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Influence of permeation modes on oxygen permeability of the multichannel mixed-conducting hollow fibre membrane

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HIGHLIGHTS

- A multichannel mixed-conducting hollow fibre membrane was prepared.
- The membrane has high oxygen permeation flux and excellent mechanical strength.
- Surface oxygen exchange reaction is the rate-limiting step for oxygen permeation.
- When oxygen permeates from lumen side to shell side, it can obtain higher oxygen flux.

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ABSTRACT

A multichannel mixed-conducting hollow fibre (MMCHF) membrane, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$, has been successfully prepared by a combined phase inversion and sintering technique. Two possible permeation modes can be used in the hollow fibre membrane. One mode is that oxygen permeates from the shell side of the membrane to the lumen side (SL mode), with the other mode being in the direction from the lumen side to the shell side (LS mode). Thus, it is necessary to study oxygen permeability in these two modes to make better use of the membrane. In this work, the influences of oxygen permeation modes on separation performance of MMCHF membrane were investigated systematically. In LS mode, the MMCHF membrane obtains a high oxygen flux of 3.22 ml min^{-1} cm^{-2} which is higher than that in SL mode. The surface reaction is the rate-limiting step for oxygen transport in the two modes and the surface reaction resistance of LS mode is smaller than that of SL mode. Our work demonstrates that when the MMCHF membrane adopts LS mode, it is beneficial to obtain higher oxygen flux.

1. Introduction

In the last decades, mixed ionic and electronic conducting (MIEC) membranes have attracted considerable attention because of their versatile functionality and wide applications, including oxygen production (Liang et al., 2010; Wang et al., 2006, 2005; Zhu et al., 2009), partial oxidation of hydrocarbons to value-added products (Jiang et al., 2008, 2013; Jin et al., 2000) and solid oxide fuel cells (Chen et al., 2014a, 2014b; Shao and Haile, 2004), etc. The promising property of the MIEC membranes is that they can separate oxygen from air with a theoretical selectivity of 100% at elevated temperature, which could have potential benefits on energy and environment (Hashim et al., 2011; Stiegel and Maxwell, 2001). However, several challenges, including chemistry and engineering issues, exist in developing MIEC membrane technique before large-scale industrial and commercial applications. In order to solve these issues, many researchers focused on the development of advanced membrane materials with high performance and the optimization of membrane configuration.

It is well known that the overall oxygen permeation through a MIEC membrane can be divided as two processes: (i) bulk diffusion and (ii) surface reaction on both sides of the membrane (Diethelm and Van herle, 2004). Normally, the overall oxygen permeation is controlled by the oxygen bulk diffusion rate in the membrane as well as the surface oxygen exchange kinetics on both sides of the membrane (Xu and Thomson, 1999). According to oxygen transport mechanism of the membrane, reducing the thickness of the membrane dense layer (Liu et al., 2012; Watenabe et al., 2010; Yashima et al., 2010) and modifying porous catalytic layers on either side or both sides of the membrane (Pan et al., 2013; Teraoka et al., 2002) are effective methods for enhancing oxygen permeability. Recently, MIEC hollow fibre membranes prepared by phase inversion and sintering technique with asymmetric structure (a thin separating dense layer

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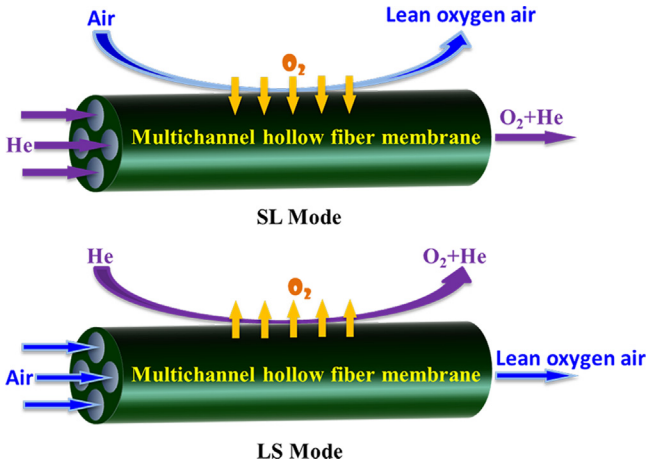

Fig. 1. Schematic diagram of permeation modes of MMCHF membranes.

integrated with porous layers on either side or both sides) based on $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (Tan et al., 2005, 2010; Zydorczak et al., 2009), $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) (Leo et al., 2011; Liu et al., 2006a; Wei et al., 2011), $BaBi_{0.05}Sc_{0.1}Co_{0.85}O_{3-\delta}$ (Sunarso et al., 2011), $BaCo_{0.7}Fe_{0.2}Ta_{0.1}O_{3-\delta}$ (Liao et al., 2012) and $BaCo_xFe_yZr_zO_{3-\delta}$ $(x+y+z=1)$ (Schiestel et al., 2005) have been proposed. Because of the thin dense layer of hollow fibre membrane, the resistance to oxygen permeation is substantially reduced compared to that of symmetric thick membranes. In addition, the porous layers on either side or both sides of the hollow fibre membrane provide large gas–membrane interface for surface exchange reactions, leading to an enhancement of oxygen permeation rate. The two above advantages of the MIEC membranes in hollow fibre configurations would position these membranes into industrial applications in the foreseeable future.

Very recently, a multichannel mixed–conducting hollow fibre (MMCHF) membrane with superb performance has been developed in our previous work, which could be a competitive candidate for industrial application (Zhu et al., 2014). In fact, two possible permeation modes can be used in the MMCHF hollow fibre membrane. Fig. 1 illustrates the two permeation modes of MMCHF membranes. One mode is that oxygen permeates from shell side of the membrane to the lumen side (designated as SL mode), with the other mode being in the direction from the lumen side to the shell side (designated as LS mode). Thus, it is necessary to study oxygen permeability in these two modes from the viewpoint of choosing an appropriate oxygen permeation mode to make better use of the membrane. Therefore, the objective of this study is to systematically investigate the influences of permeation modes on oxygen permeability of the MMCHF membrane.

2. Theory

2.1. Estimation of the rate-limiting step for oxygen transport through the MIEC membrane

The oxygen permeation flux of MIEC membrane is correlated with both the ionic and electronic conductivity of the MIEC oxides. When the oxygen transport through the membrane is limited by bulk diffusion, the oxygen permeation flux can be given by the following Wagner equation (Lin et al., 1994; Qi et al., 2000; Xu and Thomson, 1999):

$$J_{O_2} = -\frac{RT}{4^2F^2L}\int_{\ln P_1}^{\ln P_2}\frac{\sigma_{el}\sigma_{ion}}{\sigma_{el}+\sigma_{ion}}d\ln P \tag{1}$$

where J_{O_2} is the oxygen permeation flux through the membrane; R is the gas constant; F is the Faraday constant; L is the membrane thickness; P_1 is the oxygen partial pressure on the feed side; P_2 is the oxygen partial pressure on the sweep side; σ_{el} and σ_{ion} are the electronic and ionic conductivity, respectively. However, when the oxygen permeation flux is controlled by both bulk diffusion and surface oxygen exchange kinetics, the oxygen permeation flux can be expressed by the modified Wagner equation (Hong and Choi, 2010):

$$J_{O_2} = -\frac{1}{1+(2L_c/L)}\frac{RT}{4^2F^2L}\int_{\ln P_1}^{\ln P_2}\frac{\sigma_{el}\sigma_{ion}}{\sigma_{el}+\sigma_{ion}}d\ln P \tag{2}$$

where L_c is the characteristic membrane thickness. Since $\sigma_{el} \gg \sigma_{ion}$ for BSCF oxide (Zeng et al., 2007), it is reasonable to simplify Eq. (2) into the following equation:

$$J_{O_2} = -\frac{1}{1+(2L_c/L)}\frac{RT}{4^2F^2L}\int_{\ln P_1}^{\ln P_2}\sigma_{ion}d\ln P \tag{3}$$

The oxygen ionic conductivity σ_{ion} is related with the oxygen vacancy and calculated by Nernst–Einstein equation (Sunarso et al., 2008):

$$\sigma_{ion} = \frac{4F^2[V_O^{\infty}]D_V}{RTV_m} \tag{4}$$

where V_O^{∞} is the concentration of oxygen vacancy; D_v is the oxygen vacancy diffusion coefficient and V_m is the perovskite molar volume. σ_{ion} can be further related with oxygen partial pressure by the empirical equation (Qi et al., 2000; Sunarso et al., 2008):

$$\sigma_{ion} = \sigma_{ion}^{o}P^n \tag{5}$$

where σ_{ion}^{o} is the ionic conductivity when the oxygen partial pressure is 1 atm. Combing Eqs. (3) and (5) to give:

$$J_{O_2} = -\frac{1}{1+(2L_c/L)}\frac{\sigma_{ion}^{o}RT}{4^2F^2Ln}(P_2^n-P_1^n) = a(P_2^n-P_1^n) \tag{6}$$

The rate-limiting step of oxygen permeation can be identified from the value of n. In general, for $n \geq 0.5$, the oxygen permeation process is controlled by the reaction of the molecular oxygen with the membrane surface. For $0 < n < 0.5$, the oxygen permeation is controlled by both the surface reaction and the bulk diffusion, whereas for $n < 0$, the oxygen permeation is predominantly controlled by bulk diffusion of the oxygen ion (Huang and Goodenough, 2001; Liao et al., 2012; Wei et al., 2011; Zhang et al., 2007).

2.2. Calculation of the resistance for oxygen permeation through the MIEC membrane

In a steady state, the oxygen permeation flux through a MIEC membrane can be correlated with the current density by the following equation (Zeng et al., 2007):

$$J_{O_2} = \frac{I_{O_2}}{4F} \tag{7}$$

The nomenclature of I_{O_2} is the current density.

$$I_{O_2} = \frac{\Delta\mu}{Ar_{total}} = \frac{\Delta\mu}{A(r_S+r_{ion}+r_{el})} \tag{8}$$

where A, r_S, r_{ion}, r_{el} and r_{total} are the membrane area, the resistance to surface oxygen exchange at both feed side and sweep side, the resistance for oxygen bulk diffusion, the resistance for electronic transport and the total transport resistance, respectively. $\Delta\mu$ is the chemical potential difference on both sides of the MIEC membrane. According to the literatures (Liu et al., 2006b; Zeng et al., 2007), the chemical potential difference can be described as follow