Thickness dependence of oxygen permeation through erbia-stabilized bismuth oxide–silver composites

C.S. Chen*a,b,*, H. Kruidhof*a, H.J.M. Bouwmeester*a, H. Verweija, A.J. Burggraaf*a

aLaboratory of Inorganic Materials and Science, Faculty of Chemical Technology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands
bDepartment of Materials Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, China

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Abstract

Oxygen permeation measurements were performed on erbia-stabilized bismuth oxide–silver (40 v/o) composite membranes in the range of thickness of 1.60–0.23 mm and temperature of 850–650°C. Air was fed at one side of the membranes while permeated oxygen on the other side was swept away with helium. An oxygen flux as high as $1.56 \times 10^{-3}$ mol/cm²s was observed for a 0.23 mm thick membrane at 750°C and $p_{O_2}(l)=0.056$ atm. The examination of the dependence of permeance on the membrane thickness reveals that (a) the oxygen transport kinetics are controlled by the diffusion of oxygen ions in the bulk of membrane with thickness down to about 1.0 mm; (b) with further decrease in thickness, the oxygen permeation becomes partially limited by surface oxygen exchange. The surface exchange rate has been found to decrease less pronouncedly than the bulk process as temperature decreases. The mass transfer is suggested to be the rate-limiting step for the surface process.

Keywords: Oxygen permeation; Oxygen separation membranes; Stabilized bismuth oxide; Silver

1. Introduction

The solid material exhibiting high oxygen ion and electron mixed conductivity at elevated temperatures is very permeable to oxygen if an oxygen pressure difference is applied across the material. As an oxygen separation membrane it has infinite permselectivity to oxygen, i.e., imperious to other gas components, provided the membrane is made dense, i.e., without gas-through pores and cracks [1]. Some significant technological applications have been suggested including production of oxygen by separation from air and manipulation of oxygen-involved chemical reactions such as conversion of methane to synthesis gas (CO/H₂) [1–3].

Dense erbia-stabilized bismuth oxide containing 40 v/o silver metal has been found to possess large oxygen permeability at intermediate temperatures (850–650°C) [4]. Oxygen permeation through the dual phase composite membranes consists of bulk and surface process. The bulk process involves diffusion of oxygen ions in the oxide phase and of electrons in the metal phase. The surface process

*Corresponding author. Tel: +86-551-360-3234; fax: +86-551-363-1760; e-mail: ccsm@dmse.mse.ustc.edu.cn

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involves oxygen exchange at the three-phase boundary of the gas–oxide–metal. The oxygen transport kinetics varies with the membrane thickness, the applied oxygen partial pressure difference and operating temperature [5]. The aim of this paper is to identify the rate-limiting step of the oxygen transport kinetics by investigating the thickness dependence of oxygen permeation through the membranes.

2. Experimental

Bismuth oxide stabilized with 25 m/o erbia (denoted as BE25) was prepared by a solid reaction. To this end Bi$_2$O$_3$ (Merck) and Er$_2$O$_3$ (Serva) were thoroughly mixed, pre-fired at 825°C for 16 h and finely ground. The appropriate amount of silver (Specpure, Johnson Matthey) powder was mixed with BE25 powder in mortar to prepare a composite powder containing 40 v/o silver. Powder compacts of the composite were pre-pressed in a steel die under a pressure of 0.5 bar for 5 min followed by isostatically pressing at 400 MPa for 5 min. The compacts thus obtained were sintered in air at 860°C for 16 h using both heating and cooling rate of 0.3°C/min. Densities of the sintered compacts were above 95% of the theoretical density as determined by the Archimedes method (in mercury).

Prior to oxygen permeation measurement the sintered compacts were sliced into disks with a diameter of 14.75 mm and thicknesses of 1.60, 0.90, 0.60 and 0.23 mm. The disks were sealed into a quartz reactor with a volume of about 3 ml using a Pyrex glass ring (trade name Duran, Schott Netherlands) by heating to 850°C in stagnant air. Oxygen permeation experiments were conducted by feeding air at one side of the disk specimen, while sweeping the opposite side with high purity helium (UCAR Specialty Gases, p$_o$$_2$= 0.2 atm; 1 atm = 101 325 Pa). Due to the partial failure of the glass sealing, a considerable amount of oxygen leaked into the low p$_o$$_2$$_2$ side, as revealed by the presence of nitrogen. Since the leaked oxygen flux is equal to the nitrogen flux times the ratio of oxygen to nitrogen in the feeding gas, the oxygen flux that permeates through the bulk of the dense membranes is estimated by subtracting the leaked oxygen flux from the total oxygen flux measured.

Due to the glass sealing method, the gas exposed surface area at the permeate side of the membrane was somewhat reduced compared with that at the feed side. In the present study, the oxygen flux, J$_o$$_2$ (mol/cm$^2$/s), was normalized to the geometric surface area at the permeate side of the membrane. The permeance, F$_o$$_2$ (mol/cm$^2$/s), i.e., the oxygen flux per unit driving force $E$, was calculated from

$$ F_{O_2} = \frac{1}{G} \frac{J_{O_2}}{E} $$

where $G$ is a dimensionless factor that accounts for the above mentioned effect of non-axial diffusion. The value for $G$ can be obtained from a two-dimensional analysis of Fick's diffusion equation (in cylindrical coordinates) solved under the appropriate boundary conditions assuming an isotropic diffusion coefficient [6]. For 1.60, 0.90, 0.60 and 0.23 mm thick specimens, $G$ takes a value of 1.24, 1.13, 1.09 and 1.03, respectively.

The value of electrochemical driving force $E$ was calculated from

$$ E = \frac{RT}{4F'} \ln \frac{p_{O_2}(h)}{p_{O_2}(l)} $$

where $F'$ is the Faraday constant, $p_{O_2}(h)$ and $p_{O_2}(l)$ are the oxygen partial pressures maintained at the feed and permeate side, respectively. Note that the quantity $E$ is synonymous with the effective overvoltage when the composite membrane is viewed as an internally short-circuited oxygen concentration cell. Other parameters in Eq. (2) have their usual meaning.

3. Results and discussion

Fig. 1 gives the Arrhenius plots of the oxygen flux and the calculated permeance for the composite membranes. The oxygen pressure at the feed side was fixed at 0.209 atm by sweeping the membrane surface with air. Typical values for oxygen partial
Fig. 1. Temperature dependence of the (a) oxygen flux and (b) permeance of ( ▲, △) 1.6 mm thick specimen \( [p_{O_2}(l)=0.024 \text{ atm at 850°C}, \ p_{O_2}(l)=0.016 \text{ atm at 750°C}] \), ( ●, ○) 0.90 mm thick specimen \( [p_{O_2}(l)=0.032 \text{ atm at 850°C}, \ p_{O_2}(l)=0.016 \text{ atm at 750°C} ] \), ( ▼, □) 0.60 mm thick specimen \( [p_{O_2}(l)=0.043 \text{ atm at 850°C}, \ p_{O_2}(l)=0.043 \text{ atm at 750°C}] \), ( ■, □) 0.23 mm thick specimen \( [p_{O_2}(l)=0.046 \text{ atm at 850°C}; \ p_{O_2}(l)=0.056 \text{ atm at 750°C}] \). The solid symbols represent the cases that oxygen leakage accounts for less one-third of the oxygen detected at the permeated side.

Pressure at the permeate side, \( p_{O_2}(l) \), are given in the caption of Fig. 1. The solid symbols correspond to the cases that the oxygen flux which permeates through the dense membrane accounts for more than two-thirds of the oxygen detected at low \( p_{O_2}(l) \) side. The open symbols represent the cases that the leaked flux makes up more than one-third of the oxygen detected. The open symbols fall on the same line as the solid symbols, indicating that the applied correction procedure is reliable.

Fig. 1a shows that the dual phase composite membranes are very permeable to oxygen. For the 0.23 mm thick membrane, an oxygen flux of \( 3.08 \times 10^{-7} \text{ mol/cm}^2/\text{s} \) was measured at 852.5°C with \( p_{O_2}(l)=0.046 \text{ atm} \). The estimated value of oxygen flux at 750°C was \( 1.56 \times 10^{-7} \text{ mol/cm}^2/\text{s} \) with \( p_{O_2}(l)=0.056 \text{ atm} \). For the 1.6 mm thick membrane an oxygen flux was observed at 750°C and \( p_{O_2}(l)=0.016 \text{ atm} \), which is 2.7 times of the flux measured for a 2.0 mm thick La\(_{0.5}\)Sr\(_{0.5}\)Co\(_{3-x}\) membrane at the same temperature and \( p_{O_2}(l)=0.021 \text{ atm} \).

It can be seen from Fig. 1b that the permeance for the thin membrane decreases less pronouncedly than that for the thick membrane with decreasing temperature. For 0.23 and 1.60 mm thick membranes, the apparent activation energy calculated from Fig. 1b is 48.9, 75.9 kJ/mol, respectively. The difference in the value of the activation energy indicates the change of the kinetics of the oxygen permeation.

Fig. 2a and b show the permeance against the reciprocal of the membrane thickness at 850 and 750°C, respectively. It is clear that when the membrane thickness is larger than about 1 mm, the permeance is proportional to the reciprocal of the thickness, and the linear part of the line passes through the origin with a slope of \( 1/(4F_n \sigma_{amb}) \), where \( \sigma_{amb} \) is called ‘ambipolar’ conductivity as described in Ref. [6]. This reveals that under the given conditions the oxygen permeation is controlled by the bulk process, i.e., the transport of oxygen ions in the oxide phase is the rate-limiting step. With further decreasing of thickness, the permeance increases less pronouncedly. At 0.23 mm, the permeance value is considerably smaller than the value extrapolated from the linear part of the line. This suggests that the oxygen permeation is partially limited by the surface oxygen exchange process.

It has been established that the extent of the surface limitation can be described in term of interface resistance \( R_s \), which can be calculated from [6,8].
Calculation reveals that for the 0.23 mm thick membrane the surface resistance accounts for 58% and 32% of the total resistance $R$, at 850 and 700°C, respectively. Obviously, the oxygen transport kinetics is jointly controlled by the bulk and surface processes.

The surface oxygen exchange consists of charge and mass transfer steps. Assuming that mass transfer step is rate-limiting, it follows that

\[ \eta = \frac{RT}{4F} \ln \left( 1 - \frac{I}{I_L} \right) \]  
\[ (4) \]

where $\eta$ is the driving force consumed by the surface process, $I$ is the internal current density and $I_L$ the limiting current density. The value of $\eta$ can be calculated using $\eta = 4F'J_{o_2}R_s$. Inserting $I = 4F'J_{o_2}$ and $I_L = 4F'J_L$ into Eq. (4) yields

\[ \eta = \frac{RT}{4F} \ln \left( 1 - \frac{J_{o_2}}{J_L} \right) \]  
\[ (5) \]

where $J_L$ is the limiting oxygen flux.

Fig. 3 shows the Arrhenius plot of the limiting oxygen flux $J_L$. The activation energy was calculated to be 39.1±3.4 kJ/mol, which is much smaller than that for the bulk process (75.9±4.9 kJ/mol). Note that the value of the apparent activation energy related to the permeance of the 0.23 mm thick membrane (48.9 kJ/mol) is in between the values related to the bulk and surface processes. The calculated value for $J_L$ is $0.53 \times 10^{-6}$ mol/cm²/s at 850°C and $0.39 \times 10^{-6}$ mol/cm²/s at 750°C. The as-derived value is at least one order of magnitude higher than the surface oxygen exchange rate for the erbia-stabilized bismuth oxide with sputtered gold electrode determined using oxygen isotope exchange technique [9]. This provides evidence that silver metal possess much higher catalytic activity towards the surface oxygen exchange process than gold metal [4].

The assumption that the mass transfer is the rate-limiting step for the surface process is possible to be
verified with relevant electrochemical technology [10]. If the assumption holds, the as-derived \( J_L \) sets the maximum of the oxygen flux that can be obtained with the given membranes. However, it is possible to increase \( J_L \) by control of the surface microstructure of the membranes.

4. Conclusions

(1) The erbia-stabilized bismuth oxide–silver (40 v/o) composite shows great oxygen permeability. For example, oxygen permeation flux through a 0.23 mm thick membrane can reach \( 0.3 \times 10^{-6} \) mol/cm\(^2\)/s at 852.5°C with \( p_{O_2}(l) = 0.046 \) atm, and \( 0.16 \times 10^{-16} \) mol/cm\(^2\)/s at 750°C with \( p_{O_2}(l) = 0.056 \) atm.

(2) Oxygen transport kinetics is believed to be controlled by the diffusion of oxygen ions in the oxide phase for the membranes with thickness down to about 1.0 mm. As the thickness further decreases, it becomes jointly controlled by bulk and surface processes.

(3) The oxygen surface exchange rate decreases less pronouncedly with decreasing temperature than the diffusion of oxygen ions in the bulk of membranes. The mass transfer is suggested to be the rate-limiting step for the surface process.

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