Journal of Membrane Science 491 (2015) 90–98

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Oxygen permeation modeling for $Zr_{0.84}Y_{0.16}O_{1.92}$–$La_{0.8}Sr_{0.2}Cr_{0.5}Fe_{0.5}O_{3-\delta}$ asymmetric membrane made by phase-inversion

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ARTICLE INFO

Article history:
Received 10 November 2014
Received in revised form
21 February 2015
Accepted 4 May 2015
Available online 25 May 2015

Keywords:
Model
Dual-phase
Asymmetric membrane
Phase-inversion
Percolation

ABSTRACT

An oxygen permeation model for an asymmetric membrane made by phase-inversion is developed to link the permeation performance directly to measurable variables, such as experimental conditions and geometric parameters. $Zr_{0.84}Y_{0.16}O_{1.92}$–$La_{0.8}Sr_{0.2}Cr_{0.5}Fe_{0.5}O_{3-\delta}$ (YSZ–LSCrF) membrane is selected as representative membrane. The percolation theory is used to describe the effective properties of the composites. Two permeation modes in asymmetric membrane are compared. One mode is oxygen permeation from the Support to the thin Dense layer (SD mode), and the other oxygen permeation flux is the opposite way (DS mode, from dense layer to support). In these two modes, the maximum oxygen permeation rate is achieved at an ionic phase fraction of 0.5 under air/CO gradient. It is also found that it is beneficial for the membrane to obtain higher oxygen permeation flux when DS mode is adopted for the supported membrane. In addition, the surface exchange on lean side in SD mode limits the whole oxygen permeation. The resistances of support layer and dense layer in asymmetric membrane are calculated. The rate-limited step is identified by distribution of these resistances.

1. Introduction

Dense ceramic membrane made of mixed oxygen ionic and electronic conductors are permeable to oxygen under an oxygen gradient at elevated temperatures [1]. There are two main types of permeable ceramic membrane. One type is mixed oxygen-ion and electron conducting single phase membranes. Most of this type materials found so far are oxygen-deficient perovskite-structured oxides such as (Ln, A)(Co, B)$O_{3-\delta}$ (Ln=rare earth elements, A=Ca, Sr, Ba, B=transition metal elements) [2–6]. Another type is composite materials which involve an oxygen ionic conducting phase and an electronic conducting phase. These dual-phase composites show improved stabilities, but their oxygen permeability is significantly lower than the single-phase materials [7–12]. However, this low permeability can be improved by fabricating the dual-phase composites into asymmetric structure [13,14], especially made by phase-inversion [15–22].

Phase-inversion method has been the widely used technology for membrane preparation since it was successfully used by Loeb and Sourirajan to develop cellulose acetate membranes for seawater desalination in 1960s [23]. The method was first adapted for fabrication of porous ceramics especially those with the hollow fiber geometry in 1990s [24,25], and then some ceramic membranes for oxygen permeation were also prepared by phase-inversion [26,27]. In this method, the formation of membrane structure is controlled by both the thermodynamics of the solution and the kinetics of transport process. Usually, an asymmetric finger-like structure can be obtained, the thick layer with large finger-like pores provides the membrane with sufficient mechanical strength and low mass transport resistance, while the thin lower layer, free of large pores, provides the separation function.

Recently, some models to describe the oxygen permeation of membrane have been proposed, with an aim to get a deep insight into the mechanism and promote the development of ceramic separation membrane. For example, the oxygen ion permeation flux across an ionic-conducting membrane can be calculated using the Wagner equation, assuming the oxygen bulk diffusion to be the rate limiting step [28]. Lin et al. developed a model for thin mixed-conducting membranes considering the surface exchange [29]. Xu et al. investigated the permeation of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ membrane based on the origin theory of Lin [30]. Chang studied a model for asymmetric model for $SrCo_{0.4}Fe_{0.5}Zr_{0.1}O_{3-\delta}$ membrane [31]. Unfortunately, these

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http://dx.doi.org/10.1016/j.memsci.2015.05.026
0376-7388/

models are all about single phase, the ceramic membrane with two phases, the effective properties of each phase are quite different from bulk phase. In the present study, a model using the percolation theory is developed to describe the oxygen permeation properties of dual-phase supported membrane made by phase-inversion. A dual-phase composite membrane comprising of $Zr_{0.84}Y_{0.16}O_{1.92}$ (YSZ) as oxygen ionic conductor and $La_{0.8}Sr_{0.2}Cr_{0.5}Fe_{0.5}O_{3-\delta}$ (LSCrF) as electronic conductor is selected as representative membrane materials, which have been found to be structurally stable with appreciable oxygen permeation flux [18–20].

2. Theoretical model

In this paper, the model about the dual-phase membrane for oxygen permeation is mainly based on the following assumptions:

1. The diffusion coefficient of dual-phase is independent of oxygen partial pressure and is uniform throughout the entire membrane.
2. LSCrF phase in YSZ–LSCrF dual-phase membrane has low oxygen ion conductivity, so the oxygen ions only transfer in YSZ phase. The surface exchange reaction happens on the TPB area on the surface and the surface exchange area is independent with oxygen partial pressure.
3. For introducing the percolation theory, all powders to constitute the membrane are viewed as spherical particles, neglecting their irregular shapes and radius distribution.

2.1. Oxygen transport in dense layer

A typical asymmetric membrane consists of a thin dense layer and a porous support layer, so the oxygen transport in the two parts should be investigated. Firstly, a dual-phase membrane without support layer, called symmetric membrane is studied. Oxygen permeation through a symmetric membrane is driven by oxygen partial pressure gradient, and involves surface exchange on high oxygen pressure side, bulk diffusion and surface exchange on low oxygen pressure side. The processes of oxygen ion diffusion and surface exchange affect the oxygen permeation flux, and properties of these processes are related to morphology and microstructure in dual-phase membrane, which can be described by percolation theory [32–34]. Percolation theory is usually used for SOFC electrode to describe the effective properties, such as effective triple phase boundary (TPB) length and effective conductivity of composite electrode. In this paper, the percolation theory is adapted to describe the effective properties of the membrane and the support. Percolation probability (P) and coordination number (Z) are two major parameters, and the details is expressed as:

$$Z_{io}=Z\frac{V_{io}/r_{io}}{V_{io}/r_{io}+V_{el}/r_{el}} \tag{1}$$

$$Z_{el}=Z\frac{\frac{\phi_{el}}{r_{el}}}{\frac{\phi_{io}}{r_{io}}+\frac{\phi_{el}}{r_{el}}} \tag{2}$$

$$Z_{io-el}=\frac{Z}{2}\left(1+\frac{r_{io}^2}{r_{el}^2}\right)\frac{\frac{\phi_{el}}{r_{el}}}{\frac{\phi_{io}}{r_{io}}+\frac{\phi_{el}}{r_{el}}} \tag{3}$$

$$P_{io}=\left(1-\left(\frac{4.236-Z_{io}}{2.472}\right)^{2.5}\right)^{0.4} \tag{4}$$

$$P_{el}=\left(1-\left(\frac{4.236-Z_{el}}{2.472}\right)^{2.5}\right)^{0.4} \tag{5}$$

where the subscripts *io* and *el* represent ionic and electronic phase respectively. r is the radius of corresponding particles, Z is the average coordination number of all particles, which is widely assumed that $Z=6$. The ϕ_{io} and ϕ_{el} represent the volume fraction of ionic and electronic phases to the total solid materials, excluding the porosity.

The effective TPB is a geometrical parameter that is of crucial importance for the performance of surface exchange in membrane. According to percolation theory, the effective TPB length and diffusion coefficient of ionic phase are expressed as:

$$L^{eff}=2\pi r_{io-el}\ \sin\ \theta\frac{(1-\phi_g)\phi_{io}}{\frac{4\pi r_{io}^3}{3}}Z_{io-el}P_{io}P_{el} \tag{6}$$

$$D^{eff}=D_0((1-\phi_g)\phi_{io}P_{io})^{\mu} \tag{7}$$

where L^{eff} is effective TPB length per unit volume. r_{io-el} is the smaller radius of the two phase particles. θ is the contact angle, and ϕ_g is the porosity which here is assumed as 0. D_0 is bulk diffusion coefficient for ionic phase and μ is Bruggement factor that is used to include the effects of tortuous conduction paths (μ is typically 1.5).

At 800 °C, the electronic conductivity of LSCrF is $\sim$6.45 S cm^{-1} in air [35] while the YSZ ionic conductivity is just 0.03 S cm^{-1} [36]. The electronic conductivity of LSCrF is dramatically larger than the ionic conductivity of YSZ at elevated temperature, indicating that the transport of oxygen ion in YSZ rather than that of electrons in LSCrF limits the oxygen permeation in membrane bulk. Assuming the charged species in membrane are oxygen vacancies ($V_{O}^{\cdot\cdot}$) and electron–hole ($h^{\cdot}$), the resistance of electron–hole transport is small and they can move freely in the bulk in comparison with the oxygen vacancies. At the high oxygen pressure side, surface exchange happens at TPB area, which can be described as: $(1/2)O_2+V_{O}^{\cdot\cdot}\leftrightharpoons 2h^{\cdot}+O_{O}^{x}$, and the reverse reaction $(2h^{\cdot}+O_{O}^{x}\leftrightharpoons(1/2)O_2+V_{O}^{\cdot\cdot})$ happens at the lean side. With a high electron conductivity, the concentration of the electron–hole can be considered as constant at both side of membrane. Therefore, under steady state, the surface reaction rate of the each side and flux through the bulk can be calculated as Eqs. (8)–(10) (Ref [30]):

At high oxygen partial pressure side:

$$J_{O_2}=(K_f p_h^{0.5}c_h-K_r a^2)L^{eff}wr_{io} \tag{8}$$

A low oxygen partial pressure side:

$$J_{O_2}=(K_r a^2-K_f p_l^{0.5}c_l)L^{eff}wr_{io} \tag{9}$$

In Bulk:

$$J_{O_2}=\frac{1}{2}D^{eff}\frac{c_{l-}c_h}{L} \tag{10}$$

where c_h and c_l are the concentrations of oxygen vacancies at high and low oxygen pressure side of the membrane respectively, a is the concentration of electron–hole in the membrane, p_h and p_l are the oxygen partial pressures at high and low oxygen pressure side of the membrane respectively, w is the width of the TPB line, K_r and K_f are forward and reverse reaction rate constant for reaction which happens at surface $((1/2)O_2+V_{O}^{\cdot\cdot}\leftrightharpoons 2h^{\cdot}+O_{O}^{x})$, L is the thickness of membrane.

By solving Eqs. (8)–(10) and assuming $K_1=K_f L^{eff}wr_{io}$, $K_2=K_r a^2L^{eff}wr_{io}$, the steady-state oxygen permeation flux through a symmetric membrane can be readily correlated to oxygen partial pressure