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MIXED-CONDUCTING CERAMIC MEMBRANES FOR PARTIAL  
OXYGENATION OF METHANE\*

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U. Balachandran, J. T. Dusek, P. S. Maiya, and R. L. Mieville  
Energy Technology Division  
Argonne National Laboratory  
Argonne, IL 60439

M. S. Kleefisch and C. A. Udovich  
Amoco Corporation  
Naperville, IL 60566

A. C. Bose  
U.S. Department of Energy  
Pittsburgh Energy Technology Center  
Pittsburgh, PA 15236

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# MIXED-CONDUCTING CERAMIC MEMBRANES FOR PARTIAL OXYGENATION OF METHANE

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Energy Technology Division  
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## INTRODUCTION

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.  $(\text{La,Sr})(\text{Fe,Co})\text{O}_x$  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 [3–7]. 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 that uses air as the oxidant for methane–conversion reactions.

## EXPERIMENTAL

Three ceramic powders (SFC–1, SFC–2, and SFC–3) in the La–Sr–Fe–Co–O system, with different stoichiometries, were made by solid–state reaction of the constituent cation salts. The stoichiometry of SFC–1 is  $\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.6}\text{Co}_{0.4}\text{O}_x$ , which has been reported by Teraoka et al. [1,2]. The stoichiometry of SFC–2, an improved version of SFC–1, is  $\text{SrFeCo}_{0.5}\text{O}_x$ , and that of SFC–3 is  $\text{SrFe}_{0.2}\text{Co}_{0.8}\text{O}_x$ . All three powders were made by mixing appropriate amounts of  $\text{La}(\text{NO}_3)_3$ ,  $\text{SrCO}_3$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{Fe}_2\text{O}_3$  and grinding in isopropanol with  $\text{ZrO}_2$  media for 15 h. After drying, the mixtures were calcined in air at  $850^\circ\text{C}$  for 16 h with intermittent grinding. After final calcination, the powders were ground with an agate mortar and pestle to an average particle size of  $\approx 7 \mu\text{m}$ . The resulting powders were characterized by X–ray diffraction (XRD), scanning electron microscopy, and thermal analysis, and analyzed for particle–size distribution.

The powder was made into a slip containing a solvent, dispersant, binder, and plasticizer. Membrane tubes were fabricated by extruding the slip to an outside diameter of  $\approx 6.5 \text{ mm}$ , lengths up to  $\approx 30 \text{ cm}$ , and wall thicknesses of  $0.25\text{--}1.20 \text{ mm}$ . The tubes were sintered at  $\approx 1200^\circ\text{C}$  for 5–10 h in stagnant air.

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 [8]; and Young's modulus, shear modulus, and Poisson ratio, by ultrasonic methods [9]. The thermal expansion coefficient was measured in a dilatometer.

The ceramic materials were evaluated for performance in a quartz reactor system, as shown in Fig. 1. The quartz reactor supports the ceramic membrane tube with Pyrex hot seals. This design creates an isothermal environment for the ceramic tube. To facilitate reactions and equilibration of gases in the reactor, an Rh-based reforming catalyst is 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 feed gas and effluents were analyzed by gas chromatography.

Samples were prepared for conductivities and diffusional measurements by compressing the constituent powders at  $1.2 \times 10^3$  MPa into pellets 21.5 mm in diameter and  $\approx 3$  mm thick. Pellets were sintered in air at  $\approx 1200^\circ\text{C}$  for 5 h; they were then cut into small bars. The bulk densities of samples are  $\approx 95\%$  of their theoretical values.

Platinum wires were used as probes in the four-probe conductivity measurement. Specimen resistance was measured with an HP 4192A LF impedance analyzer. For measurement of oxygen ion conduction, yttria-stabilized zirconia (YSZ, with 8 mol%  $\text{Y}_2\text{O}_3$ ) was used for the electron (hole) blocking electrode [10].

The oxygen diffusion coefficient was measured by a 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 [11].

## RESULTS AND DISCUSSION

Tubes of SFC-1 lasted only a few minutes when operated 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<sub>2</sub> gas mixtures. The phase behavior of SFC-1 in 1 and 20% O<sub>2</sub> is shown in Fig. 2. In an oxygen-rich (20% O<sub>2</sub>) 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<sub>2</sub>). 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<sub>2</sub>) was shifted to the low-angle (larger d-spacing) side of the corresponding peak in the cubic perovskite phase (in 20% O<sub>2</sub>).

Detailed thermogravimetric analysis (TGA) [12] showed that the oxygen content,  $x$ , of the SFC-1 sample in 1% O<sub>2</sub> was  $\approx 0.1$  lower than that in a sample in 20% O<sub>2</sub>. Dependence of the unit cell volume on oxygen content of the sample has been established by comparing lattice parameters. For example, the volume of the primitive perovskite cell,  $V_p$ , is 57.51 Å<sup>3</sup> for  $x = 2.67$  and 59.70 Å<sup>3</sup> for  $x = 2.48$ . These results show that this material expands as oxygen is removed. Such behavior suggests 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  $V_p$  by  $\approx 2\%$ .

Both XRD results and TGA data [12] give a clear picture of the state of SCF-1 under reaction conditions. When the membrane tube is operating, high oxygen pressure is maintained outside the tube and low oxygen pressure is maintained inside the tube. Before the tube is brought up to high temperature, oxygen distribution is uniform. Upon heating, the tube material begins to lose oxygen that was incorporated during the fabrication process. Moreover, the material on the inner wall loses more oxygen than that on the outer wall. As a result, a stable oxygen gradient is generated between the outer and inner walls. It follows that the material, depending on its location in the tube, may contain different phase constituents. It is probable that the inner zone of lower oxygen content contains more ordered oxygen vacancies and hence less oxygen permeability.

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

In comparison, SFC-2 exhibited a 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 shown in Table 1.

Table 1. Physical and mechanical properties of SFC-2

Property	Value
Bulk density, g·cm <sup>-3</sup>	4.81 ± 0.04
Percent of theoretical density	93
Coefficient of thermal expansion x 10 <sup>-6</sup> /°C (200–800°C)	14.0
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

Figure 4 shows the probability of failure vs. flexural strength (Weibull statistics) for SFC-2 [13]. The Weibull modulus was 15, 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. Figure 5 shows the computed allowable external pressure on SFC-2 as a function of tube wall thickness. These calculations were based on the assumptions that the tensile strength is ≈0.67 times the flexural stress and that the compressive strength of SFC-2 is greater than its tensile strength by a factor of 8. These results suggest an ability of this ceramic



material to undergo 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.

Differences between SFC-2 and SFC-3 are seen in their electronic and ionic conductivities shown in Table 2, together with those of other materials of this same type. It is clear that SFC-2 is unique in that the ratio of ionic to electronic conductivity is close to unity.

Table 2. Conductivities measured in air at 800°C for (La,Sr)(Fe,Co)O<sub>x</sub> systems

Sample	Electronic $\sigma_{el}$ (S·cm <sup>-1</sup> )	Ionic $\sigma_i$ (S·cm <sup>-1</sup> )	Method for $\sigma_i$ measurement	Ref.
SFC-2	10	7	4-terminal, YSZ electron block	10
SFC-3	76	4	4-terminal, YSZ electron block	10
La <sub>0.6</sub> Sr <sub>0.4</sub> Co <sub>0.2</sub> Fe <sub>0.8</sub> O <sub>3</sub>	300	0.01	4-terminal, YSZ electron block	14
La <sub>0.6</sub> Sr <sub>0.4</sub> Co <sub>0.2</sub> Fe <sub>0.8</sub> O <sub>3</sub>	300	0.003	2-terminal, electron block	15
La <sub>0.8</sub> Sr <sub>0.2</sub> Co <sub>0.8</sub> Fe <sub>0.2</sub> O <sub>3</sub>	600	15	4-terminal, YSZ electron block	16
La <sub>0.8</sub> Sr <sub>0.2</sub> Co <sub>0.8</sub> Fe <sub>0.2</sub> O <sub>3</sub>	250	0.10	4-terminal, YSZ electron block	17
La <sub>0.75</sub> Sr <sub>0.25</sub> FeO <sub>3</sub>	50	0.03	<sup>18</sup> O/ <sup>16</sup> O exchange	18

Furthermore, limited SFC-2 diffusion data obtained from the time-relaxation method [11] indicate that transport of oxygen ions is associated with an activation energy of 0.89 eV. This is consistent with the high diffusion coefficient of  $9 \times 10^{-7}$  cm<sup>2</sup> s<sup>-1</sup> at 900°C.

Performance in generating syngas is demonstrated in Fig. 6, 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<sub>2</sub> 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. 7. The feed gases are the same as before. In the absence of a catalyst, the oxygen that was transported through the membrane reacted with methane and formed CO<sub>2</sub> and H<sub>2</sub>O. As seen in Fig. 8, methane conversion efficiency was ≈35% and CO<sub>2</sub> selectivity was ≈90%. Under our operating conditions, the measured oxygen flux was ≈0.3 std cm<sup>3</sup>/cm<sup>2</sup>/min. Figure 8 shows the result of a reactor run made under more severe conditions and in the presence of a catalyst for >500 h. Conversion and selectivities are similar to those of the 350 h run but the oxygen flux was one order of magnitude greater. Some small deactivation in oxygen permeation rate was observed.

Further confirmation of the stability of this membrane tube is shown in Fig. 9, which shows the 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<sub>2</sub>, and H<sub>2</sub>. 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  $9 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$  measured by the time-relaxation method [11].

## CONCLUSIONS

Mixed-conducting ceramic materials have been produced from mixed-oxide systems of the La-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 were measured and found to be adequate for a reactor in the case of SFC-2. Electronic and ionic conductivities were measured; SFC-2 is unique in the sense that the ratio of ionic to electronic conductance is close to unity.

Performance of the membrane tubes was good only with 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.

## ACKNOWLEDGMENTS

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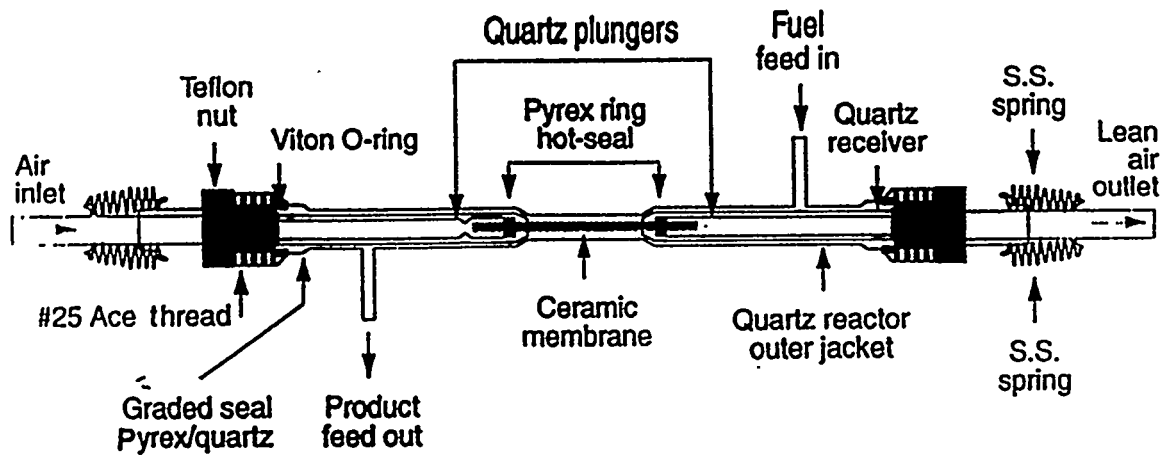


Fig. 1. Schematic diagram of ceramic membrane reactor.

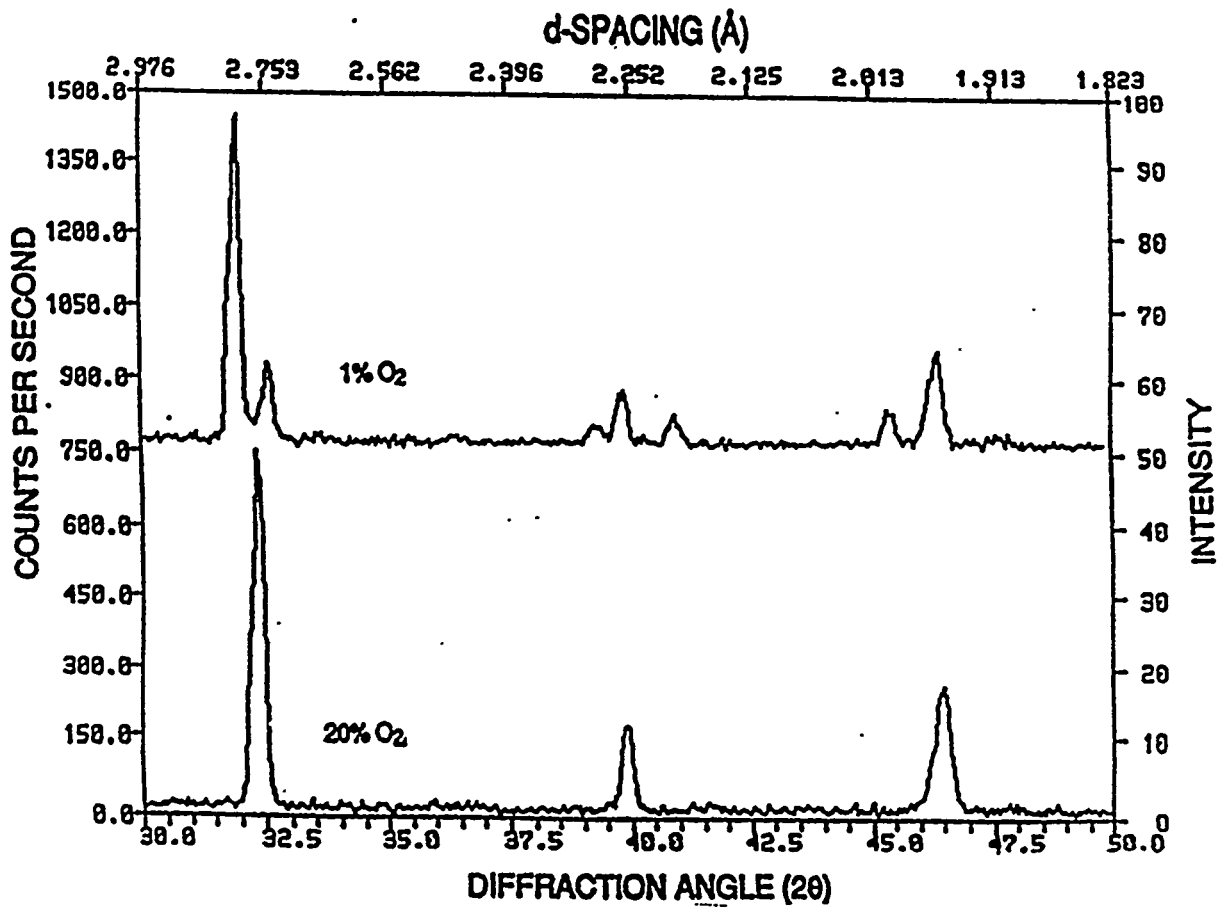


Fig. 2. XRD of SFC-1 at 850°C in 1 and 20% O<sub>2</sub> (balance is Ar).

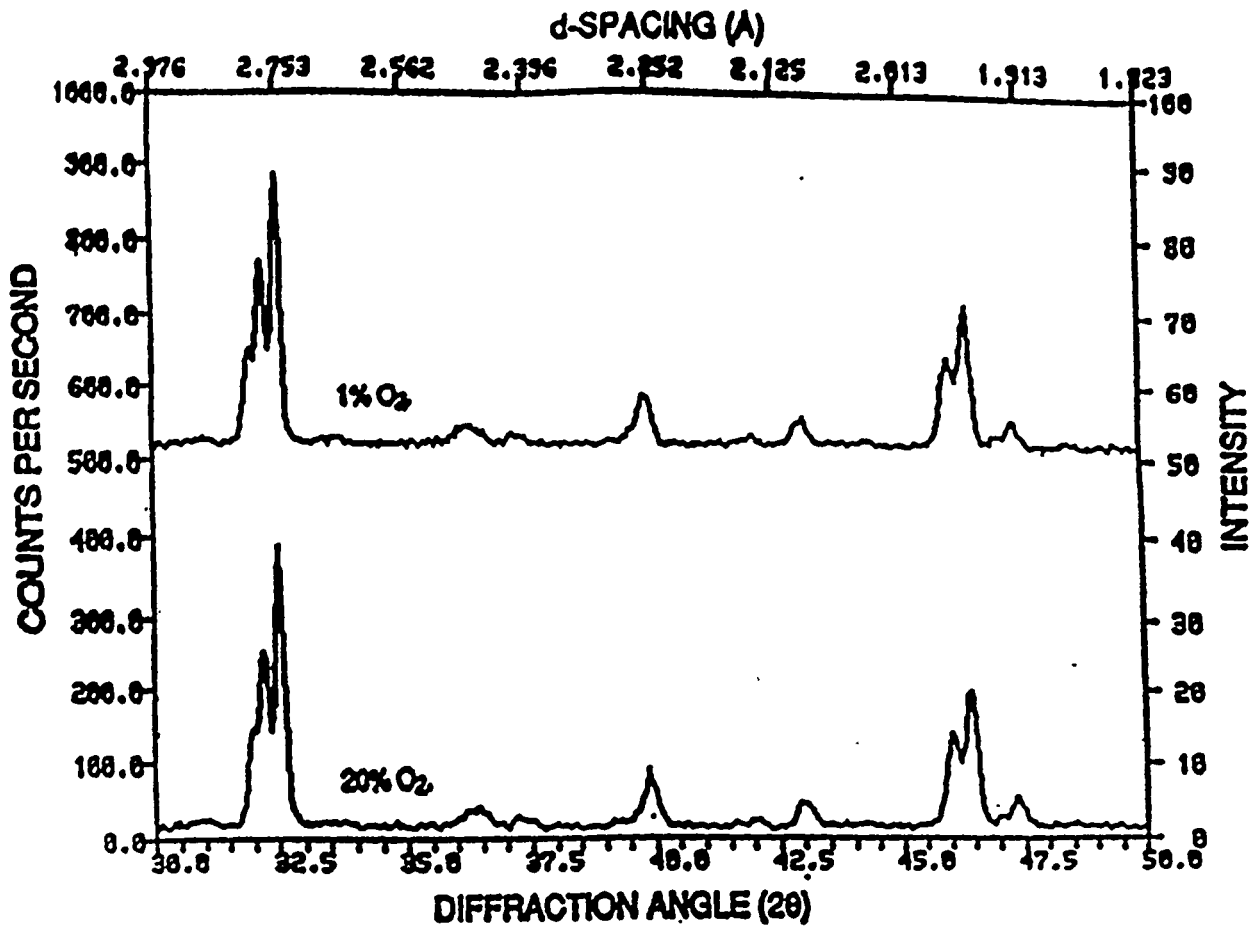


Fig. 3. XRD of SFC-2 at 850°C in 1 and 20% O<sub>2</sub> (balance is Ar).

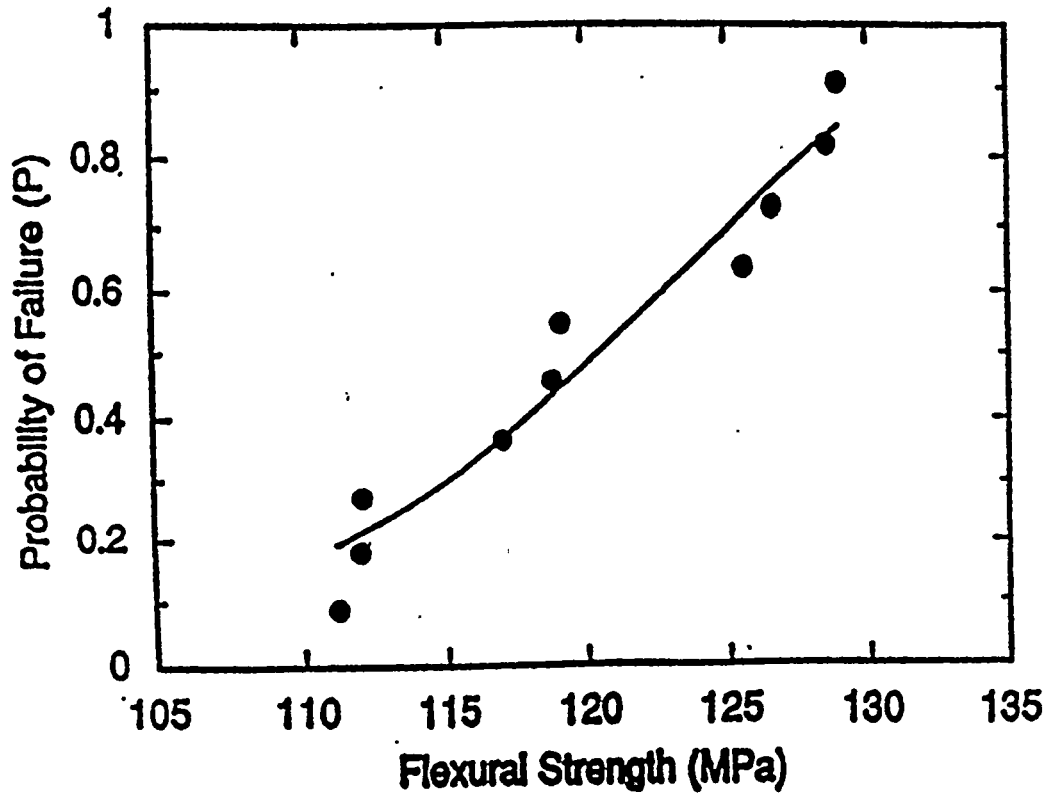


Fig. 4. Probability of failure vs. flexural strength for SFC-2 (Weibull modulus = 14.5).

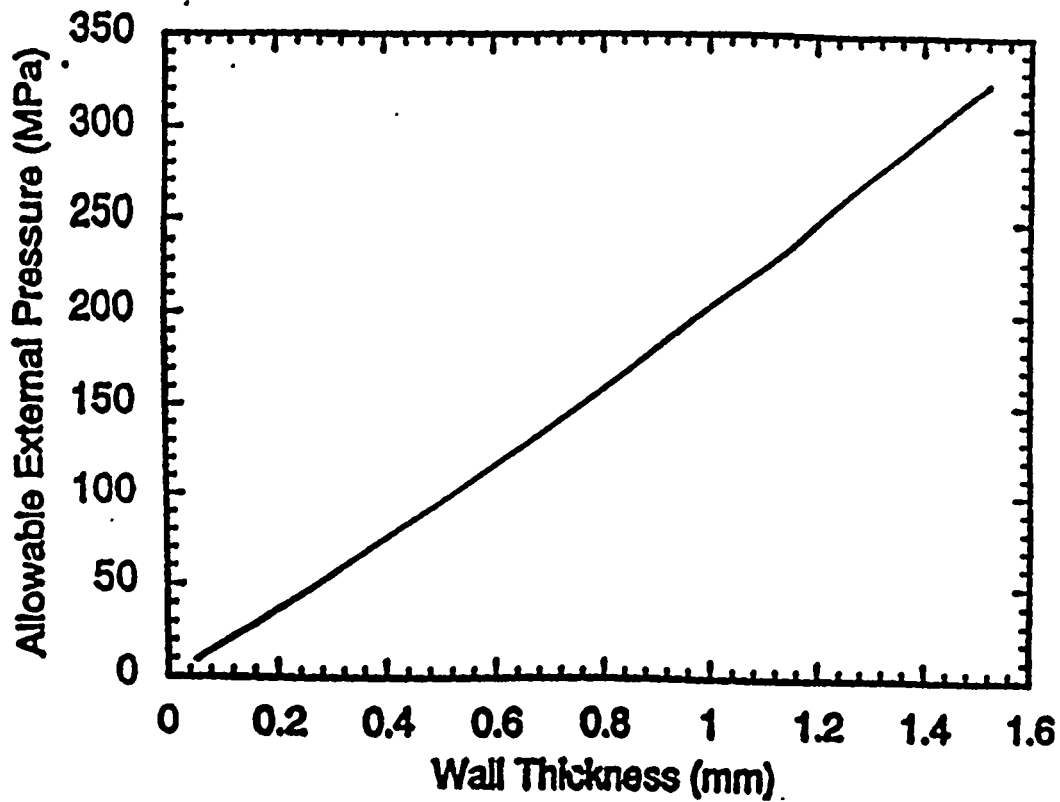


Fig. 5. Allowable external pressure on SFC-2 tubes as a function of wall thickness (outside diameter = 6.40 mm).

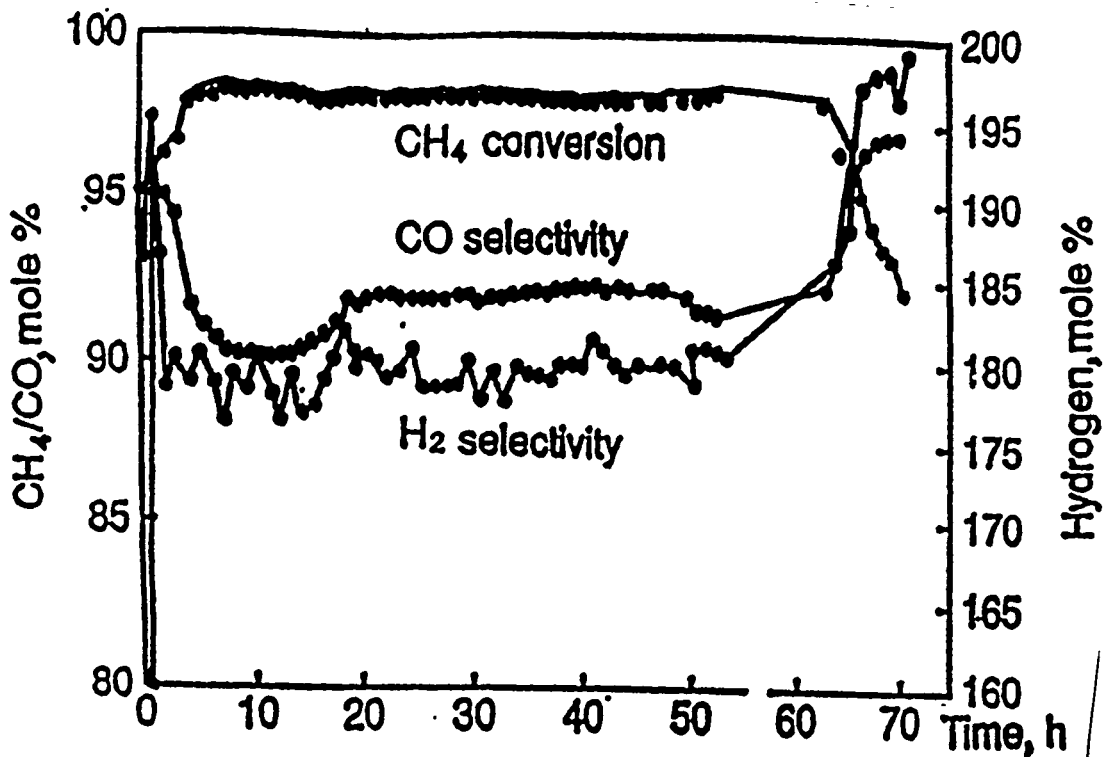


Fig. 6. Methane conversion and CO and H<sub>2</sub> selectivities in SFC-2 membrane reactor with reforming catalyst. Conditions: feed (80% CH<sub>4</sub>, 20% Ar) flow, 2.5 cm<sup>3</sup>/min; temp., 850°C; pressure 1 atm; membrane surface area, 10 cm<sup>2</sup>.



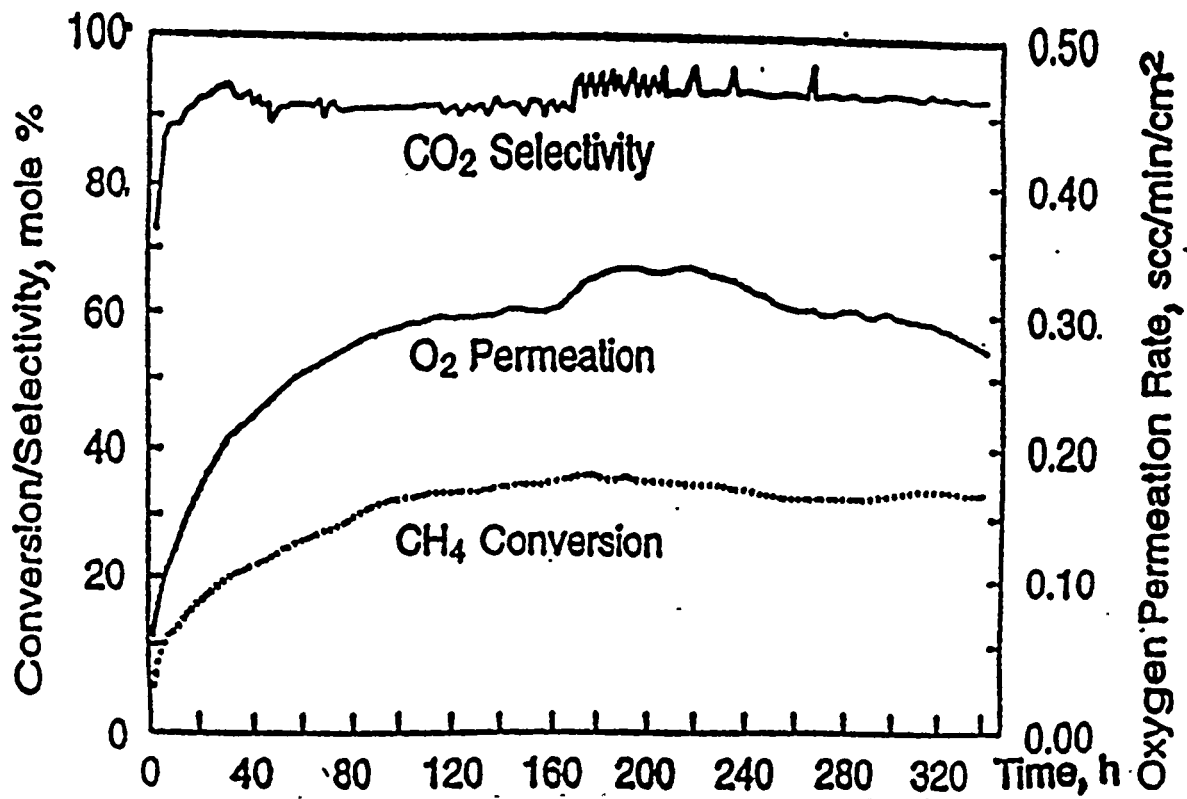


Fig. 7. Methane conversion and CO<sub>2</sub> selectivity and O<sub>2</sub> permeation in SFC-2 membrane reactor without reforming catalyst. Conditions: same as in Fig. 6.

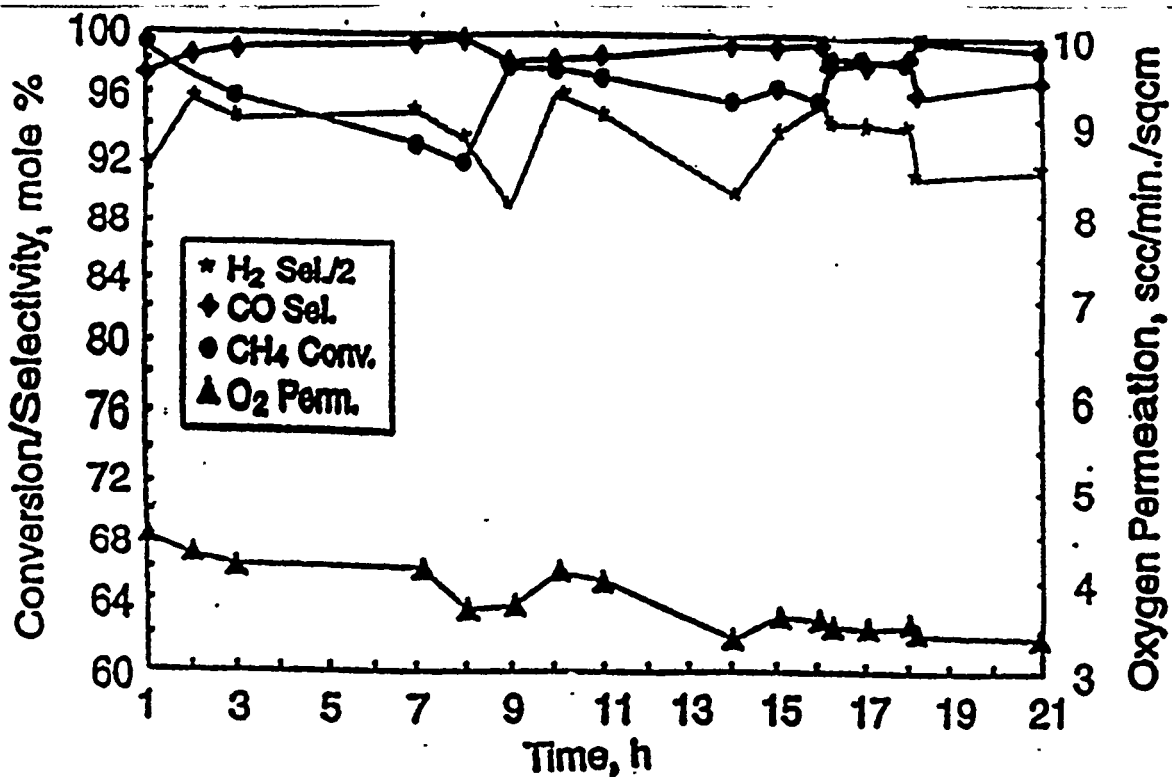


Fig. 8. Methane conversion and CO and H<sub>2</sub> selectivities and O<sub>2</sub> permeation in SFC-2 membrane reactor with reforming catalyst. Conditions: feed (80% CH<sub>4</sub>, 20% Ar) flow, 20 cm<sup>3</sup>/min; temp., 900°C; pressure 1 atm; membrane surface area, 8 cm<sup>2</sup>.

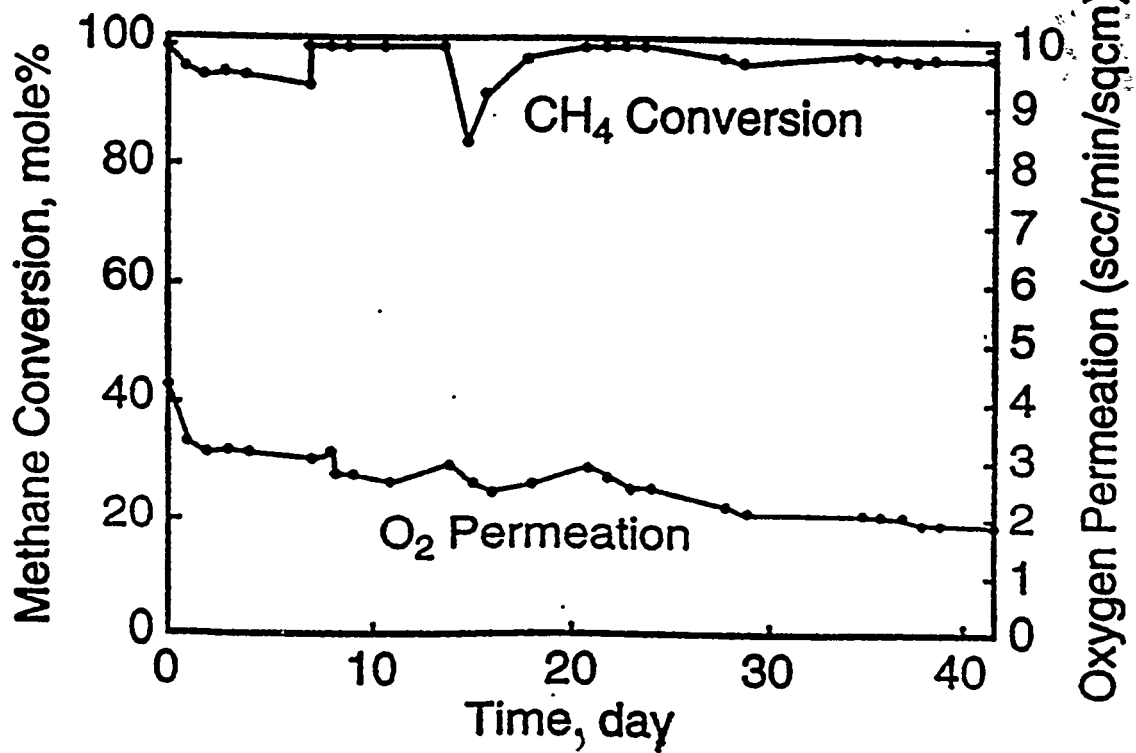


Fig. 9. Methane conversion and O<sub>2</sub> flux for a mixed feed. Conditions: feed (80% CH<sub>4</sub>, 20% Ar); temp., 900°C; pressure 1 atm; catalyst, 1.5 g; membrane surface area, 8.4 cm<sup>2</sup>.