ANL/ET/CP--91779 CONF-970163--1

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November 1996

To be presented at the 11th Intersociety Cryogenic Symposium, Energy Week Conf. & Exhibition, Houston, TX, Jan. 28-30, 1997.

*Work at Argonne National Laboratory was supported by the U.S. Department of Energy, Pittsburgh Energy Technology Center, under Contract W-31-109-Eng-38.

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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 ($CO + H_2$) 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 ≈850°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 hae 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°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 $(LaSr)(FeCo)O_x$ 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.,

1993). The most significant cost associated with conventional partial oxidation of methane is that of the oxygen plant, and this new application of the oxygen membrane offers a way to significantly reduce that cost. As an illustration of the potential of gas separation by mixed conducting membranes, we focus on this technology using a membrane of a nonperovskite structure, namely, $SrFeCo_{0.5}O_x$.

EXPERIMENTAL

$SrFeCo_{0.5}O_x$ has a unique structure (Balachandran et al., 1994) that is our present and preferred material and the focus of most of this study. In the preparation of this mixed oxide ceramic, appropriate amounts of $SrCo_3$, $Co(NO_3)_2.6H_2O$, and Fe_2O_3 were mixed and milled in isopropanol with ZrO_2 media for ≈15 h. When dry, the mixtures were calcined in air at ≈850°C for ≈16 h, with intermittent grinding. After final calcination, we ground the powder with an agate mortar and pestle to an average particle size of ≈7 μm. The resulting powders were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and thermal analysis, and also analyzed for particle-size distribution.

The powder was made into a slip containing a solvent, dispersant, binder, and plasticizer. The role of each additive has been described in an earlier publication (Balachandran et al., 1992). Membrane tubes were fabricated by extrusion of the slip to an outside diameter of ≈6.5 mm, lengths up to ≈30 cm, and wall thickness of 0.25-1.20 mm.

The extruded tubes were sintered and then characterized by SEM and XRD and finally used in our partial-oxidation studies to transport oxygen for the generation of syngas. Sintered rectangular bar samples were used to measure mechanical properties. Sintered pellet samples were prepared for conductivity and diffusion measurements.

The tubes were evaluated for performance in a quartz reactor system, as shown in Fig. 1. The quartz reactor supports the ceramic membrane tube with hot Pyrex seals. This design allows the ceramic tube to be in an isothermal environment. To facilitate reactions and equilibration of gases in the reactor, an Rh-based reforming catalyst (≈1 cm^3) is loaded adjacent to the tube. A gold wire mesh is wrapped around the tube to prevent solid-state reactions between the catalyst and the ceramic. Both the feed gas (generally 80% methane, 20% argon) and the effluents were analyzed by gas chromatograph.

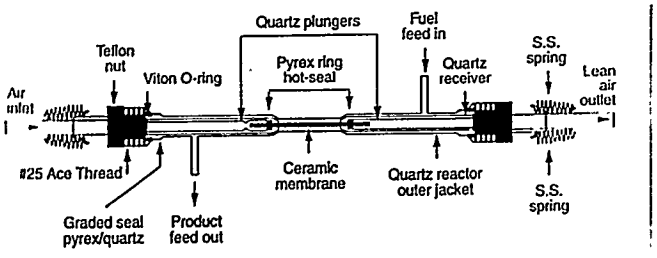

Fig. 1. Schematic diagram of ceramic membrane reactor.

Mechanical properties of the finished material were measured by conventional methods, i.e., bulk density was measured by the Archimedes principle; flexural strength, in a four-point bending mode; fracture toughness, by a single-edge notch method (Brown and Strawley, 1967); and Young's modulus, shear modulus, and Poisson ratio, by ultrasonic methods (Kraütkramer and Kraütkramer, 1983). The thermal expansion coefficient was measured in a dilatometer. Conductivity was determined by a four-probe method with a blocking electrode of yttria-stabilized zirconia (YSZ) for oxygen ion conduction (Ma et al., 1995). The oxygen diffusion coefficient was measured by a time relaxation method. The sample was subjected to a sudden increase oxygen partial pressure, and ionic conductivity was monitored as a function of time and temperature (Ma et al., 1995).

RESULTS AND DISCUSSION

The XRD pattern of an $SrFeCo_{0.5}O_x$ sample was recorded at 850°C in an Ar-O_2 gas mixture and the results are shown in Fig. 2. The $SrFeCo_{0.5}O_x$ exhibited remarkable structural stability at high temperature, and no phase transition was observed in this material as oxygen partial pressure was changed. Furthermore, the Bragg peaks stayed at the same position regardless of the oxygen partial pressure of the atmosphere. This structural stability of $SrFeCo_{0.5}O_x$, when compared with that of other mixed oxides of similar type, is reflected in its physical and mechanical properties, as shown in Table 1.

The results shown in Table 1 indicate that $SrFeCo_{0.5}O_x$ has adequate mechanical properties. Application of Weibull statistics to the fracture strength data show that the Weibull modulus was 15, indicating only moderate scatter in the strength data. Limited fractural strength data obtained at 900°C suggest no degradation of strength at elevated

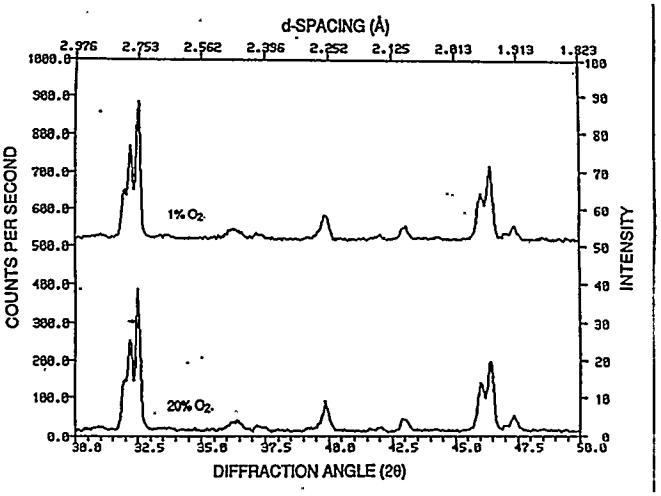

Fig. 2. XRD of $SrFeCo_{0.5}O_x$ at 850°C in 1% and 20% O_2 (balance is Ar).

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 x 10^{-16}/°C (200-800°C)
Flexural strength, MPa	120.4 ± 6.8
Fracture toughness, MPa$\sqrt{m}$	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

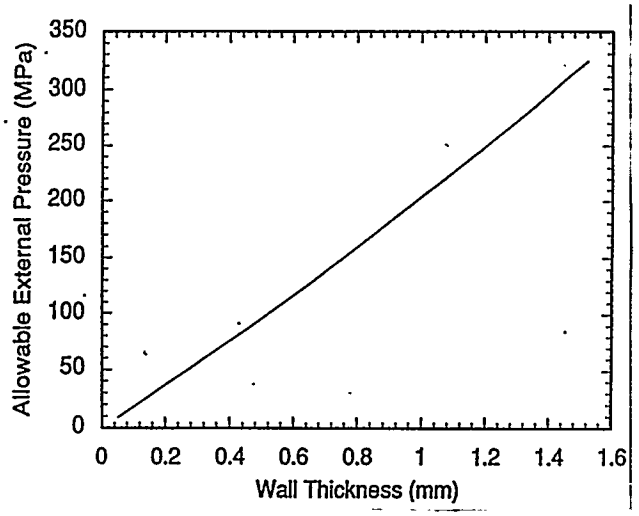

Fig. 3. Allowable external pressure on $SrFeCo_{0.5}O_x$ tubes as a function of wall thickness (O.D. = 6.40 mm).

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 x 10^{-7} cm^2 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 H_2 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

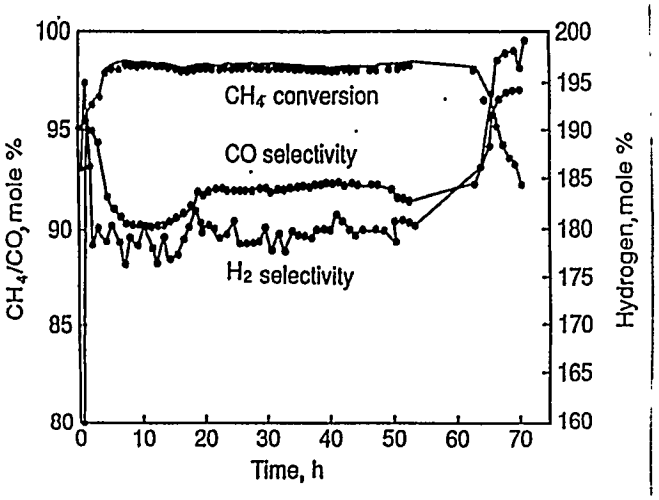

Fig. 4. Methane conversion and CO and H_2 selectivity in $SrFeCo_{0.5}O_x$ membrane reactor with reforming catalyst. Conditions: feed, 80% CH_4, 20% Ar; flow, 2.5 cm^3/min; temp., 850°C; pressure 1 atm; membrane surface area, 10 cm^2.

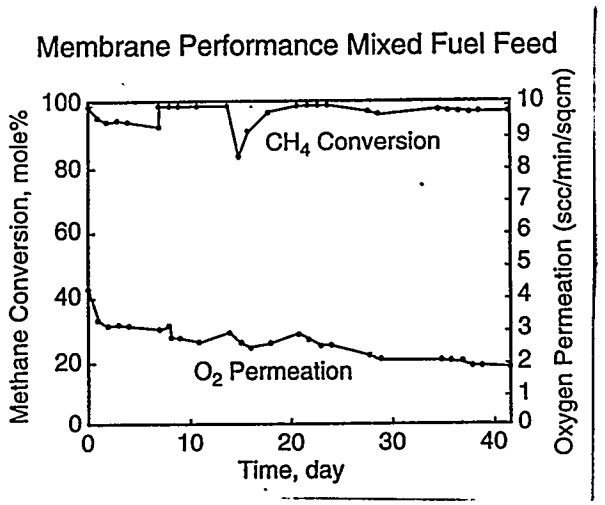

Fig. 5. Methane conversion and O_2 flux for a mixed feed. Conditions: feed, mix CH_4, CO, H_2 and CO_2, temp., 900°C; pressure 1 atm; catalyst, 1.5 g; membrane surface area, 8.4 cm^2.

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, CO_2, and H_2. 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 9×10^{-7} cm^2 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.

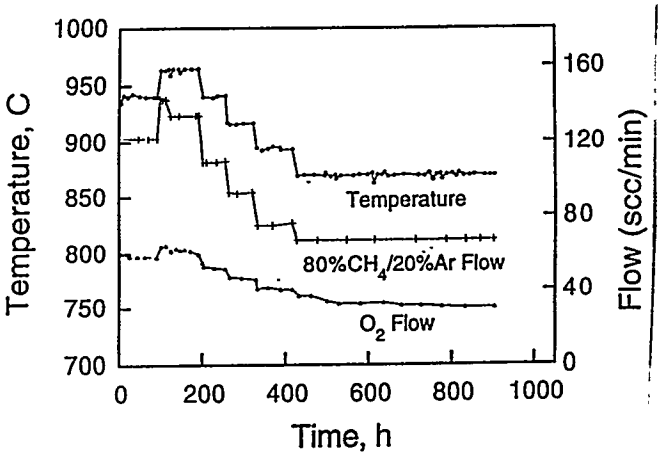

Fig. 6. Temperature profile and O_2 feed flow. Conditions: feed, pressure 1 atm; membrane surface area, 4.4 cm^2.

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.

ACKNOWLEDGMENTS

Work at Argonne National Laboratory was supported by the U.S. Department of Energy, Pittsburgh Energy Technology Center, under Contract W-31-109-Eng-38.

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