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Oxygen Permeation Properties of Dense Bi_{1.5}Er_{0.5}O₃-Ag Cermet Membranes

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ABSTRACT

Oxygen permeation experiments were performed on dense mixed-conducting ceramic-metal composite membranes (thickness 0.2 to 2 mm) Bi_{1.5}Er_{0.5}O₃-Ag with 10.0, 27.8, and 40.0 volume percent (v/o) silver, respectively, in the temperature range 873 to 993 K and oxygen partial pressure range 10^{-3.5} to 1 bar O₂. The oxygen fluxes increased with increasing silver content. In the cermets with a nonpercolative silver phase (10.0 and 27.8 v/o), the increased oxygen flux relative to that of pure Bi_{1.5}Er_{0.5}O₃ was attributed to faster kinetics of surface oxygen exchange in the presence of silver. Percolativity of the silver phase in the 40 v/o Ag composition enhances the ambipolar diffusion of oxygen ions and electrons. High oxygen fluxes (~0.25 mmol m⁻² s⁻¹ at 873 K) were observed with the latter composition, which were shown to be fully limited by the surface exchange kinetics. The activation energy for oxygen permeation in the temperature range 848 to 1003 K is about 85 to 95 kJ/mol for the compositions without percolativity of silver and 115 kJ/mol for the composite with 40 v/o Ag, which reflects a change of the rate-limiting step upon passing the percolation threshold. Results from both permeation and isotopic exchange measurements on the composition with Ag percolativity indicated the kinetic order of the surface process in oxygen to be 1/4, indicating a process fundamentally different from that on pure Bi_{1.5}Er_{0.5}O₃.

Introduction

The high-temperature face-centered cubic (fcc) δ -phase of the defect fluorite-type Bi₂O₃ is the best oxygen ion conductor known. Its anomalously high ionic conductivity is related to the cubic crystal structure, the nature of the bismuth ion, and the intrinsically large concentration of vacant sites in the oxygen sublattice, which equals 25% of the total number of crystallographic sites available. The temperature range in which the δ -phase is stable is rather narrow (1002 to 1097 K), and the transition from the δ -phase to the low-temperature α -phase is accompanied by a conductivity decrease of two to three orders of magnitude. The more conductive cubic phase can be stabilized down to room temperature by partial doping with rare earth elements or yttria,¹⁻³ although the conductivity decreases with increasing dopant concentration. The maximum conductivity below the transition temperature of δ -Bi₂O₃ is therefore obtained at the minimum doping level necessary to stabilize the fcc phase.¹ Doping with erbia or yttria has shown the best preservation of ionic conductivity.² The conductivity of compositions Bi_{2-x}(Y,Er)_xO₃ have been investigated extensively.¹⁻⁷ In the Bi_{2-x}Er_xO₃ system, the maximum conductivity is reached at 20 to 25 mole percent (m/o) Er ($x = 0.4$ to 0.5).⁴ The ionic conductivity of Bi_{1.5}Er_{0.5}O₃ (denoted as BE25) has an activation energy of 72 ± 4 kJ/mol above 873 K and reaches an absolute value of $25 \Omega^{-1} \text{ m}^{-1}$ at 973 K. The ionic conductivities of several compositions Bi_{2-x}Y_xO₃ have been shown^{5,6} to be independent of oxygen pressure.

The partial electronic conductivity of Bi_{1.46}Y_{0.54}O₃ at elevated temperatures has been investigated by Takahashi *et al.*⁷ The electronic conductivity, σ_e , is predominantly p-type at high oxygen pressures and has an activation energy, E_{act} , of 106 kJ/mol. In Kröger-Vink notation,⁸ the oxygen incorporation reaction under these conditions can be written as

Since the concentrations of oxygen anions O_O[×] and oxygen vacancies V_O^{••} are virtually constant, it follows that

$$\sigma_e \propto [\text{h}^{\bullet}] \propto p_{\text{O}_2}^{1/4} \quad [2]$$

At low oxygen partial pressures ($p_{\text{O}_2} < 10^{-6}$ to 10^{-8} bar), n-type conductivity with a $-1/4$ dependence on oxygen pressure is predominant ($E_{\text{act}} = 213$ kJ/mol). The literature on Bi₂O₃-based electrolytes has been reviewed recently.⁹

The surface exchange kinetics of BE25 has been investigated by Boukamp *et al.*^{10,11} by means of ¹⁸O/¹⁶O isotopic exchange. The following mechanism was proposed for the dissociative adsorption of oxygen in order to account for the $p_{\text{O}_2}^{1/2}$ dependence of the exchange rate experimentally observed

The second step in this scheme is thought to be rate determining.

The mutual occurrence of ionic and electronic conductivity makes it possible to use these materials as oxygen separation membranes in oxygen pressure gradients. The oxygen semipermeability of 0.2 to 2.85 mm thick dense BE25 membranes has been studied by Bouwmeester *et al.*¹² who found that permeability in the temperature range 883 to 1083 K in air/He gradients is determined partly by bulk diffusion of electron holes and partly by the oxygen exchange process at the gas/solid interfaces. In modeling the data, a $5/8$ power dependence of the oxygen exchange rate on oxygen partial pressure was assumed. Experimentally observed fluxes were in the range 10^{-3} to 0.1 mmol m⁻² s⁻¹.

Enhancement of both the electronic conductivity and the surface exchange of oxygen are therefore required to make application of Bi_{2-x}(Y,Er)_xO₃-based membranes possible. The electronic conductivity can be increased to some extent by partial substitution of bismuth by terbium.¹³ An alternative approach is to disperse a percolative second

phase with high electrical conductivity, *e.g.*, Au or Ag, beyond a critical volume fraction (percolation threshold) in the oxide matrix.¹⁴

Preliminary measurements on both 40 v/o gold and 40 v/o silver-doped Bi₂O₃-based cermets by Chen *et al.*¹⁵ indicated much higher fluxes through the latter. Shen *et al.*¹⁶ found that 33 v/o silver needs to be introduced in Bi_{1.5}Y_{0.5}O₃ in order to obtain percolative networks of both phases. In membrane applications, a particular advantage of the use of silver as the electronically conducting phase is its high activity in the dissociation of molecular oxygen O₂ → 2O_{ads}.¹⁷ Ag is also known to be permeable to oxygen,¹⁸ but the magnitude is negligible in comparison with that of Bi_{2-x}(Y,Er)_xO₃. Oxygen fluxes up to 8 mmol m⁻² s⁻¹ at 1023 K were reported through dense membranes of (Bi_{1.5}Y_{0.5}O₃)_{65v/o}(Ag)_{35v/o} 0.2 to 2 mm thick. Although the fluxes tended to increase with decreasing thickness, the authors showed from the thickness dependence of the permeation flux that a partial rate control was exerted by the surface exchange process for the thinnest specimens used in their study.

The present study investigates the oxygen permeation characteristics of Bi_{1.5}Er_{0.5}O₃-Ag cermet membranes with different silver contents. The attention is mainly focused on the composition with 40.0 v/o, in which the silver phase is percolative.

Modeling of Oxygen Permeation

Bulk diffusion.—Consider a cermet membrane with percolative ionic and electronic conducting phases. If both interfaces are in equilibrium with the imposed ambients (*i.e.*, the surface exchange kinetics are rapid) having oxygen partial pressures p_{ox} and p_{red} , respectively, then the magnitude of the driving force for permeation is the negative of the Nernst potential E .

To maintain overall charge neutrality, the ionic flux through the oxide phase is counterbalanced by that of electrons through the electronically conducting phase in the opposite direction. The ambipolar conductivity σ_{amb} is the effective conductivity originating from this charge-coupled diffusion of ions and electrons and is defined by

$$\frac{1}{\sigma_{amb}} = \frac{\tau_i}{v_i \sigma_i} + \frac{\tau_e}{v_e \sigma_e} \quad [6]$$

in which σ_i and σ_e are the ionic and electronic conductivity of the oxide and metal phase, respectively. v_i and v_e are the volume fractions of the ionic and electronically conducting phases in the composite, and τ_i and τ_e are dimensionless factors to include the effect of geometry on the partial conductivities. Note that this equation is valid only when both phases are percolative. As can be seen from Eq. 6, the value of the ambipolar conductivity is determined by the phase with the smallest effective conductivity. For a percolative metal/ceramic composite, the ionic conductivity of the oxide phase is generally much smaller than the electronic conductivity of the metal phase, in which case $\sigma_{amb} = v_i \sigma_i / \tau_i$.

Under the assumption that the ionic and electronic conductivity are independent of oxygen partial pressure, the net flux of O₂ through the membrane bulk at steady state can be calculated with¹⁹

$$j_{O_2} = \frac{\sigma_{amb}}{4FL} E = \frac{\sigma_{amb}}{4FL} \left(\frac{RT}{4F} \ln \frac{p_{ox}}{p_{red}} \right) \quad [7]$$

where L is the membrane thickness, F is Faraday's constant, and T is temperature.

Surface exchange.—In the absence of an oxygen chemical potential difference, the surface exchange of oxygen will be in a dynamic equilibrium. The net rate of reaction at each interface is zero. The exchange flux j_{ex}^0 generally found under these conditions²⁰ can be expressed by the empirical relationship

$$j_{ex}^0 = j_{ex}^* p_{O_2}^n \quad [8]$$

where n is the apparent kinetic order of the surface reaction and j_{ex}^* is the oxygen exchange rate at 1 bar O₂. Both parameters can be obtained from ¹⁸O/¹⁶O isotopic exchange experiments.

Under nonequilibrium steady-state conditions, there will be an oxygen chemical potential difference between the gas phase and the surface layer. The resulting net transport of oxygen through an interface can be approximated by $j_{O_2} = j_{ex}^* \Delta p_{O_2}^n$, yielding for the feed-side interface of the membrane

$$j_{O_2} = j_{ex}^* (p_{O_2}' - p_{O_2}^n) \quad [9]$$

and for the permeate-side interface of the membrane

$$j_{O_2} = j_{ex}^* (p_{O_2}^n - p_{O_2}') \quad [10]$$

In these equations p_{O_2}' and $p_{O_2}^n$ are the oxygen partial pressures in the ambients at the membrane feed and permeate side, respectively, and p_{ox} and p_{red} are virtual oxygen pressures in the surface layers at feed and permeate side, corresponding to certain local oxygen chemical potentials.

If diffusion is sufficiently fast in the steady state, then the oxygen flux is determined only by the exchange process. Thus $p_{ox} = p_{red}$. It then follows from combination of Eq. 9 and 10 that

$$j_{O_2} = 1/2 j_{ex}^* (p_{O_2}' - p_{O_2}'') \quad [11]$$

To calculate the overall flux through a membrane in which partial rate limitations are exerted by diffusion and exchange, the set of equations 7, 9, and 10 has to be solved simultaneously.

Experimental

Membrane preparation.—Bi_{1.5}Er_{0.5}O₃ powders were prepared by both the conventional ceramic route and the coprecipitation technique reported by Kruidhof *et al.*²¹ The Bi₂O₃/Er₂O₃ mixtures were calcined at 1010 K for 8 h, yielding phase-pure BE25. Calcined BE25 and Ag₂O were mixed and milled in the appropriate ratio in acetone in a planetary mill for several hours to obtain a physical mixture with a median agglomerate size smaller than 5 μm. Compositions containing 10.0, 27.8 and 40.0 v/o Ag were prepared, referred to as BE25Ag10, BE25Ag278, and BE25Ag40, respectively. The powders were pressed uniaxially into pellets having 25 mm diam followed by isostatic pressing at 4000 bar. The pellets were sintered at 1113 to 1123 K for 14 to 16 h (heating/cooling rate 0.5 K/min) and cut into membranes of 14.83 mm diam and thicknesses varying between 0.2 and 2.0 mm. The membranes were polished on both sides with 1000 MESH SiC.

Permeation experiments.—The experimental setup and methods for the oxygen permeation experiments have been described in detail elsewhere.²² The membranes were sealed into the reactor using low-melting glass rings (AR glass) 1 mm thick. The reactor was heated at 3 K/min to 980 to 1000 K, at which temperature it was kept for 1 h to let the glass ring seal the membrane. No reaction was observed between the glass and the membranes. The reactor was then cooled to its lowest operating temperature at 1 K/min. Air or an O₂/N₂ mixture with oxygen partial pressures of 10⁻² to 1 bar was supplied to the feed side of the membrane. Helium was supplied to the permeate side. The concentrations of O₂ and N₂ were measured by a Varian 3300 GC containing a molecular sieve 13X. The oxygen flux was calculated from

$$j_{O_2} = \frac{1}{G} \frac{F c_{O_2}}{A_{He}} \quad [12]$$

F is the flow rate at the outlet of the reactor [m³ s⁻¹ standard temperature, pressure (STP)], c_{O_2} is the oxygen concentration in the effluent stream (mol m⁻³), and A_{He} is the geometric surface area at the helium side of the membrane (1.13 cm²). The dimensionless factor G corrects for the effect of nonradial diffusion, since the applied method of sealing results in different membrane surface areas at opposite sides of the membrane.²³ In the case of surface-

controlled permeation, G is equal to 1 when the limitation occurs at the permeate side, whereas $G = A_{\text{air}}/A_{\text{He}}$ (A_{air} is the geometric surface area at the O_2/N_2 side of the membrane, 1.77 cm^2) upon limitation at the feed side. Details of the calculation of G in case of a diffusion-controlled flux can be found elsewhere.²³ In this study, the value of G is taken to be unity.

Isotopic exchange analysis.—The experimental setup for the $^{18}\text{O}/^{16}\text{O}$ isotopic exchange experiments is described in detail elsewhere.²⁴ Measurements were performed at 873 K at several oxygen pressures in the range 0.15 to 0.88 bar. The samples with geometric surface areas $A = 1.36$ to 1.60 cm^2 (mass 327 to 358 mg) were made from 13.7 to 14.0 mm diam disks that were cut in half. After mechanical polishing to submicron size and ultrasonic cleaning, the samples were placed in a quartz tube with a volume of 54.9 cm^3 and heated to 973 K, where the samples were pre-annealed for 1 h in dry natural oxygen at a pressure of 0.2 bar. The quartz tube was then quenched to room temperature and evacuated. After repeated flushing with AR and evacuating the chamber, an amount of natural oxygen necessary to establish the desired pressure at 873 K was introduced into the tube. The tube was heated quickly to 873 K, at which temperature it was kept for 1 h. Again the tube was rapidly cooled to room temperature and flushed with argon and evacuated several times. Precisely the same amount of gas as in the previous equilibration step, but now from a reservoir with 97.5% ^{18}O -enriched gas, was entered into the tube. The tube was heated quickly to 873 K. The exchange was monitored by measuring the mass 32 ($^{16}\text{O}_2$), 34 ($^{16}\text{O}^{18}\text{O}$), and 36 ($^{18}\text{O}_2$) quadrupole signals. The atomic fraction of ^{18}O in the gas phase at time t was calculated from

$$x_{18}(t) = \frac{p_{18\text{O}_2}(t) + \frac{1}{2}p_{18\text{O}^{16}\text{O}}(t)}{p_{18\text{O}_2}(t) + p_{18\text{O}^{16}\text{O}}(t) + p_{16\text{O}_2}(t)} \quad [13]$$

with $p_{16\text{O}_2}$, $p_{18\text{O}^{16}\text{O}}$, and $p_{18\text{O}_2}$ being the oxygen pressures of the respective isotopic fractions.

Phase analysis and microstructure.—X-ray diffraction (XRD) spectra were taken on a Philips PW1710 with Ni-filtered $\text{Cu K}\alpha$ radiation. The bulk mass concentrations of bismuth and erbium were determined by x-ray fluorescence spectroscopy (XRF) using a Philips PW 1480/10 x-ray spectrometer. The silver content was determined by atomic adsorption spectroscopy (AAS) using a Varian SpectraAA-10. The membrane surface morphology was examined by high-resolution scanning electron microscopy (HR-SEM) using a Hitachi S-800 field emission microscopy operating at 15 kV, which was coupled to a Kevex Delta Range EDX (energy dispersive x-ray analysis) system for surface element analysis.

Results and Discussion

Phase analysis and microstructure.—The densities of the membranes were in the range 96 to 98% of theoretical. XRD spectra of all investigated compositions indicated the presence of two separate phases identified as $\text{Bi}_{1.5}\text{Er}_{0.5}\text{O}_3$ and Ag. No other diffraction peaks were observed. The experimental mass fractions of bismuth and erbium in both freshly prepared and used BE25Ag40 membranes varied between 39.3 to 39.6% and 10.5 to 10.6%, respectively, close to the theoretical values of 39.5 and 10.5%, respectively. The silver fractions as found by AAS were 43.9 and 44.2 mass%, in agreement with the theoretical value of 43.9 mass%.

An SEM picture of the surface structure of a polished BE25Ag40 membrane before use is shown in Fig. 1. EDX analysis indicated the dark parts to be the silver phase and the white areas to be the oxide phase. Figure 2 shows the surface of a membrane exposed to a temperature of 993 K for 2 h. Severe agglomeration of silver on the membrane surface can be observed clearly. When the maximum temperature was kept below 973 K, a much smaller degree of

Fig. 1. SEM picture of a freshly polished BE25Ag40 membrane surface.

Fig. 2. SEM picture of BE25Ag40 membrane surface after thermal treatment at 993 K.

agglomeration was found. The agglomeration is probably due to the nonwetting character of silver and its large diffusivity at these temperatures and may be suppressed by using PdAg alloys instead of pure Ag. The use of these alloys in cermet membranes has already been demonstrated by Shen *et al.*¹⁶

Variation of silver content on flux.—The existence of a percolative silver network was checked for by measuring the dc electrical resistance at room temperature. BE25Ag40 was found to have a resistance of about 0.5 to 3 Ω , while the resistances of the other compositions were in the range 0.1 to 1 M Ω . An electronic short circuit was therefore concluded to exist only in BE25Ag40, which is expected based on the results of Shen *et al.*¹⁶

Arrhenius curves of 0.7 to 0.8 mm thick membranes are given in Fig. 3. All measurements were performed in fixed oxygen partial pressure gradients. The Arrhenius curve obtained by Bouwmeester *et al.*¹² on a 0.7 mm thick BE25 membrane in a 0.15 bar O_2/He gradient is shown for comparison. In comparison with phase-pure BE25, the substitution of 10.0 v/o of ceramic by silver increases the permeation rate by more than half an order of magnitude. Although silver increases the effective electronic conductivity of the bulk, its beneficial effect can only be small because the silver phase is nonpercolative, thus being able to enhance the electronic conductivity only on a microscopic scale. The ambipolar diffusion process will therefore still be limited by the electronic conductivity. For this reason it may be assumed that the major contribution of the substituted silver is its activity in the surface exchange of oxygen. Further addition of silver to a total of 27.8 v/o has a relatively small effect. The rate-determining steps

Fig. 3. Arrhenius curves of 0.7 to 0.8 mm membranes of varying silver content in air/He fixed partial pressure differences. Details in Table I.

are probably the same as in BE25Ag10, so that the increase of the permeation rate compared to that of the latter composition can be attributed mainly to the increased silver concentration at the surface.

Upon increasing the silver content from 27.8 to 40.0 v/o the permeation rate increases by almost an order of magnitude. This can be understood by considering that the silver phase becomes continuous upon passing the percolation threshold at 33 to 35 v/o Ag,¹⁶ thus creating a continuous path for transport of electronic species parallel to that in the BE25 phase but with a much large conductivity. Under these conditions, it can safely be assumed that $\sigma_{\text{amb}} = v_i \sigma_i / \tau_i$, i.e., the rate-determining effect due to a limited electron hole conduction in the oxide phase is eliminated.

Calculated activation energies and experimental condition are listed in Table I. Based on these results, a distinction can be made between phase-pure BE25, the nonpercolative Ag-doped compositions, and percolative BE25Ag40. Doping with small amounts of silver (below the percolation threshold) causes a fundamentally different exchange mechanism that on pure BE25, which is reflected in a decrease of the apparent activation energy. Upon passing the percolation threshold, the ambipolar diffusion process becomes enhanced considerably as an electronic short circuit now exists in the bulk. The ambipolar diffusion process changes from being governed by the electronic conductivity to being governed by the ionic conductivity, which is reflected in an increase of the activation energy to 116 kJ/mol.

It follows from Eq. 7 that for a diffusion-controlled flux the activation energy of j_{O_2} is the same as that of the ambipolar conductivity, i.e., the ionic conductivity in the case of BE25Ag40. Verkerk *et al.*⁴ reported an activation energy of 72 kJ/mol for the ionic conductivity of BE25. As the value derived from oxygen permeation measurements through BE25Ag40 is much higher, this implies the involvement of a process other than diffusion to control (partially) the flux.

Influence of thickness on flux.—Oxygen fluxes through BE25Ag40 membranes at 873 K are shown *vs.* the reciprocal thickness in Fig. 4. The partial pressure difference was fixed at 0.21 (air)/0.003 bar O₂. The flux of $0.24 \pm 0.04 \text{ mmol m}^{-2} \text{ s}^{-1}$ remains constant with decreasing thickness, indicating a surface-exchange-limited flux within experimental error.

Table I. Activation energies of oxygen semipermeability of 0.7 to 0.8 mm thick membranes with varying silver contents.

$V_{\text{Ag}} (\%)$	$L (\text{mm})$	$-\log(p_{\text{O}_2}''/\text{bar})$	$E_{\text{act}} (\text{kJ/mol})$
0.0	0.70		121 ± 4
10.0	0.77	2.70 to 2.80	88 ± 10
27.8	0.79	2.80	95 ± 1
40.0	0.75	2.25	116 ± 9

Fig. 4. Thickness dependence of oxygen flux of BE25Ag40 membranes at 873 K in fixed air/0.003 bar O₂ partial pressure difference.

The permeance, defined as the ratio of flux and driving force, j_{O_2}/E , is $2.9 \pm 0.5 \text{ mmol m}^{-2} \text{ s}^{-1} \text{ V}^{-1}$ at this temperature, much smaller than the value of $22.1 \text{ mmol m}^{-2} \text{ s}^{-1} \text{ V}^{-1}$ that can be calculated from the data of Shen *et al.*¹⁶ for 0.2 mm thick $(\text{Bi}_{1.5}\text{Y}_{0.5}\text{O}_3)_{65\text{v/o}}(\text{Ag})_{35\text{v/o}}$ under similar conditions. The reason for this large discrepancy is not clear.

Effect of oxygen pressure on flux.—The effect of variation of the feed-side pressure on the flux (the permeate-side pressure was kept constant) through BE25Ag40 is shown in Fig. 5. Assuming the permeation rate to be controlled by the surface exchange process only, the experimental data were fitted to Eq. 11. The best fits yielded values $n = 0.26, 0.27$, and 0.23 , at 873, 913, and 953 K, respectively, suggesting that $n = 1/4$. The data were then fitted to $j_{\text{O}_2} = 1/2 j_{\text{ex}}^* [(p_{\text{O}_2}')^{1/4} - (p_{\text{O}_2}'')^{1/4}]$, as shown graphically in Fig. 5b. The same pressure dependence was found for other membrane thicknesses.

In Fig. 6 the permeate side dependence of BE25Ag40 is shown when air was supplied to the feed side. The drawn

Fig. 5. Feed-side pressure dependence of oxygen flux of 1.02 mm BE25Ag40 membrane.

Fig. 6. Permeate-side pressure dependence of oxygen flux through 1.03 mm BE25Ag40 membrane.

lines indicate the best fits of Eq. 11 with $n = 1/4$ to the experimental data. Oxygen exchange rates j_{ex}^* determined from pressure variation experiments are listed in Table II.

Results of feed-side-pressure variation experiments on nonpercolative BE25Ag278 at 953 K are shown in Fig. 7. The best fits to Eq. 11 with $n = 1/4$ are indicated by drawn lines in the figure. As demonstrated earlier, it is plausible that ambipolar diffusion in the oxide phase exerts a partial control of the permeation rate through the nonpercolative Ag-containing compositions. Taking into account that in the oxide phase $\sigma_e \ll \sigma_i$ and $\sigma_e \propto p_{O_2}^{1/4}$, the rate of diffusion will be governed by electron hole conductivity and thus be proportional to $p_{O_2}^{1/4}$.¹² Furthermore, under the assumption that the surface process is essentially the same as on BE25Ag40, a 1/4 power dependence on oxygen pressure is expected for the surface reaction rate as well. No conclusion can therefore be drawn about the nature of the rate-determining step for BE25Ag278 based on oxygen pressure variation.

Isotopic exchange.—Oxygen isotopic exchange analysis was performed on percolative BE25Ag40 to verify the indications of an exchange-controlled flux described previously. An equilibration of isotopic fractions between the gas and solid phase that is completely rate-determined by the surface exchange reaction follows first-order kinetics. For the atomic fraction of ^{18}O in the gas phase it can be shown²⁴ that

$$x_{18}(t) = x_{18}(\infty) + [x_{18}(0) - x_{18}(\infty)] \exp \left[-A r_s \left(\frac{1}{n_{ox}} + \frac{1}{n_{gas}} \right) t \right] \quad [14]$$

where n_{ox} is half the total number of moles O^{2-} in the bulk, n_{gas} the total number of moles O_2 in the surrounding gas phase, r_s the equilibrium exchange rate, and A the sample surface area. Figure 8 displays an exchange curve of BE25Ag40 in the form $\ln[(x_{18}(t) - x_{18}(\infty))/(x_{18}(0) - x_{18}(\infty))]$ vs. t . The absence of a deviation from linearity indicates that diffusion does not exert a partial rate limitation.

Calculated values of r_s at 873 K at selected oxygen pressures are given in Fig. 9. The best fit to the data, indicated by the drawn line, has a slope $n = 0.30 \pm 0.08$, reasonably close to 1/4. The exchange rate $j_{ex}^* = 0.56 \pm$

Table II. Oxygen exchange rates j_{ex}^* (mmol m⁻² s⁻¹) on BE25Ag40 at 1 bar O₂ determined from oxygen permeation and isotopic exchange experiments.

T (K)	Permeation measurements	Isotopic exchange	Feed-side permeate-side
873	0.55 ± 0.03	0.54 ± 0.02	0.56 ± 0.08
913	1.43 ± 0.05	1.20 ± 0.12	
953	2.43 ± 0.06	2.37 ± 0.16	
993		3.69 ± 0.30

Fig. 7. Feed-side pressure dependence of oxygen flux of 0.79 mm BE25Ag278 membrane at 953 K.

0.08 mmol m⁻² s⁻¹ at 873 K, in very close agreement with the exchange rates determined from permeation data listed in Table II.

One may speculate about the nature of the rate-determining step in the exchange mechanism. For instance, the 1/4 power dependence can be explained by assuming the rate-determining step to involve surface diffusion of electron holes on the BE25 surface. The observed activation energy of 116 ± 9 kJ/mol is close to the value of 106 kJ/mol reported for electron hole conduction in Bi_{1.5}Y_{0.5}O₃.¹⁷ However, surface diffusion of adsorbed O⁻ species would also be in agreement with the observed kinetic order. Additional work is required to gain more insight into the mechanism of the surface oxygen exchange mechanism.

Conclusions

Oxygen permeation experiments were conducted on BE25Ag10, BE25Ag278, and BE25Ag40 membranes, with a relative density of 97 to 98%, thickness in the range 0.2 to 2.0 mm, under various p_{O_2} differences. The observed

Fig. 8. Decay curve of ^{18}O gas-phase atomic fraction $x_{18}(t)$ in isotopic equilibration of BE25Ag40 at 873 K.

Fig. 9. Oxygen exchange rates obtained from $^{18}\text{O}/^{16}\text{O}$ isotopic exchange at 873 K and various pressures. The best fit to the data, indicated by a drawn line, has a slope $n = 0.30 \pm 0.08$.

fluxes increased with increasing fraction of silver. The oxygen flux through BE25Ag10 and BE25Ag278 is at least partly determined by diffusion of electron holes through the BE25 oxide phase. The activation energies for oxygen permeation for these compositions is in the range 80 to 100 kJ/mol.

The flux through BE25Ag40 membranes is entirely limited by the surface kinetics. At 873 K the permeance is $2.9 \pm 0.5 \text{ mmol m}^{-2} \text{ s}^{-1} \text{ V}^{-1}$. The ambipolar diffusion in BE25Ag40 is high due to the percolativity of the silver phase, which allows fast transport of electrons. The activation energy for the surface exchange process is $116 \pm 9 \text{ kJ/mol}$. Both oxygen permeation and isotopic exchange experiments on BE25Ag40 indicate an oxygen pressure dependence of $n = 1/4$ for the oxygen exchange rate. This value indicates that the surface process is different from that observed on pure BE25, where $n = 1/2$.

Acknowledgments

The support of the Commission of the European Communities in the framework of the Joule programme, sub-programme Energy from Fossil Resources, Hydrocarbons, is gratefully acknowledged.

Manuscript submitted April 21, 1997; revised manuscript received Sept. 10, 1997.

The University of Twente assisted in meeting the publication costs of this article.

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ERRATUM

In the article, "The Effect of Salt Concentration in Electrolytes on the Maximum Energy Storage for Double Layer Capacitors," by J. P. Zheng and T. R. Jow [*This Journal*, Vol. 144, No. 7, pp. 2417-2420 (1997)], the following corrections should be made. On p. 2417 after Eq. 1b, $C = 1/4c_p\Omega_e$. Seven lines below that, the sentence which describes Eq. 2a and b should read, "On the other hand, the energy density, E_b , and the total energy, U_b , based on the electrolyte only are limited by the ion concentration or the quantity of free ions in the electrolyte and can be expressed, respectively, as Eq. 2a and 2b." In the Experimental section, the unit for the thickness of the carbon electrode was about 76 μm and the porous paper used as the separator was 50 μm thick. In the Results and

Discussion section, on p. 2419, right column, the last line of the continued paragraph should read "...words, the value of α in Eq. 2a should be less than 1." Thirteen lines from the bottom of the same page, the value of the salt concentration should be 0.2 M and two lines from the bottom, the high salt concentration should be $> 0.2 \text{ M}$. The publication information for Ref. 2 is J. P. Zheng, J. Huang, and T. R. Jow, *This Journal*, **144**, 2026 (1997) and for Ref. 3 is *J. Power Sources*, **62**, 155 (1996). The present address for T. R. Jow is the Army Research Laboratory, Sensors and Electron Directorate, Attn: AMSRL-SE-DC, Adelphi, MD 20783-1197, USA. The present address for J. P. Zheng is FAMU-FSU, College of Engineering, Tallahassee, FL 32310-6046, USA.