AIM

Association for Information and Image Management

1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910

301/587-8202

Centimeter

Inches

MANUFACTURED TO AIM STANDARDS
BY APPLIED IMAGE, INC.

1 of 1

ANL/ET/CP--81069
Conf-940713--1

DENSE CERAMIC MEMBRANES FOR PARTIAL OXYGENATION OF METHANE*

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

M. S. Kleefisch, S. Pei, and T. P. Kobylinski
Amoco Research Center
Naperville, IL 60566

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

May 1994

The submitted manuscript has been authored
by a contractor of the U. S. Government
under contract No. W-31-109-ENG-38.
Accordingly, the U. S. Government retains a
nonexclusive, royalty-free license to publish
or reproduce the published form of this
contribution, or allow others to do so, for
U. S. Government purposes.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Submitted for presentation at the 3rd International Conference on Inorganic Membranes, July 10-14, 1994, Worcester, MA.

*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.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER
87D
RECEIVED

JUL 14 1994

OSTI

Dense Ceramic Membranes for Partial Oxygenation of Methane

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

M. S. Kleefisch, S. Pei, and T. P. Kobylinski
Amoco Research Center
Naperville, IL 60566

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

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 that is based on dense ceramic membranes and that uses air as the oxidant for methane-conversion reactions, thus eliminating the need for the 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 anions, not oxygen molecules.

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 can have potential applications for improving the economics for methane conversion processes [1-11].

In principle, the 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. The surfaces can also be reversed. The membrane is permeable to oxygen at high temperatures, but not to nitrogen or any other gas. Thus, only oxygen from air can

be transported through the membrane to the inside of the reactor surface, where it reacts with the methane. Other geometric forms, such as honeycombing or corrugation, of the reactor are possible and can provide substantially greater surface areas for reaction [12].

Experimental

Two ceramic powders of the La-Sr-Fe-Co-O system with differing 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 $\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.6}\text{Co}_{0.4}\text{O}_x$, which was used by Teraoka et al. [1,2]. SFC-2 is an improved version of SFC-1. Appropriate amounts of $\text{La}(\text{NO}_3)_3$, SrCO_3 , $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 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 $\approx 850^\circ\text{C}$ 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, 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 [13]. 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 heated slowly ($\approx 5^\circ\text{C}/\text{h}$) in the temperature range of 150–400°C to facilitate removal of gaseous species formed during decomposition of the organic additives. After the organics were thus removed, the heating rate was increased to $\approx 60^\circ\text{C}/\text{h}$ and the tubes were sintered at $\approx 1200^\circ\text{C}$ for 5–10 h. All heating was in stagnant air. 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.

An Rh-based reforming catalyst was used inside the tubes. In addition to 80% methane, the feed gas contained 20% argon, which 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. Later reactor runs were also performed with flowing air on the inside of the tube and methane gas on the outside.

Results and Discussion

Tubes of SFC-1 lasted only a few minutes operating as conversion reactors at 850°C; they then broke into several pieces. XRD patterns of the original SFC-1 samples were recorded at 850°C in Ar-O₂ gas mixtures. The phase behavior of SFC-1 in 1 and 20% O₂ is shown in Fig. 1. In an oxygen-rich atmosphere (20% O₂), the material was a cubic perovskite. However, once the oxygen partial pressure was lowered to <5%, the cubic phase changed to an oxygen-vacancy-ordered phase. New peaks appeared in the XRD pattern, as seen in Fig. 1 (1% O₂). 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% O₂) was shifted to the low-angle (larger d-spacing) side of the corresponding peak in the cubic perovskite phase (in 20% O₂).

Detailed thermogravimetric analysis (TGA) showed that the oxygen content x of the sample in 1% O₂ was ≈ 0.1 lower than that in a sample in 20% O₂ [14]. 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 57.51 Å³ for $x = 2.67$ and 59.70 Å³ for $x = 2.48$.

Fig. 1. XRD of SFC-1 at 850°C in 1% and 20% O₂.

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 [14] 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 to high temperature, oxygen distribution is uniform. Upon heating, the tube 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 may contain different phase constituents, depending on its location in the tube. 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. 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 Archimedes principle; flexural strength, in a four-point bending mode; fracture toughness, by a single-edge notch method [15]; and Young's modulus, shear modulus, and Poisson's ratio by ultrasonic methods [16]. Thermal expansion coefficient was measured in a dilatometer. The results are shown in Table I.

By application of Weibull statistics [17], the Weibull modulus was calculated to be 15, which indicates 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 the methane is expected to be under higher pressures. Tubes made of this material, unlike those made of SFC-1, should not fracture under reactor conditions. Figure 3 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. 3, methane conversion efficiency is $>98\%$, and CO selectivity is 90%. As expected, measured H_2 yield is about twice that of CO.

Fig. 2. XRD of SFC-2 at 850°C in 1% and 20% O₂.

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√m	2.04 ± 0.06
Young's modulus, GPa	124 ± 3
Shear modulus, GPa	48 ± 2
Poisson's ratio	0.30 ± 0.01

Fig. 3. Methane conversion and CO and H₂ selectivities in SFC-2 membrane reactor with reforming catalyst: temperature, 850°C; pressure, ~1 atm; feed flow, 2–3 cc/min; membrane surface area, 10 cm².

The role of the catalyst in the transport of oxygen across the membrane of an SFC-2 tube was tested without the reforming catalyst. Results from a run of ~350 h are shown in Fig. 4. 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 CO₂ and H₂O. As seen in Fig. 4, methane conversion efficiency was ~35% and CO₂ selectivity was ~90%. Under our operating conditions, the measured oxygen flux was ~0.3 std cm³/cm²/min.

Successful runs of >1000 h have been made with mixed feeds and under varying conditions. An example is shown in Fig. 5, in this case, the membrane configuration was run with air flowing inside the tube at 1.2 L/min, while methane feed gas was on the outside. Conversion and selectivities were similar to those of the 70-h run but the oxygen flow was one order of magnitude greater, partly because of the higher operating temperature. Some small deactivation in the oxygen permeation rate was observed. Feed flow rate was varied during this run, causing the small perturbations seen in the overall consistent conversions and oxygen fluxes obtained over 1000 h.

Fig. 4. Methane conversion, CO₂ selectivity, and O₂ permeation in SFC-2 membrane reactor without reforming catalyst. (Conditions same as in Fig. 3.)

Fig. 5. Methane conversion and oxygen flux for a mixed feed: temperature, 900°C; pressure, 1 atm; catalyst, 1.5 g; membrane surface area, 8.4 cm².

Conclusions

Long tubes of La-Sr-F⁺-Co-O (SFC) membrane were fabricated by plastic extrusion, and thermal 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 acceptable for a reactor 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 the reactor tubes have operated for up to ~1000 h.

Acknowledgments

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.

References

1. Teraoka, Y., Zhang, H. M., Furukawa, S., and Yamozoe, N., Chem. Lett., 1743, 1985.
2. Teraoka, Y., Nobunaga, T., and Yamazoe, N., Chem. Lett., 503, 1988.
3. Hazbun, E. A., U.S. Patent 4,791,079, Dec. 13, 1988.
4. Omata, K., Hashimoto, S., Tominaga, H., and Fujimoto, K., Appl. Catal., L1, 52, 1989.
5. Balachandran, U., Morissette, S. L., Picciolo, J. J., Dusek, J. T., Poeppel, R. B., Pei, S., Kleefisch, M. S., Mieville, R. L., Kobylinski, T. P., and Udovich, C. A., Proc. Int. Gas Research Conf., ed. by H. A. Thompson (Government Institutes, Inc., Rockville, MD, 1992), pp. 565-573.
6. Mazanec, T. J., Cable, T. L., and Frye, Jr., J. G., Solid State Ionics, 111, 53-56, 1992.
7. Gur, T. M., Belzner, A., and Huggins, R. A., J. Membrane Sci. 151, 75, 1992.
8. Cable, T. L., European Patent EP 0399 833 A1, Nov. 28, 1990.
9. Cable, T. L., European Patent EP 0438 902 A2, July 31, 1991.
10. Bose, A. C., Stigel, G. J., and Srivastava, R. D., "Gas to Liquids Research Program of the U.S. Department of Energy: Programmatic Overview," paper to be presented at the Symposium on Alternative Routes for the Production of Fuels, American Chemical Society National Meeting, Washington, DC, August 21-26, 1994.
11. Proceedings of Coal Liquefaction and Gas Conversion Contractors Review Conference, Eds. S. Rogers et al., U.S. Department of Energy, Pittsburgh Energy Technology Center, Pittsburgh, PA, September 27-29, 1993.
12. Balachandran, U., Picciolo, J. J., Poeppel, R. B., and McPheeters, C. C., Proc. 24th Intersoc. Conversion Eng. Conf., Washington, DC, 3 154, 1989.

13. Balachandran, U., Morissette, S. L., Picciolo, J. J., Dusek, J. T., Poeppel, R. B., Pei, S., Kleefisch, M. S., Mieville, R. L., Kobylinski, T. P., and Udovich, C. A., Proc. Intl. Gas Res. Conf., ed. H. A. Thompson (Government Institutes, Inc., Rockville, MD, 1992).
14. Pei, S., Zajak, G. W., Faber, J., Mieville, R. L., Udovich, C. A., and Kleefisch, M. S., to be published.
15. Brown, Jr., W. F., and Strawley, J. E., ASTM STP 410, Philadelphia, PA, 1967.
16. Krautkrämer, J., and Krautkrämer, H., Ultrasonic Testing of Materials, (Springer-Verlag, New York, 1983).
17. Weibull, W., J. Appl. Mech., 293, 18, 1951.

**DATE
FILMED**

8/24/94

END