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Electrical conductivity and oxygen permeability of $Ce_{0.8}Sm_{0.2}O_{2-\delta}$–$PrBaCo_2O_{5+\delta}$ dual-phase composites

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ABSTRACT

A novel dual-phase oxygen permeation membrane based on ion-conducting $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (SDC) and mixed conducting $PrBaCo_2O_{5+\delta}$ (PBCO) is presented. There is no obvious reaction between the two phases under preparation and oxygen permeation conditions. The percolative network of mixed conducting phase PBCO can be formed in SDC-PBCO composite when the ratio of PBCO is not less than 40 vol.%. Above this threshold, the oxygen permeability of SDC-PBCO membrane increases with increasing SDC content. Compared with pure PBCO membrane, the oxygen permeability of percolative SDC-PBCO composites is improved due to the 3D diffusion ability of SDC, which can shorten the tortuosity of the oxygen diffusion path in layered PBCO. The maximum oxygen flux based on 0.6-mm-thick SDC-PBCO (6/4) is 2.38×10^{-7} mol cm^{-2} s^{-1} at 925 °C. The dependence of the oxygen permeation flux on the membrane thickness demonstrates that the bulk diffusion is the limiting step at thickness higher than 0.8 mm and the surface exchange may play an important role when the thickness is below that. Incorporation of SDC into PBCO can not only improve the oxygen permeability but also enhance the structural stability. The SDC-PBCO (6/4) dual-phase membrane is a promising candidate for oxygen separation application.

1. Introduction

The dense ceramic membrane made of mixed oxygen ion and electron conducting oxides are considered as promising material for partial oxidation of methane (POM) to synthesize syngas (H_2–CO mixture) [1,2]. These membranes derived from perovskite type (ABO_3) display infinite oxygen selectivity from air and higher oxygen fluxes comparing with organic membranes. Some perovskites, such as $Ba_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ [3], $SrCo_{1-y}Fe_yO_{3-\delta}$ [4] and $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ [5,6] have been reported to have high oxygen permeability at elevated temperature. However, the structural stability of single phase perovskite is quite limited under reducing atmosphere. For example, $SrCoFeO_3$ was reported to show very high oxygen permeation (3.1 ml cm^{-2} min^{-1} for 1.0 mm thickness membrane at 850 °C). However, an abrupt first-order phase transition at 790 °C and a decomposition in reducing atmospheres occurred [7,8], causing the long-term instability which

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prevent it from membrane reactor applications. Many efforts are made to improve the stability of perovskite-type membrane, including doping with fixed valence elements [9,10]. Recently, several researchers reported the potential application of dual-phase composite for membrane oxygen separators [11–13]. In contrast to single-phase membrane, oxygen ions and electrons of the composite membrane transport through different phases, and hence leading to the maintenance of both the high oxygen permeability and structural stability under operation conditions [14,15]. Furthermore, the higher mechanical strength and lower thermal expansion coefficient (TEC) of dual-phase membrane ensure the elegant sealing and the good cooperation with other components in the practical applications.

The layered oxygen-deficient perovskites $LnBaCo_2O_{5+\delta}$ (Ln = rare earth) have been attracting much attention as IT-SOFC cathodes [16,17], chemical gas sensors [18] and magnetic materials [19]. The ideal structure of these compounds can be generated by the stacking sequence $CoO_2|LnO_\delta|CoO_2|BaO|CoO_2$, and the oxygen vacancies are mainly located in the LnO_δ rare earth planes [17,20]. This particular distribution of oxygen vacancies could improve the oxygen transport properties compared to non-ordered perovskites, and supply surface defect sites with enhanced reactivity with oxygen molecular [21]. $PrBaCo_2O_{5+\delta}$ (PBCO) has been reported to have the faster oxygen bulk diffusion (10^{-5} cm s^{-1}) and surface exchange (10^{-3} cm s^{-1}) than other layered $LnBaCo_2O_{5+\delta}$, and exhibit a high electrical conductivity of 900 S cm^{-1} at 500 °C [22]. However, its oxygen permeability is lower than expected, around 5.09×10^{-7} mol cm^{-2} s^{-1} at 900 °C under high oxygen pressure, due to its particular structure characteristic, the two-dimensional oxygen-ion diffusion path [23]. Recently, it is found that in the SOFC cathode the introduction of fluorite structure $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (SDC) with a three-dimensional diffusion path into layered oxygen-deficient perovskites could reduce the tortuosity of the oxygen diffusion path [24]. On the other hand, the average thermal expansion coefficient (TEC) of PBCO is efficiently decreased from 21.5×10^{-6} K^{-1} to 20.1×10^{-6} K^{-1} when the SDC (12.5×10^{-6} K^{-1}) content is just 25 wt.% [25], which can improve the long-term stability of the membrane. Therefore, the incorporation of SDC into PBCO has the possibility of improving the oxygen permeability and structural stability of dense membrane, considering the high 3D ionic conduction and the excellent structural stability under reducing atmosphere of SDC. To our best knowledge, however, there is no report about the oxygen permeability, electrical conductivity and structural stability of SDC-PBCO composite membranes.

In this study, dual-phase membranes of SDC-PBCO with different volume ratios (5:5, 6:4 and 7:3) were fabricated via a conventional ceramic process. The chemical compatibility between the two phases and the effect of their ratio on the electrical conductivity and oxygen permeability of SDC-PBCO composite membrane were investigated with comparison to that of the pure phase PBCO. The thickness dependence of oxygen permeation flux of the dual-phase membrane was measured and the kinetic process of oxygen permeation through the membrane was discussed. The phase changes of the membrane surface on both sides after oxygen permeation test were also examined.

2. Experimental

2.1. *Membrane fabrication*

All the chemical reagents used in the experiments were obtained from commercial sources as guaranteed-grade reagents and used without further purification. Nanocrystalline $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ was obtained by the surfactant-assisting method as that described in our previous work [26]. $PrBaCo_2O_{5+\delta}$ powders with double-perovskite structure were prepared by EDTA-citrate complexing method [23]. Stoichiometric amount of Pr_6O_{11}, $Ba(NO_3)_2$ and $Co(NO_3)_3 \cdot 6H_2O$ were used as metal-ion sources. Pr_6O_{11} was dissolved in concentrated nitric acid (65%) under heating until a homogeneous solution was obtained, then a solution of $Ba(NO_3)_2$ and $Co(NO_3)_3 \cdot 6H_2O$ were added under vigorous stirring. When the mixing solution became homogeneous, an EDTA-ammonia aqueous solution and solid citric acid were added at EDTA: citric acid: metal ions molar ratio of 1:1:1 (pH ∼ 8). After stirring for 2 h, the mixed solution was dried at 80 °C to form purple dry gel. The gel was pre-fired at 300 °C and followed by grinding and subsequent calcination at 850 °C for 6 h to achieve pure double-perovskite oxide. The SDC and PBCO powders were mixed at different volume ratios of 5:5, 6:4, and 7:3, which were noted as SDC-PBCO (5/5), SDC-PBCO (6/4) and SDC-PBCO (7/3), respectively. Powders were milled by planetary milling at 400 rpm for 4 h. Ethyl alcohol was used as the media. After fully mixed by ball-milling, the composites were pressed into disks or bars under a pressure of ∼135 MPa, and subsequently sintered in air at 1140–1150 °C for 6 h at a heating/cooling rate of 3 °C min^{-1}. As comparison, pure PBCO disks or bars were also fabricated by the aforementioned pressure, and densified at 1130 °C for 6 h. The disk-shaped membranes were used for the oxygen permeation measurement.

2.2. *Microstructure characterization and oxygen permeation measurement*

The crystal structure of the samples were investigated by X-ray powder diffraction (XRD, Rigaku D/MAX-A powder diffractometer, Cu K_α radiation, $\lambda = 1.54056$ Å). The data were collected over the angle range from 20° to 80° with a step of 0.02° and a scan speed of 9° min^{-1}. The microstructure of sintered membranes was observed by scanning electron microscopy (SEM, LEO-1450) and the chemical composition of grains was examined by energy dispersive spectroscopy (EDS). The electrical conductivity was measured in air by four-terminal DC method upon heating from 200 to 900 °C at 50 °C per step. Four silver leads were attached to the rectangular bar with silver paste to obtain good electrical contacts between the silver leads and the sample. A direct current was passed through the two outside leads, and the voltage was measured between the two inside leads.

The oxygen permeation flux measurements were performed with a gas chromatograph method. Membranes were sealed with a silver ring onto the dense quartz tube, which were heated up to 960 °C at the rate of 2 °C min^{-1} to ensure the effective sealing. A synthetic air (21 vol.% O_2 + 79 vol.% N_2) was