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Dense mixed-oxide ceramics capable of conducting both electrons and oxygen ions are promising materials for partial oxygenation of methane to syngas. We are particularly interested in an oxide based on the Sr-Fe-Co-O system. Dense ceramic membrane tubes have been fabricated by a plastic extrusion technique. The sintered tubes were then used to selectively transport oxygen from air through the membrane to make syngas without the use of external electrodes. The sintered tubes have operated for >1000 h, and methane conversion efficiencies of >98% have been observed. Mechanical properties, structural integrity of the tubes during reactor operation, results of methane conversion, selectivity of methane-conversion products, oxygen permeation, and fabrication of multichannel configurations for large-scale production of syngas will be presented.

Mixed-oxide conductors find wide application in high–temperature solid–state electrochemical devices such as solid–oxide fuel cells, batteries, and sensors. The same materials also hold particular promise as ceramic membranes designed to separate oxygen from air, because they are impervious to other gaseous constituents. High oxygen permeability, usually associated with high oxygen ionic conductivity, is desirable in the separation process. (La,Sr)(Fe,Co)O_x systems have been shown by Teraoka et al. (1,2) to exhibit not only mixed (electronic and ionic) conductivities but also appreciable oxygen permeability (two orders of magnitude higher than that of stabilized zirconia at 800°C.)

No external electrodes are required for oxygen separation in these systems, which will operate without an external applied potential. Furthermore, the oxygen flux obtainable from the separation of air is considered commercially feasible for syngas generation by the partial oxidation of methane (3–5). The most significant cost associated with the conventional partial oxidation of methane is that of an oxygen plant. Our new technology offers a way to lower this cost, and in this paper we explore the technology that is based on dense ceramic membranes and uses air as the oxidant for methane–conversion reactions. We discuss how dense ceramic materials can be shaped into a hollow-tube reactor, with air passed over the outside of the membrane and methane through the inside (or vice versa).

Because the membrane is permeable only to oxygen at high temperatures, no dilution with nitrogen or other gases occurs. Thus, only oxygen from air can be transported through the membrane to the inside of the reactor surface, where it reacts with methane. Other geometric designs of the reactor, such as honeycombing or corrugation, are possible and can provide substantially greater surface areas for reaction (6).

EXPERIMENTAL

Several La-Sr-Fe-Co mixed oxides (known as SFCs) of various stoichiometries were prepared by solid-state reaction of the constituent cationic salts. In this paper, we consider only two mixed oxides: SFC-1, which has the formula $Sr_1Fe_{0.2}Co_{0.8}O_x$ and is a perovskite, previously studied and described by Teroaka et al. (1,2); and SFC-2, which has a stoichiometry of $Sr_1Fe_1Co_{0.5}O_x$ and a unique structure that is not a perovskite (7). SFC–2 is currently preferred and is the focus of most of this study. In the preparation of these mixed-oxide ceramics, appropriate amounts of $La(NO_3)_3$, $SrCO_3$, $Co(NO_3)_2.6H_2O$, 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; they were also analyzed for particle–size distribution.

The powder for the study was made into a slip that contained a solvent, dispersant, binder, and plasticizer. The role of each additive is described in Ref. 8. Membrane tubes were fabricated by extrusion of the slip to an outside diameter of ≈6.5 mm, lengths up to ≈30 cm, and wall thicknesses of 0.25–1.20 mm. After extrusion, the tubes were sintered. The sintered tubes were characterized by SEM and XRD and then used in our partial–oxidation studies to transport oxygen for the generation of syngas. Sintered rectangular bar samples were used to measure mechanical properties, and sintered pellet samples were prepared for measuring conductivity and diffusion.

The tubes were evaluated for performance in a quartz reactor system, 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) was loaded adjacent to the tube. 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 chromotography.

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 (9); and Young's modulus, shear modulus, and Poisson ratio, by ultrasonic methods (10). Thermal

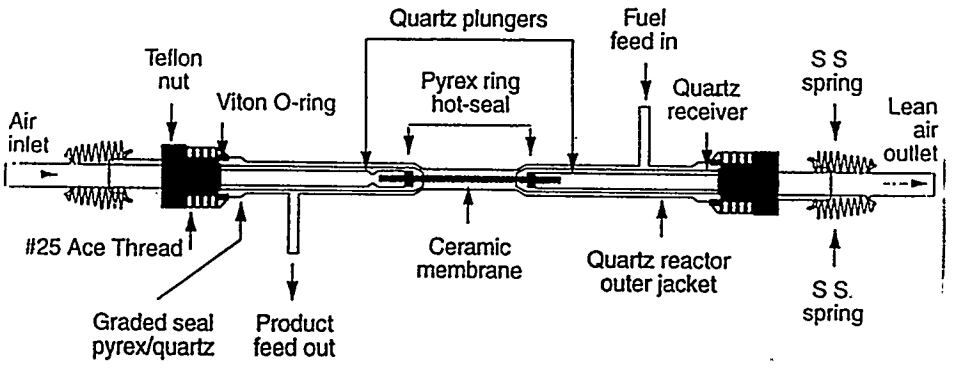

Fig. 1. Schematic diagram of ceramic membrane reactor.

expansion coefficients were measured in a dilatometer. Conductivities were measured by a four-probe method with a blocking electrode of yttria–stabilized zirconia for oxygen-ion conduction (11). Oxygen diffusion coefficients were measured by a time relaxation method. The sample was subjected to a sudden change in oxygen partial pressure, and ionic conductivity was monitored as a function of time and temperature (12).

RESULTS AND DISCUSSION

Tubes of SFC–1 survived only a few minutes when used as a conversion reactor at 850°C; they then broke into several pieces. XRD patterns of the original samples of SFC–1 were recorded at 850°C in Ar-O_2 gas mixtures. The phase behavior of SFC-1 in 1 and 20% O_2 is shown in Fig. 2. In an oxygen-rich (20% O_2) atmosphere, the material was a cubic perovskite. However, once the oxygen partial pressure was lowered below 5%, the cubic phase transformed to an oxygen-vacancy-ordered phase.

New peaks appeared in the XRD pattern, as seen in Fig. 2 (1% O_2). It is important to note that this material expanded substantially after the phase transition; this can be seen from the change in the position of the Bragg peak near 32°. Evidently, this peak in the oxygen-vacancy-ordered phase (in 1% O_2) shifted to the low–angle (larger d-spacing) side of the corresponding peak in the cubic perovskite phase (in 20% O_2).

Detailed thermogravimetric analysis (TGA) [13] showed that the oxygen content x of the SFC–1 sample in 1% O_2 was ≈0.1 lower than that in a sample in 20% O_2. Dependence of the unit cell volume on oxygen content of the sample was established by comparing lattice parameters. For example, the volume of the primitive perovskite cell Vp is 57.51 $Å^3$ for x = 2.67 and 59.70 $Å^3$ for x = 2.48. These results show that this material expands as oxygen is removed and suggest that an electronic effect is predominant in influencing the specific volume; otherwise, a simple size effect would cause the lattice to shrink. By linear interpolation of the above results, we predict that a decrease in x of 0.1 will result in an increase in Vp of ≈2%.

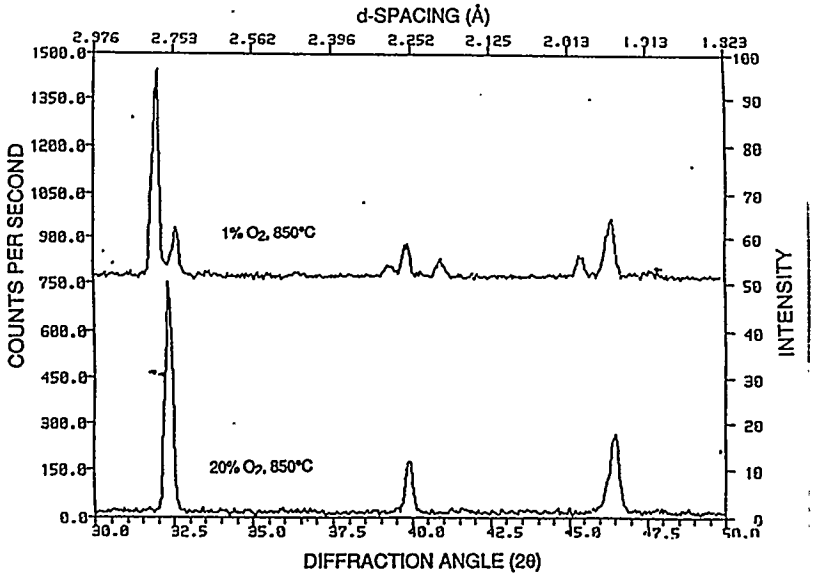

Fig. 2. XRD of SFC–1 at 850°C in 1% and 20% O_2 (balance is Ar).

Both XRD results and TGA data (13) give a clear picture of the state of SCF–1 under reaction conditions. When the membrane tube is operating, high oxygen pressure is maintained inside the tube and low oxygen pressure is maintained outside the tube. Before the tube is heated to high temperature, oxygen distribution is uniform. Upon heating, the tube material begins to lose the oxygen that was incorporated during fabrication. Moreover, the tube material on the outer wall loses more oxygen than does the material on the inner wall. As a result, a stable oxygen gradient is generated between the inner and outer walls. It follows that the material, depending on its location in the tube, may contain different phase constituents. It is probable that the outer zone of lower oxygen content contains the greater number of ordered oxygen vacancies and hence is less permeable to oxygen.

The major cause of tube fracture appears to be lattice mismatch between the materials on the inner and outer walls of the tube. The difference in composition between the inner and outer walls leads to an expansion of 2%, which is equivalent to thermal expansion caused by a 333°C temperature increase.

SFC-2 exhibited remarkable structural stability at high temperature, as shown in Fig. 3. 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. The physical and mechanical properties of SFC–2 are listed in Table I.

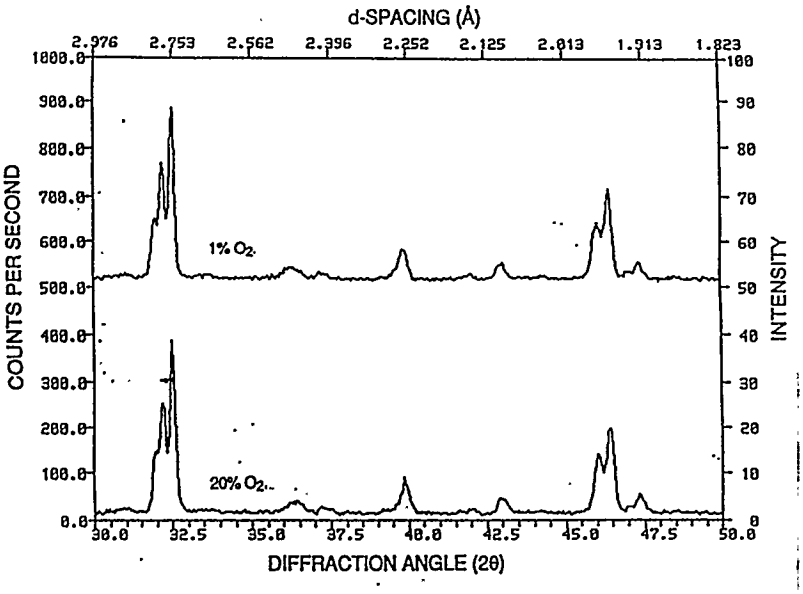

Fig. 3. XRD of SFC–2 at 850°C in 1% and 20% O_2 (balance is Ar).

Table I. Physical and mechanical properties of SFC–2

Property	Value
Bulk density	4.81 g/cm^3
Percent of theoretical density	93
Coefficient of thermal expansion	14 x 10^{-6}/°C (200-800°C)
Flexural strength	120.4 ± 0.06 MPa
Fracture toughness	2.04 ± 0.06 MPa$\sqrt{m}$
Young's modulus	124 ± 3 GPa
Shear modulus	48 ± 2 GPa
Poisson ratio	0.30 ± 0.01

The Weibull modulus was 15 (as measured by plotting the probability of failure vs. flexural strength), indicating only moderate scatter in the strength data. 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. The computed allowable external pressure for SFC-2 was 200 MPa at a tube wall thickness of 1 mm (the dependence of pressure on thickness is linear). These results suggest that this ceramic material can withstand the reasonable stresses that might occur in a commercial reactor. Tubes made of this material, unlike those made of SFC-1, are not expected to fracture under reactor conditions.

The electronic and ionic conductivities of SFC-2 were 10 and 7 s cm, respectively. When compared with other materials of this type, SFC–2 is unique in that its ratio of ionic

to electronic conductivity is close to 1 (12). Furthermore, limited SFC–2 diffusion data, obtained by the time relaxation method (13), indicate that the transport of oxygen ions is associated with an activation energy of 0.89 eV, a value that is consistent with the high diffusion coefficient of 9×10^{-7} cm^2 s^{-1} at 900°C.

Performance in generating syngas is demonstrated in Fig. 4, which shows conversion data obtained with an SFC–2 membrane tube operated at 850°C for ≈70 h. As shown, methane conversion efficiency is >98%, and CO selectivity is 90%. Measured H_2 yield is about twice that of CO, as expected.

The role of the catalyst in the transport of oxygen across the membrane of an SFC–2 tube was tested without the reforming catalyst. The results from a run of ≈350 h are shown in Fig 5. Feed gases are the same as before. In the absence of the catalyst, the oxygen that was transported through the membrane reacted with methane and formed CO_2 and H_2O. As seen in Fig. 5, methane conversion efficiency was ≈35% and CO_2 selectivity was ≈90%. Under our operating conditions, the measured oxygen flux was ≈0.3 std $cm^3/cm^2/min$.

Further confirmation of the stability of this membrane tube is shown in Fig. 6, which shows reactor results over a period of 1000 h. The feed during this period was a typical mixture expected in a commercial recycle feed, namely methane, CO, CO_2, and H_2. Throughout the run, methane conversion was high. Variations in feed flow rate caused fluctuations in conversion. A small decline in oxygen permeation was observed. However, 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 (12).

CONCLUSIONS

Mixed–conducting ceramic materials have been produced from mixed–oxide systems of the Sr–Fe–Co–O (SFC) type, in the form of tubes and bars. Thermodynamic stability of the tubes was studied as a function of oxygen partial pressure by high–temperature XRD. Mechanical properties of SFC–2 were measured and found to be adequate for a reactor. Measured electronic and ionic conductivities showed that SFC–2 is unique in that the ratio of ionic to electronic conductance is close to 1.

Performance of the membrane tubes was good only when the tubes were made of SFC–2. Fracture of other SFC tubes was the consequence of an oxygen gradient that introduced a volumetric lattice difference between the inner and outer walls. SFC–2 tubes provided methane conversion efficiencies of >99% in a reactor. These tubes have operated for >1000 h.

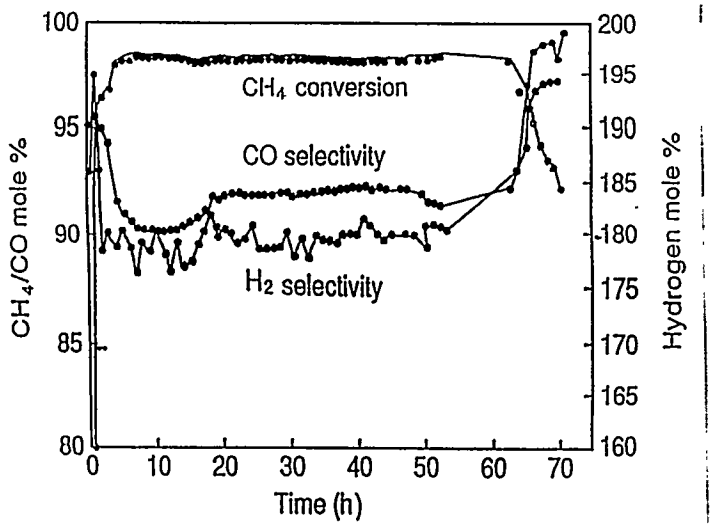

Fig. 4. Methane conversion and CO and H_2 selectivities in SFC–2 membrane reactor with reforming catalyst. Conditions: feed, 80% CH_4, 20% Ar; flow, 2.5 cm^3/min; temperature, 850°C; pressure 1 atm; surface area, 10^2.

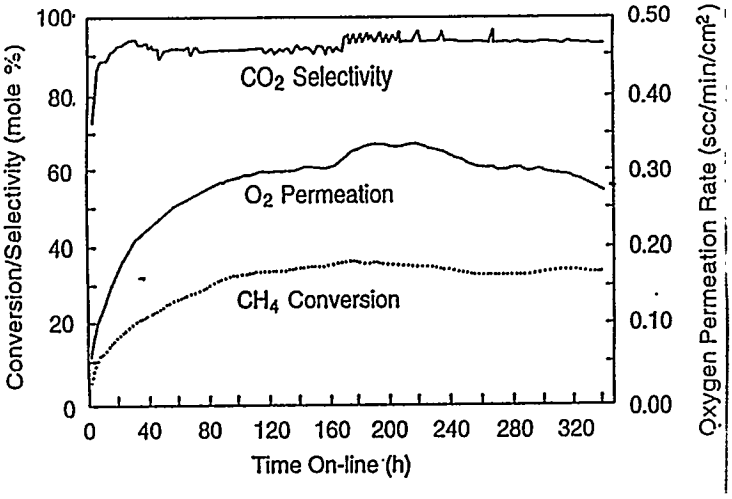

Fig. 5. Methane conversion and CO_2 selectivity and O_2 permeation in SFC–2 membrane reactor without reforming catalyst. Conditions: same as in Fig. 4.

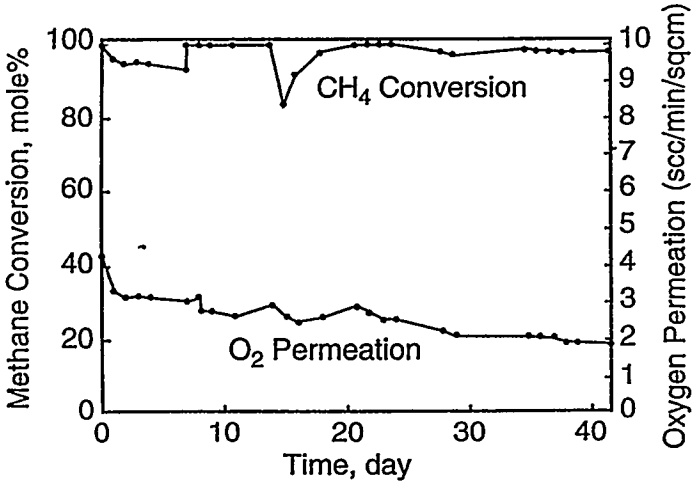

Fig. 6. Methane conversion and CO and H_2 selectivities and O_2 permeation in SFC–2 membrane reactor with reforming catalyst. Conditions: mixed feed, 20 cm^3/min; temperature, 900°C; pressure 1 atm; membrane surface area, 8 cm^2.

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