Development of Ceramic Membranes for Conversion of Methane into Syngas*

U. Balachandran and B. Ma
Energy Technology Division
Argonne National Laboratory
Argonne, Illinois 60439

September 1999

For submittal to the Proceedings of the Advanced Gas Technology '99 Conference, Houston, TX, Oct. 6-7, 1999.

*Work supported by the U.S. Department of Energy, Federal Energy Technology Center, under Contract W-31-109-Eng-38.

DISCLAIMER

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Development of Ceramic Membranes for Conversion of Methane into Syngas

U. Balachandran and B. Ma

Energy Technology Division, Argonne National Laboratory

Argonne, Illinois 60439

ABSTRACT

The abundantly available natural gas (mostly methane) discovered in remote areas has stimulated considerable research on upgrading this gas to high-value-added clean-burning fuels such as dimethyl ether and alcohols and to pollution-fighting fuel additives. Of the two routes to convert methane to valuable products, direct and indirect, the indirect route involving partial oxidation of methane to syngas (a mixture of CO and H_2) is preferred. Syngas is used as feedstock to produce a variety of petrochemicals and transportation fuels. A mixed-conducting dense ceramic membrane was developed from Sr-Fe-Co oxide. Extruded and sintered tubes of $SrFeCo_{0.5}O_x$ have been evaluated in a reactor operating at ≈850°C for conversion of methane into syngas in the presence of a reforming catalyst. Some of the reactor tubes have been run for more than 1000 h, and methane conversion efficiencies of ≈98% and CO selectivities of >96% were observed.

INTRODUCTION

Over the past several years, extensive efforts have focused on conversion of methane to value-added clean-burning fuels [1,2]. These efforts were driven by the abundance of natural gas discovered in remote areas and by the price disparity of petroleum liquids versus gas on a Btu-cost basis [3,4]. Of the two methods of converting methane to value-added materials (direct and indirect conversion), direct conversion approaches require partial oxidation of methane to methanol, formaldehyde, or alkenes. This is a more difficult approach because the reaction products are more reactive than the starting reactant (methane), leading to deep oxidation and low selectivity [5].

The indirect conversion approaches requires oxidation of methane to form syngas in a first stage by either steam reforming, direct partial oxidation, or a combination of the two. The syngas is then converted to upgraded products in a second stage by either Fischer-Tropsch technology [6] or methanol synthesis [7]. The indirect route, which operates at high pressures and temperatures, is usually energy- and capital-intensive. The cost of producing syngas by steam reforming can account for at least 60% of the integrated cost of a plant.

Partial oxidation of methane with air is a potential alternative to the steam-reforming process. But because the downstream processing requirements cannot tolerate the existence of nitrogen, high-purity oxygen (produced via cryogenic separation from air) is required. Thus, the most significant cost associated with partial oxidation is that of the oxygen plant. A new technology based on oxygen-permeable dense ceramic membranes using air as the oxidant offers a potential solution to these problems in methane conversion.

Dense ceramic membranes made of mixed-conducting materials can selectively transport oxygen from the high-oxygen-partial-pressure (pO_2) side to the low-pO_2 side. As shown in Fig. 1, these materials transport not only oxygen ions from the air side to the methane side but also electrons in the opposite direction; therefore, there is no need for external electric circuitry.

The $SrFeCo_{0.5}O_x$ material was found to have desirable properties for use as dense ceramic membrane [8-11]. Extruded and sintered ceramic membrane tubes made of this material were evaluated in methane conversion reactors operating at ≈850°C for conversion of methane into syngas in the presence of a reforming catalyst. Methane conversion efficiencies of ≈98% and CO selectivities of >96% were observed. Some the reactor tubes have been in operation for >1000 h. Moreover, the oxygen flux obtained from the separation of air in this type of conversion reactor is considered to be commercially attractive. Use of this technology can significantly reduce the cost of converting methane to syngas.

EXPERIMENTAL

The $SrFeCo_{0.5}O_x$ powders were made by a solid-state reaction method with appropriate amounts of $SrCO_3$, $Co(NO_3)_2{\cdot}6H_2O$, and Fe_2O_3; mixing and grinding were conducted in isopropanol with zirconia media for 10 h. After drying, the mixture was calcined in air at 850°C for 16 h, with intermittent grinding. After final calcination, the powder was ground with an agate mortar and pestle to an average particle size of ≈7 μm. The resulting powder was characterized by room-temperature X-ray diffraction analysis with a Scintag XDS-2000 diffractometer.

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 ≈6.5 mm, length of ≈30 mm, and wall thicknesses of 0.25 to 1.20 mm. After drying, the tubes were heated to 400°C for debindering and then sintered at 1180°C for 5 to 10 h in air. Rectangular bars 7.5 mm wide, 44 mm long, and ≈5 mm thick were made by pressing the resulting powder uniaxially in a die with a 120-MPa load. The bars were then sintered in air at ≈1180°C for 5 to 10 h and used for measuring electrical and mechanical properties. Microstructure was examined on the sintered samples by using a JEOL JSM-5400 scanning microscope. Thin bars ≈ 1 x 5 x 20 mm^3 were cut from the sintered samples for measurement of conductivity and oxygen diffusion coefficient [10,11].

True density was measured with an AccuPyc 1330 pycnometer. Bulk density was determined by the Archimedean method, with isopropanol as the liquid medium. Calculated relative density of air-sintered $SrFeCo_{0.5}O_x$ samples was >90% of theoretical value. Mechanical properties were measured on the sintered bars by conventional methods, i.e., flexural strength in a four-point bending mode; fracture toughness, by a single-edge notch method [12]; and Young's modulus, shear modulus, and Poisson ratio, by ultrasonic methods [13]. Conductivity of the sample was determined by the four-probe method [10]. Oxygen diffusion coefficient was determined with a time relaxation method [11] by abruptly changing oxygen partial pressure in the surrounding environment. The thermal expansion coefficient was measured in air with a dilatometer.

The sintered membrane tubes were evaluated for performance in a methane conversion reactor, as shown in Fig. 2. 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 faciliate reactions and equilibration of gases in the reactor, a rhodium-based reforming catalyst is loaded adjacent to the ceramic tube. Both the feed gas (generally 80% methane and 20% argon) and the effluents were analyzed by gas chromatograph.

RESULTS AND DISCUSSIONS

The room-temperature X-ray diffraction pattern of sintered $SrFeCo_{0.5}O_x$ is plotted in Fig. 3. Its primary phase has a layered structure and can be thought of as consisting of alternating $SrFeO_3$ and Fe_2O_3 blocks [14]. Perovskite-phase $SrFe_{1-x}Co_xO_{3-\delta}$ was found in the material as a secondary phase [15]. SEM images reveal a dense and homogeneous structure. Energy-dispersive X-ray (EDX) elemental analysis showed that the overall atomic ratio of the metal elements is consistent with that given in the chemical formula.

Thermal expansion of $SrFeCo_{0.5}O_x$ in air is plotted in Fig. 4 as a function of temperature. Over a wide temperature range (100 to 900°C), good linear dependence was observed. The thermal expansion coefficient derived from its slope is 14 x 10^{-6} °C^{-1}.

The total, electronic, and ionic conductivities and ionic transference number of the $SrFeCo_{0.5}O_x$ material is shown in Fig. 4 as a function of temperature. Both the electronic and ionic conductivities increase with increasing temperature, while the ionic transference number is nearly independent of temperature. At 800°C, electronic and ionic conductivities are ≈10 and ≈7 S·cm^{-1}, respectively, and this leads to an ionic transference number of ≈0.4.

Table 1. Physical and Mechanical Properties of $SrFeCo_{0.5}O_x$ Material

Property	Value
Bulk density	4.81 g·cm^{-1}
Percent of theoretical density	93
Coefficient of thermal expansion	14 x 10^{-6} °C^{-1}
Electronic conductivity	10 S·cm^{-1} (at 800°C)
Ionic conductivity	7 S·cm^{-1} (at 800°C)
Ionic transference number	0.4
Oxygen diffusion coefficient	9 x 10^{-7} cm^2·s^{-1} (at 900°C)
Flexural strength	120.4 ± 0.6 MPa
Fracture toughness	2.04 ± 0.06 MPa·$m^{0.5}$
Young's modulus	124 ± 3 GPa
Shear modulus	48 ± 2 GPa
Poisson ratio	0.3 ± 0.01

The physical and mechanical properties of the $SrFeCo_{0.5}O_x$ material are summarized in Table 1. Measured room-temperature properties were used to develop the failure criteria for the membrane during actual reaction conditions in a plant where the methane is expected to be at higher pressures. The computed allowable external pressure on the membrane tube as a function of wall thickness was calculated. These calculations were based on the assumptions that the tensile strength is ≈0.67 times the flexural stress and that the compressive strength of the material is greater than its tensile strength by a factor of 8. The computed results showed that this ceramic membrane material has sufficient strength to maintain structural integrity during methane conversion in a commercial reactor. Tubes made of this material should not fracture under reactor conditions.

Data obtained on an actual methane conversion reactor using a $SrFeCo_{0.5}O_x$ membrane tube is plotted in Fig. 5. A rhodium-based reforming catalyst is presented in the reactor. The fuel (80% methane, 20% argon) was fed at ≈1 atm pressure. High methane conversion efficiency (≈98%) and high CO selectivity (>96%) was observed. Under these operating conditions, oxygen permeation flux observed was ≈4 $scc \cdot cm^{-2} \cdot min$. This reactor was deliberately shut down after 21 days. To further confirm the stability of this type of ceramic membrane, we operated the reactor with a different feed gas over a period of 1000 h, as shown in Fig. 6. This time the reactor was supplied with a typical mixture expected in a commercial recycle feed, namely, ≈17% CH_4, ≈20% CO, ≈9% CO_2, ≈44% H_2, and ≈10% Ar. Again, high methane conversion efficiency was observed. However, the oxygen permeation flux during this operation slowly decreased from ≈4 to ≈2 $scc \cdot cm^{-2} \cdot min$.

CONCLUSIONS

The mixed-conducting $SrFeCo_{0.5}O_x$ material was found to have good potential for use as a dense ceramic membrane in methane conversion. This material has not only high combined electronic and oxygen ionic conductivities but also adequate mechanical properties. At 800°C in air, its electronic and ionic conductivities are 10 and 7 $S \cdot cm^{-1}$, respectively; and its ionic transference number is ≈0.4. Its thermal expansion coefficient is ≈14 x 10^{-6} $°C^{-1}$. Long-length membrane tubes were fabricated by plastic extrusion. Sintered tubes were evaluated in methane conversion reactors operating at 800-900°C. With the aid of a rhodium-based catalyst, methane conversion efficiencies of ≈98%, and CO selectivities of >96% were observed. Some of the reactors have operated for more than 1000 h. The feasibility of using $SrFeCo_{0.5}O_x$ dense ceramic membranes for partial oxidation of methane to produce syngas has been demonstrated.

ACKNOWLEDGMENTS

This work is supported by the U.S. Department of Energy, Federal Energy Technology Center, under Contract W-31-109-Eng-38. We thank C. Udovich and M. Kleefisch of BP-Amoco for the methane conversion experiments and valuable discussions.

REFERENCES

1. N. D. Spenser and C. J. Pereiva, J. Catal., 116 (1989) 399.
2. H. D. Gesser and N. R. Hunter, Chem. Rev., 85 (1985) 235.
3. G. E. Keller and M. M. Bhasin, J. Catal., 73 (1982) 9.
4. G. J. Hutchings, M. S. Scurrel, and J. R. Woodhouse, Chem. Soc. Rev., 18 (1989) 251.
5. Y. Amenomiya, V. I. Buss, M. Goledzinska, and A.R. Sanger, Catal. Rev. – Sci. Eng., 32 (1990) 163.
6. G. Henrici-Olive and S. Olive, Angew. Chem. Int. Ed. Engl., 15 (1976) 136.
7. H. H. Kung, Catal. Rev., 22 (1980) 235.
8. U. Balachandran, S. L. Morissette, J. J. Picciolo, J. T. Dusek, R. B. Poeppel, S. Pei, M. S. Kleefisch, R, L. Mieville, T. P. Kobylinski, and C. A. Udovich, Proc. Intl. Gas Research Conf., H. A. Thompson, ed. (Government Institutes, Inc., Rockville, MD, 1992).
9. U. Balachandran, J. T. Dusek, P. S. Maiya, R. L. Mieville, B. Ma, M. S. Kleefisch, and C. A. Udovich, presented at 11th Intersociety Cryogenic Symp., Energy Week Conf. & Exhibition, Houston, Jan. 28-30, 1997.
10. B. Ma, J.-H. Park, C. U. Segre, and U. Balachandran, Mater. Res. Soc. Symp. Proc., 393 (1995) 49.
11. B. Ma, J.-H. Park, and U. Balachandran, J. Electrochem. Soc., 144 (1997) 2816.
12. W. F. Brown, Jr. and J. E. Strawley, ASTM STP 410, Philadelphia, 1967.

13. J. Krautkramer, Ultrasonic Testing of Materials, Springer-Verlag, Berlin, 1983.

14. A. Yoshiasa, K. Ueno, F. Kanamaru, and H. Horiuchi, Mater. Res. Bull., 21 (1986) 175.

15. B. Ma, J. P. Hodges, J. D. Jorgensen, D. J. Miller, J. W. Richardson, Jr., and U. Balachandran, J. Solid State Chem., 141 (1999) 576.

Fig. 1 Schematic drawing of oxygen-permeable membrane used in methane conversion reactor.

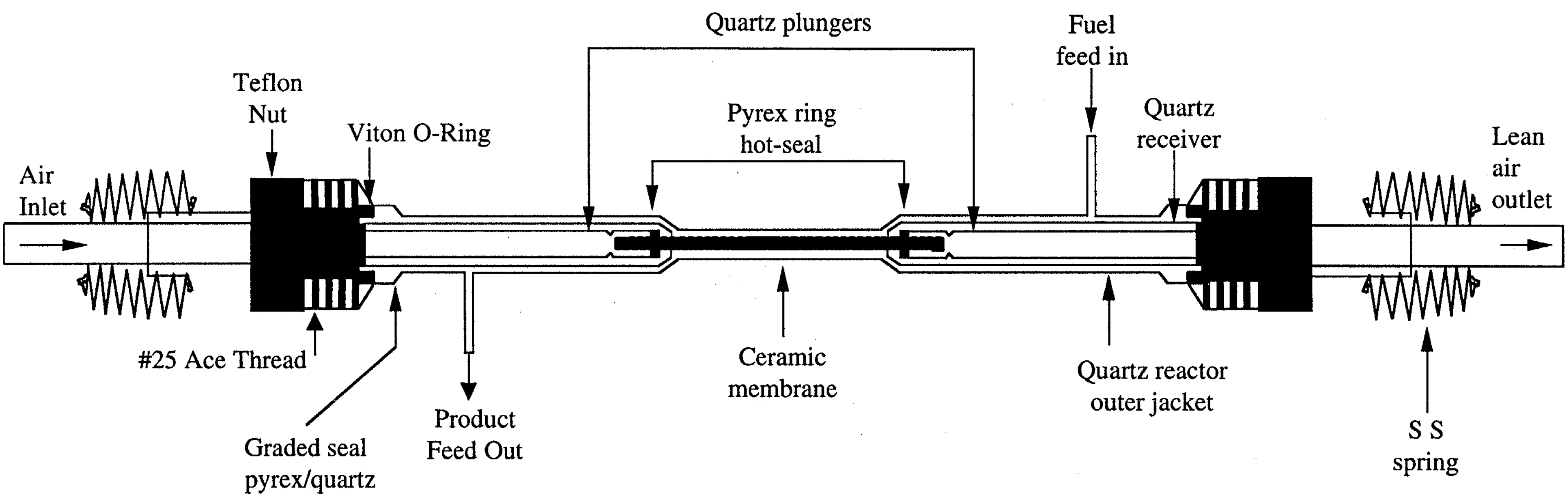

Fig. 2. Schematic drawing of ceramic membrane reactor.

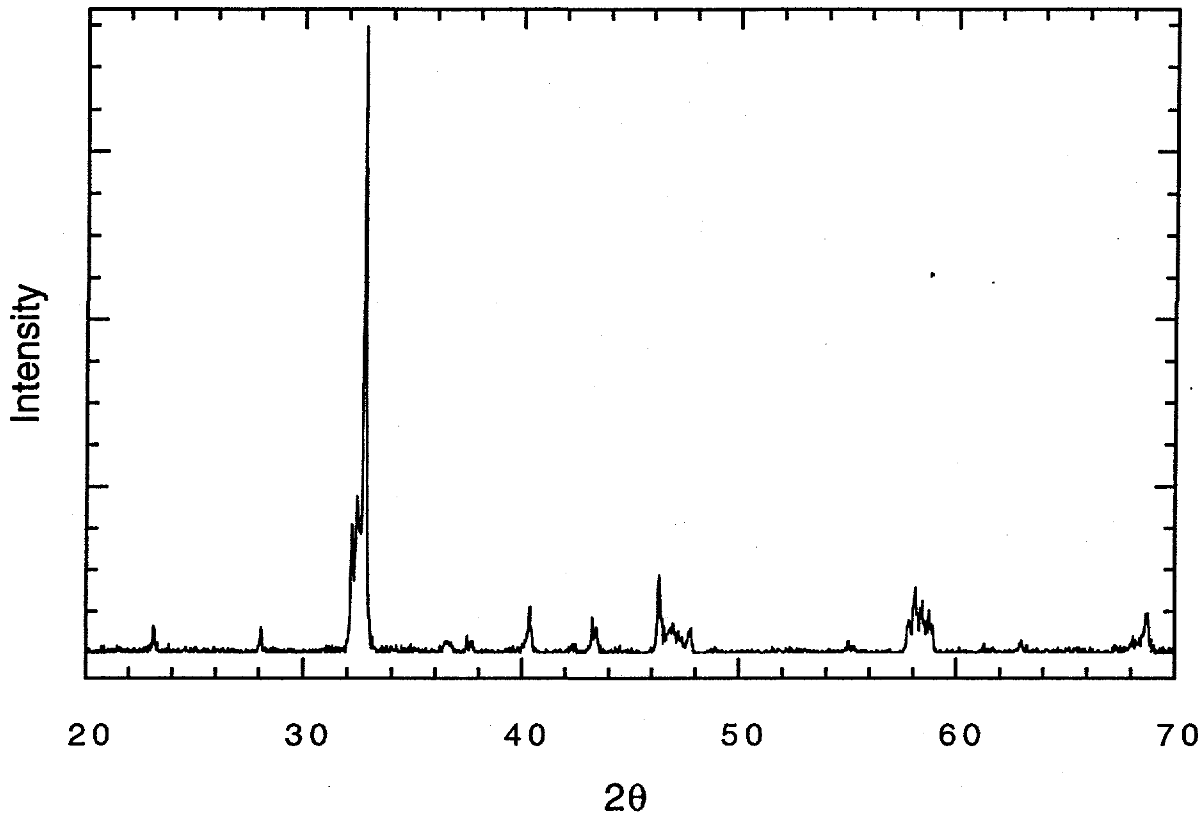

Fig. 3. X-ray diffraction patterns of sintered $SrFeCo_{0.5}O_x$ sample.

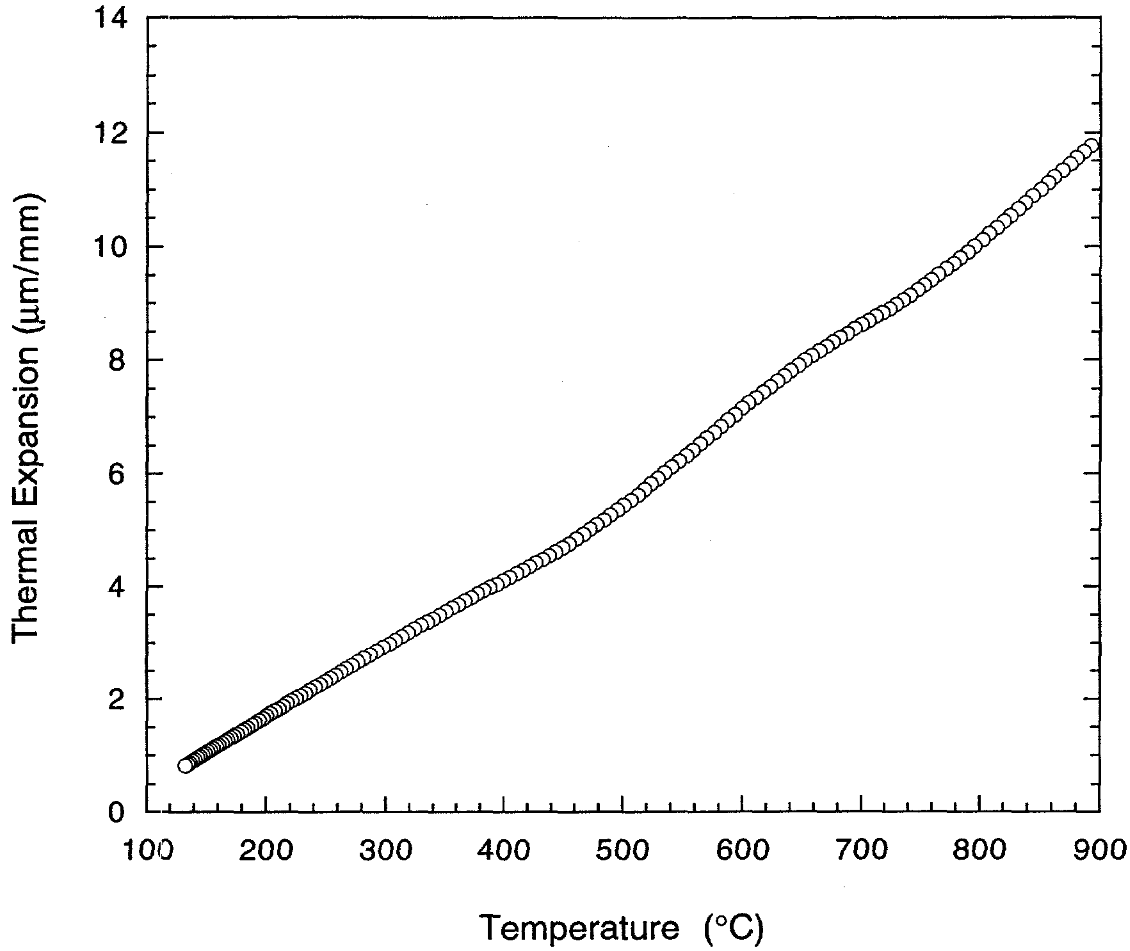

Fig. 4. Thermal expansion as a function of temperature of $SrFeCo_{0.5}O_x$ sample in air.

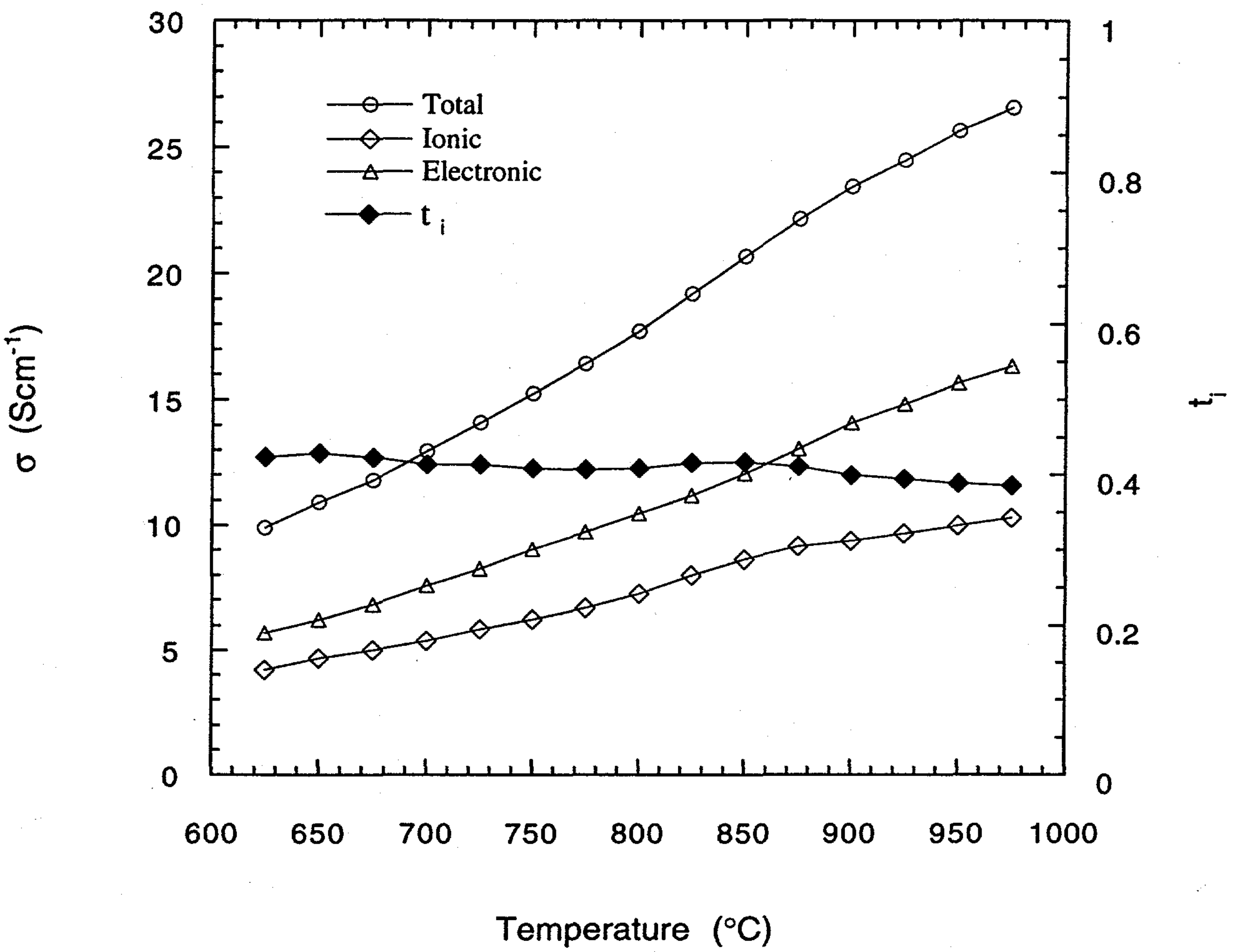

Fig. 5. Total, electronic, ionic conductivities, and ionic transference number of $SrFeCo_{0.5}O_x$ material.

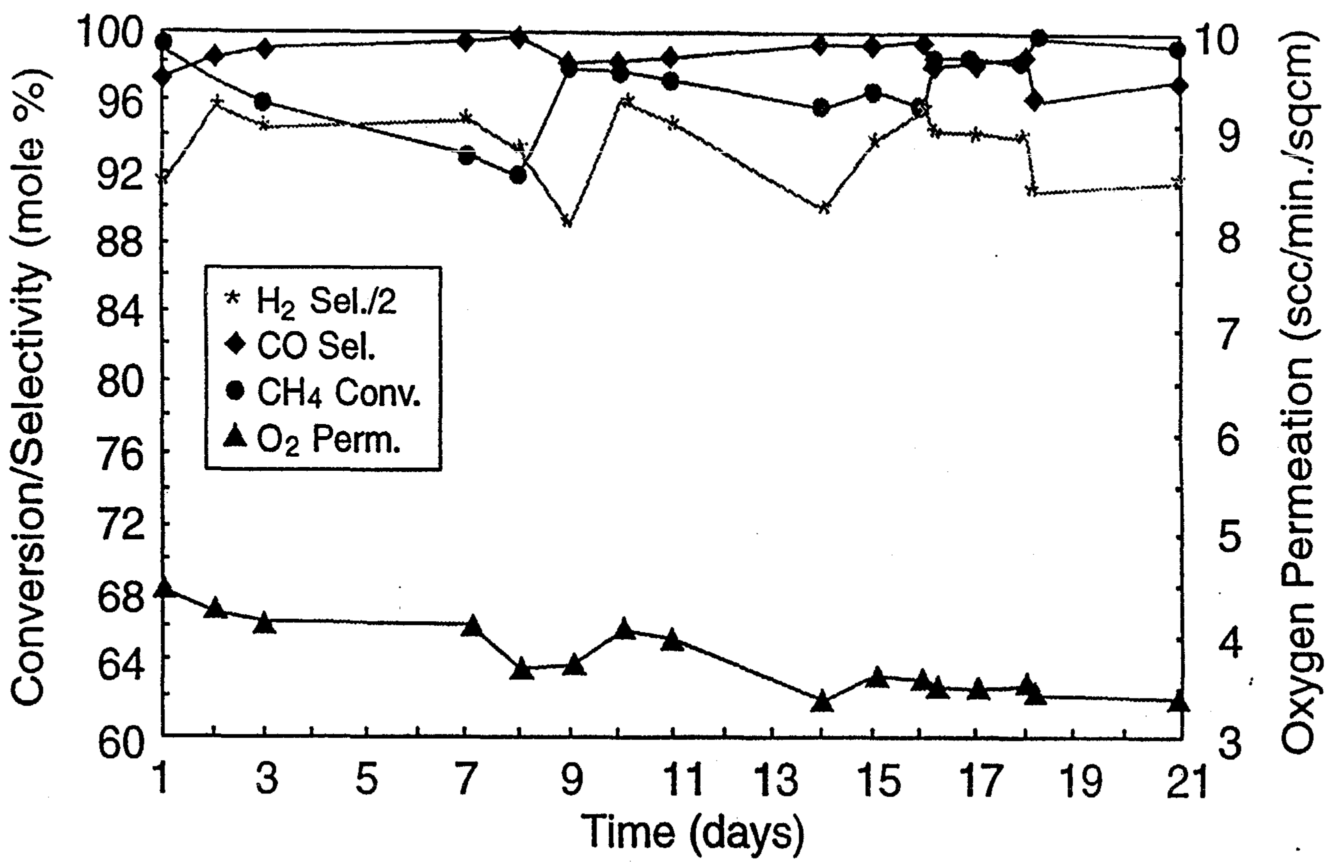

Fig. 6. Methane conversion, CO and H_2 selectivities, and oxygen-gas permeation in an $SrFeCo_{0.5}O_x$ membrane reactor operated with reforming catalyst for 21 days at 900°C (80% CH_4/20% Ar feed, pressure ≈1 atm).

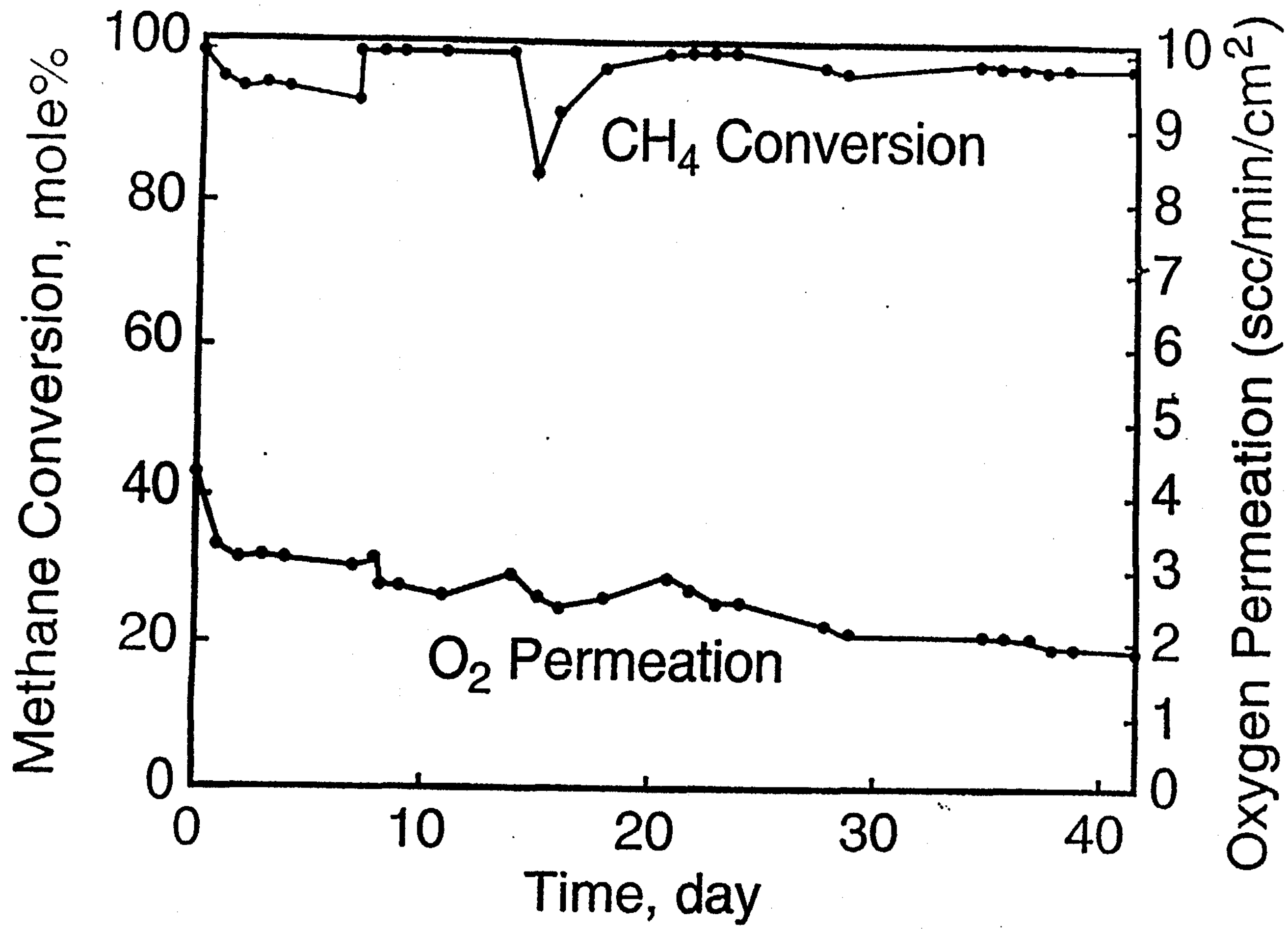

Fig. 7. Methane conversion efficiency and oxygen permeation flux for reactor using $SrFeCo_{0.5}O_x$ ceramic tubes with mixed gas feed (17% CH_4, 20% CO, 9% CO_2, 44% H_2, and 10% Ar). Conditions: temperature, 900°C; pressure, 1 atm; and flow, 20 $cm^3 \cdot min^{-1}$.