Investigation of Co–doped $Ce_{0.8}Sm_{0.2}O_{2-\delta}$–$Ba_{0.95}La_{0.05}Zr_{0.1}Fe_{0.9-x}Co_xO_{3-\delta}$ Dual–phase Oxygen Transport Membranes

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Abstract. In this study, 60 wt% $Ce_{0.8}Sm_{0.2}O_{2-\delta}$–40 wt% $Ba_{0.95}La_{0.05}Zr_{0.1}Fe_{0.9-x}Co_xO_{3-\delta}$ (SDC–BLZFC, x = 0–0.4) dual–phase oxygen transport membranes were prepared by a combined EDTA–citrate complexing sol–gol method. The effects of partial substitution of iron by cobalt on the crystal structure, phase structural stability, oxygen permeation flux and CO_2–tolerance were systematically investigated by XRD, TG and oxygen permeation experiment. The sample with x = 0.4 had the highest oxygen permeation flux of 0.42 ml min^{-1} cm^{-2} in He, while decreased most sharply after switching into pure CO_2. The result of sample with x = 0 was opposite. From all results, it could indicate that Co–doping contributes to oxygen permeation flux in inert gases and phase structural stability, but would reduce the CO_2–tolerance of SDC–BLZFC dual–phase membranes.

1 Introduction

Currently, dual–phase oxygen transport membranes (OTMs), consisting of perovskite–type membranes as electronic conducting phase (EC phase) and fluorite–type membranes as ionic conducting phase (IC phase), have been attracted great attention in the capture and storage of carbon[1–3]. And cobalt–containing oxides have a large drawback while none of the oxygen permeation flux could reach the level of cobalt–containing materials[4,5]. In this paper, a series of 60 wt% $Ce_{0.8}Sm_{0.2}O_{2-\delta}$–40 wt% $Ba_{0.95}La_{0.05}Zr_{0.1}Fe_{0.9-x}Co_xO_{3-\delta}$ (SDC–BLZFC) dual–phase OTMs with SDC (as the IC phase) and BLZFC (as the EC phase) were fabricated. Herein, the effects of cobalt substitution on the structure stability, chemical compatibility between the two phases, oxygen permeability and carbon dioxide tolerance of SDC–BLZFC were systemically studied.

2 Experimental

The $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ and $Ba_{0.95}La_{0.05}Zr_{0.1}Fe_{0.9-x}Co_xO_{3-\delta}$ (x = 0, 0.1, 0.2, 0.3, 0.4) were

synthesized by a combined EDTA–citrate complexing sol–gol method as mentioned in our earlier study[6]. The calcine temperature of $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ and $Ba_{0.95}La_{0.05}Zr_{0.1}Fe_{0.9-x}Co_xO_{3-\delta}$ are 850 ^{o}C and 600 ^{o}C for 5 h, respectively. SDC and BLZFC powder were mixed ground in a mortar in a ratio of 60:40 to ensure the uniformity of the two powders. The mixed powder was pressed to disk membranes with a diameter of 15 mm and then sintered at 1200 ^{o}C for 5 h in static air. Phase structure of the membranes and the spent membranes was investigated by X–ray diffraction (XRD, Rigaku D/MAX2550 powder diffractometer). Thermogravimetry (TG) measurements was performed to study the CO_2 resistance of SDC–BLZFC membranes. The permeation properties of SDC–BLZFC membranes were investigated with an online gas chromatography (GC–9160) system in a home–made high–temperature oxygen permeation apparatus. Air was applied as feed gas to one side of the membrane at a flow rate of 300 ml min^{-1} [STP], while He, CO_2 or a gas mixture of He and CO_2 as the sweep gas at a flow rate of 100 ml min^{-1} [STP]. The oxygen permeation flux was calculated by the external standard method according to the equation by Li[7].

3 Result and Discussion

Fig.1(a) shows the XRD pattern of SDC–BLZFC dual–phase membranes calcined at 1150 ^{o}C for 5 h in air. As is shown in the figure, the foreign phase of $BaCeO_3$ could be detected, and the amount of $BaCeO_3$ phase increased with increasing of Co content. No foreign phases were found in samples without cobalt. there was cationic mutual diffusion between IC phase and EC phase owing to Ba^{2+} ions in BLZFC electronic phase and Ce^{4+} ions in SDC ionic phase. Sun et al.[8] also found there are $BaCeO_3$ foreign phase after two phases mixed and sintered in $Ce_{0.8}Gd_{0.2}O_{2-\delta}$-$La_{0.4}Ba_{0.6}Fe_{0.8}Zn_{0.2}O_{3-\delta}$ dual–phase membranes. Rationally, the foreign phase $BaCeO_3$ hinders further diffusion of Ba^{2+} and Ce^{4+} between the two phases and maintains the integrity of electronic phases and ionic phases. The $BaCeO_3$ phase is inert phase, which oxygen permeability flux will be reduced if its concentration is too high. And the mechanism will get experimental verification in oxygen permeation experiment.
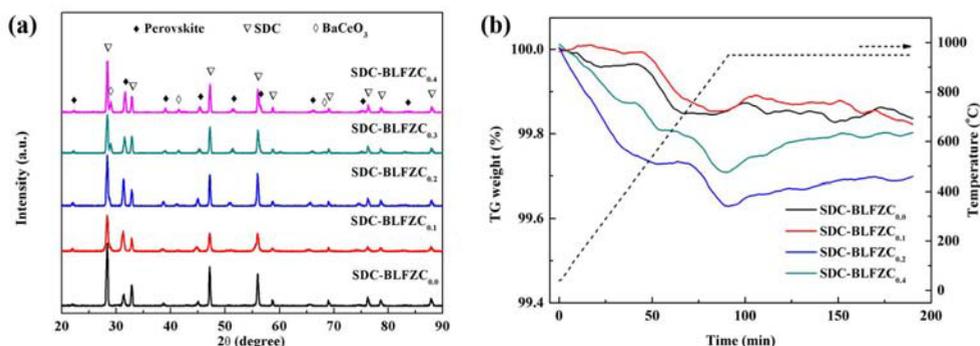

Fig. 1. (a) XRD patterns of SDC–BLZFC powder calcined at 1150 ^{o}C for 5 h and (b) TG curves of SDC–BLZFC under 50 vol% CO_2/N_2.

To verify the influence of Co content on the CO_2–tolerance of SDC–BLZFC membranes, the reactions between SDC–BLZFC membranes and CO_2 were studied by gravimetric analysis. Fig. 1(b) shows the TG curves of dual–phase SDC–BLZFC membranes. The powder which used in the experiment, comes from the membranes by fine grinding after sintering. Samples with x = 0.2, 0.4 have relatively apparent mass gain processes with temperature maintained at 950 ^{o}C, indicating that the mass gain caused by

the formation of carbonates is higher than the mass loss caused by desorption of lattice oxygen, namely the two samples have weaker CO_2–tolerance. The results also show that Co–doping is unfavorable to CO_2–tolerance of SDC–BLZFC dual–phase membranes.

Oxygen permeation fluxes through the 1.0 mm dense SDC–BLZFC membrane disks at different temperatures under air/He gradient are presented in Fig. 2 (a). The oxygen permeation fluxes have a positive relationship with the cobalt content. This is mainly ascribed to the increased oxygen vacancy concentration with Co–doping content[9,10]. Fig. 2 (b) shows the apparent activation energies (Ea) of SDC–BLZFC membranes. All membranes have their own activation energies and their fluctuation is very small with different Co–doping content. Some research shows some materials will have phase transition in temperature changing measurement, and their apparent activation energies will change obviously[11,12]. In this paper, single activation energy means that all SDC–BLZFC membranes haven't phase transition at the whole range of testing temperature, indicates Co–doped SDC–BLZFC membranes have excellent oxygen permeability and structural stability under a low oxygen partial pressure and a large oxygen pressure gradient without CO_2.
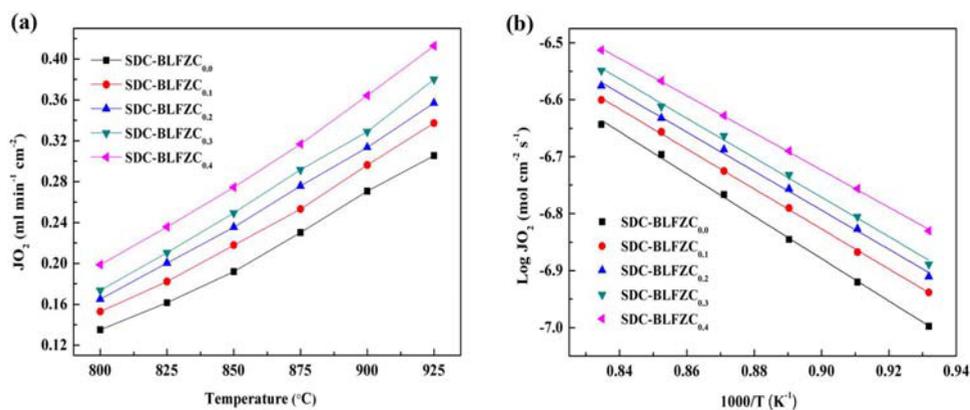

Fig. 2. (a) Temperature dependence of oxygen permeation flux though SDC–BLZFC membranes with 1.0 mm

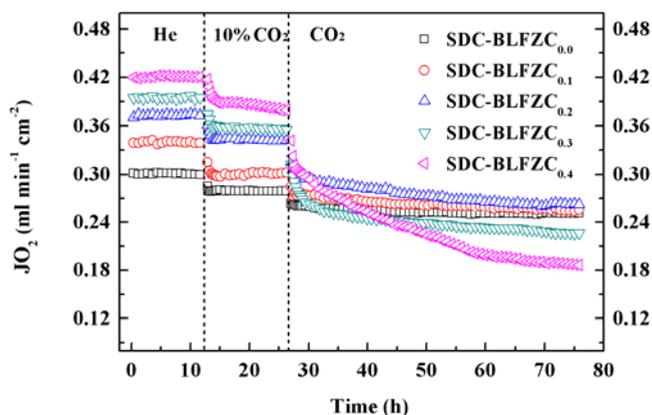thickness and (b) the apparent activation energies (Ea) of SDC–BLZFC membranes.

Fig. 3. Time dependence of oxygen permeation flux through 1.0 mm thick SDC–BLZFC membranes as a function

of CO_2 concentrations at 925 ^{o}C .

Fig. 3 shows the oxygen permeation performance of SDC–BLZFC membranes in the sweep gas of He and/or CO_2 at 925 ^{o}C. The oxygen flux of all samples didn't change

obviously under inert gas, it indicates that the membranes have excellent chemical compatibility. Upon switching the sweep gas from the CO_2–free inert gas to 10% CO_2/He, the oxygen flux decreased and then levelled off gradually. After switching the sweep gas into pure CO_2, oxygen flux of all samples decreased almost instantly and then tend to flatten out, but the decreasing degree and Co–doping content have a negative correlation. The high chemical potential of Ba^{2+} ions made the formation of carbonate quite fast in CO_2 atmosphere. Yi et al.[13,14] also prove this viewpoint. After carbonate layer reaching a certain thickness, the formation and decomposition reach equilibrium, this will make oxygen permeability stable gradually. After switching the sweep gas into pure CO_2, the increase of CO_2 partial pressure resulted in destroying the balance between formation and decomposition of carbonate. The generation of carbonate increased continuously, leading to oxygen permeability being declined. Fig. 3 indicated that Co–doping is unfavorable to CO_2–tolerance of SDC–BLZFC membranes consistent with the result of TG analysis. It maybe that Co–doping increased oxygen vacancy concentration and improved the basicity, so higher adsorption of CO_2 on material surface makes the corrosion more serious. For SDC–BLZFC membranes, the Co valence is lower than Fe, causing the alkalinity increase of samples, which is adverse to CO_2–tolerance ability[10].
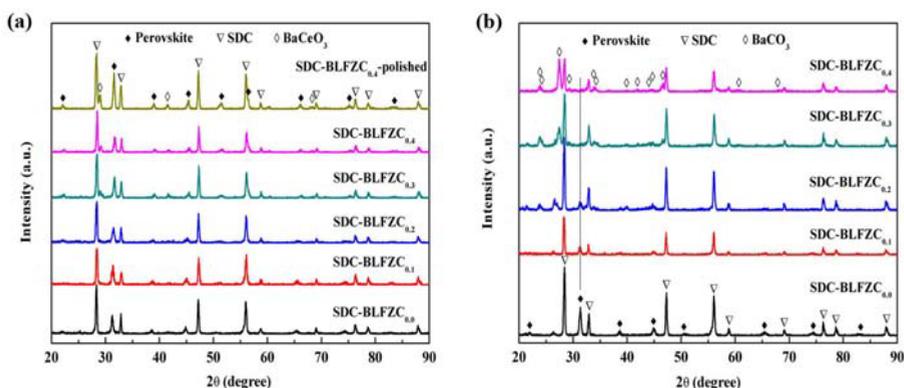

Fig. 4. XRD patterns of SDC–BLZFC after oxygen permeation tests with He and/or CO_2 as the sweep gas: (a) the feed side surface; (b) the sweep side surface.

After above oxygen permeation, phase characterization of the membranes surfaces exposed to Air was conducted by XRD, as shown in Fig. 4 (a). No other impurity phases were found on the feed side of membranes and both of SDC phase and BLZFC phase were stable, suggesting that these membranes possesses good phase structural stability and the two phases have good chemical compatibility under large oxygen partial pressure gradient and air atmospheres. Fig. 4 (b) shows the XRD pattern of samples on the sweep side. With Co–doping increasing, the diffraction peaks corresponding to $BaCO_3$ increased, and the diffraction peaks corresponding to perovskite phase reduced after the experiment. The result suggests Co–doping is bad for phase structural stability of BLZFC and CO_2–tolerance ability of SDC–BLZFC, probably caused by Co–doping increasing oxygen vacancy concentration and basicity on the surface, making CO_2 absorbed on material surface and corrode it easily, which is consistent with thermal–gravimetric analysis and oxygen permeation experiment.

4 Conclusions

The result of oxygen permeation indicated the oxygen permeation flux increased with

the improvement of Co–doping content in SDC–BLZFC system under inert gas. A stable oxygen permeation flux of 0.42 ml min^{-1} cm^{-2} was achieved with 1 mm thickness for samples in pure He at 925 ^{o}C. But with Co–doping content increasing, the oxygen permeation flux of SDC–BLZFC in pure CO_2 drops. In summary, Co–doping is favorable to improve the phase structural stability and oxygen permeation flux in inert gas, but will reduce CO_2–tolerance of SDC–BLZFC dual–phase membrane.

5 Acknowledgment

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