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DISCLAIMER

DEVELOPMENT OF MIXED-CONDUCTING CERAMICS FOR GAS SEPARATION APPLICATIONS

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ABSTRACT

Mixed-conducting oxides are used in many applications, including fuel cells, gas separation membranes, sensors, and electrocatalysis. This paper describes mixed-conducting ceramic membranes that are being developed to selectively remove oxygen and hydrogen from gas streams in a nongalvanic mode of operation (i.e., with no electrodes or external power supply). Because of its high combined electronic/ionic conductivity and significant oxygen permeability, the mixed-conducting Sr-Fe-Co oxide (SFC) has been developed for high-purity oxygen separation and/or partial oxidation of methane to synthesis gas, i.e., syngas, a mixture of carbon monoxide and hydrogen. The electronic and ionic conductivities of SFC were found to be comparable in magnitude and are presented as a function of temperature. The oxygen flux through dense SFC tubes during separation of oxygen from air is compared with the oxygen flux during methane conversion.

Unlike SFC, in which the ionic and electronic conductivities are nearly equivalent, $BaCe_{0.80}Y_{0.20}O_3$ (BCY) exhibits protonic conductivity that is significantly higher than its electronic conductivity. To enhance the electronic conductivity and increase hydrogen permeation, metal powder was combined with the BCY to form a cermet membrane. Nongalvanic permeation of hydrogen through the cermet membrane was demonstrated and characterized as a function of membrane thickness. A sintering aid was developed to avoid interconnected porosity in and improve the mechanical properties of the cermet membrane.

INTRODUCTION

Mixed-conducting oxides, with both ionic and electronic charge carriers, have received increased attention in recent years because they are technologically important in electrocatalysis and high-temperature electrochemical devices such as sensors and electrodes in solid-state fuel cells. If the ionic conductivity of these oxides is high enough, they can be used as dense membranes for gas separation; if the electronic and ionic conductivities are adequate, they can be used to separate gases nongalvanically, i.e., without the need for electrodes or an external power supply. It is generally accepted that dense, mixed-conducting, oxygen-permeable membranes have great potential to meet the needs of many segments of the oxygen market. The envisioned applications range from small-scale oxygen pumps for medical applications to large-scale usage in combustion processes such as coal liquefaction. Dense, mixed protonic/electronic conductors are likewise being considered as high temperature membranes for separating hydrogen from coal gasification and other partial-oxidation-product streams.

Iwahara and coworkers [1] first reported protonic conduction in $SrCeO_3$-based materials in the early 1980s. $BaCeO_3$-based materials, which were later found to exhibit higher conductivities, have been extensively studied [2-3]. Discovered in the late 1980s by Teraoka et al. [4], perovskites with mixed electronic and oxygen ionic conductivities and appreciable oxygen permeability were investigated [5-7] but were found to be rather unstable. Recently, Balachandran and coworkers [8] showed that $SrFeCo_{0.5}O_x$ oxide (SFC) exhibits not only high

combined electronic and oxygen ionic conductivities but also structural stability. Extruded SFC tubes have been evaluated in a reactor that was operated at ≈850°C to convert methane to synthesis gas (syngas) in the presence of a reforming catalyst; methane conversion coefficients of >98% [9] were observed, and some of the reactor tubes were operated for more than 1000 h.

This paper reports recent results on oxygen-permeable SFC and hydrogen-permeable $BaCe_{0.80}Y_{0.20}O_3$ (BCY) membranes. The electronic and ionic conductivities of SFC materials were measured, and the oxygen permeation rate through dense tubes is reported. To compare the relative importance of bulk and interfacial properties, the permeation rate of hydrogen through BCY/metal composites is presented as a function of membrane thickness. Hydrogen permeation rates measured for BCY/metal composite membranes with a range of sintering-aid concentrations, show that membrane density can be increased without degrading performance.

EXPERIMENTAL

Using $SrCO_3$, Fe_2O_3, and $Co(NO_3)_2 \cdot 6H_2O$ as starting materials, we prepared SFC samples by solid-state reaction. A mixture made from appropriate amounts of the starting materials was calcined at ≈850°C for 16 h in air with intermittent grinding. After obtaining powder with good phase purity (as determined by X-ray diffraction [XRD]) the resultant powders were pressed into pellets and sintered in air at 1200°C for 5 h. The sintered pellets were polished and used for permeation tests. Likewise, BCY was prepared by mixing the appropriate amounts of $BaCO_3$, CeO_2, and Y_2O_3 and calcining the mixture at 1000°C for 12 h in air. This powder was then ball-milled and calcined again at 1200°C for 10 h in air. After obtaining phase-pure powder (as determined by XRD), the BCY powder was mixed with 0.5-2.0 wt.% sintering aid and metallic powder to increase its electronic conductivity. This powder mixture was then uniaxially pressed and sintered for 5 h at 1400-1450°C in an atmosphere of 4% hydrogen/balance argon. Densities of the sintered pellets were measured by the Archimedes method.

The total and ionic conductivities of SFC were measured as a function of pO_2 by conventional and electron-blocking four-probe methods [8,10], respectively. The experimental setup used to study oxygen permeation of SFC membranes has been described earlier [11]. Hydrogen permeation rates through BCY/metal composites were measured with an experimental apparatus described elsewhere [12].

RESULTS AND DISCUSSION

Oxygen Ionic Conductor SFC

The total and ionic conductivities of SFC were measured by conventional and electron-blocking four-probe methods. Electronic conductivity was calculated by subtracting ionic conductivity from the total conductivity. The results, shown in Fig. 1 as a function of temperature, show that the electronic and ionic conductivities of SFC are comparable to one another in magnitude. This makes SFC unique among mixed conductors, because it is typical that one of the transference numbers significantly outweighs the other. Using the conductivity data and Eq. 1 below, and ignoring polarization effects, one can estimate the oxygen permeation flux jO_2 for a membrane, of thickness L, that is exposed to a known difference in pO_2.

$$jO_2 = \frac{RT}{16F^2L} \int_{pO_2}^{pO_2} \sigma_{tot} t_{ion} t_{el} \, d\ln(pO_2), \qquad (1)$$

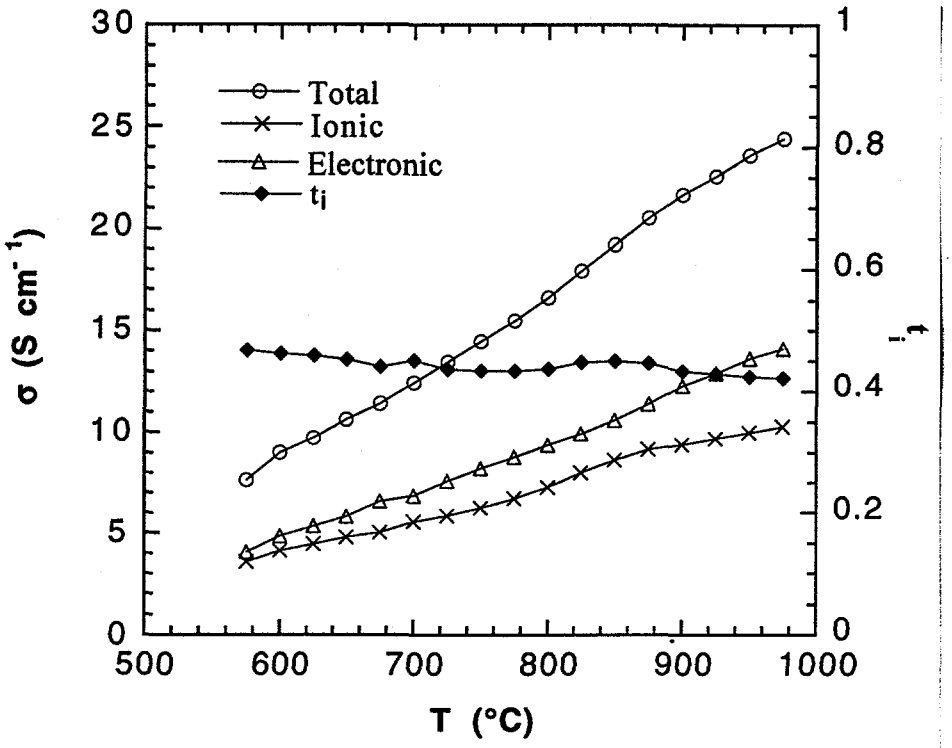

Fig. 1. Ionic transference number and ionic and electronic conductivities vs. temperature for $SrFeCo_{0.5}O_x$ (SFC) in air.

where σ_{tot} is the total conductivity, t_{ion} is the ionic transference number, t_{el} is the electronic transference number, R is the gas constant, and F is Faraday's constant. This equation shows that the oxygen permeation rate is maximized when the electronic and ionic transference numbers are comparable in magnitude, as they are in SFC. Oxygen permeation flux, determined from reactor experiments with a tubular SFC membrane [13] and from experiments with a gas-tight electrochemical cell [10], are plotted as a function of temperature in Fig. 2. The wall thickness of the tubular membrane used in the methane conversion reactor was 0.75 mm. For comparison, the permeation flux determined from the gas-tight electrochemical cell was normalized to that of a 0.75-mm-thick membrane. These data show that the two experiments are in good agreement and that the oxygen permeation flux is significant.

Protonic Conductor BCY

Unlike SFC, in which the ionic and electronic conductivities are comparable in magnitude, BCY in hydrogen-containing environments exhibits a protonic transference number that is 3-10 times larger than its electronic transference number [14]. Analogous to oxygen permeation, described by Eq. 1, hydrogen permeation is maximized when the protonic and electronic transference numbers are both equal to 0.5. To increase electronic conductivity (and hydrogen permeation), membranes were prepared from a mixture of BCY and metallic powder (referred to as cermet membranes). The hydrogen permeation rate for such cermet membranes is shown in Fig. 3 as a function of membrane thickness (with hydrogen 4%/balance argon on one side of the membrane and argon on the other side). From these data [12], it was found that the ambipolar conductivity increased while the interfacial polarization resistance decreased dramatically as temperature increased from 600 to 800°C. At 800°C, bulk resistance was much greater than interfacial resistance (for sample thickness >0.095 cm), whereas the interfacial resistance

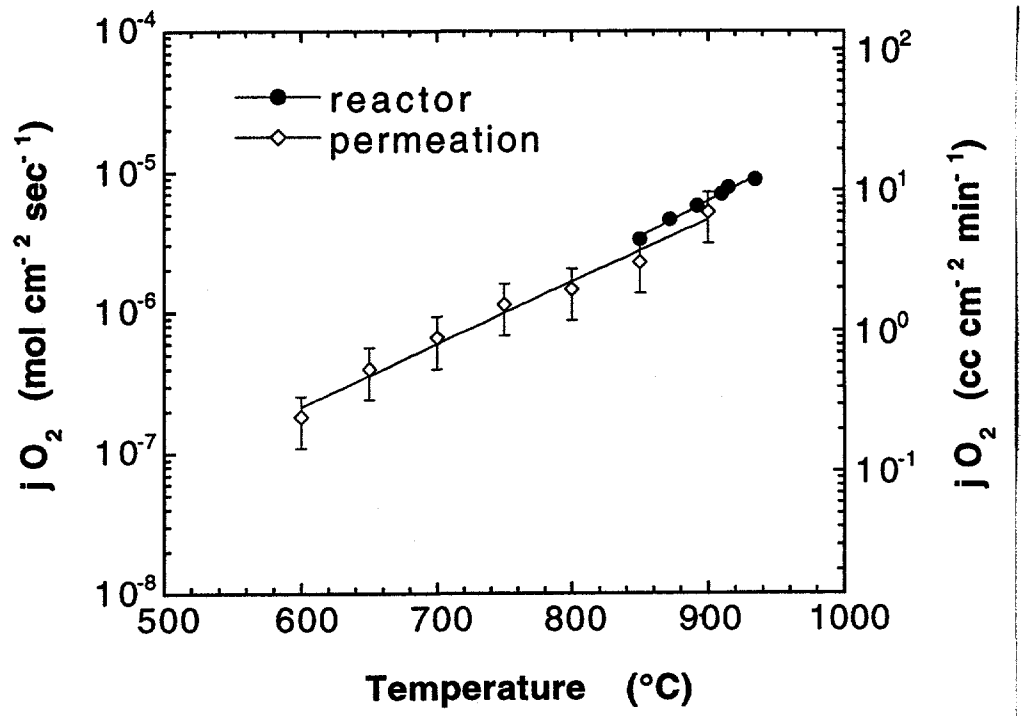

Fig. 2. Oxygen permeation rate vs. temperature for SFC membranes, as determined by independent measurements with a gas-tight electrochemical cell and a methane conversion reactor.

dominated at low temperatures (<600°C). This finding indicates that the permeation rate might be increased by reducing the membrane thickness for gas separations that are performed at higher but not lower temperatures.

To avoid interconnected porosity (to ensure high selectivity for hydrogen permeation) and improve the mechanical properties of the membrane, a sintering aid was developed to increase the density of the membrane. Figure 4 shows the permeation rate through cermet membranes that were fabricated with 0.0-2.0 wt.% sintering aid. The permeation rates were measured with a significantly higher hydrogen concentration in the feed gas, so they are significantly higher than the permeation rates shown in Fig. 3. The membrane densities were 94.5% of theoretical density (no sintering aid), 98.8% (0.5 wt.% sintering aid), and 98.5% (2.0 wt.% sintering aid). These results indicate that the sintering aid can be added without exerting deleterious effects on membrane performance, because the addition of 0.5 wt.% sintering aid produced the highest density with essentially no effect on permeation rate.

CONCLUSIONS

SFC, a mixed-conducting oxide with high electronic and oxygen ionic conductivities, has been developed. Because its electronic and ionic transference numbers are comparable in magnitude, SFC is unique among mixed conductors. The oxygen permeability of SFC membranes is high, as determined by measuring the oxygen permeation rate in both a gas-tight electrochemical cell and a methane conversion reactor. Oxygen permeability of the SFC membranes increased with increasing temperature and decreasing membrane thickness. Oxygen permeation flux for a 2.9-mm-thick specimen was ≈2.5 scc·cm^{-2}·min^{-1} at 900°C.

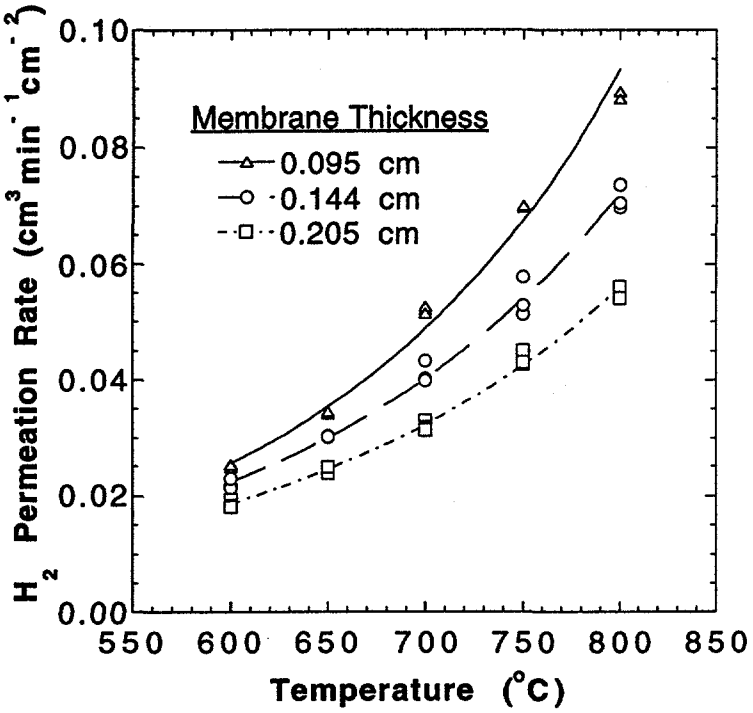

Fig. 3.
Temperature and thickness dependence of hydrogen permeation rates through BCY/metal membranes with 4% hydrogen/balance argon as feed gas and argon as sweep gas.

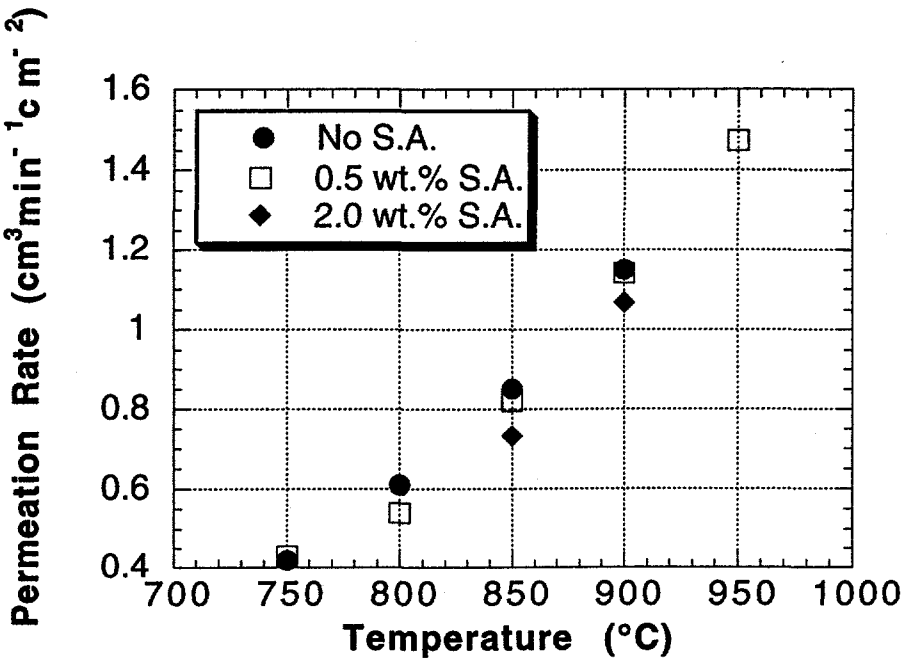

Fig. 4. Hydrogen permeation rates through BCY/metal membranes that were fabricated with various amounts of sintering aid (S.A.). Feed gas was 99.995% hydrogen and sweep gas was argon.

Measurements 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 not for separations that are performed at lower temperatures. Addition of a sintering aid can significantly increase the density of the membranes without degrading hydrogen permeation through the membrane.

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