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Stabilized bismuth oxide–noble metal mixed conducting composites as high temperature oxygen separation membranes

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Oxygen concentration cells, with dense dual phase composite membranes made from erbia-stabilized bismuth oxide and a noble metal (Au, Ag), were investigated in the temperature range 650–850 °C under controlled oxygen partial pressure gradients. An electrochemical treatment was applied to interpretation of the oxygen permeation data. It is found that the composite membranes exhibit high oxygen permeability relative to the single phase bismuth oxide, since oxygen ions and electrons are allowed to transport through the oxide and metal phase, respectively. The oxygen permeability of the silver-containing composite is at least one order higher than that of the gold-containing one, which can be explained by the fact that silver has a higher catalytic activity than gold for the surface oxygen exchange reaction and thus less limitations are exerted on the overall oxygen transport.

Keywords: *dense membranes*, *oxygen permeation*, *stabilized bismuth oxide*, *silver*, *gold*

1. Introduction

Oxygen ion-electron mixed conducting materials hold promise as dense membranes for separation of oxygen from air [1] and manipulation of chemical reactions especially at elevated temperatures such as conversion of methane to synthesis gas (CO/H_2) [2]. Mixed-conducting oxides with the fluorite and perovskite structure have been found to possess good oxygen permeability at elevated temperatures, typically above 700 °C. Besides the high oxygen permeability, membranes should possess sufficient thermodynamic stability over the used ranges of temperature and oxygen activity, chemical stability and compatibility in contact with other membrane components, and mechanical stability [3]. It is difficult to meet all these requirements in one single-phase material. The improvement in some aspects is often accompanied by the deterioration of others. To avoid this dilemma, dual phase composite membranes made from an oxygen-ion conducting oxide and an electron conducting metal have been investigated [4–8]. In this paper, an electrochemical approach is adopted to interpret the results from oxygen permeability measurements on dual phase composites of stabilized bismuth oxide [9] and noble metal.

2. Concept and theory

Figure 1a gives a schematic representation of oxygen permeation through the dual phase composite membrane, in which the composite of erbia-stabilized bismuth oxide and silver is used for the sake of illustration. The equivalent circuit is also given in Fig. 1b, which is established by viewing the oxygen permeation as an electrochemical process [10]. As shown in Fig. 1a, the permeation process consists of transport of oxygen ions and electrons through the respective phase, and oxygen exchange at three-phase boundaries of oxide, metal and gas phase. Each of these steps corresponds to a resistance in the equivalent circuit.

As the oxygen permeation is driven by an oxygen partial pressure difference across the membrane, it is appropriate to express the driving force in terms of

$$E = \frac{\mu_{O_2}(\mathrm{h}) - \mu_{O_2}(\mathrm{l})}{4F'} = \frac{RT}{4F'} \ln \frac{p_{O_2}(\mathrm{h})}{p_{O_2}(\mathrm{l})} \qquad (1)$$

where $\mu_{O_2}(\mathrm{h})$ and $\mu_{O_2}(\mathrm{l})$ are the oxygen chemical potential at the high and low oxygen partial pressure side, respectively, $p_{O_2}(\mathrm{h})$ and $p_{O_2}(\mathrm{l})$ are the respective oxygen partial pressure, F' is the Faraday constant.

With the help of the given equivalent circuit (Fig. 1b), one can arrive at the expression for the internal current circulating in the oxide and metal phase

$$i = \frac{E - |\eta(\mathrm{h})| - |\eta(\mathrm{l})|}{R_e + R_i} \qquad (2)$$

where $\eta(\mathrm{h})$ and $\eta(\mathrm{l})$ are the driving force consumed by the surface process at the high p_{O_2} and low p_{O_2} side,

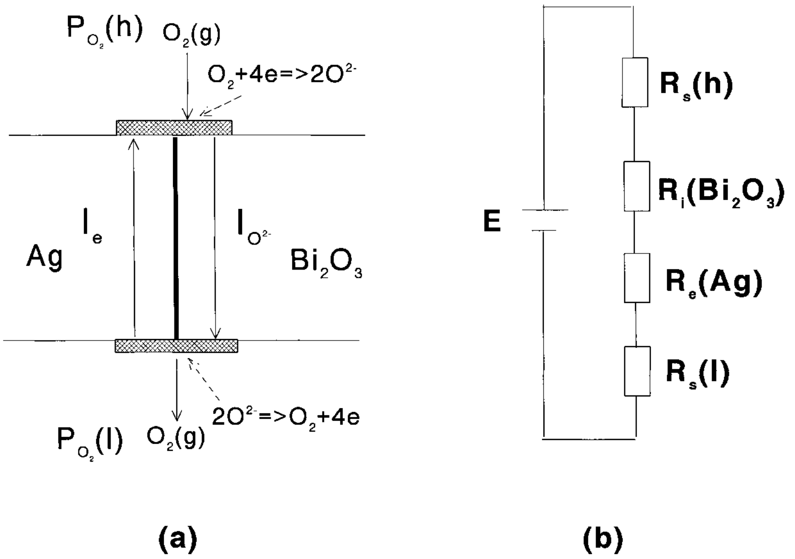

Fig. 1. Schematic representation of oxygen permeation through bismuth oxide–silver composites. (a) Simplified scheme for surface oxygen exchange and bulk transport processes; (b) equivalent circuit for oxygen permeation.

respectively; R_i, R_e are the electronic resistance in the metal phase and the oxygen ionic resistance in the oxide phase.

Inserting $R_i = L/\sigma_i$, $R_e = L/\sigma_e$ into Equation 2 yields

$$i = \frac{\sigma_i \sigma_e}{\sigma_i + \sigma_e} \frac{E - |\eta(l)| - |\eta(h)|}{L} \tag{3}$$

where L is the thickness of the membranes, σ_i and σ_e are the conductivity of the oxide and metal phase, respectively. Note that the term $\sigma_i\sigma_e/(\sigma_i + \sigma_e)$ is usually called the ambipolar conductivity σ_{amp}, which was originally introduced to describe the joint movement of ions and electrons in a medium.

In characterizing the membrane materials, permeation flux J_{O_2} and permeance F_{O_2} (i.e., the flux per unit driving force) are the two key quantities, and in this case they can be connected to the internal current density i and the total resistance R_t via Faraday law:

$$\begin{aligned} J_{O_2} &= \frac{i}{4F'} = \frac{\sigma_{amb}}{4F'L}(E - |\eta(l)| - |\eta(h)|) \\ &= \frac{\sigma_{amb}}{4F'L}\left(\frac{RT}{4F'}\ln\frac{p_{O_2}(h)}{p_{O_2}(l)} - |\eta(l)| - |\eta(h)|\right) \end{aligned} \tag{4}$$

and

$$\begin{aligned} F_{O_2} &= \frac{J_{O_2}}{E} = \frac{i}{4F'E} = \frac{1}{4F'R_t} \\ &= \frac{1}{4F'(R_i + R_e + R_s(h) + R_s(l))} \end{aligned} \tag{5}$$

Equations 4 and 5 provide us fundamental expressions for oxygen permeation through the dual phase composite. Now let us examine the two extreme cases. When the surface oxygen exchange process is sufficiently fast relative to the transport of charged species in the bulk of the membrane (i.e., $\eta(h)$, $\eta(l) = 0$, $R_s(h)$, $R_s(l) = 0$), oxygen permeance is inversely proportional to the bulk resistance and thus the thickness of the membrane. In this case, Equation 4 simplifies to the one for oxygen permeation through the single phase mixed conducting oxide based on Wagner theory [1]. For the other extreme case that the surface oxygen exchange process is much slower than the bulk process, the oxygen permeance is then determined by the surface resistance and thus independent to the thickness of the membrane.

3. Experimental details

3.1. *Sample preparation*

Bismuth oxide powder stabilized with 25 mol % erbia (denoted BE25) was prepared by a solid state reaction [9]. The appropriate amount of gold (Analar, BDH) or silver (Specpure, Johnson-Matthey) powder was mixed in a mortar with BE25 powder to prepare a composite powder containing 40 v/o gold (denoted BEAu40) or silver (denoted BEAg40). The composite powder compacts were sintered in air at 860 °C for 16 h using both heating and cooling rates of 0.3 °C $\min^{-1}$. The sintered samples had 95% of the theoretical density as determined by the Archimedes technique (in mercury). The electrical resistance of the samples measured at room temperature was found to be very small, indicating that a three-dimensional continuous network was formed, thus allowing transport of electrons.

3.2. *Oxygen permeation measurements*

Oxygen permeation experiments were performed with disc-shaped specimens. The gold-containing specimen had a thickness of 1.0 mm and a diameter of 15 mm, and the silver-containing specimen a thickness of 1.6 mm and a diameter of 15 mm. The discs were sealed into a quartz reactor with a volume of about 3 ml using a Pyrex glass ring (trade name Duran, Schott Netherlands BV) by heating to 850 °C in stagnant air. Ambient air was then fed into one side of the disc specimen, while high purity helium (UCAR Specialty Gases NV, $p_{O_2} = 1.1 \times 10^{-4}$ atm) was introduced to the other side to sweep away the permeated oxygen. The oxygen and nitrogen concentrations in the effluent at the gas outlet of the permeate side were measured by gas chromatography (Varian model 3400) with a molecular sieve column (80–100 mesh, 6 ft s.s.). Due to the partial failure of the glass sealing at temperatures below 750 °C, a considerable amount of oxygen leaked into the low p_{O_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 feed gas, the oxygen flux that permeated through the bulk of the dense membranes was estimated by subtracting the leaked oxygen flux from the total oxygen flux measured.

In the permeation cell, the membrane surface area exposed to the gas phase at the permeate side was somewhat reduced compared with that at the feed side due to the glass sealing method. This complicates the flux profile in the bulk of the membrane, and an appropriate data processing method has to be used. In the present study, the oxygen flux, J_{O_2} (mol cm^{-2} s^{-1}), was normalized on the available geometric surface area at the permeate side of the membrane, and the permeance F_{O_2} (mol cm^{-2} s^{-1}) was calculated from

$$F_{O_2} = \frac{1}{G}\frac{J_{O_2}}{E} \tag{6}$$

Where G is a dimensionless factor that accounts for the above mentioned effect of nonaxial diffusion. The values of G were obtained from a two-dimensionless analysis of Fick's diffusion equation (in cylindrical coordinates) solved under the appropriate boundary conditions assuming an isotropic diffusion coefficient [10]. For the 1.6 mm thick silver-containing composite membrane a value of 1.24 for G was calculated. For the 1.0 mm thick gold-containing composite the corresponding value was 1.15.

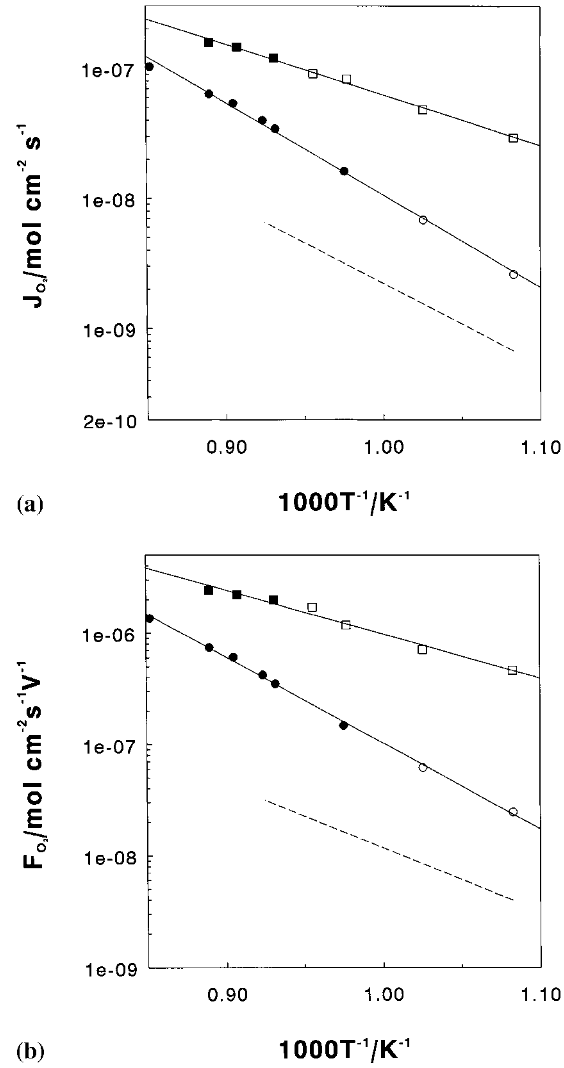

Fig. 2. Temperature dependence of the (a) oxygen flux and (b) permeance of (○, ●) 1.0 mm thick BEAu40 composite (p_{O_2}(l) = 0.0096 atm at 850 °C; p_{O_2}(l) = 0.0021 atm at 750 °C), (□, ■) 1.6 mm thick BEAg40 composite (p_{O_2}(l) = 0.024 atm at 850 °C; p_{O_2}(l) = 0.016 atm at 750 °C). Data obtained for 0.7 mm thick single phase BE25 (p_{O_2}(l) = 0.0001 atm) from previous work [11] is given for comparison (dashed lines). The filled symbols represent the case that the permeate flux rather than leaked flux is dominant, while the open symbols represent the case that considerable amount of oxygen leaked into low pressure side (see also Table 1).

4. Results and discussion

The oxygen permeation flux and the calculated permeance for the 1.0 mm thick gold-containing and the 1.6 mm thick silver-containing composite membranes are plotted in Fig. 2 as a function of temperature. For comparison, the oxygen flux values through a 0.7 mm thick single phase bismuth oxide and the permeance are also given [11]. The oxygen partial pressure at one side of the permeation cell, p_{O_2}(h), was kept at 0.209 atm by passing ambient air, while at the other side the oxygen partial pressure, p_{O_2}(l), was maintained in the range 2.5×10^{-2} to 2.0×10^{-3} atm by sweeping the membrane surface with high purity helium. The given oxygen fluxes have been corrected for the leakage that resulted from the partial failure of the glass sealing. The percentages of the correction can be found in Table 1. The permeated fluxes are dominant for BEAg40 at T ≥ 800 °C and for BEAu40 at T ≥ 750 °C, as marked by the filled symbols in Fig. 2. The open symbols in Fig. 2 represent the case where a considerable amount of oxygen detected at the low p_{O_2} side had leaked from the high p_{O_2} side. The open points fall on the same straight lines as the filled points which gives confidence in the reliability of the applied correction procedure.

As can be seen from Fig. 2, the presence of the percolative metal network in both composite membranes results in a net increase in the oxygen permeation flux. Compared with that observed through the single phase bismuth oxide, the oxygen flux through

Table 1. Relative amount of permeated and leaked oxygen fluxes

BE25/Au (40 v/o)			*BE25/Ag (40 v/o)*		
T /°C	*Perm. flux* /%	*Leaked flux* /%	*T* /°C	*Perm. flux* /%	*Leaked flux* /%
900	100	0			
831	100	0	850	96	4
809	100	0	828	96	4
800	100	0	801	70	30
			773	42	58
752	86	14	750	38	62
702	47	53	702	25	75
650	19	81	650	13	87

the gold-containing composite is less than one order of magnitude higher, while an increase of almost two orders of magnitude occurs for the silver-containing composite. The remarkable difference in the oxygen permeation behaviour for the two composite specimens is also reflected in the corresponding data for oxygen permeance as given in Fig. 2b. For example, at 850 °C, for the silver-containing composite an oxygen flux of 1.6×10^{-7} mol cm^{-2} s^{-1} and 2.5×10^{-6} mol cm^{-2} s^{-1} V^{-1} at $p_{O_2}(\mathrm{l})$ of 0.024 atm was measured, while 6.0×10^{-8} mol^{-1} cm^{-2} s^{-1} and 7.4×10^{-7} mol cm^{-2} s^{-1} V^{-1} was measured for the 1.0 mm gold-containing composite at the same temperature and $p_{O_2}(\mathrm{l}) = 0.0096$ atm. The differences in the oxygen flux and permeance between the two composites become more pronounced with decreasing temperature. At 750 °C a flux of 8.5×10^{-8} mol cm^{-2} s^{-1} and permeance of 1.2×10^{-6} mol cm^{-2} s^{-1} V^{-1} at $p_{O_2}(\mathrm{l})$ of 0.016 atm was obtained for the silver-containing composite, while 1.6×10^{-8} mol cm^{-2} s^{-1} and 1.5×10^{-7} mol cm^{-2} s^{-1} V^{-1} was obtained for the gold-containing composite at the same temperature and $p_{O_2}(\mathrm{l})$ of 0.0021 atm.

The activation energy of 76 ± 5 kJ mol^{-1} calculated from the permeance data for the silver-containing composite is close to the value of 72 ± 4 kJ mol^{-1} obtained from ionic conductivity measurements on the erbia-stabilized oxide BE25 [9]. This is taken as evidence that oxygen permeation through the silver-containing composite is mainly limited by the transport of oxygen ions through the bismuth oxide phase. This judgement is further supported by the inverse proportionality between the permeance and the thickness of the membrane [7]. On the other hand, permeation of oxygen through the gold-containing composite is suggested to be mainly limited by the oxygen exchange at the membrane surfaces, based on the close resemblance between the activation energy 148 ± 3 kJ mol^{-1} obtained from the oxygen permeance data of BEAu40 and the value of 145 ± 7 kJ mol^{-1} derived from exchange current density measurements of Au electrode on BE25 at p_{O_2} of 1.0 atm [12]. These judgements provide a basis for us to describe the bulk and surface transport properties of these two composites quantitatively, as shown below.

4.1. *Effective ionic conductivity of the composites*

For the case that the overall oxygen permeation process is limited by the bulk transport, combining Equations 4 and 5 yields that

$$F_{O_2} = \frac{\sigma_{\mathrm{amb}}}{4F'L} \tag{7}$$

With this equation, the ambipolar conductivity of the membrane can be calculated using permeance data in the bulk controlled region. For the percolative dual phase composites, the electronic conductivity of the metal phase is usually much larger than the ionic conductivity of the oxide; the value of latter is then virtually equal to the ambipolar conductivity. Figure 3 gives the ionic conductivity corrected for the volume fraction of the oxide phase (60 v/o). For comparison, the ionic conductivity of single phase BE25 ceramics is also shown. The effective ionic conductivity of the oxide phase in the composite is smaller than that of single phase bismuth oxide by a factor of about 3. The decrease in ionic conductivity of the oxide in the composite can be attributed to the presence of 'dead ends' and a large tortuosity of the oxygen ion conducting path due to the blocking of the metal phase.

4.2. *Interface resistance of BEAu40 composite*

Silver is by far the best oxygen electrode in terms of polarizability and electrode resistance [13]. It was found that the electrode resistance of silver sputtered electrodes on yttria-stabilized zirconia is much smaller than that of gold sputtered electrodes [14]. This illustrates that silver is very active for surface oxygen exchange while gold is much less active. Oxygen exchange at the surface of the silver-containing composite is thus relatively fast, imposing less limitation on the overall transport process, compared with the use of gold as the metallic phase. Since the catalytic

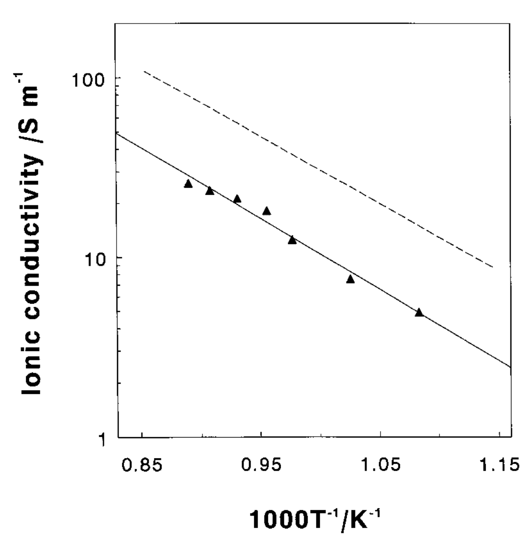

Fig. 3. Temperature dependence of the ionic conductivity of (▲) BEAg40 composite (from this study) and the dashed line is for single phase BE25 ceramics (from [9]).

activity of gold for oxygen exchange is known to be low, oxygen exchange on the gold-containing composite occurs at the bismuth oxide surface which exhibits a considerable activity in oxygen exchange [15].

The extent of the surface limitation can be expressed in terms of interface resistance R_s, which can be calculated from [10, 16]

$$R_s = R_t - \frac{L}{\sigma_{amb}} \quad (8)$$

The value of R_t is given by the ratio of driving force (E) to the internal current density (i) as shown before. The value of R_s can be readily calculated provided that data of the 'ambipolar' conductivity σ_{amb} are available.

For the calculation of R_s for the gold-containing composite, the 'ambipolar' conductivities of the gold and silver-containing composites were assumed to have similar values. The Arrhenius plot of R_s for the BEAu40 membrane is shown in Fig. 4. The activation energy was evaluated to be $156 \pm 3\,\mathrm{kJ\,mol^{-1}}$. The overall oxygen transport process thus turns out to be largely controlled by the surface process at low temperatures. The interface resistance R_s accounts for about 83% of the total resistance R_t at 850 °C, increasing up to a value of 93% at 750 °C. These values fairly agree with those obtained from oxygen pump experiments in which sputtered gold electrodes were used in solid electrolyte [12]. At 637 °C, it was found that between 86–91% of the applied overvoltage was consumed by the surface exchange process [12].

5. Conclusions

The oxygen permeation flux through the erbia-stabilized bismuth oxide electrolyte BE25 increase by introducing of 40 v/o either silver or gold relative to that exhibited by the single phase oxide ceramics. This increase is much more pronounced when silver metal is used to provide a percolative network for electronic conduction. The observed behaviour can be attributed to a greater catalytic activity of silver towards surface oxygen exchange compared with that of gold. As an example, for a 1.6 mm thick silver-containing composite a value of $8.5 \times 10^{-8}\,\mathrm{mol\,cm^2\,s^{-1}}$ was measured at 750 °C with $p_{O_2}(\mathrm{h}) = 0.209$ and $p_{O_2}(\mathrm{l}) = 0.016\,\mathrm{atm}$, while a value of $1.6 \times 10^{-8}\,\mathrm{mol\,cm^{-2}\,s^{-1}}$ was found for a 1.0 mm thick gold-containing composite at the same temperature with $p_{O_2}(\mathrm{h}) = 0.209$ and $p_{O_2}(\mathrm{l}) = 0.016\,\mathrm{atm}$.

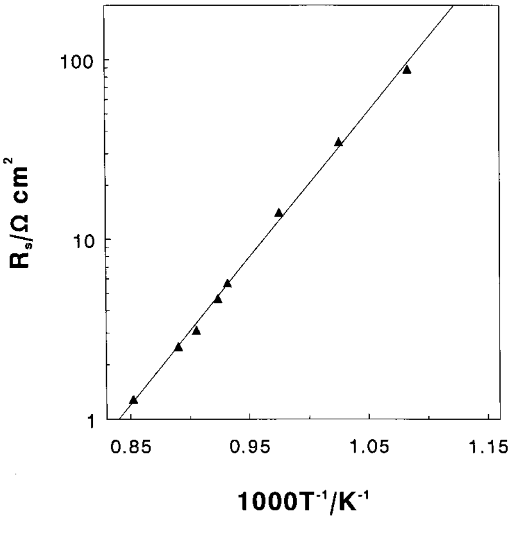

Fig. 4. Temperature dependence of the interface resistance of the BEAu40 composite.

The effective ionic conductivity of the oxide phase in the silver-containing composite is lowered by a factor of about 3 relative to that of single phase bismuth oxide. This behaviour can be attributed to the microstructure of the composite, i.e. the presence of 'dead ends' and the tortuosity of the ion conducting path. The large interfacial resistance calculated for the gold-containing composite confirms that neither gold nor the oxide phase has a sufficient catalytic activity to sustain large oxygen permeation flux.

The present results show that for optimization of oxygen fluxes through composite membranes, in addition to generating continuous pathways for ionic and electronic conduction, at least one of the consistent material should exhibit a large catalytic activity towards oxygen exchange. Provided that its volatility is not a serious problem under actual operating conditions, this work demonstrates that silver is a promising material. Extended research is required to study the performance of such membranes under prolonged use.

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