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Influence of sealing materials on the oxygen permeation fluxes of some typical oxygen ion conducting ceramic membranes

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ABSTRACT

In this study, the influences of sealing materials on the oxygen permeation fluxes of three typical dense oxygen permeating membranes, including PrBaCo₂O_{5+δ} (PBC), Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} (BSCF5582) and Ce_{0.8}Sm_{0.2}O_{1.9} (SDC), with high electronic conductivity, moderate electronic conductivity and dominant oxygen-ion conductivity, respectively, are systematically investigated. Silver and insulating ceramic are used as two different sealants. The effects of external short circuit for electronic conduction by applying silver sealant and potential contamination effect of ceramic sealant on membranes were taken into major consideration. PBC membranes with either silver or ceramic as sealant showed comparable oxygen permeation fluxes during the test. Similar conclusions were also obtained based on BSCF5582 membranes. As for SDC membrane, significant promotion of the permeation flux by applying silver sealant was clearly demonstrated. Explanations for these performance changes are proposed. The findings from this study may provide valuable insight to explain the discrepancy of oxygen permeation fluxes of some membranes as reported by different research groups in the literature.

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1. Introduction

The success of nearly all chemical industries is dependent on the efficiency of reaction and separation. In particular, gas separation becomes more and more important to develop energy-efficient and environmentally benign industrial chemical processes. Up to now, several techniques have been established for gas separation, like adsorption, cryogenic distillation, and membrane separation. Among them, membrane separation is the most attractive technology for its advantages of continuous operation with high efficiency and low energy consumption [1]. In general, gas separation membranes can be synthesized into microporous or dense structure. Defect-free dense membranes can achieve 100% permeation selectivity, exemplified by Pd membrane for hydrogen separation [2].

As one of the most important raw materials for chemical industries, oxygen is currently produced by cryogenic distillation of air, which is very mature, but intensive in energy consumption and capital cost. In some cases, pressure swing adsorption is also used to produce oxygen with less demand on purity and in

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intermediate scale. Recently, a new technology based on dense mixed conducting membranes has received considerable attention, which is characterized by 100% oxygen permeability, continuous operation, flexibility to scale up in different sizes and more importantly significant reduction in production cost [3]. The oxygen permeation through those mixed conducting membranes is based on the ionic diffusion mechanism. For example, molecular oxygen at high concentration side is first reduced to oxygen ions and electron holes over the oxygen-rich side membrane surface, followed by ionic diffusion through the membrane bulk to the oxygen-lean side membrane surface driven by the oxygen partial pressure gradient across the membrane. On the oxygen-lean side membrane surface, the oxygen ions and electron holes are recombined to form molecular oxygen, which is finally released into the surrounding atmosphere [4,5].

For practical application of oxygen permeating membrane, the oxygen permeation flux should be equal or higher than $\sim 7.5 \times 10^{-6} \text{ mol cm}^{-2} \text{ s}^{-1}$ ($10 \text{ mL cm}^{-2} \text{ min}^{-1}$, STP) [6]. Thus far, many mixed conducting materials have been developed for oxygen permeating membranes. In one case, materials with dominant oxygen ionic conductivity, such as fluorite-type oxides, had been targeted for examination [7–9]. For example, at 800 °C, the ionic conductivities of a series of doped-CeO₂ range from 0.04 S cm⁻¹ to 0.1 S cm⁻¹, while their ionic transference numbers are all close

to 1, which indicate that the electronic conductivities of these materials are at least two orders of magnitude lower than their ionic conductivities [10]. As a consequence, these single-phase membranes based on fluorite-type oxides showed poor oxygen permeability (10^{-11} – 10^{-8} mol cm⁻² s⁻¹) [11]. Then, a secondary phase with high electronic conductivity was introduced to form a composite membrane for oxygen separation, which, however, often lowered the overall oxygen-ion conductivity of the membranes [12–14]. More recently, the oxides with perovskite-type lattice structure have attracted more attention as materials of ceramic oxygen permeating membranes. This type material typically possesses high electronic conductivity. More importantly, many such perovskite-type mixed conductors also exhibit favorable oxygen ionic conductivity more than one order of magnitude higher than that of the best oxygen-ion conductors with the fluorite-type lattice structure, such as doped ceria or zirconia [11,15–18]. The oxygen permeation fluxes of these perovskite-type membranes can reach 10^{-10} – 10^{-6} mol cm⁻² s⁻¹ [11], which are close to the basic requirement of practical application of oxygen permeating membrane.

Among the reported oxygen permeation fluxes of selected membranes by different research groups, large discrepancy was observed. The reported permeation fluxes of the membranes in the same material composition can vary by several times [15,19–23]. The difference was usually explained by the different microstructures and impurity phases brought into the membranes from different preparation protocols, which could affect the grain boundary conductivity, bulk conductivity and surface oxygen exchange process [21–23]. Also, the application of different experimental set-up and test conditions would also impact the oxygen permeation flux of membranes [15,19,24]. For example, in ambient air, the oxygen permeation flux of a PrBaCo₂O_{5+δ} membrane (thickness: 1 mm) is $\sim 1.6 \times 10^{-7}$ mol cm⁻² s⁻¹ at 900 °C when the helium with a flow rate of 65 ml min⁻¹ is used as sweeping gas, while a higher flux of $\sim 3.5 \times 10^{-7}$ mol cm⁻² s⁻¹ is observed when the flow rate of helium increases to 100 ml min⁻¹ [15,19].

The oxygen permeation test is carried out at high temperatures and flux value is usually measured by a gas chromatography (GC) method. In a typical measurement, a dense disk-shape membrane was sealed onto a tube (quartz or ceramic) with one side of the membrane surface exposing to air (sometimes an oxygen based mixture gas with fixed oxygen partial pressure was used) and the other side sweeping with an inert gas (typically, helium). Under the drive of oxygen partial pressure gradient across the membrane, the oxygen can be continuously permeated from the oxygen-rich side atmosphere through the membrane to the oxygen-lean side atmosphere, which could be carried by the helium gas and directed to a GC for gas composition analysis and flux value calculation [4].

Avoiding gas leakage during an oxygen permeation test is a big thing that should be of concern. Because although the oxygen flux can be corrected due to an estimated leakage rate, a significant gas leakage will significantly reduce the driving force for oxygen permeation across the membrane and thus limit the true membrane performance. Effective sealing is critical to minimize gas leakage and to ensure the oxygen purity. Normally, two types of high temperature sealing materials have been attempted: electronic conductive sealants, i.e., gold/silver ring and silver/gold paste and non-electronic conductive, i.e., ceramic/glass paste [25–27]. Ceramic/glass paste sealing and gold/silver paste sealing are most frequently used because the membrane sidewall can also be covered with the sealant to avoid radial contribution to the oxygen permeation flux thus improving the flux value accuracy [27,28]. One big feature of electronic conductive metal sealing is that the sealant will create an external short circuit for electronic conduction. Recently, we have demonstrated that some oxide materials

with negligible electronic conductivity could be developed into ceramic oxygen permeating membranes with favorable oxygen flux by introducing short circuit for electronic conduction [29,30]. It suggests the external short circuit from metal sealant may also affect the oxygen permeation flux of mixed conducting membranes, in particular for those with lower electronic transfer number. Indeed, in an early study, the influence of such an external short circuit caused by the conductive Pt sealant on the performance of a tube membrane made of a calcium-ceria co-doped zirconia material has already been observed [31]. On the other hand, there are also some considerations about the contamination effect brought by sealing materials, which can deteriorate the oxygen permeation performance of membranes [24,27]. To get more in-depth understanding the oxygen permeation through ceramic oxygen permeating membranes, it is worthwhile to re-investigate systematically the effect of sealing material on the oxygen fluxes.

Herein, a systematic investigation of the sealing agent on the oxygen permeation fluxes of mixed conducting ceramic membrane was conducted. Two different sealing materials, silver paste and non-electronic conductive ceramic paste, were tried. Three mixed conducting materials, PrBaCo₂O_{5+δ} (PBC), Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} (BSCF5582) and Ce_{0.8}Sm_{0.2}O_{1.9} (SDC), which display high electronic conductivity, moderate electronic conductivity than oxygen ionic conductivity and dominant oxygen-ion conductivity, respectively, were investigated. The purpose of this study is to elucidate the role of external short circuit from sealing on the oxygen permeation flux of mixed conducting membranes. It may help readers to understand the discrepancy that exists in the reported oxygen fluxes for selected membranes as reported in literature.

2. Experimental

2.1. Powder synthesis and sample preparation

The PBC, BSCF5582 and SDC oxide powders were prepared via a combined EDTA and citrate complex technique. Metal nitrates in analytic grades, including Pr(NO₃)₃·6H₂O, Ba(NO₃)₂, Sr(NO₃)₂, Co(NO₃)₃·6H₂O and Fe(NO₃)₃·9H₂O, were used as the raw materials of cation sources. The detailed preparation procedure was reported earlier [32]. The solid precursors of PBC, BSCF5582 and SDC were calcined respectively at 1050, 950 and 800 °C for 5 h in air to obtain the products with targeted composition and lattice structure.

For the fabrication of oxygen permeating membranes, the oxide powders were first milled with the high-energy ball miller (FRITSCH Pulverisette 6) for 1 h; then, the powders were dry pressed into disk-shaped green membranes using a stainless steel die with an inner diameter of 15 mm. The obtained PBC, BSCF5582 and SDC green membranes were sintered respectively at 1100, 1100 and 1400 °C for 5–10 h to obtain the desired densified structure. The sintered membranes had a diameter around 12 mm. For all membranes, their surfaces were polished with 600-mesh SiC paper to obtain similar surface roughness. The thickness of PBC, BSCF5582 and SDC was controlled at 1.2, 1.0 and 0.5 mm, respectively. The decoration of membrane surface with a porous gold layer was conducted by uniformly brushing a diluted gold paste on the surface of the membrane. The diluted gold paste was obtained by dispersing the concentrated gold paste with ethanol, and minor portion of PVA was hereby added as the pore former.

2.2. Characterization and oxygen permeation tests

The phase structures of the as-synthesized powders were examined by an X-ray diffractometer (Rigaku Smartlab) equipped

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