Perovskite-Related ZrO_2-Doped $SrCo_{0.4}Fe_{0.6}O_{3-\delta}$ Membrane for Oxygen Permeation

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A typical perovskite $La_{0.2}Sr_{0.8}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) membrane and a novel perovskite-related ZrO_2-doped $SrCo_{0.4}Fe_{0.6}O_{3-\delta}$ (SCFZ) membrane were successfully prepared. The sintered membranes were characterized by an in-situ high-temperature X-ray diffraction, scanning electron microscopy and energy dispersive spectroscopy. Oxygen permeabilities of the two dense membranes were measured in the temperature range of 923 to 1,173 K under a fixed oxygen partial pressure gradient. The results of the oxygen permeation experiment and high-temperature X-ray diffraction in argon atmosphere indicate that the perovskite-related SCFZ membrane has higher oxygen fluxes and is stable than that of the LSCF membrane at elevated temperatures and reduced oxygen partial pressures.

Introduction

Mixed conducting membranes that exhibit high oxygen ionic and electronic conductivities have attracted great interest as clean, efficient, and economical means of producing oxygen from air or other oxygen-containing gas mixtures. They will be most competitive at small- and intermediate-scale levels in which flexibility of operation is desired, and may eventually challenge the present commercial status of cryogenics, pressure-swing adsorption, and polymeric membranes (Carolan et al., 1993a,b,c; Liu et al., 1993). Another application of mixed-conducting oxide membranes is to be found in the field of chemical processing, including the partial oxidation of light hydrocarbons such as the conversion of natural gas to value-added products such as ethane/ethene (Hazbun, 1989; ten Elshof et al., 1995a,b; Nozaki and Fujimoto, 1994; Wang and Lin, 1995) and syngas (Tsai et al., 1994; Pei et al., 1995; Balachandran et al., 1995, 1997), waste reduction, and recovery (Dixon et al. 1994).

To date, industrially important mixed conducting oxides have been primarily based on oxygen-deficient fluorite-related structures such as ZrO_2 and CeO_2 doped with CaO or Y_2O_3 (Bouwmeester and Burggraaf, 1996). The oxygen flux through these materials in usual ranges of temperature and oxygen pressure is negligibly low, preventing their practical use as oxygen separation membranes. Teraoka et al. (1985, 1988, 1991) were the first to report very high oxygen fluxes through cobalt-rich compositions, which are known to become highly defective because of the vacancy of the oxygen anions at elevated temperatures and reduced oxygen partial pressure. Subsequently, materials with oxygen-deficient perovskite and perovskite-related structures have received much attention for numerous applications (Gur et al., 1992; Itoh et al., 1994; van Hassel et al., 1993a,b, 1994; Kawada et al., 1995; Chen et al., 1997; ten Elshof et al., 1995a,b,c; Qiu et al., 1995; Kharton et al., 1996).

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Although recent reports have described various perovskite-type materials that could be used in oxygen permeation or as partial-oxidation ceramic membrane reactors, apparently little work has been focused on the problems associated with the stability of the membrane under reaction conditions. In fact, some perovskite-type oxides have very high oxygen permeabilities but poor stabilities under the conditions of a reducing atmosphere and an elevated temperature. One of the typical examples is $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$, which has a high reported oxygen permeation rate, 3.1 cm^3 (STP)$\cdot min^{-1} \cdot cm^{-2}$ (temperature: 1,123 K, membrane thickness: 1 mm) (Teraoka et al., 1985), but has both an abrupt first-order phase transition at around 1,063 K (Kruidhof et al., 1993) and a susceptibility to reducing atmospheres (Pei et al., 1995). The Sr-Fe-Co-O perovskite-type membrane of Pei et al. (1995) cracked due to the high oxygen pressure gradient across the membrane, immediately after the syngas synthesis reaction was initiated, indicating that the lattice structure of membrane had changed under different oxygen partial pressure. The membrane was also reduced to $SrCO_3$ and elemental cobalt and iron after two days, indicating that either the mismatch of the perovskite lattice parameters or the decomposed products had caused considerable volume expansion that led to the fracture. Takeda et al. (1986) also pointed out that the crystal structure of $SrCoO_{3-\delta}$ powder was likely to be changed by temperature, oxygen partial pressure, and synthetic conditions.

Both high permeability and structural stability are necessary for perovskite or perovskite-related membranes to be used in oxygen permeation. Stevenson et al. (1996) reported that perovskite-type membranes in strontium and cobalt exhibit very limited chemical and structural stability toward a reducing atmosphere at elevated temperatures. Tsai (1996) had also proved that the typical perovskite $La_{0.2}Sr_{0.8}Co_{0.8}Fe_{0.2}O_{3-\delta}$ not only had relatively low oxygen permeation rates, but also was unstable in a reducing atmosphere due to the cobalt-rich B site. In the study of Stevenson et al. (1996), $La_{0.2}Sr_{0.8}Co_{0.8}Fe_{0.2}O_{3-\delta}$ compositions could be considered to be viable candidate materials for oxygen permeation applications in the intermediate temperature range (such as from 1,023 to 1,073 K). Tsai (1996) studied, the $La_{0.2}Ba_{0.8}Co_{0.2}Fe_{0.8}O_{3-\delta}$ membrane, which had been shown to have a high oxygen permeation rate and structural stability under reaction conditions. Balachandran et al. (1995, 1997) developed a nonperovskite mixed oxide $SrCo_{0.5}FeO_x$ as a membrane material to be used in the reaction of methane to syngas that can be operated for over 1,000 h.

The purpose of this study was to exploit a new material for oxygen permeation which will have the following properties: (1) a high oxygen permeability; (2) a stable lattice structure under various oxygen partial pressures. It is well known that the toughness of ceramics can be substantially enhanced by adding a toughening material to control the martensitic transformation (Mcmeeking and Evans, 1982). Zirconium dioxide (ZrO_2), which is also a mixed conducting oxide, has been used as a toughening material due to its high strength, fracture toughness, and low thermal conductivity (Matsui et al., 1986). The mechanism of toughening has been reported by many researchers (Mcmeeking and Evans, 1982; Evans and Faber, 1984). In this study, ZrO_2-doped $SrCo_{0.4}Fe_{0.6}O_{3-\delta}$ (designated as SCFZ) membrane has been prepared and characterized, and the more conventional perovskite-type $La_{0.2}Sr_{0.8}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (designated as LSCF) membrane, which has the same structure as $SrCo_{0.4}Fe_{0.6}O_{3-\delta}$ (designated as SCF) and has been researched by many studies (Itoh et al., 1994; Chen et al., 1997; Stevenson et al., 1996), has also been prepared and characterized for comparison. Oxygen permeation fluxes of the two membranes have been measured carefully with a permeation reactor. The structural stability of the membranes toward reducing atmospheres at elevated temperatures is discussed.

Experimental Studies

Powder synthesis

Two ceramic powders of different stoichiometries were synthesized in the experiment reported here: $La_{0.2}Sr_{0.8}Co_{0.2}Fe_{0.8}O_{3-\delta}$, which is designated as LSCF, ZrO_2-doped $SrCo_{0.4}Fe_{0.6}O_{3-\delta}$, which is designated as SCFZ. Powders were synthesized by the solid-state reaction of the constituent cation salts, which were purchased from the Second Chemical Industry of Shanghai and the purity of 99.9%. Stoichiometric amounts of $La(NO_3)_3 \cdot 6H_2O$, $Sr(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, and 8% Y_20_3 partial stabilized ZrO_2 (ZrO_2 9 wt% in SCFZ) were mixed and milled in isopropanol for 48 h. After being dried at 353 K for 24 h, the mixtures were sintered in air at 1,173 K for 10 h, with the heating and cooling rates controlled at 2 K/min. Finally, the powders were reground in an agate mortar and pestle for 24 h.

Membrane preparation

The membranes were prepared by isostatic pressing. A die was used for the shape-forming process, which includes loading, pressing, and ejecting. A total of 12 tons of oil pressure was applied on the plunger of the die by the press, which is in a pressure of 400 MPa on the powders. After 5 min, the pressure was released and the die was removed from the press. Results showed that 1 to 2 g of powder produced a 1- to 2-mm-thick, 16-mm-dia. green disk. The green disks of LSCF were sintered in air at 1,523 K for 10 h, while SCFZ were sintered in air at 1,373 K for 5 h. The heating and cooling rates were controlled at 2 K/min.

Characterization of the membrane

The crystal types of the resulting membranes were determined by an *in-situ* high-temperature X-ray diffraction analysis using Cu Kα radiation (PAD X, Scintag Inc.). Each sample was tested at several temperatures in oxygen-rich atmosphere (in air) and oxygen-lean atmosphere (in argon) using a Pt holder. The heating rate was 4 K/min, and the sample was stabilized at every temperature for 1 h, and a range of diffraction angles from 20° to 90° was used. Data collection was accomplished using DMSNT software (Scintag inc., Cupertino, CA) and data analysis was undertaken using Jade software (Materials Data Inc., Livermore, CA).

The membrane surface morphology was examined by high-resolution scanning electron microscopy (HR-SEM) (Hitachi S-800 field emission microscope). Surface element analysis of the membranes was performed by energy dispersive spectroscopy (EDS) (U.S. Kevex-Sigma).

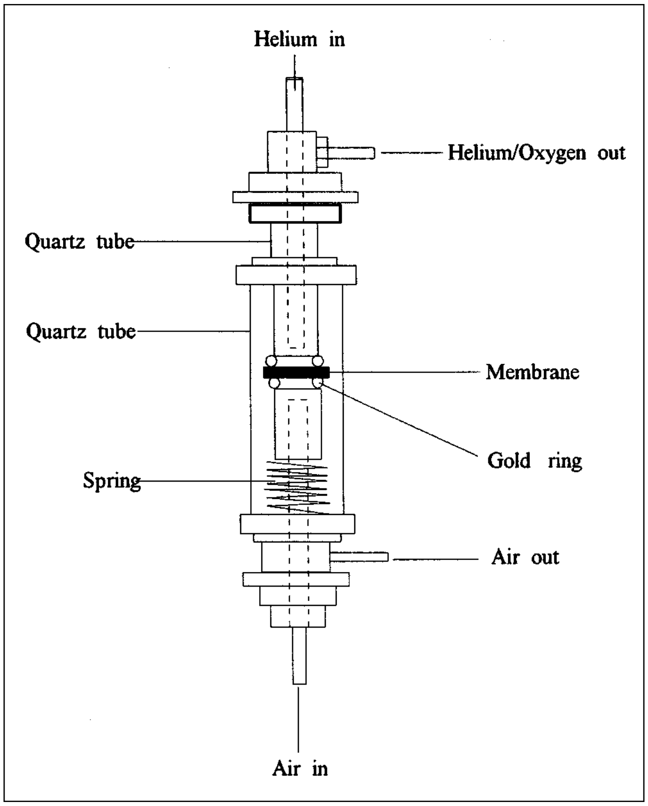

Figure 1. Oxygen permeation reactor.

The densities of the sintered membranes were determined by the Archimedes method using ethanol. These densities exceeded 90% of the theoretical in all cases.

Apparatus for oxygen permeation measurement

Details of the membrane permeation reactor design are shown in Figure 1, which is similar to the one used by Tsai (1996). A sintered-disk membrane was polished to the thickness of interest and then mounted on a quartz tube using a gold ring seal. Gold, which is the most ductile element with a melting point of 1,337 K has an inertness for most chemical reactions. Its thermal expansion coefficient (1.44×10^{-5} K^{-1}) is between that of quartz (5.4×10^{-8} K^{-1}) and perovskite-type or perovskite-related membranes ($3\sim6\times10^{-5}$K^{-1}).

Pure gold foils of 0.05-mm thickness were cut into rings. The sintered disk membranes, which had diameters of about 14 mm, were hand-polished. A pressure of approximately 0.1 M Nm^{-2} was applied by releasing an air-cooled spring from the bottom of the ring to provide close contact for quartz/gold/membrane joints, while the temperature was controlled at 1,293 K for 10 h (AI-708PA Temperature Controller). A heating rate of 1.5 K/min was used to form the bonding. The furnace was then cooled to the temperature of interest at a 1.5 K/min cooling rate. Experimentally results showed that the air tight sealing could be sustained at temperatures from 473—1,273 K and pressure drops up to 0.02 MPa between permeate and retentive sides, depending on the strength of the perovskite membranes.

The oxygen permeation rate through the prepared disk membrane in this study was measured in the range of 973 to 1,243 K with the apparatus shown in Figure 2. Helium gas was introduced to sweep the permeate oxygen, and the product gases, including the permeated oxygen, were analyzed by an on-line gas chromatography equipped with two automatic valves, a sampling valve, and a bypass valve. The amount of oxygen passing through the membrane was calculated from the measured outlet flow rate and the oxygen concentration.

Results and Discussion

SEM results

SEM pictures of the surface and the cross-section of a sample are shown in Figure 3 and Figure 4. Big crystals without significant grain boundaries were seen. Closed porosity can be seen in these photos, which might be due to the grain

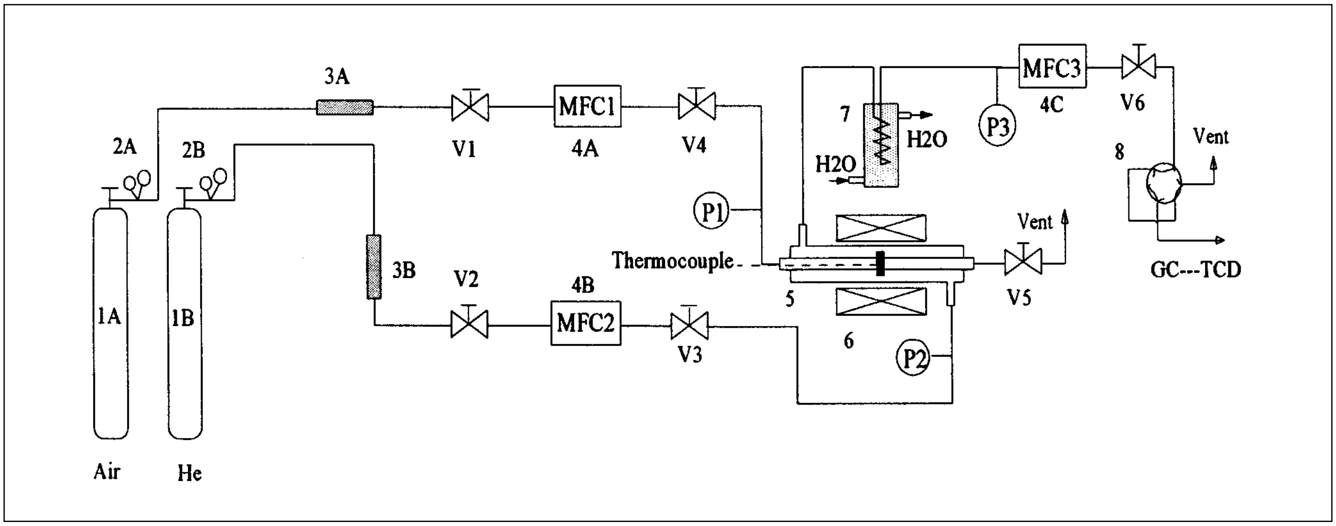

Figure 2. Apparatus used for measuring oxygen permeation rate.

(1A, 1B) gas cylinders; (2A, 2B) gas regulators; (3A, 3B) purifying traps; (4A, 4B) mass-flow controller; (5) permeation reactor; (6) furnace; (7) cooler; (8) six-way valves; (V1-V6) flow control valves.

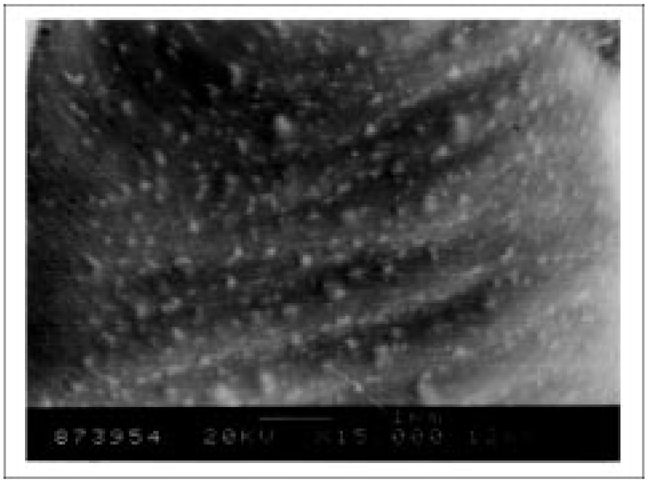

Figure 3. SEM photograph of surface of membrane.

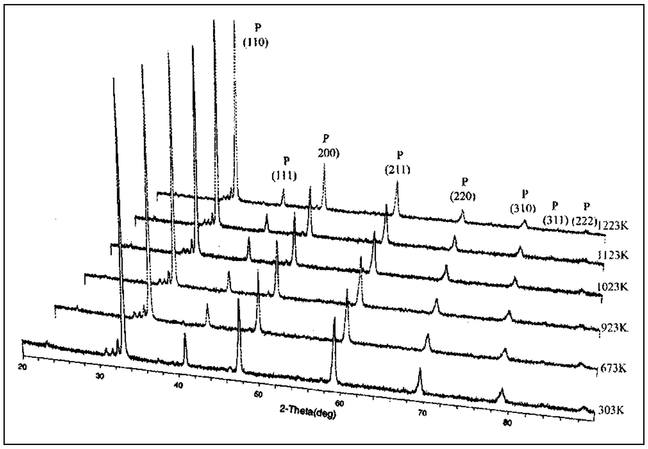

Figure 5. X-ray diffraction patterns of LSCF membrane at various temperatures in air.

(P) Perovskite; inscriptions below the symbols are the Miller indexes (*hkl*).

growth, or air trapped during the pressing. However, nitrogen permeation rate measurement confirmed that open porosity did not exist.

High-temperature x-ray diffraction results

Figure 5 shows the X-ray diffraction patterns of the LSCF membrane at temperatures of 303, 673, 923, 1,023, 1,123, and 1,223 K in air. Since the patterns are quite similar to those of $SrCo_{0.5}Fe_{0.5}O_{3-\delta}$, which is a cubic perovskite-type oxide, the LSCF membrane is considered to have the perovskite-type structure and is a single-phase material.

Figure 5 also shows that the LSCF membrane is very stable at temperatures up to 1,223 K in oxygen-rich atmosphere (air).

Figure 6 shows the x-ray diffraction patterns of the SCFZ membrane at temperatures of 303, 673, 923, 1,023, 1,123, 1,223, 1,323, 1,432, 1,523, and 1,623 K in air. It is clear from Figure 6 that the crystal type of SCFZ is not a single-phase perovskite structure. The high-temperature x-ray diffraction pattern of SCFZ consists of three distinct phases: $SrCo_{0.5}Fe_{0.5}O_{3-\delta}$ perovskite-type structure, and ZrO_2 and $SrZrO_3$ structure, which indicates that some ZrO_2 and SrO have reacted at the high temperature and the membrane is not a single-phase material. Therefore, the SCFZ membrane can be called perovskite-related oxide. Molar fractions of the three materials can be estimated to be 0.9679, 0.0245, 0.0076, respectively, according to the intensities and weight-absorption coefficients. Figure 6 also indicated that the SCFZ membrane is very stable at temepartures up to 1,423 K in oxygen-rich atmosphere (air).

EDS results

Whether the element of the membrane materials will change at high temperature for several hours is very important for the membrane's oxygen permeability for the stoichiometric ratio will influence the oxygen vacancies of the mem-

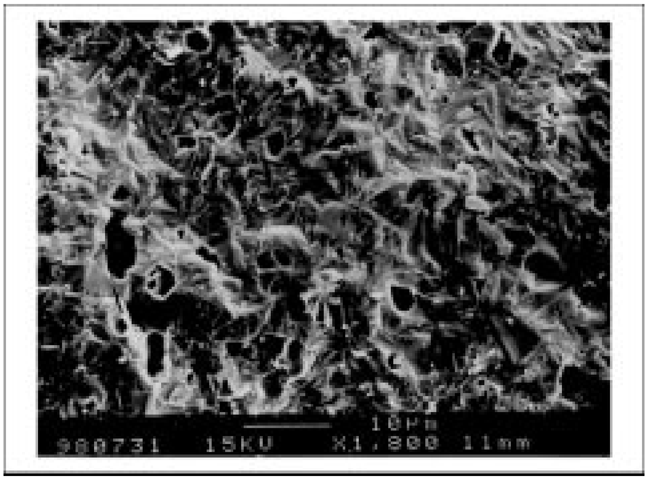

Figure 4. SEM photograph of cross-section of membrane.

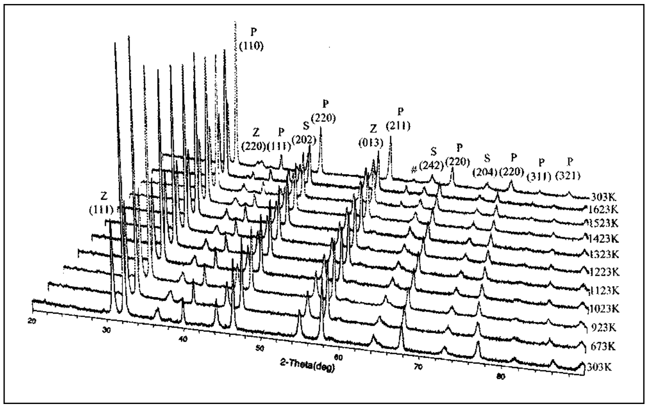

Figure 6. X-ray diffraction patterns of SCFZ membrane at various temperatures in air.

(P) Perovskite; (Z) ZrO_2; (S) $SrZrO_3$; (#) peaks due to the thermal expansion of the Pt holder; inscriptions below the symbols are the Miller indexes (hkl).

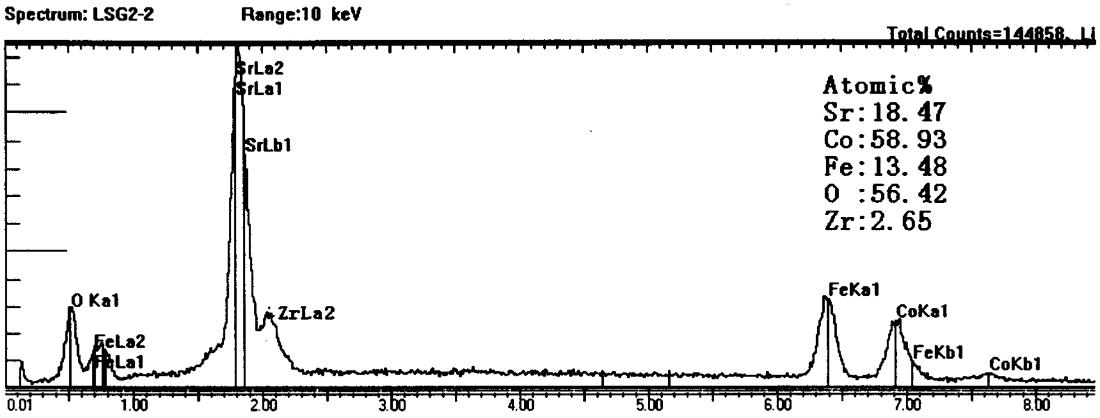

Figure 7. EDS results of SCFZ membrane.

brane materials, further impacting the oxygen permeability. EDS results of SCFZ membrane are shown in Figure 7, which indicated that the chemical elements are stable after several hours of calcination and the molar fraction of Zr is similar to the total molar fractions of ZrO_2 and $SrZrO_3$ calculated from the XRD results.

Oxygen permeation

The membrane was further tested for oxygen permeation after the temperature dropped to 1,173 K after sealing. Helium was introduced to the line, and, in turn, one of the membrane sides was changed from high oxygen partial pressure to low oxygen partial pressure. Therefore, the membrane would adapt to the newly applied gradient by losing oxygen. The tested oxygen flux would include two parts: the time-independent, steady-state contribution, and a time-dependent contribution due to the loss of lattice oxygen. This is the reason why the oxygen flux was very high when helium was introduced to the line. From Figure 8, the second part finally disappeared 1 h later, and the oxygen flux became stable.

At each tested temperature, a specified time was required before the permeation flux reached equilibrium. The variation of the permeation fluxes with temperature for the LSCF and SCFZ membranes, each of which had a diameter of 14 mm and a thickness of 2 mm, is shown in Figure 9. On the feed side, air at a pressure of 0.1 MPa was applied at a flow rate of 200 mL/min. The sweep gas (He) was used at a pressure of 0.1 MPa and at a flow rate of 15 mL/min. The oxygen partial pressure could be estimated by summing these flow rates with the content of the product gases being analyzed by gas chromatography.

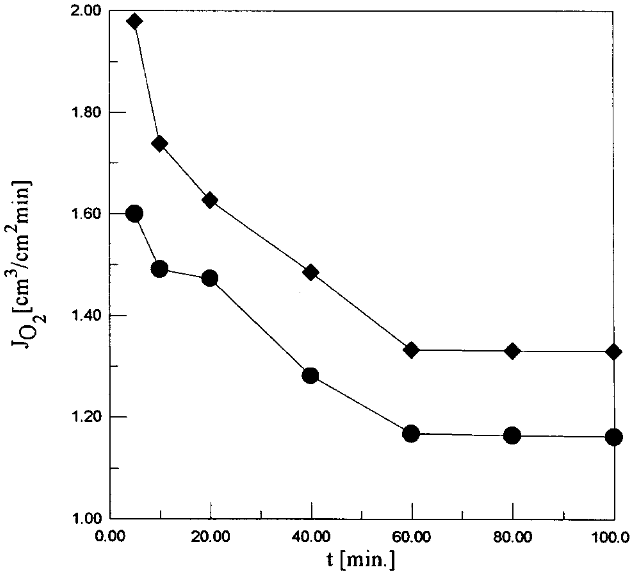

Figure 8. TIme-dependent permeation study of SCFZ membranes at the temperature of 1,223 K.

(◆) membrane thickness of 1.2 mm; (●) membrane thicknes of 1.6 mm; partial pressure of the oxygen: 0.21 atm/2.1 $\times 10^{-3}$ atm.

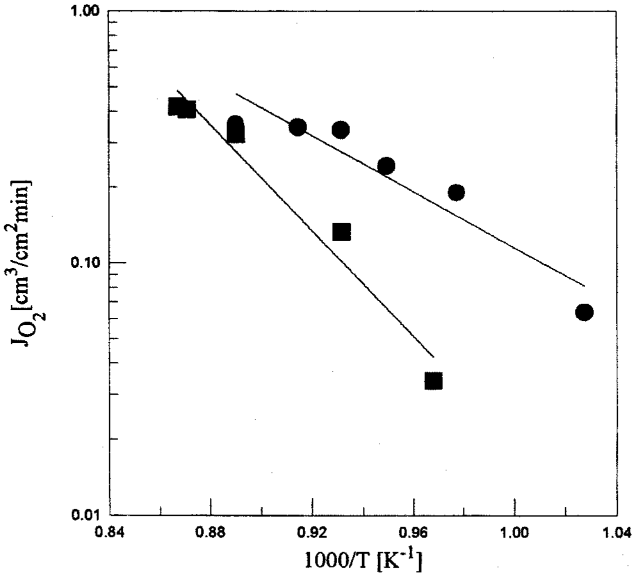

Figure 9. Temperature dependence of the oxygen permeability of SCFZ membrane (●) and LSCF membrane (■).

Membrane thickness of 2 mm; partial pressure of the oxygen of 0.21 atm/2.1 $\times 10^{-3}$ atm.

Figure 9 shows that the oxygen fluxes become substantial above 1,023 K and increase with increasing temperature, which is due to the increasing diffusion rate. The oxygen fluxes of the SCFZ membrane are higher than those of the LSCF membrane. For example, at 1,123 K, the oxygen fluxes of the LSCF and SCFZ membranes are 0.325 and 0.355 cm^3 (STP)/$cm^2 \cdot$ min, respectively. The SCFZ membrane has higher oxygen flux than that of the LSCF membrane due to its higher strontium and cobalt contents, since the strontium and cobalt introduce oxygen defects in the lattice. The response of the oxygen flux to temperature changes yielded apparent activation energies over the temperature range (obtained from the slopes of plots of ln (σ_i/T) vs. $1/RT$). The value of the LSCF membrane is 192.21 KJ/mol, which is similar to the result of the $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ membrane reported by Xu and Thomson (1998). The value of the SCFZ membrane is 97.756 KJ/mol., which is similar to the result of $La_{0.75}Sr_{0.25}FeO_{3-\delta}$ reported by van Hassel et al. (1994).

Both ZrO_2 and perovskite $SrCo_{0.4}Fe_{0.6}O_{3-\delta}$ are mixed conducting oxides, which can be used as dense membrane materials. The rate at which oxygen permeates through a dense membrane is essentially controlled by two factors: the rate of oxygen diffusion across the membrane, and the rate of interfacial oxygen exchange. The oxygen flux can be increased by reducing the thickness of membrane, until its thickness becomes less than a characteristic value (μm) L_c at which point the flux of oxygen is under conditions of mixed control of the surface exchange kinetics and bulk diffusion. Below L_c, the oxygen flux can only marginally be improved by making the membrane thinner (Bouwmeester and Burggraaf 1996). They calculated the characteristic thickness for several La-Sr-Co-Fe perovskite-type oxides to be in the 20 to 500 μm range at 1,173 K. In this study, all membrane thickness were larger than 1 mm, so the oxygen flux is limited by bulk oxygen diffusion.

When the oxygen flux (mol/$cm^2 \cdot$ min) is governed by bulk oxygen diffusion, it is generally described by Wagner's equation (Itoh et al., 1994) as

$$Jo_2 = \frac{1}{16F^2} \frac{RT\sigma_e\sigma_i}{(\sigma_e + \sigma_i)t_m} \ln(P_h/P_l), \qquad (1)$$

Here J_{o_2} (mol/$cm^2 \cdot$ min) is the oxygen flux, σ_e (S/cm) is the electronic conductivity, σ_i (S/cm) is the ionic conductivity, R (J/mol·K) is the gas constant, F (C/mol) is the Faraday constant, T (K) is the temperature, t_m (cm) is the thickness of the membrane, and P_h, P_l(Pa) are the partial pressures of oxygen upstream and downstream, respectively. Increasing either the ionic or electronic conductivity will lead to a rise in the oxygen permeability of the membrane with a maximum oxygen permeability being attained when the values of σ_e and σ_i become close. For some perovskite membranes, the electronic conductivity is several orders of magnitude larger than the ionic conductivity (Elshof et al., 1995c). In this study, ionic conductivity were calculated from the measured flux rates, using the following relation (Stevenson et al., 1996)

$$\sigma_i = (4FJ_{o_2}t_m)/[RT\ln(P_h/P_l)] \qquad (2)$$

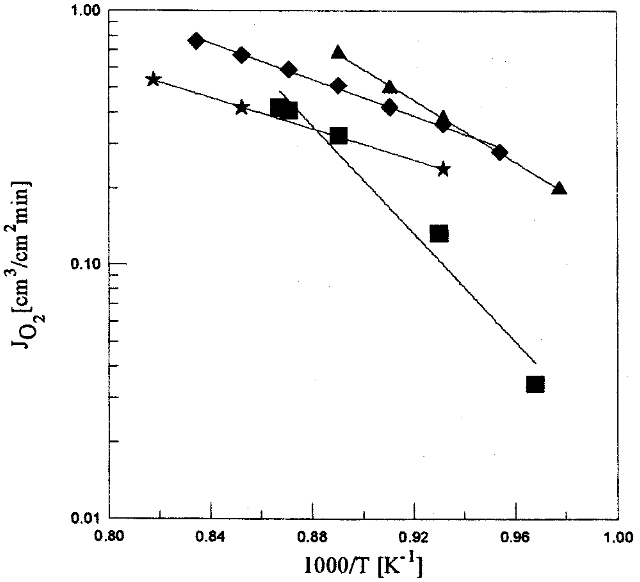

Figure 10. Oxygen fluxes: previous report vs. this study.

(▲): Teraoka et al. (1985) ($La_{0.2}Sr_{0.8}Co_{0.4}Fe_{0.6}O_{3-\delta}$, 1 mm, 0.21 atm/1 × 10^{-3} atm); (♦) Stevenson et al. (1996) ($La_{0.2}Sr_{0.8}Co_{0.2}Fe_{0.8}O_{3-\delta}$, 2 mm, 1 atm/2 × 10^{-4} atm); (★) Chen et al. (1997) ($La_{0.3}Sr_{0.7}CoO_{3-\delta}$, 2.15 mm, 0.21 atm/1.6 × 10^{-2} atm); (■) our study ($La_{0.2}Sr_{0.8}Co_{0.2}Fe_{0.8}O_{3-\delta}$, 2 mm, 0.21 atm/2.1 × 10^{-3} atm).

At 1,123 K, the results of LSCF and SCFZ membrane are 0.583 and 0.673 $(\Omega \cdot cm)^{-1}$, respectively.

The oxygen flux of the $SrCo_{0.4}Fe_{0.6}O_{3-\delta}$ membrane is larger than that of ZrO_2 membrane since the oxygen-ion conductivity of $SrCo_{0.4}Fe_{0.6}O_{3-\delta}$ can be 1 to 2 orders of magnitude higher than that of the stabilized ZrO_2 in the usual ranges of temperature and oxygen partial pressure (Bouwmeester and Burggraff, 1996). The operational temperature of this study is between 923 K and 1,473 K, a temperature range throughout which the oxygen permeability of $SrCo_{0.4}Fe_{0.6}O_{3-\delta}$ remains predominant. Qiu et al. (1995) reported the fluxes of the $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ membrane to be 0.673 mL/cm^2min at 1,123 K, while Kruidof et al. (1993) reported the same material to be 0.268 mL/cm^2min at the same temperature. The oxygen fluxes of the SCFZ membrane are similar in magnitude to the results reported by literature. So the doped ZrO_2 might not obviously change the oxygen permeability of SCFZ membrane.

Many researchers have studied La-Sr-Co-Fe-O oxide, which is a typical perovskite structure material. A comparison of the oxygen fluxes determined in their work with these in the present study is shown in Figure 10. Our oxygen permeation data are close to those of Chen et al. (1997). The difference may be due to the different value of the oxygen partial pressure gradient across the membrane. Stevenson et al. (1996) prepared the same membrane material $La_{0.2}Sr_{0.8}Co_{0.2}Fe_{0.8}O_{3-\delta}$. The reported oxygen permeation data are higher than those of this study, which might be the difference of the membrane preparation technique and the process conditions, such as the oxygen partial pressure gradient, using oxygen as the source gas with nitrogen as the carrier gas. The oxygen permeation rates reported by Teraoka et al. (1985) were

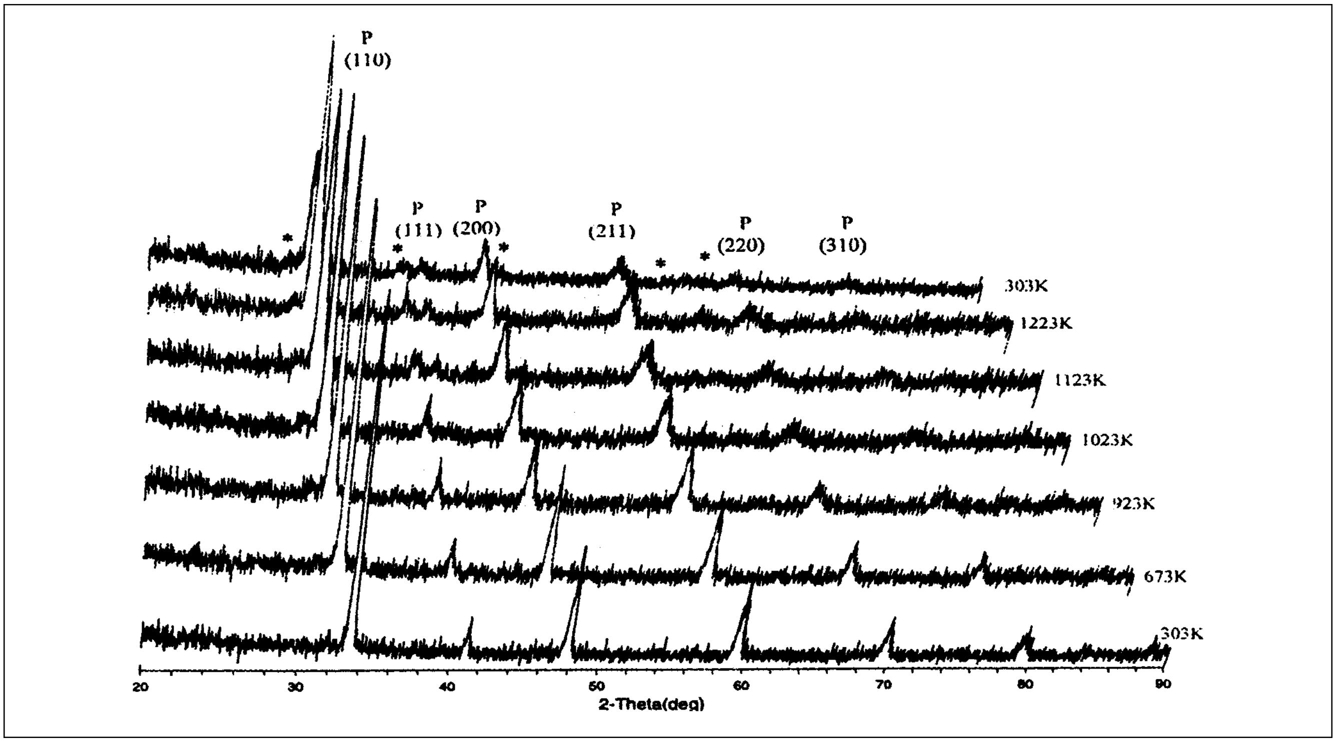

Figure 11. X-ray diffraction patterns of LSCF membrane at various temperatures in argon.

(P) Perovskite; (*) new peaks due to the expansion of the lattice; inscriptions below the symbols are the Miller indexes (*hkl*).

higher than those of others. This disagreement might be attributed to the preparation technique or to the fact that the data reported here were obtained at steady state, while the data of Teraoka et al. (1985) were likely obtained using initial time rates (Tsai, 1996).

Structural stability at elevated temperatures and reduced oxygen partial pressures

Teraoka et al. (1985) have shown how the oxygen permeability was affected by cation substitution and have reported that oxygen flux could be increased by increasing the amount of acceptor doping. In addition to the desired oxygen flux values, an ideal material for oxygen permeation must exhibit sufficient mechanical strength and structural stability toward reducing atmospheres at elevated temperatures.

During the oxygen permeation experiment with prepared LSCF membrane, 90% of the membranes (about 20 membranes were tested) broke when helium was introduced to the line, or it fractured into several pieces when the membrane was cooled to room temperature. From Figure 5, the structure of the LSCF membrane is a cubic perovskite-type material in oxygen-rich (air) atmosphere. Results of high-temperature x-ray diffraction experiments conducted at high temperature in argon atmosphere are shown in Figure 11. However, at the temperatures higher than 1,023 K, new peaks appeared near the characteristic peak and the characteristic peak was not obvious, which indicated that the lattice was beginning to expand and the structure of LSCF membrane had changed in the oxygen-lean atmosphere at high temperatures. This result is consistent with the conclusion of Balachandran et al. (1995, 1997) that the structure of the perovskite membrane transforms from the cubic phase to an oxygen-ordered vacancy phase.

From the results shown in Figure 11, the failure mechanism of the LSCF membrane can be explained as follows. The distribution of oxygen was uniform before helium was introduced to the line. As helium started to sweep the air, oxygen concentration became small and the membrane began to lose oxygen. Moreover, the material on the oxygen-lean side lost more oxygen than that on the oxygen-rich side. As a result, a stable oxygen gradient was generated between the oxygen-rich and the oxygen-lean sides, leading to the lattice mismatch and the membrane fracture. Xu and Thomson (1998) declared that stability can be dramatically affected by small oxygen concentrations, which coincided with the analysis mentioned above.

In comparison, the SCFZ membrane exhibited a remarkable structural stability at high temperatures in argon atmosphere, as shown in Figure 12. The high-temperature x-ray diffraction results show that the SCFZ membrane is especially stable when the temperature is lower than 1,223 K, and no phase transition was observed in this material as the oxygen partial pressure was changed. This stability can be explained by the mechanism of toughening. It has been shown that yttria-containing tetragonal zirconia with high strength, fracture toughness and low thermal conductivity exhibited plastic deformation with a maximum bending strain of 0.8% due to the stress-induced tetragonal to monoclinic transformation accompanied by lattice-invariant shear deformation

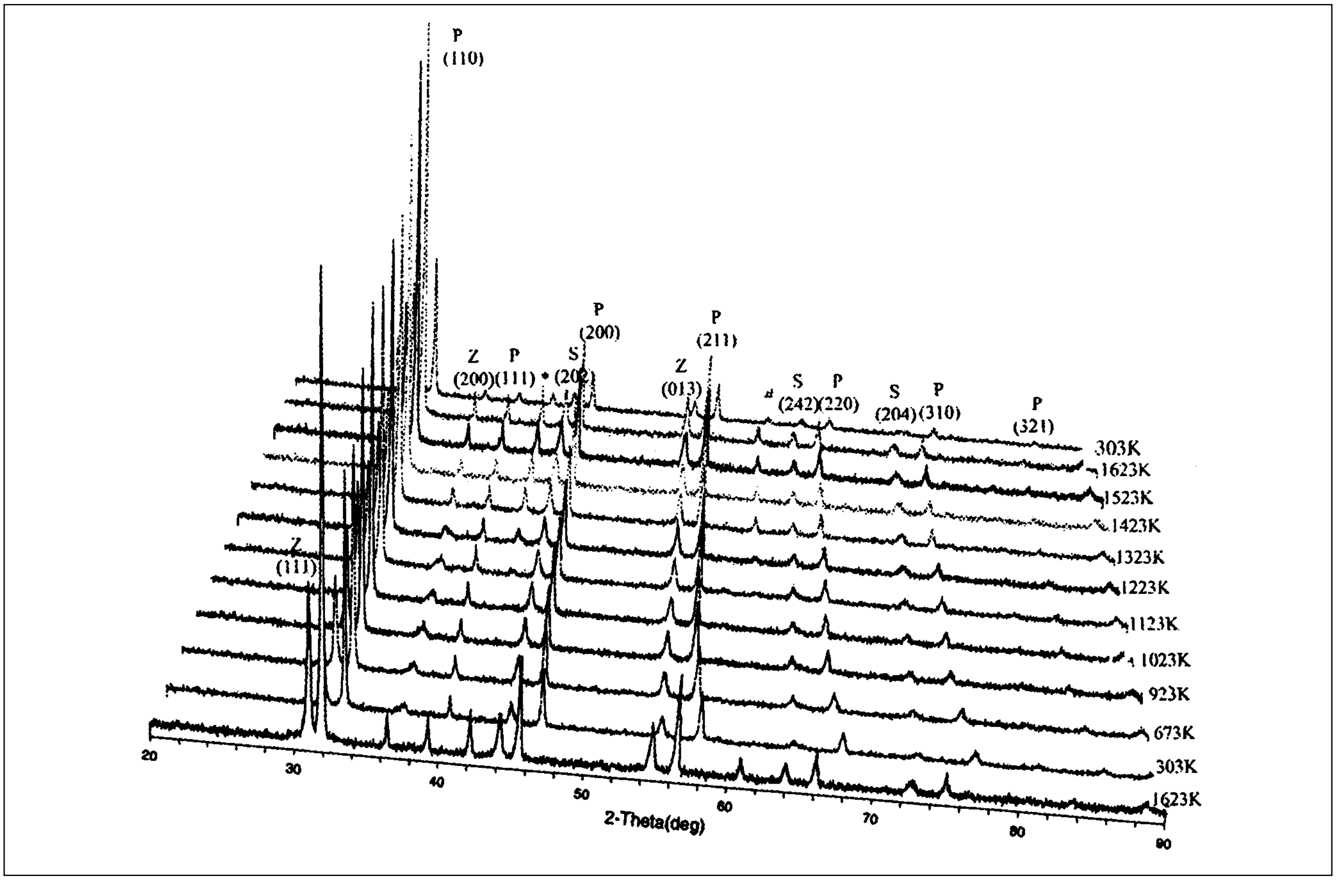

Figure 12. X-ray diffraction patterns of SCFZ membrane at various temperatures in argon.

(P) Perovskite; (Z) ZrO_2; (S): $SrZrO_3$; (*), (#) peaks due to the thermal expansion of Pt holder; inscriptions below the symbols are the Miller indexes (*hkl*).

(Matsui et al., 1986). The transformation causes microcracking, which absorbs the energy from the expansion of the main phase. The enhanced toughness can be considered to originate from the transformation and tends to limit the crack opening (Mcmeeking and Evans, 1982). The oxygen permeation experiments also proved that the perovskite-related SCFZ membrane did not break when helium was introduced to the line. Further confirming the stability of this membrane, 20 SCFZ membranes of different thickness were tested at the temperature range of 873 to 1,223 K and the partial pressures of oxygen were 0.1 MPa upstream and 1×10^{-4} to 1×10^{-2} MPa downstream. Each of them was stable over a period of 50 h. With its higher oxygen permeabilily, SCFZ can be used as membrane material for long-term oxygen permeation.

Conclusions

(1) Both the LSCF membrane and the SCFZ membrane, whose crystal types are peroviskite-type and perovskite-related, respectively, are very stable at high temperatures in air atmosphere.

(2) The rates of oxygen permeation were measured at different temperatures. At 1,123 K, the oxygen fluxes of the LSCF and SCFZ membranes were 0.325 and 0.355 cm^3 (STP)/$cm^2\cdot$min, respectively.

(3) The LSCF membrane sometimes broke during the oxygen permeation experiment due to lattice expansion in an oxygen-lean atmosphere. The SCFZ membrane, however, exhibited a remarkable structural stability at high temperatures in argon atmosphere due to the enhanced toughness, which originated from the ZrO_2 transformation and which tended to limit the crack opening. No phase transition was observed in this material as the oxygen partial pressure was decreased.

(4) The SCFZ membrane exhibited high oxygen flux and structural stability under the operating conditions of the experiments reported here.

Acknowledgments

This work was supported by the National Advanced Materials Committee of China (NAMCC, No. 715-006-0120), the National Natural Science Foundation of China (NNSFC, No. 59789201), and the U. S. Dept. of Energy, Basic Energy Sciences, Divison of Materials Sciences (USDOE/BES/DMS).

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Manuscript received July 14, 1998, and revision received Nov. 2, 1998.