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MIXED-CONDUCTING OXIDES FOR GAS SEPARATION APPLICATIONS

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ABSTRACT

Mixed-conducting oxides are attracting increased attention because of their potential uses in high-temperature electrochemical applications such as solid-oxide fuel cells, batteries, sensors, and gas-permeable membranes. We are developing mixed-conducting, dense ceramic membranes to selectively transport oxygen and hydrogen. Ceramic membranes made of Sr-Fe-Co oxide (SFC), which exhibits high combined electronic and oxygen ionic conductivities, can be used to selectively transport oxygen during the partial oxidation of methane to synthesis gas (syngas, a mixture of CO and H_2). Steady-state oxygen permeability of $SrFeCo_{0.5}O_x$ has been measured as a function of oxygen-partial-pressure gradient and temperature. At 900°C, oxygen permeability was ≈ 2.5 scc·cm^{-2}·min^{-1} for a 2.9-mm-thick membrane, and this value increases as membrane thickness decreases. We have fabricated tubular $SrFeCo_{0.5}O_x$ membranes and operated them at 900°C for >1000 h during conversion of methane into syngas. Yttria-doped $BaCeO_3$ (BCY) is a good protonic conductor; however, its lack of electronic conductivity can potentially limit its hydrogen permeability. To enhance the electronic conductivity and thus improve hydrogen permeation, a membrane composite material was developed. Nongalvanic permeation of hydrogen through the composite membrane was characterized as a function of thickness.

Key words: Mixed-Conductor, Gas Separation, Oxygen Permeation, Hydrogen Permeation, Ceramic Membrane

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1. INTRODUCTION

In recent years, mixed-conducting oxides, in which both ionic and electronic charge carriers exist, have received increased attention because of their technological importance in high-temperature electrochemical devices and in electrocatalysis. For example, they are used as sensors and as electrodes in solid-state fuel cells; if their ionic conductivity is high enough, they can be used as dense membranes for gas separation. It is generally accepted that mixed-conducting oxide membranes have great potential to meet the needs of many segments of the oxygen market. The applications envisioned a range from small-scale oxygen pumps for medical applications to large-scale usage in combustion processes such as coal liquefaction.

In the early 1980s, Iwahara et al. [1-3] first reported protonic conduction in $SrCeO_3$ materials. Later, the $BaCeO_3$ system was extensively studied because of its higher conductivities [4-7]. Following their discovery by Teraoka et al. [8,9] in the late 1980s, mixed-conducting perovskites with combined electronic and oxide ionic conductivities and appreciable oxygen permeability were investigated [10-15]. Recently, Balachandran et al. [16,17] have shown that $SrFeCo_{0.5}O_x$ (SFC) exhibits not only high combined electronic and oxygen ionic conductivities but also structural stability. Extruded tubes of these materials have been evaluated in a reactor operating at ≈850°C to convert methane to syngas in the presence of a reforming catalyst. Methane conversion coefficients >98% were observed [18,19], and some of the reactor tubes have been operated for more than 1000 h.

In this paper, we report our recent results on the oxygen permeable SFC membranes and hydrogen permeable $BaCe_{0.8}Y_{0.2}O_3$ (BCY) composite membranes. Oxygen permeation flux was measured as a function of differential oxygen partial pressure (Δp_{O_2}) and temperature. Oxygen permeation data from an actual methane conversion reactor was compared with the steady-state oxygen permeation data that were obtained with a gas-tight electrochemical cell. The permeation rate of hydrogen through a BCY composite membrane is presented as a function of membrane thickness to determine the relative importance of bulk and interfacial properties.

2. EXPERIMENTAL

Oxygen-permeable SFC samples were prepared by a solid-state reaction method, with $SrCO_3$, Fe_2O_3, and $Co(NO_3)_2{\cdot}6H_2O$ used as starting materials. Mixing and grinding were performed in isopropanol with zirconia media. After drying, the mixtures were calcined at ≈850°C for 16 h in air with intermittent grinding. Phase purity was confirmed by X-ray diffraction (XRD). The resultant powders were pressed into pellets and sintered in air at 1200°C for 5 h. Sintered pellets were polished and used for permeation tests. Proton conducting BCY was also prepared by mixing the appropriate amounts of $BaCO_3$, CeO_2, and Y_2O_3 and then calcining the mixture at 1000°C for 12 h in air. The obtained powder was ball-milled and recalcined at 1200°C for 10 h in air. Metal powder was added to the resulting powder to increase electronic conductivity, and the mixture was pressed with a 100-MPa load into pellets of ≈22.5 mm in diameter and ≈2 mm thick. The pellets were then sintered at 1550°C for 5 h in an atmosphere of 4% hydrogen balanced with argon.

Total and ionic conductivities of SFC were measured as a function of p_{O_2} by using the conventional four-probe and electron-blocking four-probe methods [17,20]. The experimental setup used to study oxygen permeation of SFC membranes has been reported earlier [21]. A sintered pellet of SFC was sealed to an yttria-stabilized zirconia (YSZ) crucible by a Pyrex glass seal. Two electrodes were placed on the bottom and side of the YSZ crucible, respectively, and serve as oxygen pump and oxygen sensor. The p_{O_2} inside the cell can be determined from the electromotive force (EMF), E, generated on the side-wall electrodes (sensor) by solving the equation

$$p_{O_2}^{II} = p_{O_2}^{I} \exp\left(\frac{4FE}{RT}\right) \qquad (1)$$

where $p_{O_2}^{II}$ and $p_{O_2}^{I}$ are the p_{O_2} values inside and outside the gas-tight cell, respectively. Other variables are as usual, i.e., F, Faraday's constant; R, gas constant; and T, absolute temperature.

The experimental setup for investigating proton transport in the BCY samples has been reported elsewhere [22]. Composite BCY samples of three thicknesses were tested. 4% hydrogen (balanced with argon) was used as feeding gas, and 99.999% argon was used as sweeping gas. Hydrogen flux through the membrane was measured by gas chromatography.

3. RESULTS AND DISCUSSION

Using the conventional four-probe and electron-blocking four-probe methods, we measured the total and ionic conductivities of SFC. Ionic transference number can be deduced from ionic conductivity divided by the total conductivity. The total and ionic conductivities and the ionic transference number of SFC in air are plotted in Fig. 1 as a function of temperature. Conductivities increase with increasing temperature, whereas the ionic transference number is almost independent of temperature. At 800°C in air, the total conductivity and oxygen ionic conductivity are ≈17 and 7 $S{\cdot}cm^{-1}$, respectively, which leads to an ionic transference number of ≈0.4. This result indicates that the electronic and ionic conductivities of the SFC sample are comparable, i.e., their ratio is close to unity. Thus the SFC materials are unique among other mixed conductors, in which electronic transference numbers are much greater than ionic transference numbers, or vice versa.

The oxygen permeation flux j_{O_2} through a membrane of thickness L can be deduced from conductivity data [20] as follows:

$$j_{O_2} = \frac{RT}{16F^2L} \int_{p^{I}_{O_2}}^{p^{II}_{O_2}} \sigma_{tot} t_{ion} t_{el} \, d\ln(p_{O_2}) \qquad (2)$$

where σ_{tot} is total conductivity, t_{ion} is ionic transference number, and t_{el} is electronic transference number. The oxygen permeability of SFC was determined

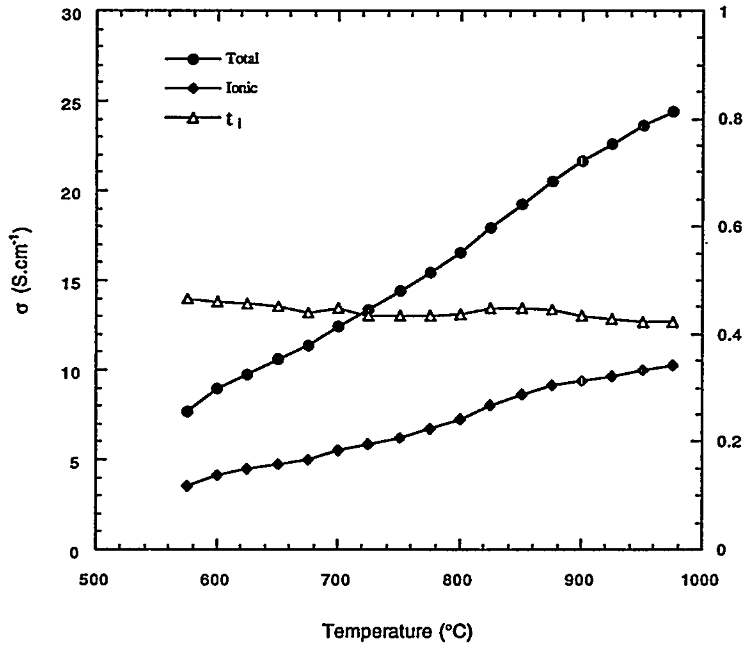

Figure 1. Temperature dependence of total conductivity ionic conductivity and ionic transference number for SFC in air.

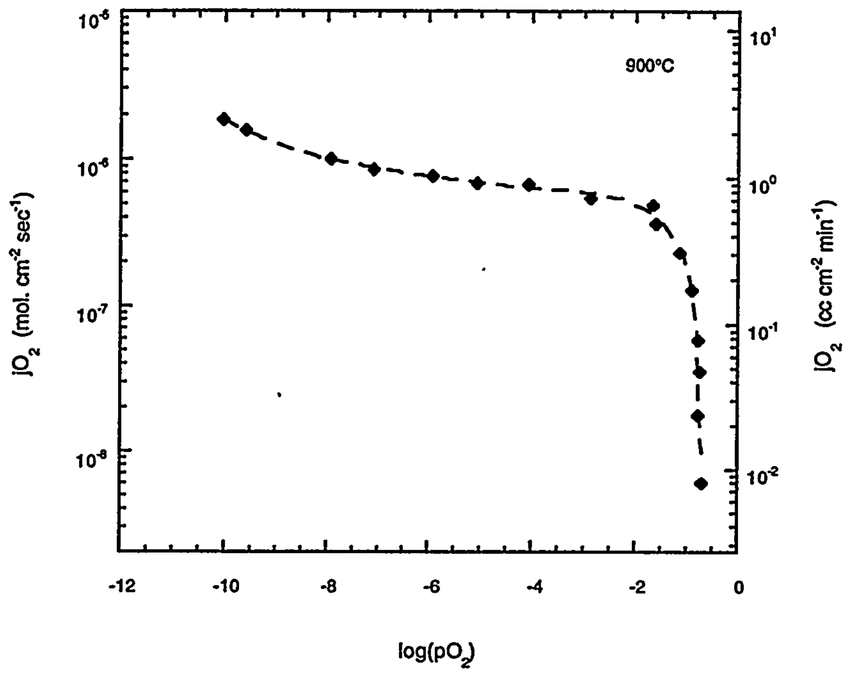

Figure 2. Oxygen permeation flux as a function of oxygen partial pressure inside a gas-tight cell. Specimen thickness = 2.9 mm.

with a gas-tight cell that was described earlier [20]. Reducing oxygen environments were achieved by pumping oxygen out of the gas-tight cell by pumping electrodes on the YSZ crucible. Oxygen permeates the SFC disk membrane because of the p_{O_2} difference on the two sides of the specimen disk. Under steady-state conditions, the amount of oxygen that enters the cell (by permeating the specimen disk) is equal to that pumped out by the YSZ oxygen pump. Therefore, the flow of oxygen through the specimen can be determined from the current applied to the YSZ oxygen pump. Oxygen permeation flux j_{O_2} is related to the applied current I as follows:

$$j_{O_2} = \frac{I}{4FS} \qquad (3)$$

where S is the effective cross-sectional area of the specimen.

Oxygen permeation flux through a 2.9-mm-thick SFC disk, obtained from Eq. 3, the experimental data of a steady-state pumping current I, and geometric parameters of the specimen, is plotted in Fig. 2 as a function of the p_{O_2} inside the gas-tight cell. Flowing air (p_{O_2} = 0.21 atm) was the reference atmosphere during oxygen permeation experiments. Figure 2 shows that j_{O_2} increases dramatically in the range between p_{O_2} = 0.21 and ≈10^{-3} atm, and its slope becomes flatter when p_{O_2} inside the cell is reduced further. Results on oxygen permeability at various p_{O_2} gradients and temperatures show that j_{O_2} increases, as expected, with temperature and p_{O_2} gradients. At 900°C, the oxygen permeability was ≈2.5 ssc·cm^{-2}·min^{-1} for a 2.9-mm-thick specimen and increases as membrane thickness decreases.

Sintered thin-wall tubes of SFC were tested in a methane conversion reactor for >1000 h [18,19,23]. Oxygen permeation flux determined from reactor experiments (with tubular SFC membrane) [23] and that determined using a gas-tight electrochemical cell have been plotted in Fig. 3 as a function of temperature. Results from these two experiments are in good agreement.

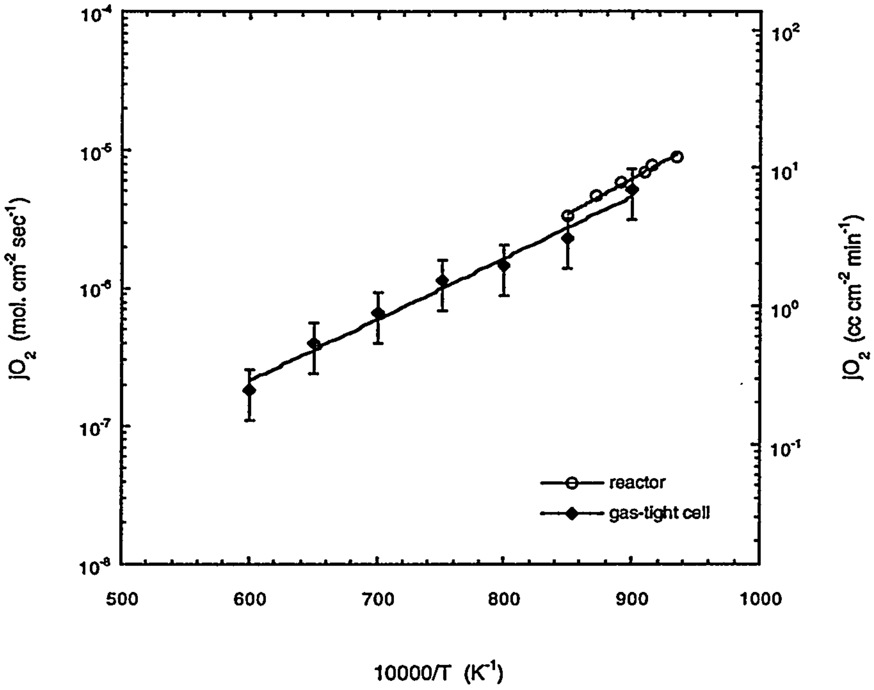

Figure 3. Temperature dependence of oxygen permeation flux determined by two independent methods.

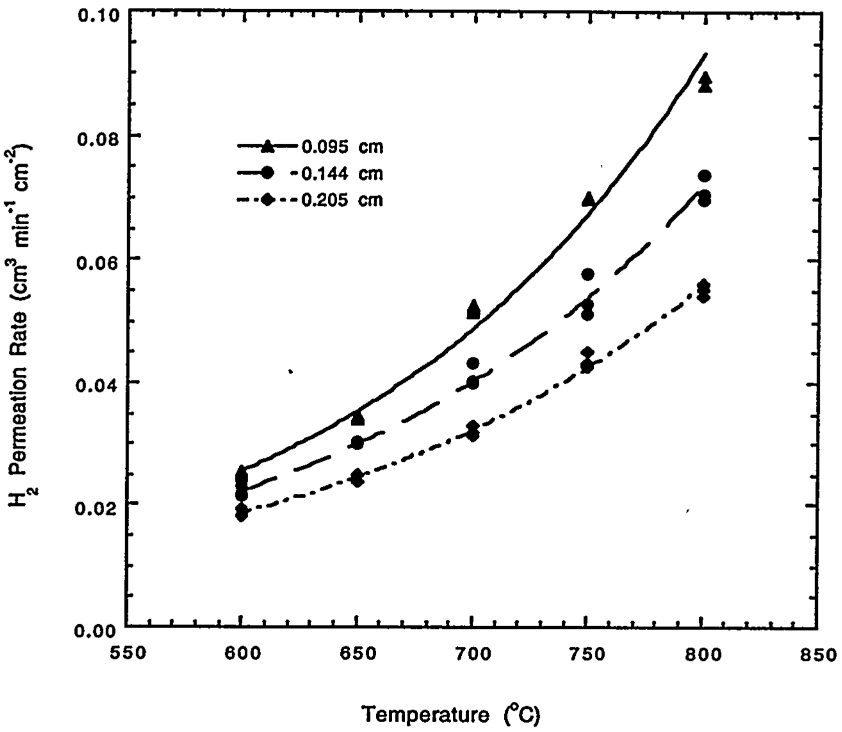

Figure 4. Temperature dependence of hydrogen permeation rate through BCY composite membranes with 4% H_2 (balanced with argon) as feed gas and argon as sweep gas.

Analogous to oxygen permeation flux (given in Eq. 2), the hydrogen permeation flux through a bulk property controlled proton permeable membrane can be written as follows:

$$j_{H_2} = \frac{RT}{4F^2L}\int_{p_{H_2}^{I}}^{p_{H_2}^{II}} \sigma_{tot} t_{ion} t_{el} d\ln(p_{H_2}) \qquad (4)$$

where σ_{tot} is the total conductivity, t_{ion} is the ionic transference number, and t_{el} is the electronic transference number. Other parameters have their usual meaning. Under constant hydrogen partial pressure difference, the hydrogen flux through a membrane would be optimized if the electronic and protonic transference numbers of the composite BCY material were both equal to 0.5. In a hydrogen-containing environment, the protonic transference number of BCY is 3-10 times greater than its electronic transference number. To increase the electronic conductivity of the material, we added metal powder to BCY material to form a composite membrane. The hydrogen permeation rate for such composite membranes of three thicknesses is shown in Fig. 4 as a function of temperature. Plotting the permeation rate against the inverse of sample thickness [22] indicates that the ambipolar conductivity increased while the interfacial polarization resistance decreased dramatically as temperature increased from 600 to 800°C. At 800°C, the bulk resistance is much greater than the interfacial resistance (for sample thickness of >1 mm), whereas the interfacial resistance dominates at low temperature (<600°C). This finding implies that the permeation rate could be increased by reducing the membrane thickness for gas separations that are performed at high temperatures but would be less affected at low temperatures.

4. CONCLUSIONS

We developed a mixed-conducting ceramic membrane material, $SrFeCo_{0.5}O_x$ (SFC) that exhibits high electronic and oxygen ionic conductivities, and has electronic and ionic transference numbers that are comparable to each other, making it unique among other mixed conductors. The oxygen permeability of membranes made of the SFC material is high. Direct measurement of oxygen permeation flux with a gas-tight electrochemical cell agrees well with values obtained from other oxygen permeation experiments and with values calculated from conductivity data. At 900°C, oxygen permeation flux, as determined with a gas-tight electrochemical cell, was ≈ 2.5 $scc \cdot cm^{-2} \cdot min^{-1}$ for a 2.9-mm-thick specimen. Oxygen permeability of the SFC membranes increases with increasing temperature and decreasing membrane thickness.

Measurement of hydrogen permeation rate through BCY/metal membranes showed that interfacial polarization is significant at lower temperatures ($T < 600°C$) but decreases dramatically at higher temperatures. Decreasing the membrane thickness may increase the permeation rate for high temperature separations, but would have smaller effect for separations performed at lower temperatures.

5. ACKNOWLEDGMENTS

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