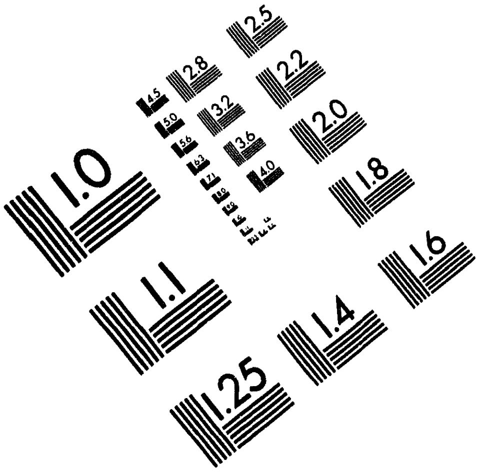

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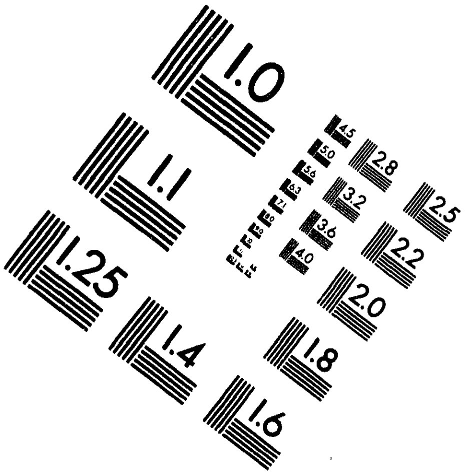

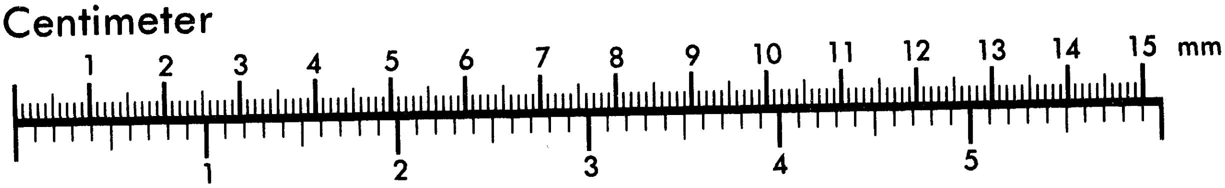

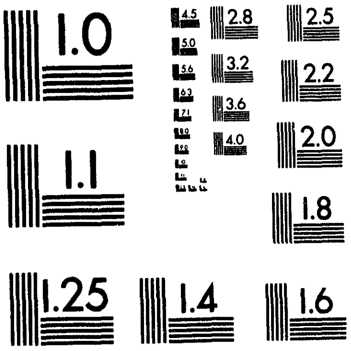

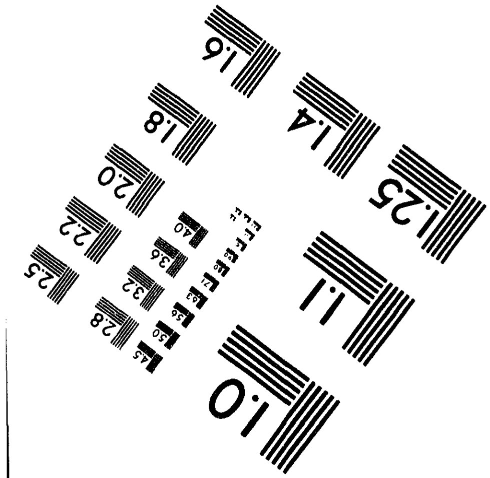

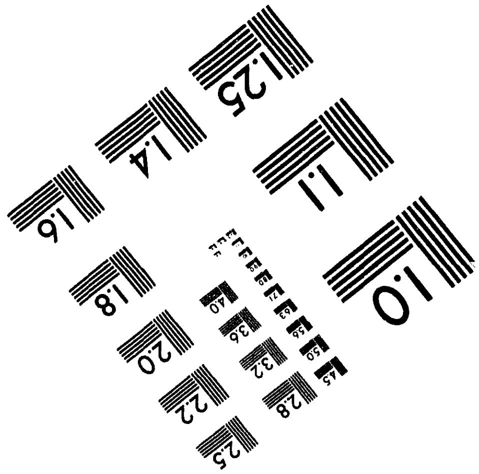

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CERAMIC MEMBRANES FOR GENERATION OF PARTIAL-OXIDATION PRODUCTS FROM METHANE*

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INTRODUCTION

The most significant cost associated with partial oxidation of methane to syngas is that of the oxygen plant. In this paper, we offer a technology, based on dense ceramic membranes, that uses air as the oxidant for methane-conversion reactions and eliminates the need for an oxygen plant. Certain ceramic materials exhibit both electronic and ionic conductivities (of particular interest is oxygen-ion conductivity). These materials transport not only oxygen ions (functioning as selective oxygen separators) but also electrons back from the reactor side to the oxygen-reduction interface. As such, no external electrodes are required and if the driving potential of transport is sufficient, the partial oxidation reactions should be spontaneous. Such a system will operate without an externally applied potential. Oxygen is transported across the ceramic material in the form of oxygen anions and not oxygen molecules.

Recent reports in the literature suggest that ceramic membranes made of these mixed conductors can successfully separate oxygen and nitrogen at flux rates that could be considered commercially feasible [1-8].

EXPERIMENTAL

Two ceramic powders of the La–Sr–Fe–Co–O system with different stoichiometries, designated SFC-1 and SFC-2, were made by solid-state reaction of the constituent cation salts. The stoichiometry of SFC-1 is the same as that of $La_{0.2}Sr_{0.8}Fe_{0.6}Co_{0.4}O_x$, which was used by Teraoka et al. [1,2]. SFC-2 is an improved version of SFC-1. Appropriate amounts of $La(NO_3)_3$, $SrCO_3$, $Co(NO_3)_2 \cdot 6H_2O$, and Fe_2O_3 were mixed and milled in isopropanol with ZrO_2 media for ≈15 h. After drying, the mixtures were calcined in air at ≈850°C for ≈16 h, with intermittent grinding. After final calcination, using an agate mortar and pestle, we ground the powder to an average particle size of ≈7 µm. The resulting powders were characterized by XRD, SEM, and thermal analysis, and analyzed for particle-size distribution.

The powder was made up into a slip containing a solvent, dispersant, binder, and plasticizer. Membrane tubes were fabricated by extrusion of the slip with an outside diameter of ≈6.5 mm and lengths up to ≈30 cm. Wall thicknesses were 0.25–1.20 mm. Tubes were sintered at ≈1200°C for 5–10 h in stagnant air.

An Rh-based reforming catalyst was used inside the tube. The feed gas contained 80% methane and 20% argon. Argon was used as an internal calibration standard for gas analysis. Both the feed gas and the effluents were analyzed with a gas chromatograph. Outside the tube, air was the source of oxygen.

RESULTS AND DISCUSSION

Tubes of SFC–1 lasted only a few minutes as a conversion reactor operating at 850°C. The tubes 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. 1. The material was a cubic perovskite in an oxygen-rich (20% O_2) atmosphere. Once the oxygen partial pressure was lowered below 5%, however, the cubic phase transformed to an oxygen-vacancy-ordered phase. New peaks appeared in the XRD, as seen in Fig. 3 (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) was shifted to the low–angle (larger d-spacing) side of the corresponding peak in the cubic perovskite phase (in 20% O_2).

A detailed thermogravimetric analysis (TGA) [10] showed that the oxygen content x of the 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 the oxygen content of the sample has been established by comparing the lattice parameters. For example, the volume of the primitive perovskite cell V_p 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. 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 ≈2%.

Both XRD results and TGA data [10] 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, the distribution of oxygen is uniform. Upon heating, the tube begins to lose oxygen that was previously incorporated in 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 has 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. 2. 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 mechanical properties of the SFC–2 were measured by conventional methods, i.e., bulk density was measured by the Archimede' principle; flexural strength, in a four-point bending mode; fracture toughness, by a single-edge notch method [11]; and Young's modulus, shear modulus, and Poisson's ratio, by ultrasonic methods [12]. The thermal expansion coefficient was measured in a dilatometer. The results are shown in Table I.

Figure 3 shows the probability of failure vs. flexural strength (Weibull statistics) for SFC-2 [13]. The Weibull modulus was observed to be 15, indicating only moderate scatter in the strength data. Measured room-temperature properties were used to develop the failure criteria for the membranes during actual reaction conditions in a plant where methane is expected to be at higher pressures. Figure 4 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, should not fracture under reactor conditions. Figure 5 shows the conversion data obtained with a membrane tube made of SFC-2 and operated at 850°C for ≈70 h. As seen from Fig. 5, methane conversion efficiency is >98%, and CO selectivity is 90%. As expected, measured H_2 yield is about twice that of CO.

The role of the catalyst in the transport of oxygen across the membrane, an SFC-2 tube was tested without the reforming catalyst. The results from a run of ≈350 h are shown in Fig. 6. 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_2 and H_2O. As seen in Fig. 6, methane conversion efficiency was ≈35% and CO_2 selectivity was ≈90%. Under our operating conditions, the measured oxygen flux was ≈0.3 std $cm^3/cm^2/min$. Figure 7 shows the result of a reactor run made under more severe conditions and in the presence of a catalyst for a period of >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 the oxygen permeation rate was observed.

CONCLUSIONS

Long tubes of La–Sr–Fe–Co–O (SFC) membrane have been fabricated by plastic extrusion. 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 material. Performance of the membrane strongly depended on the stoichiometry of the material. Fracture of certain SFC tubes was the consequence of an oxygen gradient that introduced a volumetric lattice difference between the inner and outer walls. However, tubes made with a particular stoichiometry (SFC-2) provided methane-conversion efficiencies of >99% in a reactor. Some of these reactor tubes have operated for up to ≈500 h.

ACKNOWLEDGMENTS

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TABLE I. Physical and mechanical properties of SFC-2

Property	Value
Bulk Density, g.cm^{-3}	4.81 ± 0.04
Percent of Theoretical Density	93
Coefficient of Thermal Expansion x 10^{-6}/°C (200–800°C)	14.0
Flexural Strength, MPa	120.4 ± 6.8
Fracture Toughness, MPa	2.04 ± 0.06
Young's Modulus, GPa	124 ± 3
Shear Modulus, GPa	48 ± 2
Poisson's Ratio	0.30 ± 0.01

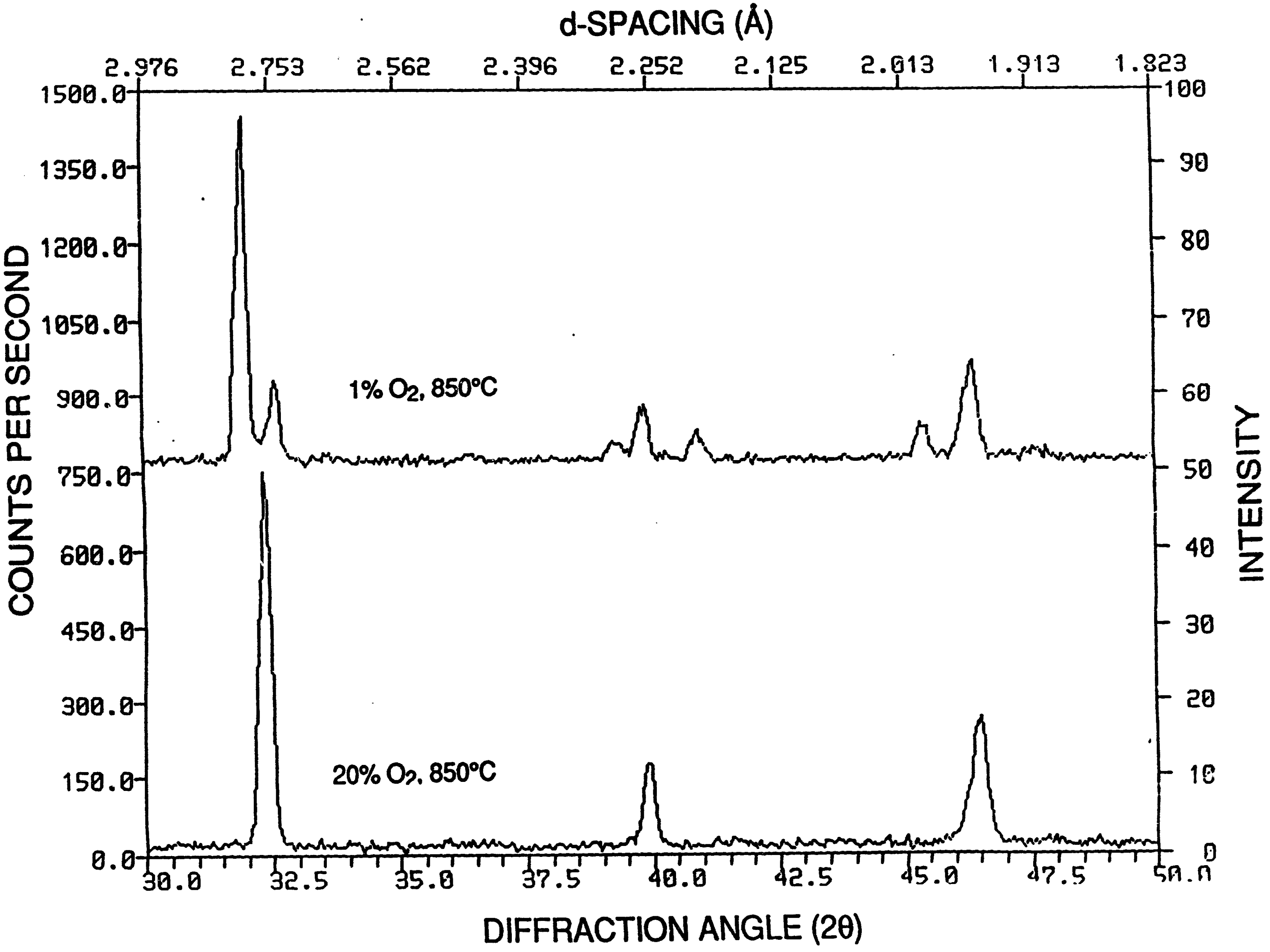

Figure 1. XRD of SFC-1 at 850°C in 1% and 20% O_2.

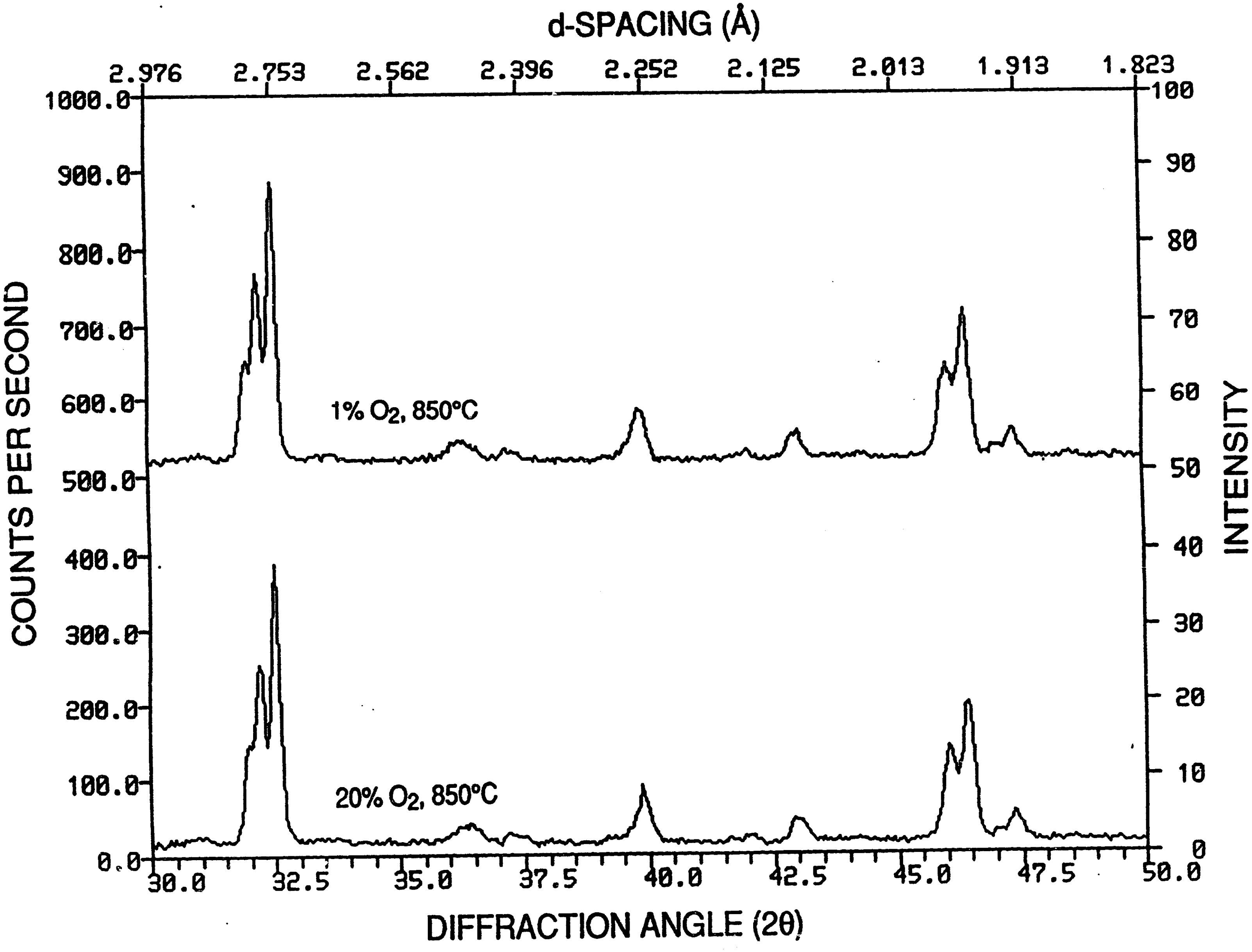

Figure ~~4~~ 2. XRD of SFC-2 at 850°C in 1 and 20% O_2.

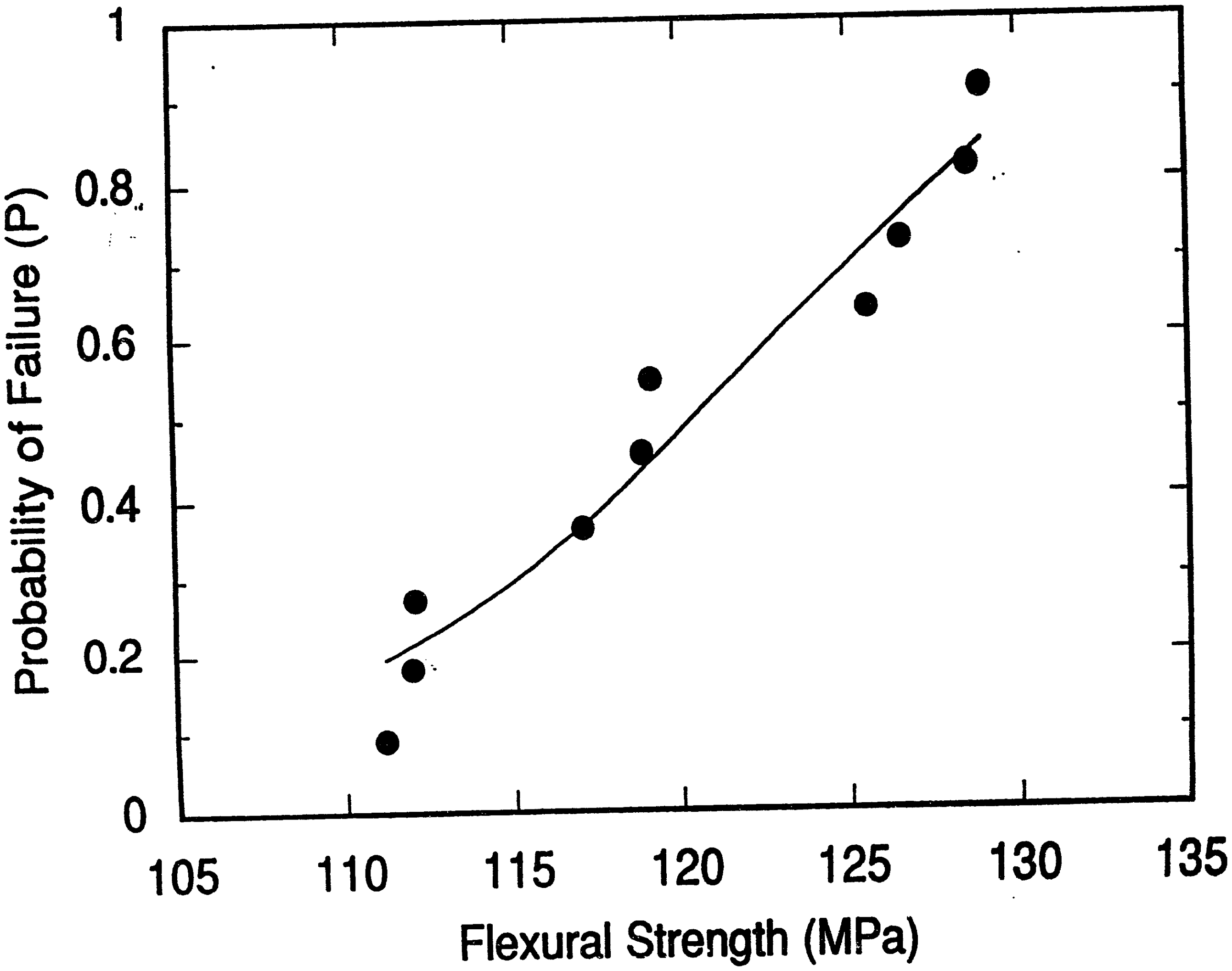

Figure [illegible]. Probability of failure vs. flexural strength for [illegible]SFC-2 (Weibull
3. modulus = 14.5).

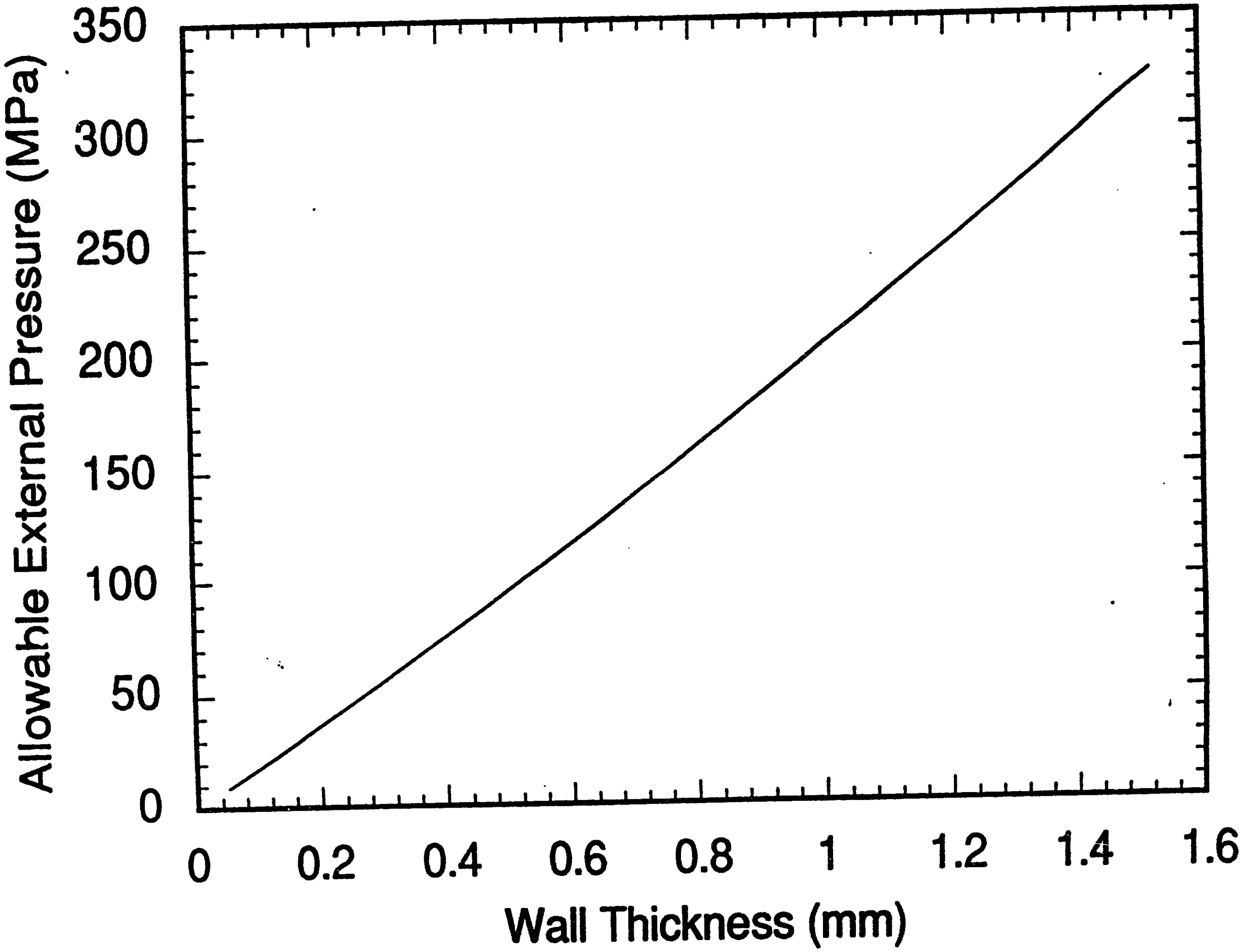

Figure 4. Allowable external pressure on [illegible]SFC-2 tubes as a function of wall
4 thickness (outside diameter of tube = 6.48 mm).

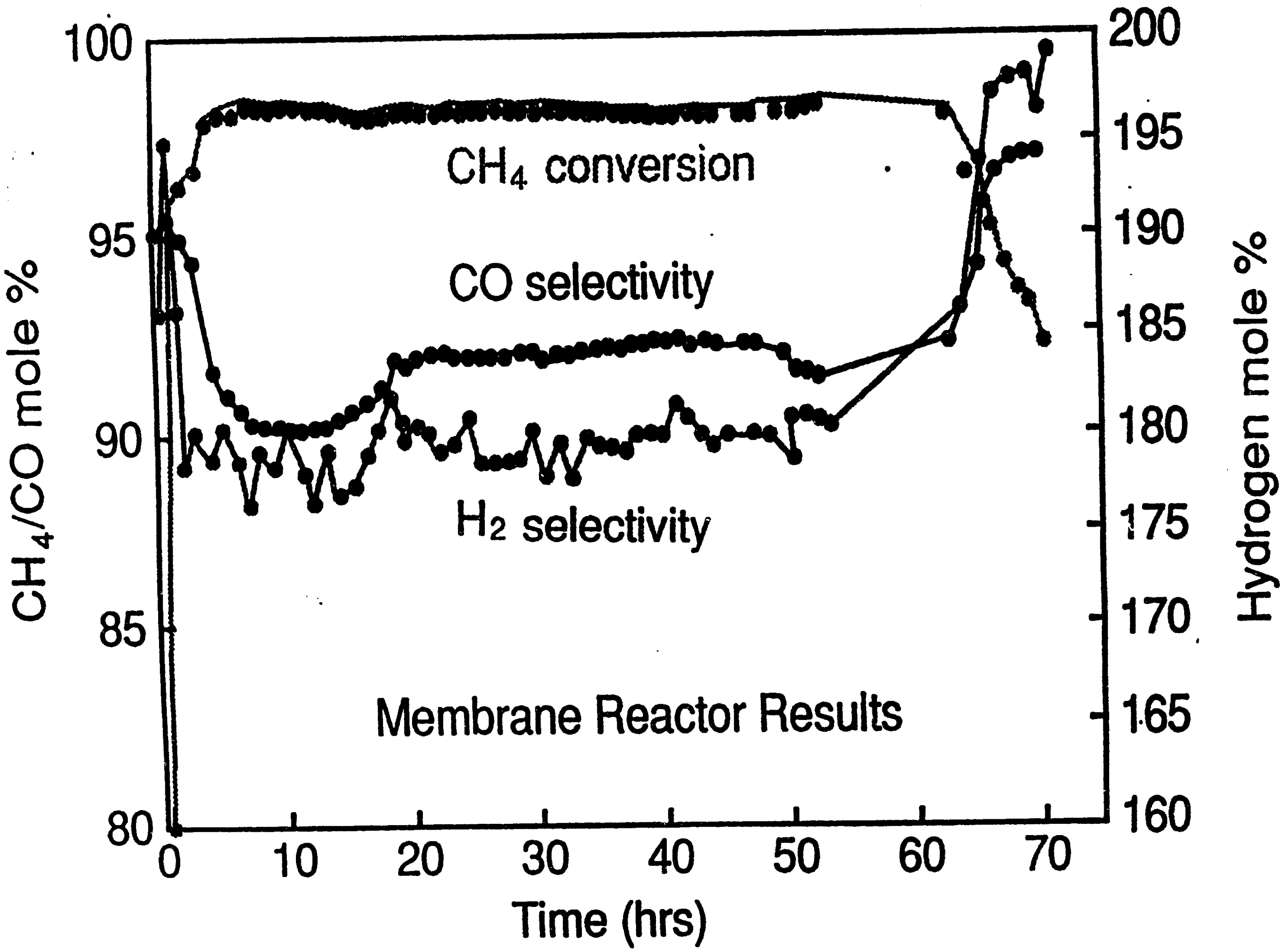

Figure [illegible]. Methane conversion and CO and H_2 selectivities in SFC-2 membrane reactor with reforming catalyst.

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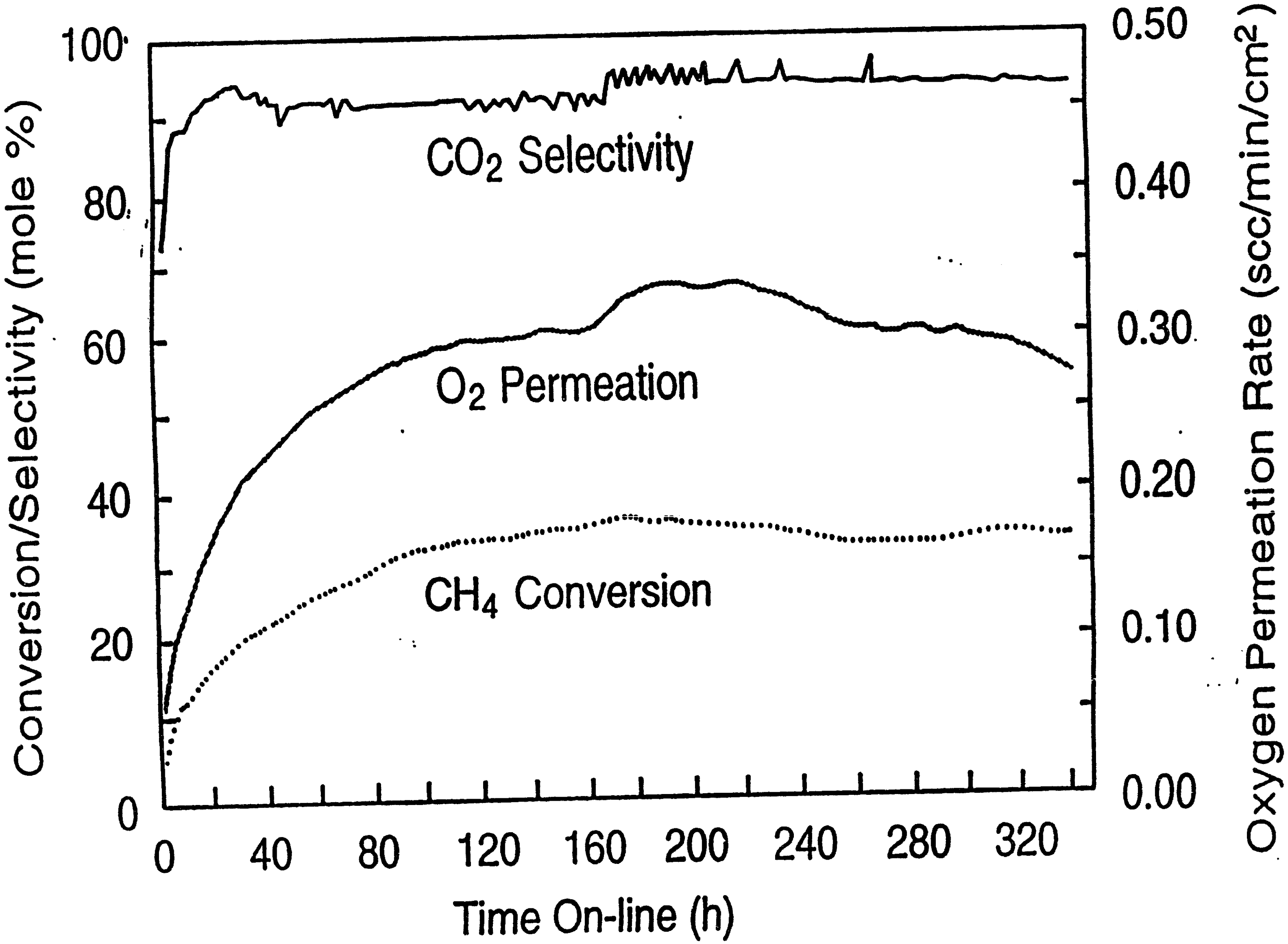

Figure [illegible]. **Methane conversion, CO_2 selectivity, and O_2 permeation in**
6 [illegible]**SFC-2 membrane reactor without reforming catalyst.**

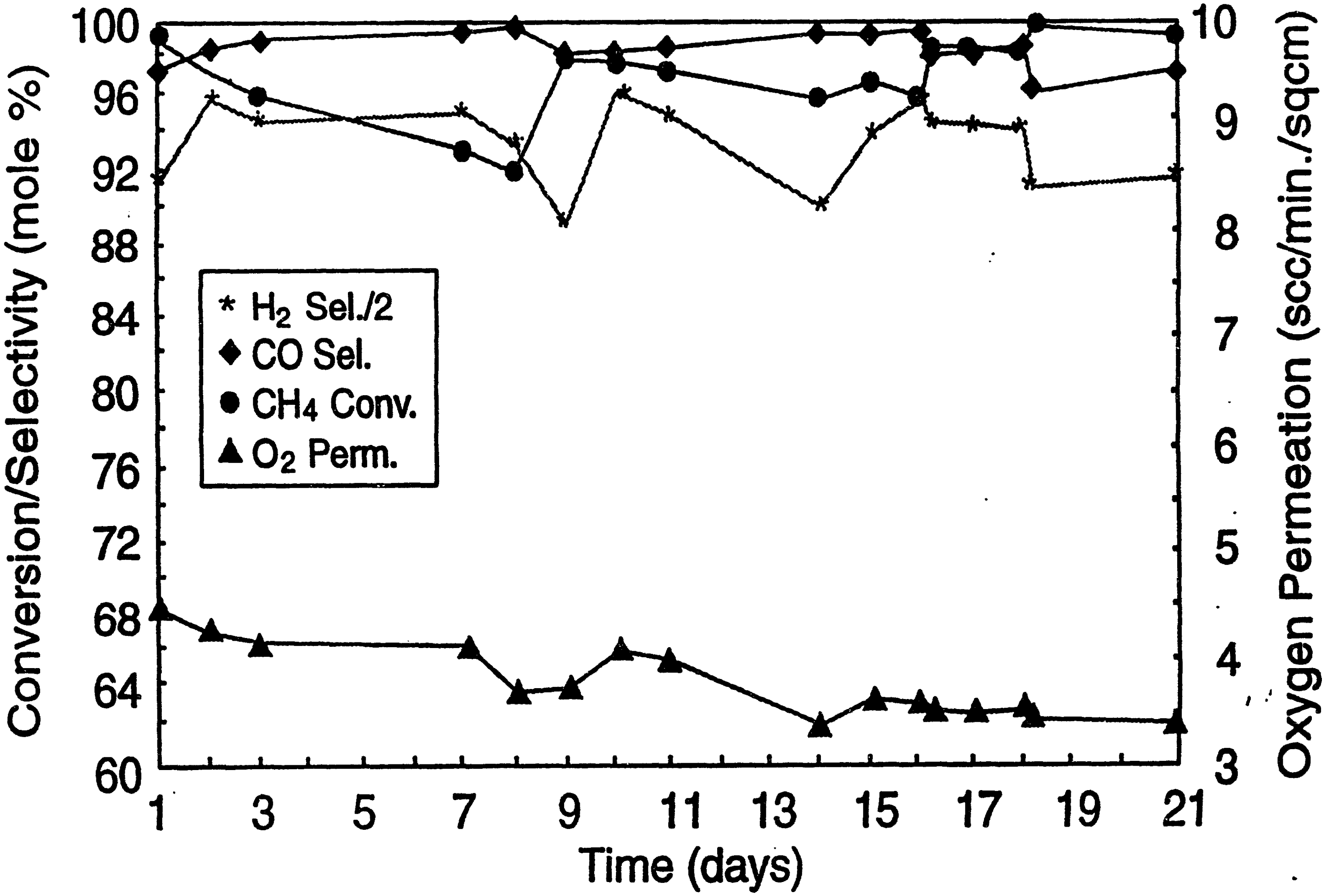

Figure ~~10~~. 7 Methane conversion, CO and H_2 selectivities, and O_2 permeation in 4SFC-2 membrane reactor operated with reforming catalyst for 21 days at 900°C (80% CH_4/20% Ar fuel, pressure ≈1 atm).

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