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SEPARATION OF GASES WITH SOLID ELECTROLYTE IONIC CONDUCTORS*

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ABSTRACT

We have developed a novel method of gas separation based on electrolyte ionic membrane technology. Separation of one gas from another occurs through an ion-conducting membrane by the passage of selected ions. Most systems studied have focused on oxygen ion conduction for the separation of oxygen from air, although protonic and halide-conducting solid materials also exist. As an example of this system, this paper concentrates on a study of a membrane reactor used in the production of syngas ($\text{CO} + \text{H}_2$) from methane. The membrane material is a modified perovskite-type oxide exhibiting mixed (electronic/ionic) conductivity. Mixed-conductivity oxides are promising materials for oxygen-permeating membranes that can operate without electrodes or external electrical circuitry. Extruded tubes of this material have been evaluated in a reactor operating at $\approx 850^\circ\text{C}$ for partial oxidation of methane into syngas in the presence of a reforming catalyst. Separated oxygen on one side of the reactor wall was obtained from air on the other side. Methane conversion efficiencies of $>99\%$ were observed, and some of the reactor tubes have been operated for >1000 h. Membrane tubes were fabricated from calcined powders by a plastic extrusion technique. Characterization of the mechanical, physical, and chemical properties of this material confirmed the stability exhibited in the reactor.

INTRODUCTION

In this paper, we consider only gas separations occurring with mixed ionic/electronic conducting membranes. This precludes single ionic conducting membranes with electrodes, porous membranes, or other dense membranes such as palladium or molecular sieves.

Mixed-conducting membranes are primarily used for the separation of O_2 or H_2 from other gases and are driven solely by the partial pressure difference of these gases on either side of the membrane. In theory, other gases such as the halogens could be separated in this manner, given the correct membrane composition and structure (Chadwick et al., 1983).

Both protonic and ionic membranes selectively permeate by a mechanism associated with defects or vacancies in their structures. For instance, in perovskites (a class of mixed oxides), vacancy concentration in the lattice can be modified by compositional changes to facilitate high oxygen transport. Similar materials such as brownmillerite have ordered oxygen

vacancies and consequently exhibit high conductivity (Kendall et al., 1995).

Limited success has been obtained also in transforming single ionic conducting materials (e.g., stabilized zirconia) to mixed conducting materials by suitable doping with electronic conducting substances (Cable 1991, 1990). However, the more popular approach appears to be the use of compositions that inherently contain both types of conduction.

In gas separation, high fluxes for these materials are required for commercial success. High fluxes also require high temperature of operation ($>700^\circ\text{C}$), but many material problems are associated with this, including stability and compatibility with other materials in terms of seals and connections. This can severely limit the choice of material. With regard to both oxygen and protonic conducting membranes, the presence of highly reducing conditions on one side of the membrane can cause stability problems (Pei et al., 1995). Thermodynamic calculations can generally allay fears or signify major concerns. In the case of hydrogen membranes, the presence of carbon dioxide might pose a hazard more serious than the problem of reduction because of the extreme stability of the alkaline earth carbonates (Scholten et al., 1993). Some examples of discrepancies between calculated thermodynamic stability and actual results indicate the importance of obtaining supporting data (Iwahara et al., 1989).

Hydrogen membranes offer a potential alternative to existing methods of separation hydrogen from other gas streams, but much development work is needed to find a suitable material containing the correct properties. Although many protonic conducting membranes exist (Kendall, et al., 1995), electronic conductivity is limited and separations can occur only by a galvanic mode of operation (i.e., with external electrodes).

On the other hand, oxygen-conducting membranes are more advanced in their development. Teraoka et al. (1985, 1988) showed that the $(\text{LaSr})(\text{FeCo})\text{O}_x$ systems exhibit not only mixed conductivity but also appreciable oxygen permeability (two orders of magnitude higher than that of stabilized zirconia at 800°C). Furthermore, the oxygen flux obtainable from the separation of air is considered commercially feasible for an application such as syngas generation by the partial oxidation of methane (Balachandran et al.,

Table 1. Physical properties of SrFeCo_{0.5}O_x

Property	Value
Bulk density, g/cm ³	34.81 ± 0.04
Percent of theoretical density	93
Coefficient of thermal expansion	14.0 × 10 ⁻¹⁶ /°C (200-800°C)
Flexural strength, MPa	120.4 ± 6.8
Fracture toughness, MPa√m	2.04 ± 0.06
Young's modulus, GPa	124 ± 3
Shear modulus, GPa	48 ± 2
Poisson ratio	0.30 ± 0.01

temperatures. Measured room-temperature properties were used to develop failure criteria for the membranes under actual reaction conditions in a plant where methane is expected to be at higher pressures. Figure 3 shows the computed allowable external pressure on SrFeCo_{0.5}O_x as a function of tube wall thickness. These calculations were based on assumptions that the tensile strength is 0.67 times the flexural stress and that the compressive strength of SrFeCo_{0.5}O_x is greater than its tensile strength by a factor of 8. These results suggest that this ceramic material can withstand reasonable stresses that might occur in a commercial reactor.

Differences between SrFeCo_{0.5}O_x and other materials of the same family are observed in their electronic and ionic conductivity (Table 2) (Ma et al., 1995; Anderson et al., 1994; Chen et al., 1994; Worrell et al., 1993; Teraoka et al., 1988; Ishigaki et al., 1988). It is clear that SrFeCo_{0.5}O_x is

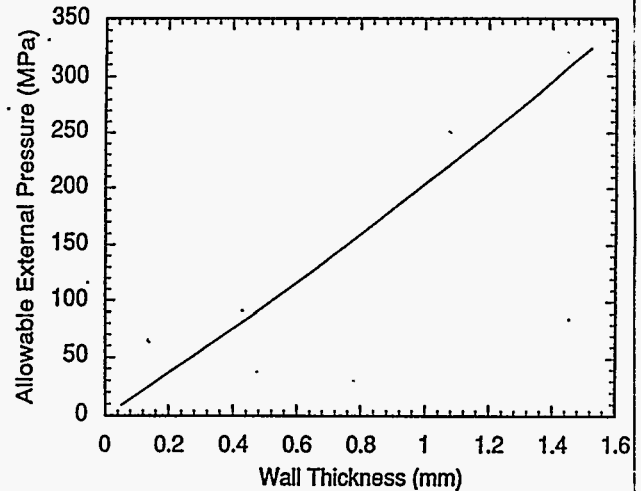


Fig. 3. Allowable external pressure on SrFeCo_{0.5}O_x tubes as a function of wall thickness (O.D. = 6.40 mm).

unique in that its ratio of ionic to electronic conductivity is close to unity.

Furthermore, limited SrFeCo_{0.5}O_x diffusion data, obtained from the time-relaxation method (Ma et al., 1995), indicate that transport of oxygen ions is associated with an activation energy of 0.89 eV. This finding is consistent with the high diffusion coefficient of 9 × 10⁻⁷ cm² s⁻¹ at 900°C.

Performance in generating syngas is demonstrated in Fig. 4, which shows conversion data obtained with an membrane tube at 850°C for 70 h. As shown, methane conversion efficiency is >98%, and CO selectivity is 90%. Measured H₂ yield is approximately twice that of CO, as expected.

Table 2. Electronic and ionic conductivities of various mixed oxides

Sample	Electronic s _{el} (S·cm ⁻¹)	Ionic s _i (S·cm ⁻¹)	Method for Measuring s _i
SrFeCo _{0.5} O _x	10	7	4-terminal, YSZ electron block
SrFe _{0.8} Co _{0.2} O _x	76	4	4-terminal, YSZ electron block
La _{0.6} Sr _{0.4} Co _{0.2} Fe _{0.8} O ₃	300	0.01	4-terminal, YSZ electron block
La _{0.6} Sr _{0.4} Co _{0.2} Fe _{0.8} O ₃	300	0.003	2-terminal, electron block
La _{0.8} Sr _{0.2} Co _{0.8} Fe _{0.2} O ₃	600	15	4-terminal, YSZ electron block
La _{0.8} Sr _{0.2} Co _{0.8} Fe _{0.2} O ₃	250	0.10	4-terminal, YSZ electron block
La _{0.75} Sr _{0.25} FeO ₃	50	0.03	¹⁸ O/ ¹⁶ O exchange

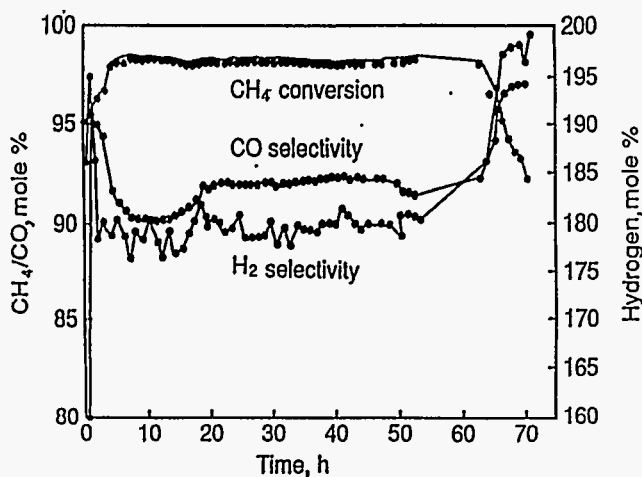


Fig. 4. Methane conversion and CO and H₂ selectivity in SrFeCo_{0.5}O_x membrane reactor with reforming catalyst. Conditions: feed, 80% CH₄, 20% Ar; flow; 2.5 cm³/min; temp., 850°C; pressure 1 atm; membrane surface area, 10 cm².

Further confirmation of the stability and high performance of this membrane tube is shown in Fig. 5, which illustrates reactor results over a period of 1000 h. The feed during this period was a typical mixture expected in a commercial recycling feed, namely methane, CO, CO₂, and H₂. Throughout the run, methane conversion was high. A small decline in oxygen permeation was observed. However, this high oxygen flux is consistent with the high diffusion coefficient of $9 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ that was measured by the time-relaxation method (Ma et al., 1995).

A further run of 1000 h, seen in Fig. 6, was made with a methane/argon feed. During this run, the temperature was changed several times. To compensate for the resulting change in reaction rate, the feed flow rate was altered accordingly. Selectivity to CO during the entire run remained >98%. Oxygen permeability followed the changes in temperature and feed flow.

CONCLUSIONS

Mixed-conducting ceramic materials have been produced from mixed-oxide systems that can produce selective permeable membranes for hydrogen and oxygen. An example of a successful oxygen-separating membrane of modified perovskite structure was discussed in terms of its fabrication, physical properties and performance in the production of syngas from the partial oxidation of methane.

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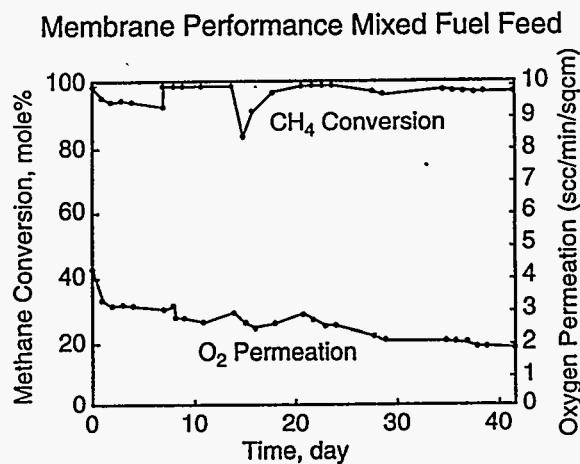


Fig. 5. Methane conversion and O₂ flux for a mixed feed. Conditions: feed, mix CH₄, CO, H₂ and CO₂, temp., 900°C; pressure 1 atm; catalyst, 1.5 g; membrane surface area, 8.4 cm².

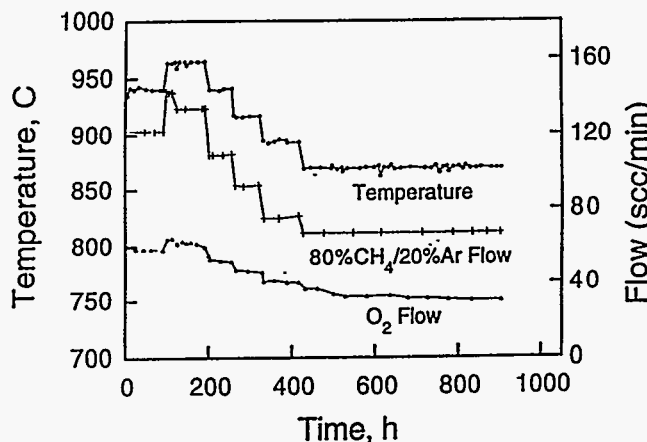


Fig. 6. Temperature profile and O₂ feed flow. Conditions: feed, pressure 1 atm; membrane surface area, 4.4 cm².

REFERENCES

- Anderson, H. U., Chen, C. C., Tai, L. W., and Nasrallah, M. M., 1994, in *Proc. 2nd Intl. Symp. on Ionic and Mixed Conduction Ceramics* (T. A. Ramanarayanan, W. L. Worrell, and H. L. Tuller, eds.) pp. 376-387, The Electrochem. Soc., Pennington, NJ.
- Balachandran, U., Morissette, S. L., Picciolo, J. J., Dusek, J. T., Poeppel, R. B., Pei, S., Kleefisch, M. S., Mieville, R. L., Kobylinski, T. P., and Udovich, C. A., 1992, in *Proc. Int. Gas Res. Conf.* (H. A. Thompson, ed.) pp. 565-573, Government Institutes, Inc., Rockville, MD.
- Balachandran, U., Morissette, S. L., Dusek, J. T., Mieville, R. L., Poeppel, R. B., Kleefisch, M. S., Pei, S., Kobylinski, T. P., and Udovich, C. A., 1993, in *Proc. Coal*

Liquefaction and Gas Conversion Contractors Rev. Conf. (S. Rogers et al., eds.), Vol. 1, pp. 138-160, U.S. Dept. of Energy, Pittsburgh Energy Technology Center, Pittsburgh, PA, Sept. 27-29.

Balachandran, U., Kleefisch, M. S., Kobylinski, T. P., Morissette, S. L., and Pei, S., 1994, International Patent WO94/24065, October.

Brown, W. F., Jr. and Strawley, J. E., 1967, ASTM STP 410, Philadelphia, PA.

Cable, T. L., 1990, European Patent EP 0 399 833 A1, Nov. 28.

Cable, T. L., 1991, European Patent EP 0438 902 A2, July 31.

Chadwick, A. G., Strange, J. H., Ramieri, G. A., and Terenzi, M., 1983, *Solid State Ionics*, **9/10**, 555.

Chen, C. C., Nasrallah, M. M., and Anderson, H. U., 1994, submitted to *J. Electrochem. Soc.*

Iwahara, H., Uchida, H., Morimoto, K., and Hosgoi, S., 1989, *J. Appl. Electrochem.*, **19**, 448.

Ishigaki, T., Yamauchi, S., Kishio, K., Mizusaki, J., and Fuek, K., 1988, *Solid State Chem.*, **73**, 179.

Kendall, K. R., Navas, C., Thomas, J. K., and zur Loye, H.-C., 1995, *Solid State Ionics*, **82**, 215.

Kraüt Kramer, J., and Kraüt Kramer, H., 1983, *Ultrasonic Testing of Materials* (Springer—Verlag, New York).

Ma, B., Park, J.-H., Balachandran, U., and Segre, C. U., 1995, "Electronic/Ionic Conductivity and Oxygen Diffusion Coefficient of the Sr-Fe-Co-O System," Materials Research Society Spring Meeting, San Francisco, CA, April 17—21.

Ma, B., Balachandran, U., Park, J.-H. Park, and Segre, C. U., 1996, *Solid State Ionics*, **83**, 65.

Pei, S., Kleefisch, M. S., Kobylinski, T. P., Faber, J., Udovich, C. A., Zhang-McCoy, V., Dabrowski, B., Balachandran, U., Mieville, R. L., and Poeppel, R. B., 1995, *Catal. Lett.*, **30**, 201.

Scholten, M. J., Schoonman, J., van Miltenburg, J. C., and Oonk, H. A. J., 1993, *Solid State Ionics*, **61**, 83.

Teraoka, Y., Zhang, H. M., Furukawa, S., and Yamazoe, N., 1985, *Chem. Lett.*, 1743.

Teraoka, Y., Nobunaga, T., and Yamazoe, N., 1988, *Chem. Lett.*, 503.

Teraoka, Y., Zhang, H. M., Okamoto, K., and Yamazoe, N., 1988, *Mater. Res. Bull.*, **23**, 51.

Worrell, W. L., Han, P., and Huang, J., 1993, in *High Temperature Electrochemical Behavior of Fast Ion and Mixed Conductors* (F. W. Poulsen, J. J. Bertzen, T. Jacobson, E. Skou, and M. J. L. Ostergood, eds.), Risø National Laboratory, Roskilde, Denmark) pp. 461-466.