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Novel cobalt-free oxygen permeable membrane

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A series of cobalt-free and low cost perovskite oxygen permeable membranes based on $BaCe_xFe_{1-x}O_{3-\delta}$ (BCF) oxides was successfully synthesized and the membrane showed both high oxygen permeability and high stability under reductive atmosphere, which will be most suitable for constructing a membrane reactor for selective oxidation of light hydrocarbons to syngas or high value corresponding oxygenates.

Dense oxygen permeable membranes, made of oxygen ion and electron mixed conductors, have attracted increasing attention due to their potential and wide applications in the separation of oxygen from air,[1–4] conversion of natural gas to syngas,[5–8] high selective oxidization of light hydrocarbons,[9–10] *etc.* Among these applications, the conversion of natural gas to syngas in oxygen permeable membrane reactors has important commercial benefits, due to a 25% reduction in the current-technology-based cost of gas-to-liquids (GTL) product.[7] During the past decades, many oxygen permeable membrane materials were synthesized, based on cobalt doping in the B site of perovskite (ABO_3), to meet the above applications. Though high oxygen flux was obtained, few membrane materials were able to tolerate the reducing syngas environment.[11] So, the development of cobalt-free and high stability oxygen permeable membrane materials with considerable oxygen permeation flux was highly desired. $La_{1-x}Sr_xGa_yFe_{1-y}O_{3-\delta}$ is a stable membrane material that is not cobalt doped, which has been developed by the Eltron Research team and is reported to be stable in operation for over 1000 h under the syngas environment.[12] However, high cost (due to expensive gallium) and low oxygen permeation flux block its large scale application.

In this report, we develop a series of new cobalt-free perovskite oxygen permeable membrane materials $BaCe_xFe_{1-x}O_{3-\delta}$(BCF), based on the fact that perovskite $BaCeO_3$ is employed as a hydrogen permeable membrane with excellent resistance to a reducing atmosphere. And summarizing the previous work, we find that oxygen permeable membrane materials doped with iron instead of cobalt in the B site can improve the stability of these materials, so iron is preferred as the B site dopant. Barium is chosen as the A site ion to decrease the oxygen permeation activation energy and increase the oxygen permeation flux[13] because it can not only enlarge the lattice free volume, but also reduce the average metal–oxygen bond energy within the lattice. Additionally, we also discover that barium is more stable than strontium in the A site by comparing long-term stability data of corresponding membrane materials under syngas conditions.[5–6,8,14–17]

The BCF oxides were prepared by a combined citrate and EDTA complexing method.[13] Powders were pressed into disks under 8–12 MPa for several minutes, and sintered at 1413–1453 K for about 5–10 h in stagnant air with a heating and cooling rate of 2 K min^{-1}. All the membrane samples tested for oxygen permeation had relative densities no less than 93%.

The phase structure of BCF was determined by X-ray diffraction (XRD, Rigaku D/Max-RB, Cu α radiation) in the 2θ range 20–80° with a step width of 0.02°. The oxygen permeation experiments were performed in a vertical high-temperature gas permeation cell as described in the literature.[13] Dried air was used as the feed at a flow rate of 100 ml min^{-1}. High purity helium (O_2 < 4 ppm) flowed on the other side of the membrane at a flow rate of 30 ml min^{-1}. The effluents were analyzed by a gas chromatograph (GC, Agilent 6890) equipped with a 3m-13X column. The oxygen concentration was calculated by the external standard method. The oxygen permeation flux through the membrane was calculated based on the helium flow rate and the oxygen concentration in the effluents. Nitrogen, if possible, in the effluents was detected by gas chromatograph due to the slight imperfections of seal, and the leak amounts of oxygen were subtracted when calculated the oxygen permeation flux. The leakage percentages of all the samples are less than 5%.

Fig. 1 shows the XRD patterns of the BCF series of oxide powders. Based on the calculation on the tolerance factor for the perovskite structure, we know that it is difficult to prepare BCF materials with pure perovskite phase due to the big differences in radii of Ce^{3+}, Ce^{4+} (1.15 Å, 1.01 Å) and Fe^{2+}, Fe^{3+} or Fe^{4+}(0.92 Å, 0.785 Å, 0.725 Å). However, $BaCe_{0.15}Fe_{0.85}O_{3-\delta}$ (BCF1585) and $BaCe_{0.85}Fe_{0.15}O_{3-\delta}$ (BCF8515) with almost pure perovskite structure were successfully synthesized in our laboratory after a lot of trial work. As shown in Fig.1, BCF1585 has a cubic perovskite structure with a = 4.1095 Å, and BCF8515 belongs to the orthorhombic structure with a = 4.3955 Å and c = 4.3644 Å. As for $BaCe_{0.2}Fe_{0.8}O_{3-\delta}$ (BCF28) and $BaCe_{0.4}Fe_{0.6}O_{3-\delta}$ (BCF46), it is found that each of the two samples comprises two kinds of perovskite oxides mentioned above (BCF1585 and BCF8515). The fraction of BCF1585 in the series of oxides increases with the increase in amount of iron doped. To test the stability of BCF1585 under reducing environment, the powder is exposed to 5% H_2 + Ar for 1 hour at elevated temperatures. XRD patterns show the pervoskite structure is even maintained at 900 °C under such a reductive atmosphere. Based on the results, we can conclude that the materials ($BaCe_{0.15}Fe_{0.85}O_{3-\delta}$) we developed have good stability under a reductive environment.

The BCF series of oxygen permeable membrane disks, prepared without cracks and pinholes, were tested in oxygen permeation experiments. Fig. 2 shows the variation of oxygen flux as a function of the temperature at a constant air flow rate of the oxygen-rich side and helium flow rate of the oxygen-lean side. The oxygen fluxes of the series of membranes increase monotonously with the increase in temperature. It also shows that the oxygen fluxes increase remarkably with the increase in the amount of iron-doping, that is the increase of the fraction of BCF1585 in the relevant samples.

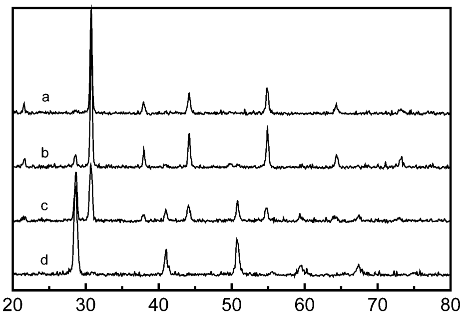

Fig. 1 XRD patterns of $BaCe_xFe_{1-x}O_{3-\delta}$ series of oxygen permeable membranes at room temperature. (a), x = 0.15; (b), x = 0.2; (c), x = 0.4; (d), x = 0.85.

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The oxygen permeability of BCF8515 is difficult to detect, so we can attribute the oxygen permeability of the series of membranes to BCF1585. The oxygen permeation fluxes of BCF1585, exhibit the highest value (0.52ml cm^{-2}·min^{-1}) among this series, which is several times higher than that of $La_{0.15}Sr_{0.85}Ga_{0.3}Fe_{0.7}O_{3-\delta}$ (0.09 ml cm^{-2}·min^{-1}) and higher than that of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (0.25ml cm^{-2}·min^{-1}) at the same temperature (1223 K) and measured on the same equipment.[18] It is well known that if the oxygen permeation is limited by oxygen ion diffusion in the bulk, oxygen flux varies with the thickness of the membrane in accordance with the Wagner equation [eqn. (1)]:

$$J_{O_2} = \frac{RT}{4^2 F^2 L}\int_{P_2}^{P_1}\frac{\sigma_e\sigma_i}{\sigma_e+\sigma_i}d\ln p_{O_2} \qquad (1)$$

where, each parameter has the usual meaning. As shown in Fig. 2, the oxygen fluxes of BCF28 (d = 1.0 mm) are evidently higher than that of BCF28 (d = 1.5 mm) at the temperatures range of experiments. The calculation values (curve b), based on the d = 1.5 mm sample shown in Fig. 2, are slightly higher than that of d = 1.0 mm sample. So, the oxygen permeation rate of the BCF28 membrane is jointly controlled by the oxygen ions diffusing in bulk and recombining on the membrane surface (*i.e.* surface exchange). However, the diffusion of oxygen ions in bulk is dominant in the studying range of thickness. The other BCF series' oxygen permeation fluxes are also mainly bulk limited. So we can gain higher oxygen flux by reducing the thickness of the membranes.

Table 1 shows the BCF series of membranes' components and oxygen permeation fluxes at 1173 K. The molar fraction of BCF1585 in the series of membranes is calculated based on the XRD results. The membranes thickness is unified to 1.0 mm for comparison according to the above result. From Table 1, we can clearly find the oxygen fluxes of this series of membranes are directly related with the molar fraction of BCF1585.

The oxygen permeation flux is difficult to detect for the BCF82 membrane, owing to the molar fraction of BCF1585 being too small to exceed the percolation limit. Carefully analysing the data listed in the table, we find that there is a sharp change of oxygen flux from BCF28 to BCF1585. Detailed reasons of this issue will be discussed in future work. The similar oxygen permeation activation energies perhaps reflect the fact that the series of membranes have the same active component.

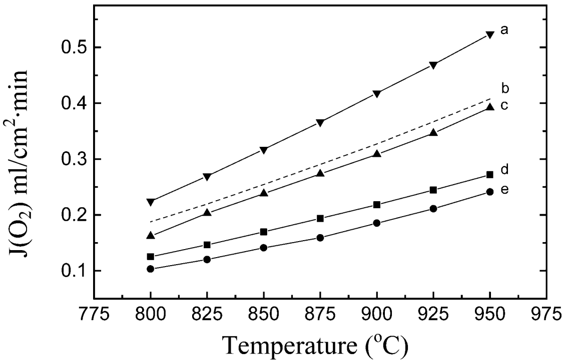

Fig. 2 Comparison of oxygen permeation fluxes of $BaCe_xFe_{1-x}O_{3-\delta}$ series of membranes as a function of temperature. Air flow rate in the oxygen-rich side is 100 ml min^{-1} and helium flow rate in the oxygen-lean side is 30 ml min^{-1}. Membrane area is range from 0.85 to 0.90 cm^2. (a), x = 0.15 (d = 1.0 mm); (b), calculation values based on (d); (c), x = 0.2 (d = 1.0 mm); (d), x = 0.2 (d = 1.5 mm); (e), x = 0.4 (d = 1.4 mm).

Table 1 Relationship of BCF series of membrane materials' components with oxygen permeation fluxes at 1173 K

Sample	BCF1585 (mol%)	BCF8515 (mol%)	J (O_2) (ml cm^{-2}.min^{-1})	E_a of J (O_2) (kJ mol^{-1})
BCF82	7.1	92.9	not detected	—
BCF46	64.3	35.7	0.260[a]	61.7
BCF28	92.9	7.1	0.308	62.2
BCF1585	100.0	0.0	0.418	61.4

[a] Adjusted values based on the fact oxygen permeation rate is primarily controlled by bulk diffusion, and all the membrane thicknees is 1.0 mm.

Based on the above results, we can conclude that this series of membrane materials possess high oxygen permeation fluxes and stability under reductive environments without using expensive metals, such as Ga, and easily reduced metals, such as Co. A pure perovskite phase is obtained when the amount of Ce^{4+} doping is 15%, and the oxygen fluxes reach the highest value of the series of membrane materials. The oxygen permeation rate is limited by bulk diffusion of all the series.

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Notes and references

1 Y. Teraoka, H. M. Zhang, S. Furuka and N. Yamazoe, *Chem. Lett.*, 1985, 1743.
2 H. H. Wang, Y. Cong and W. S. Yang, *J. Membr. Sci.*, 2002, **210**, 259.
3 A. C. van Veen, M. Rebeilleau, D. Farrusseng and C. Mirodatos, *Chem. Commun.*, 2003, 32.
4 V. V. Kharton, A. V. Kovalevsky, A. P. Viskup, F. M. Figueiredo, A. A. Yaremchenko, E. N. Naumovich and F. M. B. Marques, *J. Electrochem. Soc.*, 2000, **147**, 2814.
5 C. Y. Tsai, A. G. Dixon, W. R. Moser and Y. H. Ma, *AIChE Journal*, 1997, **43**, 2741.
6 Z. P. Shao, H. Dong, G. X. Xiong, Y. Cong and W. S. Yang, *J. Membr. Sci.*, 2001, **183**, 181.
7 P. N. Dyer, R. E. Richards, S. L. Russek and D. M. Taylor, *Sold State Ionics*, 2000, **134**, 21.
8 U. Balachandran, J. T. Dusek, P. S. Maiya, B. Ma, R. L. Mieville, M. S. Kleefisch and C. A. Udovich, *Catal. Today*, 1997, **36**, 2656.
9 H. H. Wang, Y. Cong and W. S. Yang, *Chem. Commun.*, 2002, 1468.
10 F. T. Akin and Y. S. Lin, *Catal. Lett.*, 2002, **78**, 239.
11 H. J. M. Bouwmeester, *Catal. Today*, 2003, **82**, 141.
12 M. Schwartz, J. H. White and A. F. Sammels, *US Pat.*, 6,214,757, 2001.
13 Z. P. Shao, W. S. Yang, Y. Cong, H. Dong, J. H. Tong and G. X. Xiong, *J. Membr. Sci.*, 2000, **172**, 177.
14 J. H. Tong, W. S. Yang, B. C. Zhu and R. Cai, *J. Membr. Sci.*, 2002, **203**, 175.
15 U. Balachandran, J. T. Dusek, R. L. Meiville, R. B. Poeppel, M. S. Kleefish, S. Pei, T. P. Kobylinski, C. A. Vdovich and A. C. Bose, *Appl. Catal. A*, 1995, **133**, 19.
16 W. Q. Jin, S. G. Li, P. Huang, N. P. Xu, J. Shi and Y. S. Lin, *J. Membr. Sci.*, 2000, **166**, 13.
17 C. Y. Tsai, A. G. Dixon, Y. H. Ma, W. R. Moser and M. Pascucci, *J. Am. Ceram. Soc.*, 1998, **81**, 1437.
18 Z. P. Shao, *PhD thesis*, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 2000, p. 149.