Advances in Ion Transport Membrane Technology for Oxygen and Syngas Production

Lori L. Anderson^a, Phillip A. Armstrong^a, Robert R. Broekhuis^a, Michael F. Carolan^{a,*}, Jack Chen^b, Mark D. Hutcheon^a, Charles A. Lewinsohn^b, Christopher F. Miller^a, John M. Repasky^a, Dale M. Taylor^b, Charles M. Woods^a

^a*Air Products and Chemicals, Inc., 7201 Hamilton Blvd., Allentown, PA 18195-1501, United States*

^b*Ceramtec, Inc., 2425 S 900W., Salt Lake City, UT 84119, United States*

**Corresponding author, Tel., +1 484 437 7142*

Email addresses: andersll@airproducts.com (L. Anderson), armstrpa@airproducts.com (P. Armstrong), carolamf@airproducts.com (M. Carolan), jchen@ceramatec.com (J. Chen), hutchemd@airproducts.com (M. Hutcheon), clewinsohn@ceramatec.com (C. Lewinsohn), millercf@airproducts.com (C. Miller), dtaylor@ceramatec.com (D. Taylor), woodscm@airproducts.com (C. Wood)

Abstract

Several decades of research by Air Products and Ceramtec have recently culminated in the construction and operation of a test unit with the capacity to produce up to 100 tons per day of oxygen using planar, ceramic mixed conducting, ion transport membranes (ITM). In the first tonnage operation of this unit, over 16 tons/day of oxygen were produced. Smaller scale experiments demonstrated high purity oxygen production for over 15000 hours. A parallel development effort has produced planar ceramic mixed conducting membranes to partially oxidize methane to produce syngas.

Keywords

Ion transport membrane

Ceramic membrane

Mixed conductor

Oxygen production

Syngas production

1. Introduction

Air Products and its partner Ceramtec are developing ion transport membranes (ITM) for oxygen and syngas production. ITMs are ceramic, mixed conducting membranes that conduct oxygen ions at elevated temperatures. They have significant potential in the industrial gas and energy industries. The focus of the development program at Air Products and Ceramtec are ITM membranes for the separation of a pure oxygen product from air, ITM Oxygen, and ITM membranes for the conversion of methane to synthesis gas, a mixture of carbon monoxide and hydrogen, ITM Syngas. Many different organizations have been

involved in their own developments of similar membranes and those developments have been reviewed by other authors [1-5]. The purpose of this paper is to review the state of the art of the technology being jointly developed by Air Products and Ceramtec, in particular the scale-up of the technology to large scale process demonstration facilities.

Air Products and Ceramtec have been developing ITM membranes together since the mid 1990's [6]. Significant progress has been made since then. The ITM team currently holds over 90 US patents in the ITM field, with equivalent patents issued in jurisdictions around the world. The patents cover membrane materials [7, 8, 9, 10], membrane designs [11, 12, 13, 14, 15], ceramic to metal seals [16, 17, 18, 19], and processes using ITM membranes [20, 21, 22, 23, 24, 25, 26, 27]. Progress in both technologies has been aided by cooperative agreements with the US Department of Energy and alliances with industrial partners.

The planar membrane configuration offers a high degree of flexibility in designing membrane modules for optimum flux performance and reliability. The modular membrane systems developed by Air Products and Ceramtec affords a high packing density of membrane for a given volume of reaction vessel and a low ratio of ceramic-to-metal seals to membrane surface area. It is well known that planar compact heat exchangers can achieve higher convective heat transfer coefficients than shell and tube heat exchangers since the heat transfer coefficients are inversely proportional to the hydraulic diameter and planar compact heat exchangers can have smaller hydraulic diameters than tubular heat exchangers [28]. Analogously, planar membranes should achieve improved convective heat and mass transfer coefficient relative to tubular membranes resulting from the planar membrane's smaller hydraulic diameters due to the internal micro-channels and close external membrane spacing. Furthermore, the microchannel architecture reduces stresses due to external pressure in the membrane layers of components and, hence, improves reliability.

ITM Oxygen membranes operate under an imposed gradient of oxygen partial pressure to produce a pure oxygen product. Hot, high pressure air is supplied to one side of a membrane and a pure oxygen product is recovered from the permeate side of the membrane. Favorable economics can be obtained when ITM Oxygen is integrated with other high temperature processes such as Integrated Combined Cycle Gasification [29, 30]. Recovery of the energy contained in the hot, high pressure vitiated air stream after oxygen has been extraction by the ITM membranes permits the co-production of power and steam as co-products [31]. This has been one of the drivers for continued development of ITM Oxygen technology by various research groups around the world [32].

The driving force for oxygen flux through ITM Syngas membranes is produced by supplying heated air and a hydrocarbon such as methane to opposite sides of the membrane [33]. Oxygen permeating the membrane oxidizes the methane to produce synthesis gas (syngas), a valuable feedstock for many industrial processes, including ultraclean liquid fuels, hydrogen production, and chemical production. Previously published studies indicated that ITM Syngas could improve the economics of syngas production for gas-to-liquids production [34, 35]. The disk membrane designs described previously could not support a significant pressure differential across the disk. Also, the reactor systems in which the disks were evaluated were not rated for pressurized operation. To evaluate performance of new membrane configurations and compositions at elevated pressure, both the reactor design and the disk membrane module had to be modified. The benefits of introducing porous layers and components was described in a previous publication [36], for a disk membrane system operated at near-atmospheric pressure on both sides of the membrane, and whose porous layer composition is identical to that of the dense membrane. This previous work has been extended in two directions: demonstration of operation with an elevated pressure on the reducing side of the membrane, and further flux enhancement by the introduction of catalytic components into the porous layers.

2. Material and methods

2.1 ITM Membrane Fabrication

Membrane components for ITM Oxygen and ITM Syngas applications are manufactured by similar methods. As shown in the flowchart presented in Figure 1, the first step of manufacturing is to synthesize powders with the desired ITM material composition using solid state synthesis methods. Subsequently, powder is milled to the appropriate particle size for forming and sintering. Milled powder is combined with solvents, dispersants, binders, and plasticizers to make a suspension with a well-defined viscosity. The slip is cast onto a carrier film and dried to obtain ceramic tapes of varying thicknesses. The tape is then featured, by laser-cutters or mechanical punches, into the dimensions and architecture required for the individual layers of the membrane components. The correct combination of layers is laminated together and then sintered. Modules are made by joining sintered components together in a separate thermal process [37, 38, 39].

Figure 1. Flowchart of manufacturing of ceramic ITM membranes

2.2 ITM Syngas Membrane Fabrication

2.2.1 Fabrication of Green Tapes

The powder with a composition of $\text{La}_{1-x}\text{Ca}_x\text{FeO}_{3-\delta}$ (LCF), where δ makes the compound charge neutral, was prepared through a conventional solid state reaction method. The LCF powder was combined with a dispersant, a binder, a plasticizer, and a solvent to form a slip suitable for tape casting. The slip was first mixed and then rolled ~16 hours to ensure the complete dissolution of the binder. The slip was filtered through a screen and degassed prior to casting on the polyester film by a doctor-blade tape casting method. Four different tapes (thick porous, thin porous, thick dense, and thin dense tapes) were cast for fabrication of different disk architectures. The thickness of the tape was adjusted by the gap of the doctor blade to control a green thickness of <150 μm and <600 μm for a thin and a thick tape respectively. The porous tapes were fabricated by introducing a suitable pore former to form the porous tape with an open porosity of 30-40%.

2.2.2 DS, PDS, PDPS, PDPS_p Disks Manufacture

Fabrication of DS Disks

Dense-Slotted (DS) disks are composed of 2 different layers: A thin dense membrane layer (D, <100 μm sintered) and the slotted (S) with rim layers made of thick dense tapes (~500 μm sintered). Two different tapes (1 thin dense, and 2 thick dense tapes) were cut into 16.5 cm x 16.5 cm tiles for the final lamination

size. Both slotted and rim layers are first obtained from thick dense tapes and cut by the laser cutting. The DS and rim layers are laminated by a solvent bonding process. After the solvent bonding operation, the DS assembly is further laser cut into 28 individual PDS disks for thermal processing.

Fabrication of PDS Disks

Porous-Dense-Slotted (PDS) disks are composed of 3 different layers: a thick porous layer (P, ~500 μm sintered, 30-40% open porosity), thin dense membrane layer (D, <100 μm sintered) and the slotted (S) with rim layers both made of thick dense tapes (~500 μm sintered). Three different tapes (1 thick porous, 1 thin dense, and 2 thick dense tapes) were cut into 16.5 cm x 16.5 cm tiles for the final lamination size. The P and D layers were heat laminated together between two sheets of Mylar. After lamination, the new PD sub-assembly is completed with alignment holes cut with a laser beam. Both slotted and rim layers are obtained from thick dense tapes and cut by the laser cutting. Finally, the PDS and rim layers are laminated by a solvent bonding process. After the solvent bonding operation, the PDS assembly is further laser cut into 28 individual PDS disks for thermal processing.

Fabrication of PDPS Disks

Porous-Dense-Porous-Slotted (PDPS) disks are composed of 4 different layers: a thick porous layer (P, ~500 μm sintered, 30-40% open porosity), thin dense membrane layer (D, <100 μm sintered), thin porous layer with dense rim (P, <100 μm sintered, 30-40% open porosity), and the slotted (S) with rim layers both made of thick dense tape (~500 μm sintered). The fabrication of PDPS disk follows largely the same process used for the fabrication of PDS disks with the addition of the thin porous layer with a dense rim.

Fabrication of PDPS_p Disks

Porous-Dense-Porous-Porous Slotted (PDPS_p) disks are composed of 4 different layers: thick porous layer (P, ~500 μm sintered, 30-40% open porosity), thin dense membrane layer (D, <100 μm sintered), thin porous layer (P, <100 μm sintered, 30-40% open porosity), and the porous slotted layer (S_p) and dense outer rim layer both made of thick tapes (~500 μm sintered). The processes used for the fabrication of PDPS_p disks are similar to those used for the PDS disks with the exception of the additional thin porous layer and thick porous slotted layer with dense rim.

All disks with different architectures were bisqued with a low-temperature, binder removal schedule tailed to burnout the binder, followed by a high temperature sintering at >1573 K to achieve hermetic disks of ~1.9 cm diameter for the reactor tests. The leak tests of the disks are conducted on a Helium Leak Detector instrument. All disk membranes must be hermetic for further testing in the reactors. Figure 2 shows typical hermetic PDS disks after sintering.

Figure 2. Sintered PDS disks are shown with the porous layer visible on the left, and the slotted layer on the right.

2.2.3 Disks Membrane Microstructure

Sacrificial disk membranes are cross-sectioned to verify their microstructure by Scanning Electron Microscopy (SEM). The membranes are observed at different magnifications to examine the microstructure. Figure 3 shows cross-section SEM images of the (a) Dense-Slotted (DS) membrane, (b) Porous-Dense-Slotted (PDS) membrane, (c) Porous-Dense-Porous-Slotted (PDPS) membrane, and (d) Porous-Dense-Porous-Slotted_{porous} (PDPS_p) membrane.

(a) DS disk membrane

(b) PDS disk membrane

(c) PDPS disk membrane

(d) PDPS_p disk membrane

Figure 3. Cross-section SEM of (a) DS disk membrane, (b) PDS disk membrane, (c) PDPS disk membrane, (d) PDPS_p disk membrane.

2.2.3 Disk Membrane Catalyzation

On-membrane catalyst was applied to some of the disk modules to improve the kinetics of syngas-side oxygen transfer and combustion reactions. Various formulations (single metal, bimetallic) and loadings were applied during the broader experimental program, and were found to have approximately equal effectiveness at promoting flux. The experimental results described below were achieved with a specific loading of Rh and Pd, whose application is briefly described below.

Solutions were prepared of $[\text{Rh}_3\text{Ac}_6\text{-}\mu\text{-O}(\text{H}_2\text{O})_3]\text{Ac}$ in ethanol (62 mg/ml) and PdAc_2 in chloroform (43 mg/ml). For each impregnation step, 65 μl of the organic solution was applied to the syngas-side porous layer of a 20-mm diameter disk using a syringe, which was sufficient to just fill the pores. The disk was then air-dried, and calcined in air at 500°C. Each metal solution was impregnated twice using this method, in sequence Rh-Pd-Rh-Pd, to achieve loadings of 0.99 mg Rh/cm² and 0.84 mg Pd/cm².

3. Experimental

3.1 ITM Oxygen process demonstration

From the earliest development of ITM Oxygen technology, the vehicles used to demonstrate the concept and implementation have undergone continuous scale-up. Experimentation continues at all scales, in support of the various development goals, but the focus in recent years has shifted to installations to demonstrate multi-wafer membrane stacks, a step up from apparatuses to test small disk membranes and single-wafer membrane modules. Membrane stacks containing up to 12 wafers can be tested in a Technology Demonstration Unit (TDU), whose feed flow rates and process conditions match those of anticipated commercial operation. The TDU uses electric furnaces to heat air compressed up to 1.7 MPa. The hot, compressed air then flows over the 12 wafer module at up to 60 Nm³/hr. A vacuum pump is used to withdraw the oxygen permeate, whose flux and purity are measured using a mass flow meter and a paramagnetic analyzer. At the next scale, the Subscale Engineering Prototype (SEP), shown in Figure 4, is configured to test up to six full-sized (144-wafer) stacks, arranged in 3 rows of 2 modules. The SEP also heats the compressed feed air to the modules using electrically heated metal pipes. The modules are housed in an internally insulated flow duct inside a pressure vessel. A vacuum pump withdraws the oxygen permeate from each module, and the flow rate and purity of each module is measured independently. At the largest scale, the Intermediate Scale Test Unit (ISTU), shown in Figure 5, is designed to produce up to 100 ton/day of oxygen and 1 MW of net power. A block flow diagram of the ISTU is shown in Figure 6. Modules installed in the flow duct are shown in Figure 7. Air is compressed and then heated against the hot non-permeate gas exiting the ITM vessel. An indirect fired heater is used to heat the feed air to the process temperature. Energy from the hot, pressurized non-permeate gas is recovered in a hot gas expander, producing up to 1 MW of electricity. The oxygen permeate is cooled before venting. Its membrane vessel is configured the same as an anticipated commercial vessel design; the overall unit contains all unit operations required for commercial operation of the technology.

Figure 4. Subscale Engineering Prototype capable of testing up to six 144 wafer ITM Oxygen modules.

Figure 5. Intermediate Scale Test Unit, capable of producing up to 100 tpd of Oxygen

Figure 6. Flow diagram of the ISTU.

Figure 7. ITM Oxygen Modules installed in the flow duct of the ISTU.

3.2 ITM Syngas

An exploded view of the modified membrane module design is shown in Figure 8. To withstand the pressure differential, the thin membrane layer is backed by robust support layers, which define flow channels for the feed air. The multi-layer disk is joined to a tube composed of the membrane material, to form a tubular module. This design eliminates leaks and minimizes stresses due to thermal expansion. The reactor system was redesigned to accommodate this membrane module, and is described in the Appendix.

Figure 8. Exploded view of High pressure ITM Syngas membrane, Sx and Sy layers provide mechanical support.

4. Results and Discussion

4.1 ITM Oxygen

Several recent milestone achievements have furthered the development of commercial ITM Oxygen technology. In the TDU, a 12-wafer membrane stack was operated for over 15,000 hours at full process conditions. During this time, it underwent several planned and unplanned temperature and pressure cycles, as well as variations in pressure and temperature to evaluate membrane performance at a range of conditions. Performance versus time at a single temperature and pressure condition is shown in Figure 10. Product purity was maintained at >99% oxygen throughout the run, while oxygen flux decreased slightly. Post-test analysis revealed that creep due to the pressure load on the wafer had resulted in a compressive creep strain of the entire stack of wafers of 3.4% resulting in the macroscopic wafer displacements seen in Figure 11. A large fraction of the creep strain was accommodated by decreasing the cross-sectional area of the internal flow channels of the membrane wafers at the central manifold, an example of which can be seen in Figure 12, which could result in a higher pressure drop on the permeate side of the membrane. This higher pressure drop would decrease the driving force for oxygen permeation. This is a possible reason for the slight decay in flux. Initial results from laboratory experiments suggest that methods for reducing the creep rate to acceptable levels are feasible, and are the subject of on-going development.

Figure 10. Long term testing of 12 wafer module in the TDU showing steady oxygen purity and only a minor decay in flux.

Figure 11. Before testing (left) and after testing (right) pictures of the 12 wafer module tested for over 15000 hrs, showing evidence of compressive creep.

Figure 12. Example of deformation and decreased cross sectional area of the channels due to creep, as seen in the channels at the bottom middle of the image.

The SEP has accumulated over 1100 total days of operation while demonstrating the commercial flux target for full size modules. Pressure and temperature cycling of full size modules have also been demonstrated, as shown in Figure 13. The modules in this run maintained >99.9% oxygen product purity and steady oxygen flux through the temperature and pressure cycles.

Figure 13. Oxygen purity and flux of a full size ITM Oxygen module through temperature and pressure cycles demonstrating stable permeate purity and flux.

The ISTU has operated at $\approx 1/4$ capacity with 2 rows of modules installed. Oxygen production of 16 ton/day was achieved during a 300-hour run, which met expectations based on the number of installed modules. Additionally, several other necessary technology components in the areas of heat transfer and contaminant mitigation were successfully demonstrated. Figure 14 shows the oxygen production rate and purity remaining steady with no indication of decay during this large-scale demonstration. Figure 15 shows the flux from each module normalized to the flux expected from a first-row module without an air-side porous layer. Modules with an air-side porous layer had $\sim 9\%$ higher flux than modules without a porous layer. Modules in the second row had $\sim 4\%$ lower flux than the modules in the first row, due to the lower oxygen partial pressure in the air reaching the second row after the first row has extracted some of the oxygen.

Figure 14. Qualitative oxygen purity and production rate during the tonnage oxygen production run in the ISTU.

Figure 15. Comparison of the fluxes of modules with and without air side porous layers and fluxes of modules in the first and second rows.

4.2 ITM Syngas

Figure 16 demonstrates the effect of catalyzing the fuel-side porous layer. The blue bars represent the previously reported oxygen flux at 900°C achieved by non-catalyzed membranes, with flux enhancement through the introduction of porous layers. The red bars show the flux achieved by applying catalyst to the fuel side of the membrane. The first two bars demonstrate that the catalyst is even more effective than the porous layer at reducing the kinetic resistance of fuel-side combustion reactions. Even catalyst applied to a bare dense membrane is sufficient to boost flux performance. The flux can then be further enhanced by including an air-side porous layer.

Figure 16. Comparison of oxygen flux from catalyzed (red) and uncatalyzed membranes (blue) with or without air and permeate side porous layers.

These flux enhancements by membrane configuration and catalysis have subsequently been demonstrated at larger scale in the Process Development Unit, through months of operation at a variety of temperatures and compositions, and pressures exceeding 18 bar abs.

The high-pressure reactor enables comparison of process performance at both high and low temperatures, with both catalyzed and uncatalyzed membranes. This provides insights into the mechanisms at play in the reaction-driven flux process. As an example, Table 1 lists activation energies measured between 790 and 940°C, during operation at high (23 mol%) and low (3 mol%) hydrogen concentration in the fuel-side feed.

Table 1. Measured activation energies over the temperature range 790-940°C, in kJ/mol. For all experiments, $y_{H_2O}=19\%$, balance nitrogen.

	P=1.1 bar abs		P=11.3 bar abs	
	uncatalyzed	catalyzed	uncatalyzed	catalyzed
$y_{H_2}=3\%$	57	20	56	27
$y_{H_2}=23\%$	75	30	83	63

The much lower activation energies for the catalyzed membranes confirm that the fuel-side combustion and oxygen transfer processes are among the rate-determining steps in the overall flux process. For both uncatalyzed and catalyzed membranes, regardless of pressure, the activation energy is lower at the lower hydrogen concentration, which suggests that the mechanism for oxygen transfer may be shifting as less hydrogen is available to drive the surface processes. While the activation energies for uncatalyzed membranes are similar in the low-pressure and high-pressure cases, catalyzed membranes appear to be significantly less temperature-activated at low pressure than at high pressure. This may be evidence that the surface reactions are inhibited by a fuel-side component, such as water vapor. Besides the few examples highlighted above, the versatile high- and low-pressure reactors have been used to study the effects of ITM composition, dense and porous layer properties and thicknesses, and effects of process contaminants. They are powerful tools in the development and optimization of ITM membrane systems for reaction-driven oxygen transport and syngas

5. Conclusions

Oxygen production using ceramic, mixed conducting ion transport has now been demonstrated at a significant scale, producing tonnage quantities of oxygen for the first time. Very long term testing has shown that the ITM membranes can operate for the times required for commercial applications while maintaining high purity oxygen production. The advantages of using either or both enhanced surface area and catalysts on the oxygen flux for oxidation reactions have also been demonstrated.

6. Acknowledgements

This technology development has been supported in part by the U.S. Department of Energy under Contract No. FC26-98FT40343. The U.S. Government reserves for itself and others acting on its behalf a royalty-free, nonexclusive, irrevocable, worldwide license for Governmental purposes to publish, distribute, translate, duplicate, exhibit and perform this copyrighted paper. Neither Air Products and Chemicals, Inc. nor any of its contractors or subcontractors nor the United States Department of Energy, nor any person acting on behalf of either:

1. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
2. Assumes any liabilities with respect to the use of, or for damages resulting from the use of, any information, apparatus, method, or process disclosed in this report.

Reference herein to any specific commercial products, 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 Department of Energy. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Department of Energy.

7. References

- 1) Dong, X., W. Jin, et al. (2011). "Dense ceramic catalytic membranes and membrane reactors for energy and environmental applications." Chemical Communications 47(39): 10886-10902.
- 2) Habib, M. A., H. M. Badr, et al. (2011). "A review of recent developments in carbon capture utilizing oxy-fuel combustion in conventional and ion transport membrane systems." International Journal of Energy Research 35(9): 741-764.
- 3) Jiang, Q., S. Faraji, et al. (2011). Chapter 11 - A Review of Mixed Ionic and Electronic Conducting Ceramic Membranes as Oxygen Sources for High-Temperature Reactors. Membrane Science and Technology. S. T. Oyama and M. S.-W. Susan, Elsevier. Volume 14: 235-273.
- 4) Zhang, K., J. Sunarso, et al. (2011). "Research progress and materials selection guidelines on mixed conducting perovskite-type ceramic membranes for oxygen production." RSC Advances 1(9): 1661-1676.
- 5) Wei, Y., W. Yang, et al. (2013). "Dense ceramic oxygen permeable membranes and catalytic membrane reactors." Chemical Engineering Journal 220(0): 185-203.
- 6) Paul N. Dyer, Robin E. Richards, Steven L. Russek, Dale M. Taylor, Solid State Ionics 134 (2000) 21-33
- 7) Carolan, M.F.; Dyer, P.N.; Motika, S. A.; Alba, P. B.; Compositions capable of operating under high carbon dioxide partial pressures for use in solid-state oxygen producing devices, US Patent 5,712,220, January 27, 1998.
- 8) Carolan, M.F.; Dyer, P.N.; Motika, S. A.; Compositions capable of operating under high oxygen partial pressures for use in solid-state oxygen producing devices, US Patent 5,817,597, October 6, 1998.
- 9) Carolan, M.F.; Dyer, P.N.; Motika, S. A.; Alba, P. B.; Fluid separation devices capable of operating under high carbon dioxide partial pressures which utilize creep-resistant solid-state membranes formed from a mixed conducting multicomponent metallic oxide, US Patent 6,056,807, May 2, 2000.
- 10) Dyer, P.N.; Carolan, M.F.; Butt, D.; Van Doorn, R. H. E.; Cutler, R. A.; Mixed conducting membranes for syngas production, US Patent 6,492,290, December 10, 2002
- 11) Thorogood, R. M.; Srinivasan, R.; Yee, T. F.; Drake, M. P.; Composite mixed conductor membranes for producing oxygen, US Patent 5,240,480, August 31, 1993.
- 12) Taylor, D. M. et, al., Planar solid-state membrane module, US Patent 5,681,373, October 28, 1997.
- 13) Carolan, M.F. et. al., Planar ceramic membrane assembly and oxidation reactor system, US Patent 7,279,027, October 9, 2007.
- 14) Gordon, J. H. and Taylor, D. M., Solid-state membrane module, US Patent 7,955,423,
- 15) Hinklin, T. R. and Lewinsohn, C. A.; Solid-state membrane module, US Patent 9,067,172, June 30, 2015
- 16) Rynders, S. W.; Minford, E.; Tressler, R. E.; Taylor, D. M.; Compliant high temperature seals for dissimilar materials, US Patent 6,302,402, October 16, 2001.

- 17) Minford, E.; Seal assembly for materials with different coefficients of thermal expansion, US Patent 7,581,765, September 1, 2009.
- 18) Carolan, M. F.; Minford, E.; Cooke, J. A.; Calianno, T. J.; Composite seal, European Patent 1983236B1, October 22, 2008.
- 19) Underwood, R. P. and Tentarelli, S. C.; Seal between metal and ceramic conduits, US Patent 8,944,437, February 3, 2015
- 20) Kang, D.; Thorogood, R. M.; Allam, R. J.; and Topham, A. K. J.; Integrated production of oxygen and electric power, US Patent 5,657,624, August 19, 1997.
- 21) Russek, S. L.; Knopf, J. A.; Taylor, D. M.; Oxygen production by ion transport membranes with non-permeate work recovery, US Patent 5,753,007, May 19, 1998.
- 22) Nataraj, S.; Moore, R. B.; Russek, S. L.; Production of synthesis gas by mixed conducting membranes, US Patent 6,048,472, April 11, 2000.
- 23) Nataraj, S.; Russek, S. L.; Synthesis gas production by ion transport membranes, US Patent 6,077,323, June 20, 2000.
- 24) Nataraj, S.; Russek, S. L.; Utilization of synthesis gas produced by mixed conducting membranes, US Patent 6,110,979, August 29, 2000.
- 25) Nataraj, S.; Russek, S. L.; Dyer, P. N.; Synthesis gas production by mixed conducting membranes with integrated conversion into liquid products, US Patent 6,114,400, September 5, 2000.
- 26) Nataraj, S.; Russek, S. L.; Synthesis gas production by ion transport membranes, US Patent 6,214,066, April 10, 2001.
- 27) Repasky, J. M., Ion transport membrane reactor systems and methods for producing synthesis gas, US Patent 9,028,720. May 12, 2015.
- 28) John Hesselgreaves, *Compact heat exchangers: selection, design and operation*, Pergamon, 2001, pages 3-8,
- 29) C. Lewinsohn, J. Chen, D.M. Taylor, P.A. Armstrong, L.L. Anderson, and M.F. Carolan, "Ceramic Gas-separation Membranes for Advanced Energy Applications," *Cer. Engng. & Sci. Proc.*, vol. 34, issue 9, 2013
- 30) A. Bose, P. A. Armstrong and E. P. Foster, Progress in Ion Transport Membranes for Gas Separation Applications in *Inorganic Membranes for Energy and Environmental Applications*, Springer-Verlag New York, 2009, pp 3-25
- 31) *ibid.*
- 32) Tonziello, J. and M. Vellini (2011). "Oxygen production technologies for IGCC power plants with CO₂ capture." *Energy Procedia* 4: 637-644.
- 33) M. Carolan, Syngas Membrane Engineering Design and Scale-Up Issues. Application of Ceramic Oxygen Conducting Membranes, *Nonporous Inorganic Membranes For Chemical Processing*, Wiley, 2006
- 34) Dr. Duke du Plessis, Gas to Liquids Technologies with Potential for Adding Value to Alberta's Natural Gas Resources, CERI Natural Gas Conference, Calgary (March 3-4, 2014)
- 35) Repasky, John M., Michael F. Carolan, David W. Studer, Clifford M. Lowe, Karl F. Gerdes, Joris Smit, and Berthold Bremen. "ITM Syngas: ceramic membrane technology for lower cost conversion of natural gas." In *AIChE Spring National Meeting*, vol. 4. 2010
- 36) C.F. Miller, J. Chen, M. F. Carolan and E. P. Foster, *Catalyst Today*, 228 (2014) 152-157
- 37) Butt, D. P.; Cutler, R. A.; Rynders, S. W.; Carolan, M. F.; Method of joining ITM materials using a partially or fully-transient liquid phase, US Patent 7,011,898, March 14, 2006.
- 38) Butt, D. P.; Cutler, R. A.; Rynders, S. W.; Carolan, M. F.; Method of forming a joint, US Patent 7,094,301, August 22, 2006.
- 39) Cutler, R. A.; Hutching, K. N.; Kleinlein, B. P.; Carolan, M. F.; Method of forming a ceramic to ceramic joint, US Patent 7,695,580. April 13, 2010

Appendix: Design of the ITM Syngas cold-wall reactor

Figure A-1. Schematic of the ITM Syngas cold-wall reactor (not to scale). See text for descriptions of the numbered items.

Figure A-1 shows schematically the design of the redesigned reactor system. Pressurized operation is achieved by using a cold-wall approach, in which the pressure-containing outer shell (1) is cooled and insulated (2) from an inner zone heated by electric heating elements (3). The annular zone containing the insulation and heating elements is not hermetically sealed from the inner flow path, and is therefore at process pressure; it is purged with argon to prevent accumulation of process gas and extend the life of the heaters. The hot flow tube (4) is constructed from inert materials such as pure nickel metal. The reducing gas, typically consisting of hydrogen, nitrogen, and steam, passes through a pre-heating and guard bed section (5) and impinges on the top of the disk membrane module (6), before exiting through the main flow path. The disk module is ceramically joined to a ceramic tube of the same material (7), forming a hermetic seal. The ceramic tube engages into a metal tube (9), using a U-ring sealing arrangement (8). Feed air is delivered through an alumina tube (10) that extends through the center of the tubular module and terminates in a nozzle that engages with the central air inlet slot of the membrane module. Air flows through the channels adjacent to the thin membrane, and out through the air exit slots, leaving the reactor through the annular space around the air feed tube. The oxygen flux is evaluated from the oxygen concentration measured in the air effluent.