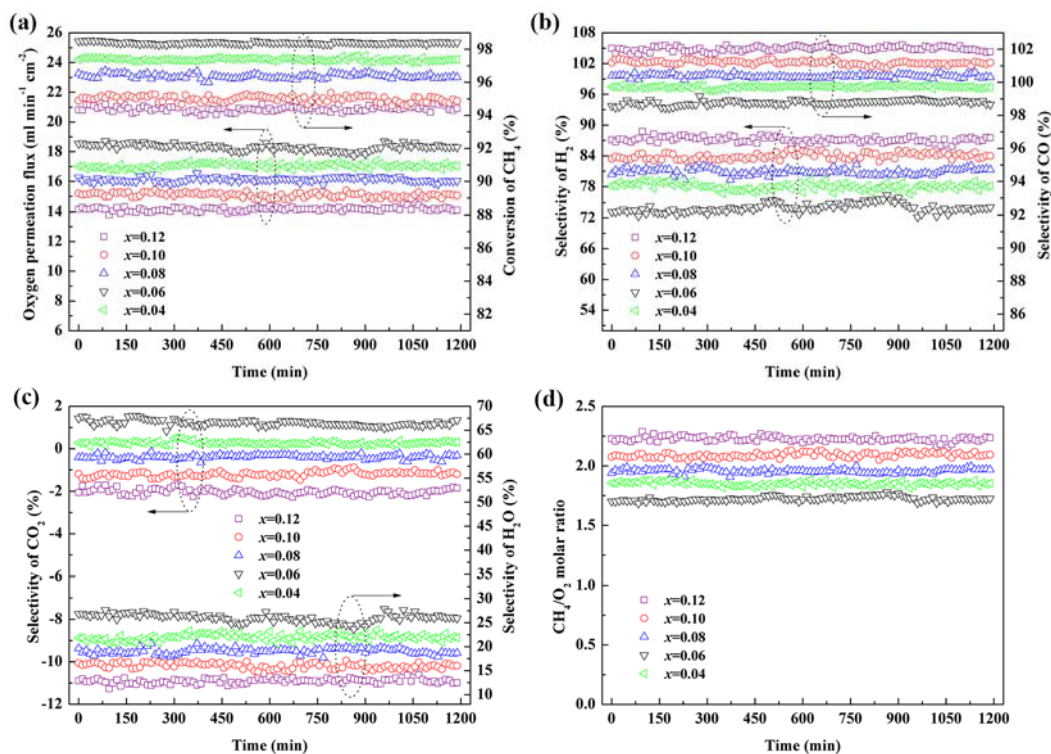
Fig. 3 – The performance of BCFZ membrane reactors for the catalytic partial oxidation of COG: (a) the oxygen permeation flux and CH4 conversion; (b) the selectivity of H2 and CO; (c) the selectivity of H2O and CO2; (d) the CH4/O2 molar ratio. Reaction conditions: COG = 100 ml min-1; air = 300 ml min-1; membrane thickness = 1.0 mm; temperature = 900 °C.

Fig. 2(b) shows the temperature dependence of the oxygen permeation flux through the 1-mm-thick BCFZ ($x = 0.04–0.12$) membranes under an air/COG gradient. The oxygen permeation fluxes of all the membranes were considerably high, i.e., several times or even one order of magnitude higher than that in the air/He gradient. This enhancement might be caused by the generation of more oxygen vacancies under the lower oxygen partial pressure on the permeation side because of the rapid reaction between the COG and penetrating oxygen. In addition, the oxygen permeation flux of the BCFZ membranes first increases, and then decreases with increasing Zr content, which is consistent with the oxygen flux behavior under an air/He gradient. Similar to the results under an air/He gradient, the highest oxygen permeation flux of 19.4 ml·min^{-1}·cm^{-2} at 925 °C was achieved by the $x = 0.06$ BCFZ membrane. Hence, it can be concluded that the oxygen permeability in the catalytic partial oxidation of COG in the BCFZ membrane reactor can be improved by the introduction of a certain amount of Zr to BCFZ membranes.
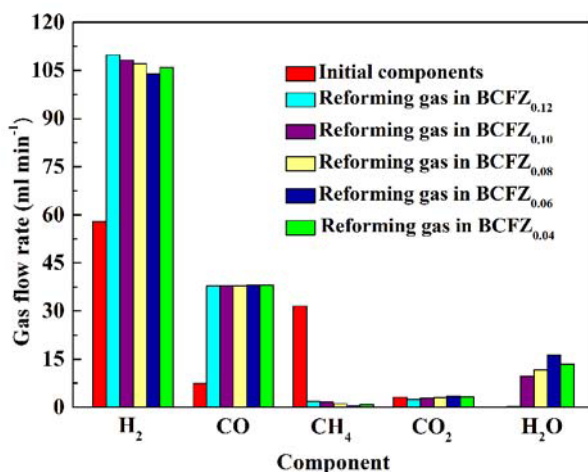
Fig. 4 Variation of components in the COG before and after undergoing catalytic reforming in BCFZ membrane reactors.

The effects of Zr content on the performance of the BCFZ membrane reactors at 900 °C are shown in Fig. 3. It can be seen that the oxygen permeation flux, CH_4 conversion, and the product yields remain constant during 20 h tests of the BCFZ membrane reactors. In Fig. 3(a), the average oxygen permeation flux and CH_4 conversion first increase and subsequently decrease with increasing Zr concentration. Of all the membranes, the $x = 0.06$ BCFZ membrane reactor shows the highest average oxygen permeation flux of 18.3 ml·min^{-1}·cm^{-2} and CH_4 conversion of 98.4%, while those of the $x = 0.12$ membrane are the lowest at 14.2 ml·min^{-1}·cm^{-2} and 94.4%, respectively. Furthermore, the product yields are affected by the different oxygen permeation fluxes and reactant conversions resulting from the different Zr contents of the BCFZ membranes. Fig. 3(b) shows the influence of Zr content on the selectivity of H_2 and CO. The average selectivity of H_2 and CO changed from 73.9% and 98.8% ($x = 0.06$) to 87.1% and 102.0% ($x = 0.12$), respectively, which is in contrast to the oxygen permeation flux results. The decreased selectivity of H_2 is attributed to the enhancement of reaction between H_2 and permeated oxygen, which improves the H_2O yields, as shown in Fig. 3(c) [11]. For the $x = 0.08$, 0.10, and 0.12 membranes, the CO selectivity exceeds 100% because of the partial conversion of CO_2 in the COG to CO through the dry reforming reaction, which corresponds with the negative values of CO_2 selectivity in Fig. 3(c) [12]. This phenomenon might be caused by the CH_4/O_2 molar ratio, as presented in Fig. 3(d). It can be seen that the average CH_4/O_2 molar ratio varies from 1.7 to 2.2, indicating that the oxygen permeation flux varies from an excess of oxygen to a shortage of oxygen for the partial oxidation reaction. Moreover, after the catalytic reforming in the BCFZ membrane reactor (Fig. 4), the flow rates of H_2 and CO were greatly improved, reaching 103.8–109.8 and 37.8–38.08 ml·min^{-1}, respectively. As shown in Fig. 4, the amount of hydrogen after reforming is 1.8–1.9 times the original hydrogen in the COG.

4 Conclusions

Mixed ionic–electronic conducting (MIEC) materials composed of $BaCo_{0.7}Fe_{0.3-x}Zr_xO_{3-\delta}$ (BCFZ, $x = 0.04$–0.12) were synthesized with a sol–gel method. After being sintered at 1110 °C for 8 h, a pure cubic perovskite structure was obtained for $x = 0.04$–0.10. While, traces of a $BaZrO_3$ phase were detected for $x = 0.12$. All the BCFZ membranes exhibit a dense ceramic structure. The oxygen permeability of the BCFZ membranes increased with

increasing operating temperature. The oxygen permeation flux first increased and then decreased with increasing Zr content under He and COG atmospheres. The $BaCo_{0.7}Fe_{0.24}Zr_{0.06}O_{3-\delta}$ membrane showed the highest oxygen permeation flux of 2.72 $ml \cdot min^{-1} \cdot cm^{-2}$ at 925 °C under an air/He gradient. The good long-term operation stability and highest permeation flux of 18.3 $ml \cdot min^{-1} \cdot cm^{-2}$ at 900 °C under an air/COG gradient were achieved in the $BaCo_{0.7}Fe_{0.24}Zr_{0.06}O_{3-\delta}$ membrane reactor, which is a promising membrane material for the catalytic partial oxidation of COG to produce hydrogen.

5 Acknowledgments

References

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