ELSEVIER

Catalysis Today 36 (1997) 265–272

CATALYSIS TODAY

Ceramic membrane reactor for converting methane to syngas [1]

U. Balachandran [a,*], J.T. Dusek [a], P.S. Maiya [a], B. Ma [a], R.L. Mieville [a], M.S. Kleefisch [b], C.A. Udovich [b]

[a] *Energy Technology Division, Argonne National Laboratory, Argonne, IL 60439, USA*
[b] *Amoco Research Center, Naperville, IL 60566, USA*

Abstract

Certain perovskite-type oxides (ABO_3) containing transition metals on the B-site show mixed (electronic/ionic) conductivity. These mixed-conductivity oxides are promising materials for oxygen-permeating membranes that can operate without electrodes or external electrical circuitry. Oxides in the system Sr–Fe–Co–O permeate large amounts of oxygen, and extruded tubes of these materials have been evaluated in a reactor operating at ≈ 850°C for direct conversion of methane into syngas ($CO + H_2$) in the presence of a reforming catalyst. Methane conversion efficiencies of > 99% were observed, and some of the reactor tubes have been operated for more than 1000h. Membrane tubes were fabricated from calcined powders by a plastic extrusion technique. Ceramic powders in the Sr–Fe–Co–O system were made by solid-state reaction of the constituent carbonates, oxides, and/or nitrates. The chemical-phase behavior of the ceramic powders with varying stoichiometries were studied by high-temperature in-situ X-ray diffraction (XRD) as a function of oxygen partial pressure. The sintered extruded tubes were also characterized by XRD and scanning electron microscopy.

Keywords: Membrane reactor; Methane conversion; Syngas; Perovkites; Ceramics

1. Introduction

Over the past several years, extensive efforts have focused on both direct and indirect conversion of methane to value-added products, particularly easily transportable fuels [1,2]. Direct-conversion approaches require some form of partial oxidation of methane to methanol, formaldehyde, or olefins. This is the more difficult approach because the desired products of reaction are more reactive than the starting reactant (methane), which then leads to deep oxidation and low selectivities [3].

Indirect approaches for methane conversion require oxidation of methane to form syngas ($CO + H_2$) in a first stage by either steam reforming or direct partial oxidation, or a combination of both. The syngas is then converted into upgraded products in a second stage by Fischer–Tropsch technology [4] or methanol synthesis [5]. The indirect route is usually very energy- and capital-intensive (steam reforming is highly endothermic), operating at high pressures and temperatures. The cost of syngas production by steam reforming can account for at least 60% of the integrated cost of the total plant. Although direct partial oxidation of methane with air as the oxygen source is a

---

[*] Corresponding author.

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

PII S0920-5861(96)00229-5

potential alternative to steam-reforming processes, downstream processing requirements cannot tolerate nitrogen (recycling with cryogenic separations is required) and therefore pure oxygen is required. Thus, the most significant cost associated with conventional partial oxidation of methane to syngas is that of the oxygen separation plant.

In this paper we explore a new technology that can lower this cost, based on a dense ceramic membrane reactor that uses air as the oxidant for the methane conversion reactions thus saving 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. 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 ions, not oxygen molecules.

In principle, the dense ceramic materials can be shaped into a hollow-tube reactor, with methane passed over the outside of the membrane and air through the inside. The surfaces can also be reversed. The membrane is permeable to oxygen at high temperatures, but not to nitrogen or other gases. Thus, only oxygen from air can be transported through the membrane to the other surface, where it reacts with methane. Other geometric reactor forms, such as honeycombing or corrugation, are possible and can provide substantially greater surface areas for reaction [6].

Recent reports in the literature suggest that dense ceramic membranes made of these mixed conductors can successfully separate oxygen from air at flux rates that could be considered commercially feasible, and thus have potential application for improving the economics for methane conversion processes [7–15].

2. Experimental

Several Sr–Fe–Co mixed oxides (designated as SFC) of differing stoichiometry were prepared by the solid state reaction of the constituent cationic salts. In this paper, we concentrate on two mixed oxides. SFC-1 has the formula of $SrFe_{0.2}Co_{0.8}O_x$ and is a perovskite, previously studied and described by Teroaka et al [7,8]. SFC-2 has a stoichiometry of $Sr_1Fe_1Co_{0.5}O_x$ with a unique structure that is not a perovskite [16]. It is our present and preferred material and is the focus of most of this study. The comparison between these two materials highlights the properties necessary for a successful dense membrane reactor for production of syngas from the partial oxidation of methane. In the preparation of these mixed-oxide ceramics, appropriate amounts of $SrCO_3$, $Co(NO_3)_2 \cdot 6H_2O$, and Fe_2O_3 were mixed and milled in isopropanol with ZrO_2 media for ≈ 15h. When dry, the mixtures were calcined in air at ≈ 850°C for ≈ 16h, 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 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 [11]. 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.

The extruded tubes were sintered and 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. Sintered pellet samples were prepared for conductivities and diffusional 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, 1.25 cm long, 0.2 cm wide) 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 chromotograph.

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 [17]; and Young's modulus, shear modulus, and Poisson ratio, by ultrasonic methods [18]. The thermal expansion coefficient was measured in a dilatometer. Conductivities were measured by a four-probe method with a blocking electrode of yttria-stabilized zirconia for the oxygen ion conduction [19]. The oxygen diffusion coefficient was 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 [20].

3. Results and discussion

SFC-1 tubes survived only a few minutes when operated as a conversion reactor at 850°C; they then broke into several pieces. XRD patterns of the original SFC-1 samples were recorded at 850°C in Ar–O_2 gas mixtures. The structure of SFC-1 in 1 and 20% O_2 is shown in Fig. 2. In an oxygen-rich atmosphere (20% O_2), the material was a cubic perovskite. However, once the oxygen partial pressure dropped 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, as can be seen from the change in the position of the Bragg peak near 32° in Fig. 2. 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) [21] 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 the oxygen content of the sample has been established by comparing lattice parameters. For example, the volume of the primitive perovskite cell V_p is 57.51Å^3 for $x = 2.67$ and 59.70Å^3 for $x = 2.48$. These results

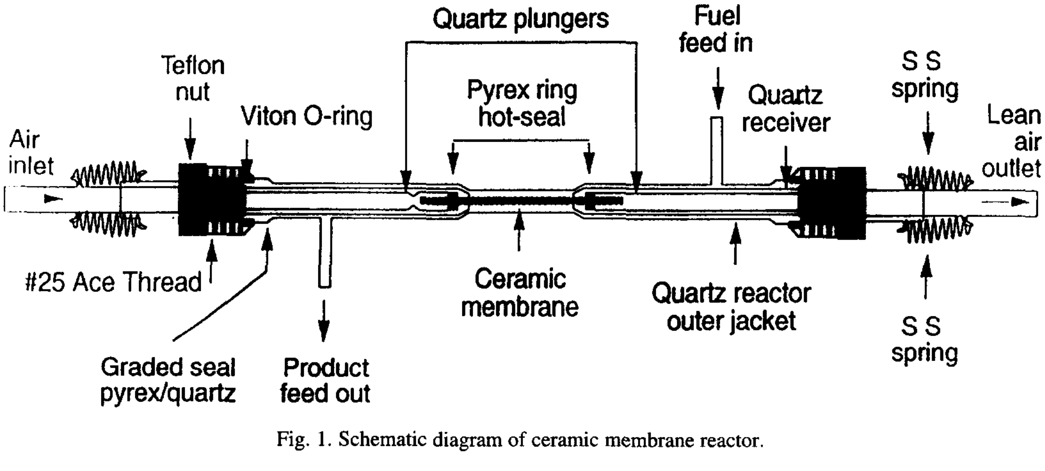

Fig. 1. Schematic diagram of ceramic membrane reactor.

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 of $\approx 2\%$ in V_p.

Based on the XRD results and the previous TGA data [21], a clear picture about the state of the SFC-1 membrane tube under reaction conditions can be obtained. The operation of the membrane tube solely as an oxygen separator is discussed first. In this case, high oxygen pressure is maintained inside the tube and low oxygen pressure is maintained outside the tube. Before the tube is brought up to high temperature, it has a uniform distribution of oxygen.

Upon heating, the tube material begins to lose oxygen that was incorporated during the fabrication. Moreover, the material on the outer wall loses more oxygen than that on the inner 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 outer zone, with less oxygen, contains more ordered oxygen vacancies and is hence less oxygen-permeable.

The most remarkable factor, and one that can cause 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 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 remarkable structural stability at high temperature, as shown in Fig. 3. No phase transition was observed in

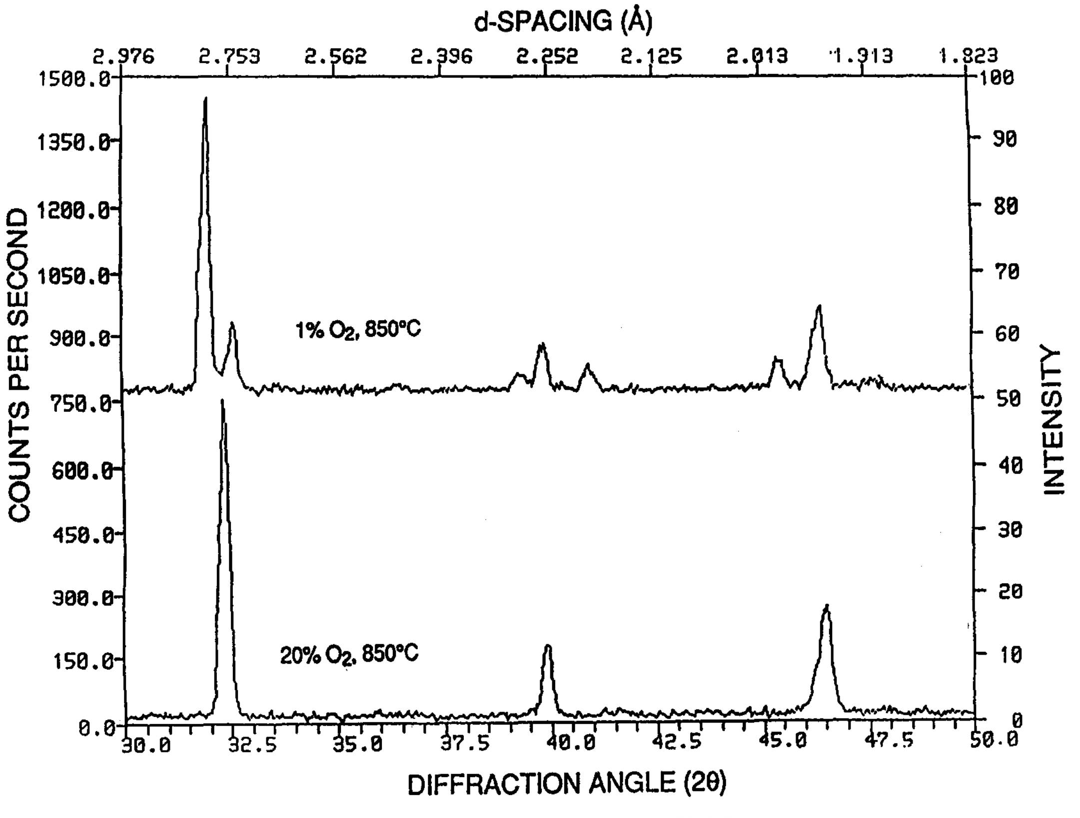

Fig. 2. XRD of SFC-1 at 850°C in 1 and 20% O_2.

Table 1
Physical and Mechanical Properties of SFC-2 Membrane Material

Property	Value
Bulk density	4.81 g·cm^{-3}
Percent of theoretical density	93
Coefficient of thermal expansion	14×10^{-6}/°C (200–800°C)
Flexural strength	120.4 ± 0.06 MPa
Fracture toughness	2.04 ± 0.06 MPa m$^{0.5}$
Young's modulus	124 ± 3 GPa
Shear modulus	48 ± 2 GPa
Poisson's ratio	0.30 ± 0.01

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 SFC-2, is reflected in its physical and mechanical properties, as shown in Table 1.

In all cases, SFC-2 shows more than adequate strength, especially in fracture toughness, which is the ability of a material to resist crack propagation. Tubes made of this material, unlike those made of SFC-1, are not expected to fracture under reactor conditions.

Differences between SFC-2 and other mixed oxides were observed in the ratio of their electronic and ionic conductivities [20]. SFC-2 was unique in that its ratio of ionic to electronic conductivity is close to unity, unlike the other oxides in which there is a preponderance of one value over another.

Furthermore, limited SFC-2 diffusion data, obtained from the time-relaxation method [20], 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 9×10^{-7} cm^2 s^{-1} at 900°C [22].

These properties are consistent with the performance of a membrane reactor of this material with a methane/argon feed. Generation of syn-

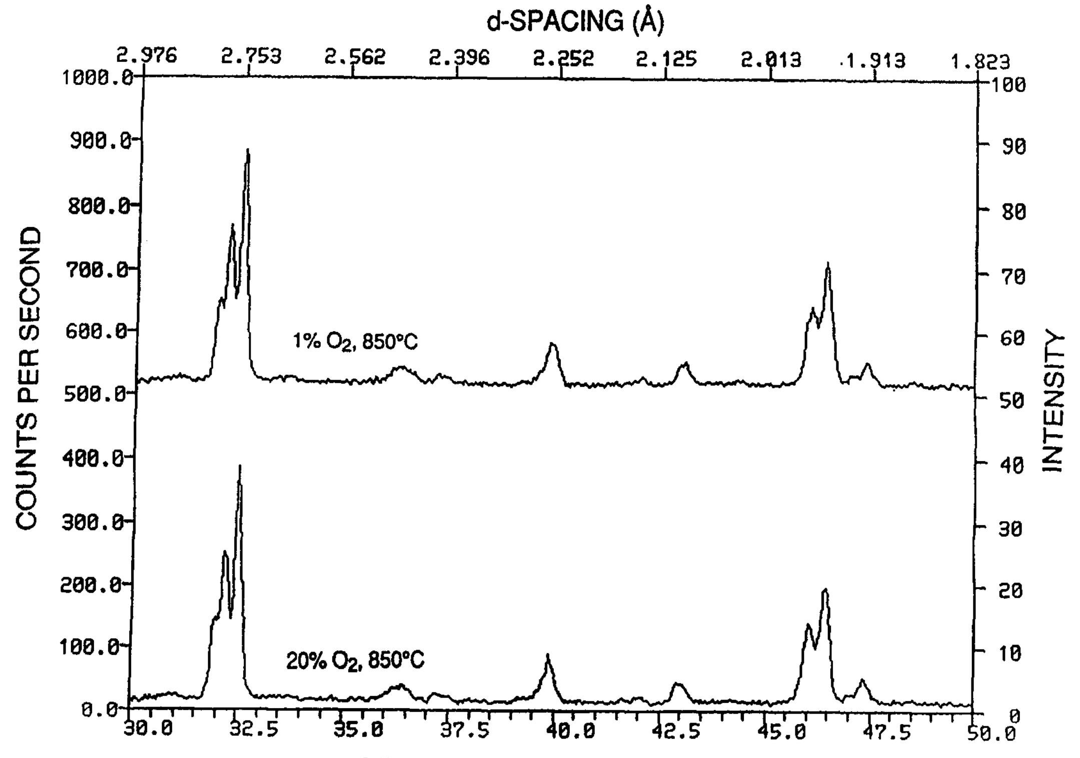

Fig. 3. XRD of SFC-2 at 850°C in 1 and 20% O_2.

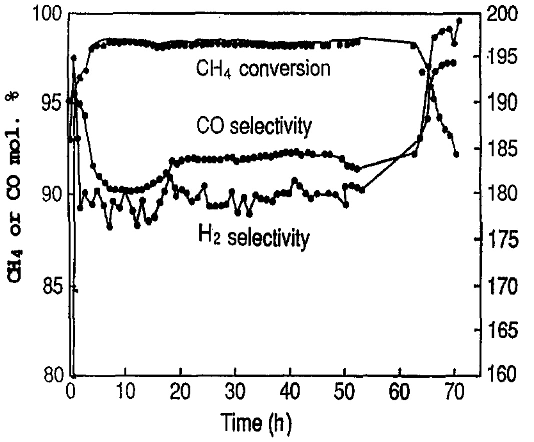

Fig. 4. Methane conversion and CO and H_2 selectivities in SFC-2 membrane reactor with reforming catalyst. Conditions: feed (80% methane, 20% argon) flow, 2.5 cm^3/min; temp., 850°C; pressure atmosphere, membrane surface area, 10 cm^2.

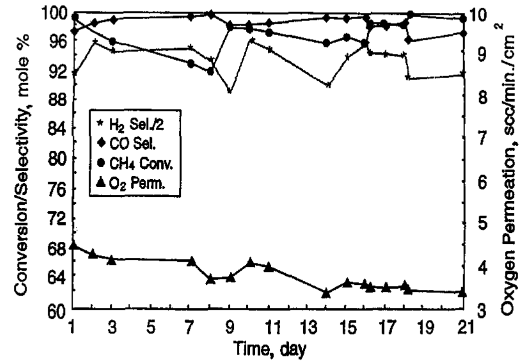

Fig. 6. Methane conversion and CO and H_2 selectivities and O_2 permeation in SFC-2 membrane reactor with reforming catalyst. Conditions: feed, 80% CH_4, 20% Ar; flow, 20 cm^3/min; temp., 900°C; pressure 1 atm; membrane surface area, 8 cm^2.

gas is demonstrated in Fig. 4, showing conversion data obtained with an SFC-2 membrane tube and a Rh catalyst at 850°C for ≈ 70h. As shown, methane conversion efficiency is > 98%, and CO selectivity is 90%. Selectivity is defined here, as the percent component produced per feed converted. Measured H_2 yield is approximately twice that of CO, as expected for partial oxidation of methane.

The role of the catalyst in the transport of oxygen flux averaged over the entire SFC-2 tube was tested without the reforming catalyst. The results from a run of ≈ 350h are shown in Fig. 5. 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. 5, methane conversion efficiency was ≈ 35% and CO_2 selectivity was ≈ 90%. Under our operating conditions, measured oxygen flux was ≈ 0.3 std $cm^3/cm^2/min$.

Fig. 6 shows the result of a reactor run made under more severe conditions and in the presence of the Rh based catalyst for > 500h. Conversion and selectivities are similar to those of the 350-h run but the oxygen flux was one order of magnitude greater. Some slight deactivation in oxygen permeation rate was observed.

Further confirmation of the stability of this membrane tube is shown in Fig. 7, which shows

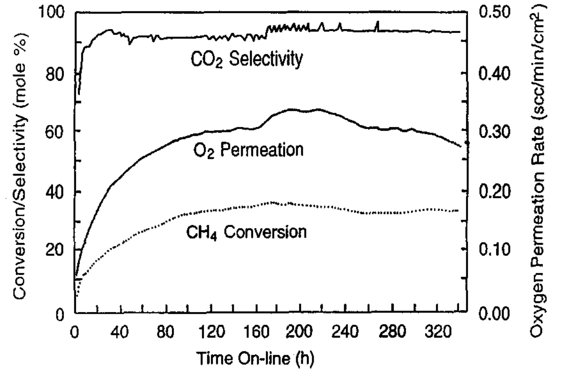

Fig. 5. Methane conversion and CO_2 selectivity and O_2 permeation in SFC-2 membrane reactor without reforming catalyst. Conditions: same as in Fig. 4.

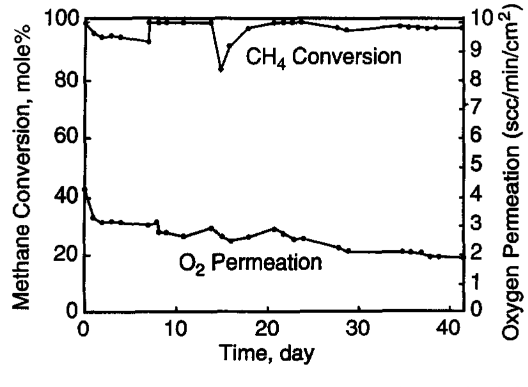

Fig. 7. Methane conversion and oxygen flux for a mixed feed. Conditions: temp., 900°C; pressure 1 atm; catalyst, 1.5 g; membrane surface area, 8.4 cm^2.

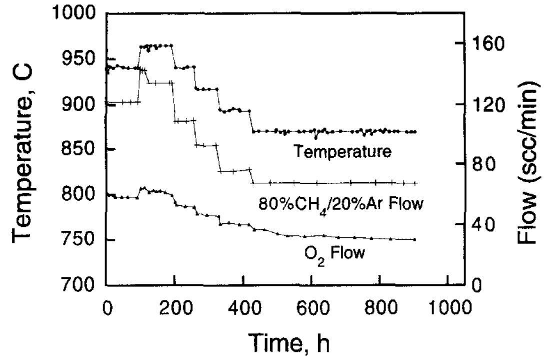

Fig. 8. Temperature profile and O_2 and feed flow for a 1000-h run. Conditions: feed, 80% CH_4, 20% Ar; pressure 1 atm; membrane surface area, 4.4 cm^2.

reactor results over a period of 1000h. 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 [20].

An additional run of 1000h, seen in Fig. 8, 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. The selectivity to CO during the entire run remained > 98%. Oxygen permeability followed the changes in temperature and feed flow, while maintaining conversion.

4. 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 the SFC-2 material were adequate for reactor use. Electronic and ionic conductivities showed that SFC-2 is unique in that its 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 and have operated successfully for > 1000h.

Acknowledgements

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

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] Y. Amenomiya, V.I. Buss, M. Goledzinszka and A.R. Sanger, Catal. Rev.-Sci. Eng., 32 (1990) 163.
[4] G. Henrici-Olive and S. Olive, Angew. Chem. Int. Ed. Engl., 15 (1976) 136.
[5] H.H. Kung, Catal. Rev., 22 (1980) 235.
[6] U. Balachandran, S.E. Dorris, J.J. Picciolo, R.B. Poeppel, and C.C. McPheeters, Proc. 24th Intersociety Energy Conversion Engineering Conf., Washington, DC, 3 (1989) 1541.
[7] Y. Teraoka, H.M. Zhang, S. Furukawa and N. Yamozoe, Chem. Lett., (1985) 1743.
[8] Y. Teraoka, T. Nobunaga and N. Yamazoe, Chem. Lett., (1988) 503.
[9] E.A. Hazbun, US Patent 4,791,079, December 13, 1988.
[10] K. Omata, S. Hashimoto, H. Tominaga and K. Fujimoto, Appl. Catal., 52 (1989) L1.
[11] 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. Int. Gas Research Conf., Orlando, FL, 1992, pp. 565–573 (1992).
[12] T.J. Mazanec, T.L. Cable and J.G. Frye, Jr., Solid State Ionics, 53–56(1992) 111.
[13] T.M. Gur, A. Belzner and R.A. Huggins, J. Membrane Sci., 75 (1992) 151.
[14] T.L. Cable, European Patent EP 0 399 833 A1, November 28, 1990.
[15] T.L. Cable, European Patent EP 0438 902 A2, July 31, 1991.

[16] U. Balachandran, M. Kleefisch, T.P. Kobylinski, S.L. Morissette and S. Pei, International Patent WO94/24065, October 1994.

[17] W.F. Brown, Jr. and J.E. Strawley, ASTM STP 410, Philadelphia, PA, 1967.

[18] J. Krautkrämer and H. Krautkrämer, Ultrasonic Testing of Materials, Springer-Verlag, Berlin, 1983.

[19] B. Ma, J.-H. Park, U. Balachandran and C.U. Segre, Mat. Res. Soc. Symp. Proc., 393 (1995) 49.

[20] B. Ma, U. Balachandran, J.-H. Park and C.U. Segre, Solid State Ionics., 83 (1996) 65.

[21] S. Pei, M.S. Kleefisch, T.P. Kobylinski, J. Faber, C.A. Udovich, V. Zhang-McCoy, B. Dabrowski, U. Balachandran, R.L. Mieville and R.B. Poeppel, Catalysis Lett., 30 (1995) 201.

[22] P.S. Maiya, M.S. Kleefisch, J.T. Dusek, R.L. Mieville, U. Balachandran and C.A. Udovich, Presented at 1st Int. Conf. on Ceramic Membranes, 188th Mtg. of Electrochem. Soc., Inc., Chicago, IL, October 8–13, 1995.