

State of Art (SOTA) Report on Dense Ceramic Membranes for Oxygen Separation from Air

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Executive Summary

Inexpensive, large scale oxygen production is crucial to the development of the next generation of integrated carbon capture and sequestration power plants based on coal gasification or oxy-fuel coal combustion technologies. The current state of the art is cryogenic distillation with no other mature technology, such as pressure swing adsorption or polymeric membranes, able to cost effectively deliver the tonnage quantities of O₂ at the required purities of >95% (vol.). However, cryogenic distillation is an energy and capital intensive mature technology with very few prospects for large performance improvements or opportunities for cost reductions. Of the embryonic technologies, ion transport membranes (ITMs) represent the most promising alternative. This research is primarily at the laboratory scale at present where the state of the art are dense ceramic membranes made from doped perovskite materials such as barium strontium cobalt iron mixed oxides (BSCF) which exhibit fluxes on the order of 10 – 15 ml min⁻¹ cm⁻² under optimal conditions. However, the more stable lanthanum strontium cobalt iron mixed oxides (LSCF) is preferred owing to its superior chemical and mechanical properties, though delivering lower oxygen fluxes. Fluorites are now being considered, particularly that these materials can operate under exposure to water and CO₂.

Commercial deployment has yet to be realised but small pilot scale facilities have been commissioned using perovskites. The largest of these was built by Air Products and Chemicals in the USA with a production capacity of 5 tonnes per day. This facility has been operational for in excess of 500 days, and its success has undoubtedly led to their decision to construct a new 100 TPD facility due to be commissioned in 2013. This is possibly the first indication that this technology can be taking over the hump in the demonstration cycle (see Figure 1), where capital and operational costs could start reducing. The membrane module design used by Air Products, a wafer-like module incorporating a central collection tube arguably represents the state of the art by virtue of the success of their pilot facilities. Other researchers, however, see future modules adopting tubular geometries to further reduce module size and membrane sealing requirements. Regardless, the rate limiting steps for further commercialisation are the fabrication of mechanically robust and chemically stable membranes (especially against water and CO₂ exposure) and the development of innovative sealing systems able to withstand the high operating temperatures required as in both cases.

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List of Acronyms and Abbreviations

ANLEC	Australian National Low Emissions Coal
ASU	Air Separation Unit
BSCF	$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$
CCS	Carbon Capture and Sequestration (or Storage)
IGCC	Integrated gasification combined cycle
ITM	Ionic transport membranes
LSCF	$\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$
MIEC	Mixed ionic electronic conducting
SOTA	State of the art
TRL	Technology Readiness Level

1 Introduction

This report addresses the first deliverable for project number 3-0510-0034 Australian National Low Emissions Coal Research and Development Ltd (ANLEC) title “**Membranes for tonnage oxygen separation suited to supply oxy-fuel and coal gasification applications**”. This report was prepared by The University of Queensland and project partners Curtin University and The University of Western Australia.

The objective of this report is on the state of art analysis (SOTA) of dense ceramic membranes for oxygen separation from air. Hence, this report considers the three stages of technology development namely: (i) embryonic, (ii) development, demonstration and deployment, and (iii) mature technologies. In this work, we have assessed the open literature via university libraries, data base, scientific journals and available web pages. Whilst there is a large number of information available, we have endeavoured to include only the most relevant works that could be constituted as state of art in this report.

2 Background

2.1 Research Drivers

Reducing the capital and operating costs of oxygen production is the major driver for the research and development of ionic transport membranes (ITMs). This is particularly important for producing the tonnage quantities of oxygen required for the next generation of integrated carbon capture and sequestration (CCS) power plants, based on gasification and/or oxyfuel coal combustion processes. Currently large scale oxygen production is carried out by cryogenic distillation, a mature technology where significant technological innovations are no longer expected. Cryogenic distillation is capital and energy intensive, operating at very low temperatures (-200°C) and at elevated pressures. Coupling a cryogenic air separation unit at the front end of an oxyfuel coal power plant is likely to reduce power generation efficiencies by 25%, for example taking a total power plant efficiency of around 40% down to 30%, which will, in turn, have profound implications for the cost of electricity. Based on reputable work from the US Department of Energy, ITMs offer the potential to separate oxygen from air and to reduce oxygen production costs by 35% or more¹ with lower efficiency penalties.

2.2 Competitive Technologies

There are multiple technology options available for oxygen production. The choice of technology used is highly dependent on the type and scale of the application, final purity requirements and the cost of energy. These technologies can be categorized according to their technology readiness level (TRL), grouped here into (i) mature, (ii) DD&D (development, demonstration & deployment) and (iii) embryonic categories for

¹ G.J. Stiegel, R.C. Maxwell, Gasification technologies: the path to clean, affordable energy in the 21st century, Fuel Processing Technology, 71 (2001) 79-97.

simplicity. Mature technologies offer a very small scope for further improvements as they have already undergone major technical developments for at least the last 20 years. However, they offer the best performance and risk minimisation profiles, and are therefore the most attractive for deployment in the first generation of CCS plants. Embryonic technologies are those that are still at the laboratory research stage. The gap between embryonic and maturity is herein referred to as DD&D, which represents those technologies that have progressed beyond the laboratory proof-of-concept stage. DD&D technologies are focussed on accelerating towards demonstration and deployment, but still must undergo further scientific and engineering development. Hence, embryonic and DD&D technologies represent the largest scope for improvement and efficiency gains but also the largest risk of failure.

Table 1 outlines the oxygen requirements for an ASU integrated with a carbon capture ready oxy-fuel or IGCC power plant. It is important to realise that the oxygen purity requirements are dependent on the combustion technology, CO₂ capture technology and CO₂ end use. A DOE NETL study² into pulverised coal oxy-combustion technology found that if a high purity CO₂ stream (> 95%) is required then it is more cost effective to use a high purity O₂ stream (99 vol%) rather than build additional capacity to remove the contaminants from a lower quality O₂ stream (95 vol%) during the CO₂ clean up and compression trains. However, for most cases the difference in cost and performance of using a higher purity or lower purity O₂ stream was marginal.

Table 1 - Typical Oxygen Requirements for ASU integration into CCS ready power plants

O ₂ characteristic	Requirement
Oxygen Flow rate	150 – 500 tO ₂ h ⁻¹
Oxygen Purity	>95 vol%
Allowed Impurities	Ar < 5%

Figure 1 shows our opinion of the current stage of development for the most prominent and promising air separation technologies. Table 2 provides more detailed information relating each technology including the typical capital costs and energy requirements of the major air separation technologies discussed in this section. Where possible we have used data where the chosen ASU technology has been integrated into either an oxyfuel coal combustion or IGCC power plant. Currently only cryogenic air separation and ITMs have undergone such a techno-economic evaluation and the data for polymeric membranes and PSA systems are indicative of standalone systems only, making a true comparison difficult.

² DOE/NETL, Pulverised coal oxycombustion power plants, volume 1: Bituminous coal to electricity. 2008.

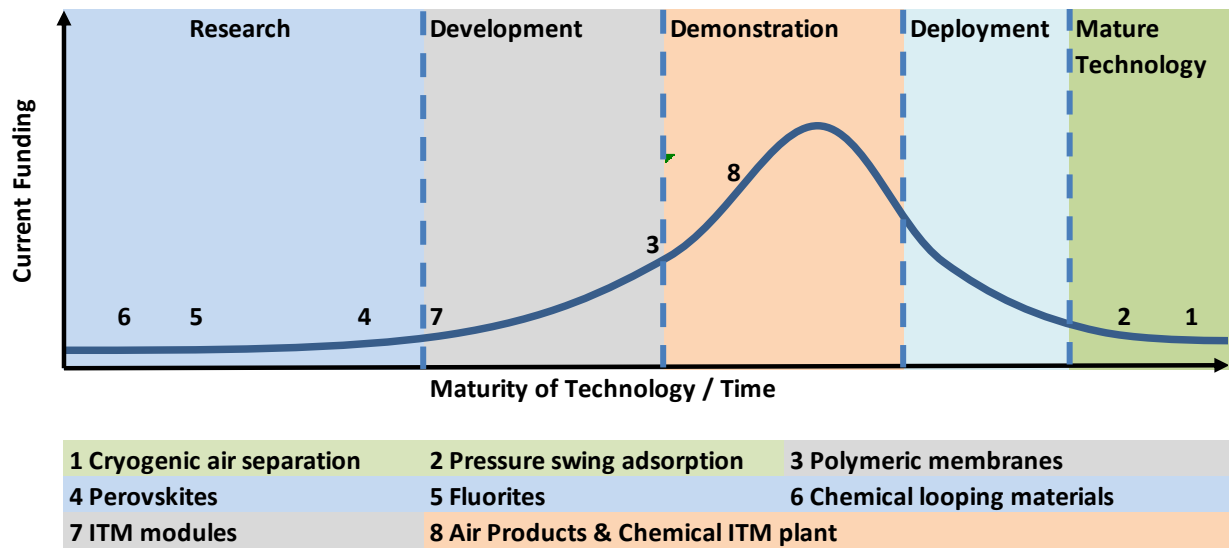


Figure 1 – Maturity versus total investment for oxygen separation technologies.

Table 2 – Details of ASU technologies

Technology	Cryogenic Air Separation	Pressure Swing Adsorption	Polymeric Membranes	Ionic Transport Membranes
Current Status	Mature	Mature	Mature	Demonstration
O₂ Purity Limit (% vol) (Remaining impurities)³	99+ (Ar)	95 (Ar)	40 (N ₂ , CO ₂ , H ₂ O)	100
O₂ Flowrate in largest commercial installations (tO₂ d⁻¹)	>3000 ⁴	<350 ⁶	<20 for oxygen enriched combustion applications	5 (soon to grow to 100 with installation of new plant)
Suitability for CCS	High	Moderate	Alone – Low Hybrid - Moderate ⁵	High
Timeframe to CCS commercialization	Immediate	Short	NA	Medium / Long
Installed Capital Cost in Oxyfuel or IGCC plant (\$US2008 kWe⁻¹)	310 – 500* ^{2,6}	150 - 200 For standalone PSA system producing <150 tO ₂ d ⁻¹⁷	95 – 160 For a 30% O ₂ stream ⁸	260 - 295 ^{2,8}
Energy Consumption in Oxyfuel or IGCC plant (kWh tO₂⁻¹)	245 – 670* ^{2,8}	~450 ⁹ -700 ⁹	<ul style="list-style-type: none"> • 260 for 40% O₂ stream¹⁰ • 190[^] – 240^{&} for hybrid membrane / cryogenic system⁷ 	100 - 655 ^{#2,8}
Energy Penalty for Integration with CCS[§]	~25% ²	NA	NA	~25% ²

*the wide range in these values reflects the differing O₂ flow rates required and energy integration opportunities available for oxy-fuel and IGCC applications

#the largest value includes heating value of NG for generating required operating temperatures for ITM, whereas the smallest value represents only the electrical energy input

§ defined as $1 - \eta_{CCS} / \eta_{Ref}$

^for plants producing > 1000 tO₂ d⁻¹

&for plants producing < 100 tO₂ d⁻¹

³ Smith, A.R. and Klosek, J., A review of air separation technologies and their integration with energy conversion processes. Fuel Processing Technology, 2001. 70(2): p. 115-134.

⁴ Castle, W.F., Air separation and liquefaction: recent developments and prospects for the beginning of the new millennium. International Journal of Refrigeration, 2002. 25(1): p. 158-172.

⁵ Burdyny, T. and Struchtrup, H., Hybrid membrane/cryogenic separation of oxygen from air for use in the oxy-fuel process. Energy, 2010. 35(5): p. 1884-1897.

⁶ DOE/NETL, Cost and Performance Baseline for Fossil Energy Plants Volume 3a: Low Rank Coal to Electricity: IGCC Cases. 2011.

⁷ Matson, S.L., et al., Membrane oxygen enrichment : II. Economic assessment. Journal of Membrane Science, 1986. 29(1): p. 79-96.

⁸ Bhide, B.D. and Stern, S.A., A new evaluation of membrane processes for the oxygen-enrichment of air. II. Effects of economic parameters and membrane properties. Journal of Membrane Science, 1991. 62(1): p. 37-58.

⁹ Meriläinen, A., Seppälä, A., and Kauranen, P., Minimizing specific energy consumption of oxygen enrichment in polymeric hollow fiber membrane modules. Applied Energy, 2012. 94(0): p. 285-294.

Mature technologies that overcame the “cost hump” for oxygen separation from air include cryogenic distillation and pressure swing adsorption (PSA). For producing tonnage quantities of high purity (> 98 vol%) oxygen, cryogenic distillation is the technology of choice whilst PSA systems find deployment at small to medium scale or where the highest purity O₂ is less of a concern¹⁰. Additionally the capital costs of PSA systems tend to scale linearly with size making them a poor choice for integration with large power plants. In the development phase, polymeric membranes typically deliver oxygen at purities less than 40%, and are therefore used primarily to enrich oxygen or nitrogen streams. In the research phase, chemical looping combustion has been proposed, though the development of stable metal oxides is in the early stages of laboratory research.

The technology that is attracting major interest from the research community and subsequent investment from government and industry sources is ionic transport membranes also known as dense ceramic membranes. This technology spans from the embryonic stage, where there is still a concerted research effort into developing new materials; to the developmental stage of membrane modules which are being investigated in Europe, USA, Australia and Asia; and even the demonstration stage where Air Products and Chemicals Inc. (USA) has operated a pilot plant for over 2 years, delivering 5 tonnes of oxygen per day (TPD) and has recently begun construction of a 100 TPD facility in Convent, Louisiana with operation due to begin in 2013¹¹.

3 Dense Ceramic Membrane Technology

3.1 Ionic Transport Materials

The primary materials of interest for the synthesis of dense ceramics are perovskites (ABO₃), fluorites (AO₂), brownmillerites (A₂B₂O₅), Ruddlesden-Popper series (A_{n+1}B_nO_{3n+1}), and Sr₄Fe_{6-x}Co_xO₁₃ compounds¹². These materials conduct oxygen ions, essentially enabling oxygen separation from air. Perovskites are the most attractive of these materials as they conduct oxygen ions and electrons spontaneously (Fig. 2b) and are often referred to as mixed ionic electronic conductors (MIEC). The advantage of a MIEC material is that it dispenses with the need for external electrical circuits (Fig. 2a) as is the case for fluorites, which operate like fuel cells. Thus the use of MIEC materials simplifies the engineering design and reduces the operational energy requirements for oxygen separation from air.

¹⁰ J.G. Jee, M.B. Kim, C.H. Lee Pressure swing adsorption processes to purify oxygen using a carbon molecular sieve. *Chemical Engineering Science*, 60 (2005) 869-882.

¹¹ J.M Repasky, L. L. Anderson, V.E. E. Stein, P. A. Armstrong, E. P. Foster, ITM Oxygen technology: scale-up toward clean energy applications, International Pittsburgh Coal Conference, Pittsburgh, Pa., U.S.A. October 15–18, 2012

¹² S. Smart, J.C. Diniz da Costa, S. Baumann, W.A. Meulenber, Oxygen transport membranes: dense ceramic membranes for power plant applications, in: A. Basile, S.P. Nunes (Eds.) *Advance membrane science and technology for sustainable energy and environmental applications*, Woodhead Publishing Ltd, Cambridge, 2011, pp. 255-294.

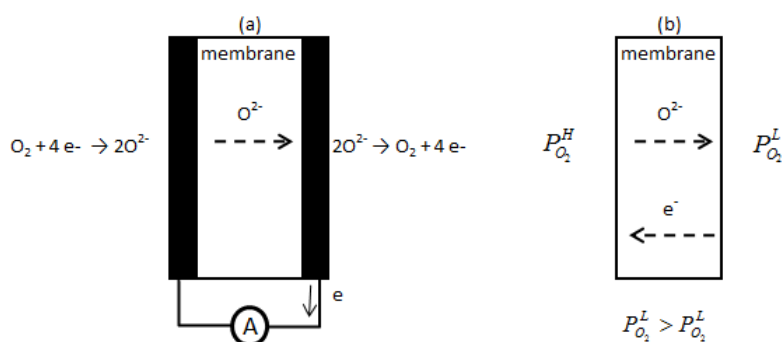


Figure 2 - Dense ceramic oxygen conducting membranes (a) solid electrolyte for O^{2-} conduction and (b) mixed ionic electronic conductor

3.1.1 Perovskites

Perovskite compounds are crystalline ceramics with a cubic structure¹³ described by the general formula ABO_3 (shown schematically in Fig. 3). The A and B sites are cations occupied by alkali or rare earth elements of the Lanthanide series and transition metals, respectively. The unit cell is a face-centred cubic crystal with the larger A cations located at the corners, the smaller B cation located in the body-centred position and the O^{2-} anions located in the face-centred positions. At high temperatures ($>700^\circ C$) they conduct oxygen ions which diffuse through the crystal lattice via oxygen vacancy sites or defects¹⁴. The pioneering work of Teraoka¹⁵ and co-workers demonstrated that vacancy defect concentration (δ), and consequently ionic diffusion, was enhanced by doping the cation sites (A or B) with other cations (A' or B') of different sizes and/or valences, resulting in the general formula $A_xA'_{1-x}B_yB'_{1-y}O_{3-\delta}$.

$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) has been the most studied perovskite as it has consistently demonstrated the highest oxygen fluxes of all the MIEC materials at $\sim 3 \text{ ml min}^{-1} \text{ cm}^{-2}$ for discs and $\sim 9 \text{ ml min}^{-1} \text{ cm}^{-2}$ for hollow fibres at around $900^\circ C$ with a transmembrane O_2 partial pressure differential of $\sim 20 \text{ kPa}$. As with all membrane technologies, the thickness of the membrane significantly influences the overall oxygen flux. Disc membranes tend to be thicker ($\sim 1 \text{ mm}$) and therefore deliver lower oxygen fluxes than the thinner hollow fibres ($\sim 0.3 \text{ mm}$). However, BSCF is unstable at temperatures below $\sim 825^\circ C$ leading to crystal phase change and membrane mechanical failure. This is significant as lower operating temperatures are more desirable to reduce additional heating requirements. Hence, the more stable $La_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCF) is generally preferred, despite its lower oxygen fluxes. LSCF hollow fibres generally give oxygen fluxes of 1 ml

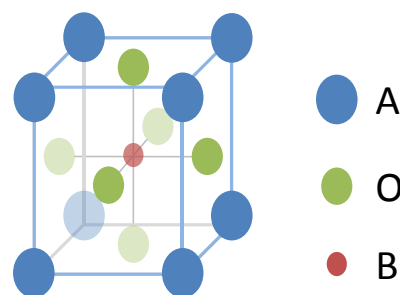


Figure 3 – Ideal crystal structure of a perovskite compound.

¹³ R.J.H. Voorhoeve, D.W. Johnson, J.P. Remeika, P.K. Gallagher, Perovskite Oxides - Materials Science in Catalysis, *Science*, 195 (1977) 827.

¹⁴ J. B. Goodenough, Ceramic technology - Oxide-ion conductors by design, *Nature*, 404 (2000) 821.

¹⁵ Y. Teraoka, H. M. Zhang, S. Furukawa, N. Yamazoe, Oxygen permeation through perovskite-type oxides, *Chemistry Letters*, 11 (1985) 1743.

$\text{min}^{-1} \text{cm}^{-2}$, although these membranes have been reported to operate for over 1000 hours. Replacing strontium in BSCF with zirconia to form BCFZ has resulted in more stable membranes which have been operated for up to 2200 hours¹⁶. Crucially for oxy-fuel coal combustion, perovskites are inherently unstable when exposed to CO_2 which reacts with perovskites components to form non-conducting carbonates.

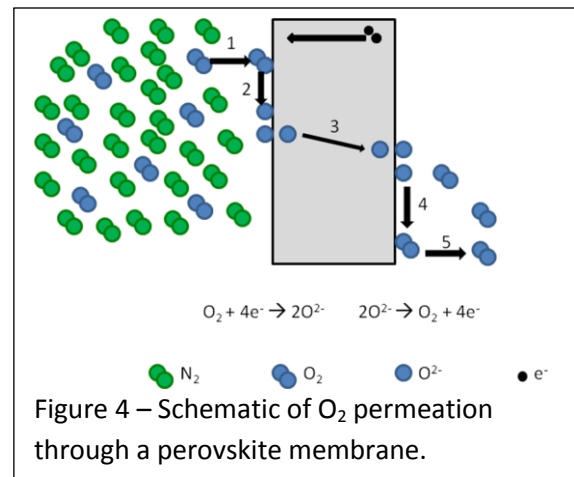
3.1.2 Fluorites

Fluorites are pure ionic conductors, and whilst they can also separate pure oxygen from air, their lack of electronic conductivity necessitates an external circuit to enable oxygen production, as depicted in Figure 2a. Several fluorite oxides such as yttria-stabilized zirconia (YSZ), samarium-doped ceria (SDC) or gadolinium-doped ceria (GDC) do possess sufficient chemical stability for use in ITM applications as these are widely applied as electrolyte layers in solid oxide fuel cells (SOFC)¹¹. Many of the SOFC operation involve exposure of these pure ionic conductors to CO_2 and H_2O . However, oxygen fluxes of fluorites are generally extremely low, on the order of less than $0.05 \text{ ml min}^{-1} \text{cm}^{-2}$. The only exception is bismuth samarium doped ceria (BiSDCSm)¹⁷ based fluorites with oxygen fluxes as high as $0.9 \text{ ml min}^{-1} \text{cm}^{-2}$ at 800°C .

3.2 Oxygen transport through membranes

Oxygen diffusion through dense ceramic membranes can occur only if there is a driving force which physically manifests as an oxygen partial pressure difference between the feed stream and permeate stream. In terms of membrane operation, oxygen transport involves five progressive steps shown schematically in Figure 4¹⁸:

- Step 1 - feed side gas transport: the oxygen molecule is transported from the gas phase to the membrane surface by gas to gas diffusion.
- Step 2 - dissociation (surface reaction) on interface I (feed side): the oxygen molecule adsorbs to the membrane surface and then disassociates due to catalytic activity of the ceramic material.
- Step 3 - ionic transport (bulk diffusion): the oxygen ions diffuse through the ceramic crystal lattices, driven by a partial pressure gradient of oxygen across the membrane. Electrons are transported in the opposite direction to maintain electrical neutrality of the membranes.
- Step 4 - association (surface reaction) on interface II (permeate side): the oxygen ions recombine into oxygen molecules and desorb from the membrane surface.



¹⁶ T. Schiestel, M. Kilgus, S. Peter, K. J. Caspary, H. Wang, J. Caro, Hollow fibre perovskite membranes for oxygen separation. *Journal of Membrane Science*, 258 (2005) 1-4.

¹⁷ K. Zhang, Z. Shao, C. Li, S. Liu, Novel CO_2 -tolerant ion-transporting ceramic membranes with an external short circuit for oxygen separation at intermediate temperatures, *Energy & Environmental Science*, 5 (2012) 5257-5264.

¹⁸ S. Smart, J.C. Diniz da Costa, S. Baumann, W.A. Meulenber, Oxygen transport membranes: dense ceramic membranes for power plant applications, in: A. Basile, S.P. Nunes (Eds.) *Advance membrane science and technology for sustainable energy and environmental applications*, Woodhead Publishing Ltd, Cambridge, 2011, pp. 255-294.

- Step 5 - permeate side gas transport : the oxygen molecules are transported to the permeate stream by gas to gas diffusion.

Perovskite materials are inherently catalytic and able to break down molecular oxygen into oxygen ions at high temperature. As a result the O₂ fluxes in steps 2 and 4 are controlled by the kinetics of the surface dissociation/association reaction, whilst the flux in step 3 is controlled by bulk diffusion associated with the membrane thickness. The oxygen flux through the entire membrane is therefore limited either by surface kinetics or by bulk diffusion. Thus the membrane materials and fabrication geometry become intrinsically important. ITM are similar to any other membrane technology in the sense that by reducing the thickness of the membrane, gas permeation or O₂ flux increases likewise. In other words thinner membranes are desirable as they deliver high oxygen throughput per area of membrane. However, a major difference of ITMs is that there is a critical length (L_c) where any further reduction in membrane thickness no longer increases O₂ flux. At this critical length, the transport resistances due to surface kinetics and bulk diffusion are equal, and the transport of oxygen becomes limited by the kinetics of the surface exchange reaction.

The L_c parameter is material and temperature dependent in the case of BSCF membranes, and it is approximately 0.7 - 1.1mm between 800 - 900°C¹⁹. Once the membrane thickness is less than L_c , the membrane transport is controlled by the kinetics of the surface reaction. Researchers have deposited palladium or platinum catalysts on the surface of thin MIEC hollow fibres (200 - 300 µm thick) to overcome surface kinetics limitations. In a recent study that employed palladium catalysts on BSCF hollow fibres researchers observed that oxygen fluxes could be increased by a factor of 10 at lower temperatures (700 °C) and recorded a maximum of 14.5 ml min⁻¹ cm⁻² at 950 °C²⁰. In the case of fluorites, the oxygen flux is controlled by the electronic conductivity as the materials are ionic conductors. Nevertheless, as the membrane thickness is decreased beyond L_c , the controlling step will no longer be bulk diffusion but the kinetics of the surface exchange reaction²¹.

4 Engineering development phase

Two types of design are being considered in the initial development phase of ITM modules as schematically shown in Figure 5. The primary difference between the operating modes is how the driving force, i.e. oxygen partial pressure difference, is established between the feed and permeate streams. Both seek to maximise this driving force, in different ways, as the higher the driving force, the larger the oxygen flux.

¹⁹ W.K. Hong, G.M. Choi, Oxygen permeation of BSCF membrane with varying thickness and surface coating. *Journal of Membrane Science* 346, (2010) 353-360.

²⁰ A. Leo, S. Smart, S. Liu, J. C. Diniz da Costa, High Performance Perovskite Hollow Fibres for Oxygen Separation, *Journal of Membrane Science*, 368 (2011) 64-68.

²¹ H.J.M. Bouwmeester, H. Druidhof, A.J. Burggraaf, P.J. Gellings, Oxygen semipermeability of erbia-stabilized bismuth oxide. *Solid State Ionics*, 53-56 (1992) 460-468.

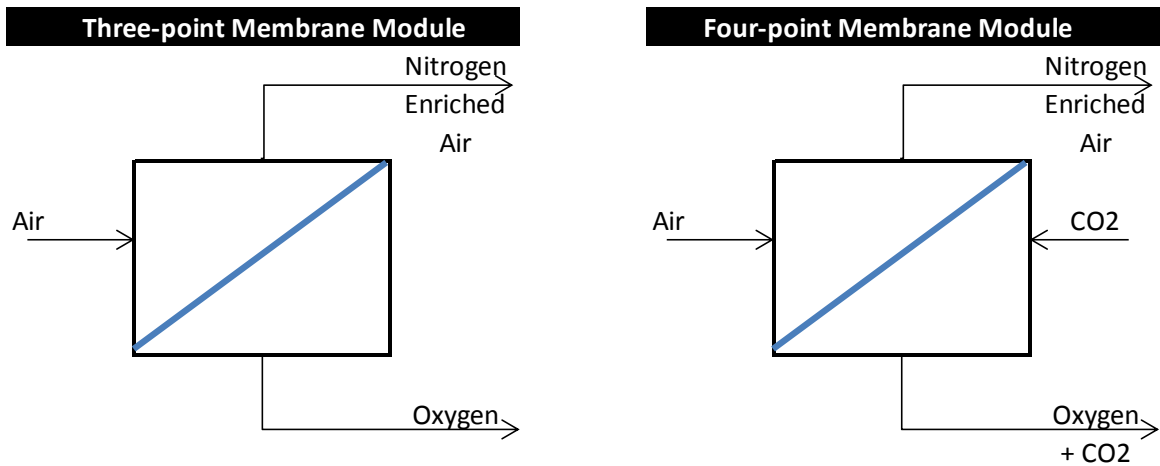


Figure 5 – Three-point and Four-point membrane modules. The box represents a membrane module and the diagonal line in the box represents a membrane.

The first type is called a three-point membrane module. In this set up, air is cleaned and dehydrated before reaching the membrane module. Hence, the feed side of the membrane will contain pure air, possibly with very small concentrations of water and CO₂ (at ppm levels or lower). In this set up, (i) the air feed stream could be pressurised in excess of 5 bars and the permeate side be maintained at 1 bar, (ii) the air feed stream could be kept at 1 bar and the permeate stream at vacuum pressure, or (iii) for maximum driving force the air feed stream could be pressurised and the permeate stream kept under vacuum pressure.

The second type is called a four-point membrane module which is envisioned for oxyfuel coal power plants. In this set up, a highly concentrated CO₂ stream (recycled from the combustion gases) is used as a sweep gas stream on the permeate side. The function of the CO₂ sweep gas is to reduce the partial pressure of O₂ in the permeate stream and thereby increase the transmembrane O₂ partial pressure driving force. This serves the dual purpose of reducing the need to pressurise the feed stream and acts as a diluent for the combustion gas to better control flame temperature in the burner. Hence, there is less of a need to pressurise the air feed stream to high pressures, although the membranes employed in this set up must, by definition, be chemically stable to water and CO₂.

4.1 Materials selection

4.1.1 Three-point Membrane Module

Currently LSCF is the state of art material for application in the three-point membrane module as it represents the best compromise between good oxygen fluxes (around 1 ml min⁻¹ cm⁻²) and long term stability. Of course, membranes with higher fluxes would be preferred, particularly since higher fluxes will reduce the requirements for membrane area, corresponding unit size, and ultimately capital costs of the

plant. However, the highest flux material, BSCF, is not stable under the desired operating temperatures of <850 °C and requires modification to significantly improve long term stability.

4.1.2 Four-point Membrane Module

Currently, there are no membrane materials under development that could be considered for development in this operating mode. Crucially, these materials must be tolerant to both CO₂ and water, which has proven a substantial obstacle to overcome. There is a thrust of research in this area with perovskites based on iron eg. BaCo_xFe_yZr_zO₃²² and fluorites based on samarium²³. Out of these, the iron based perovskites oxygen fluxes are very low and must be periodically recovered in CO₂ free conditions. Only fluorites could be considered as a potential material with oxygen fluxes reaching 0.2 ml min⁻¹ cm⁻² at 600°C partially exposed to water and CO₂. Additionally these materials must be tolerant against sulphur oxides (SO_x) and nitrogen oxides (NO_x) which may be present in trace (ppm) or low (<5%) concentrations of the recycled flue gas stream. Currently, there is a dearth of research into the stability of MIEC membrane materials against SO_x and NO_x compounds with most researchers focusing on their stability against CO₂ and water. However, several studies have reported that BSCF compounds are poisoned by sulphur during the hollow fibre fabrication process if sulphur-containing polymeric binders are used.¹⁴ Previous studies had already established that trace SO_x compounds, ever present in atmospheric air, were not responsible for poisoning BSCF during testing.²⁴ Thus BSCF at least appears to have some tolerance to SO_x compounds although the precise exposure level or timeframe has yet to be determined. Further, recent unpublished research work from Europe has apparently demonstrated that SO_x (1 vol%) in a gas mixture containing CO₂ and water degraded the crystal structure of perovskites.

4.2 Geometries

The principal geometries pursued for membrane modules include hollow fibres, capillaries, tubes and flat membranes. The state of the art at the moment with respect to membrane flux is hollow fibre membranes, due to their ability to be manufactured with very thin membrane walls, yet still retain a measure of mechanical strength. These can be produced by adapting the facile and cost effective phase inversion process, already employed in the manufacture of polymeric hollow fibres for the water processing industry. These hollow fibres can be assembled at a high packing density essentially allowing a very large surface area per unit volume due to their small outer shell diameter $\varnothing = 1\text{mm}$. The downside of the hollow fibres is that membrane modules must be designed to avoid substantial pressure drops over the system, i.e. smaller unit modules with reduced Reynolds numbers, without overtly compromising membrane flux and unit throughput. In addition, perovskite materials are inherently brittle and very prone to mechanical failure,

²² O. Czuprat, M. Arnold, S. Schirrmeister, T. Schiestel, J. Caro, Influence of CO₂ on the oxygen permeation performance of perovskite-type BaCo_xFeyZrzO_{3-δ} hollow fiber membranes. *Journal of Membrane Science* 364, (2010) 132-137

²³ K. Zhang, Z. Shao, C. Li, S. Liu, Novel CO₂-tolerant ion-transporting ceramic membranes with an external short circuit for oxygen separation at intermediate temperatures, *Energy & Environmental Science*, 5 (2012) 5257-5264.

²⁴ Liu, S. and Gavalas, G.R., Preparation of oxygen ion conducting ceramic hollow-fiber membranes. *Ind. Eng. Chem. Res.*, 2005. 44: p. 7633-7637.

especially under the vibration and frictional stresses experienced in an industrial environment. Therefore, it is expected that the optimal compromise will involve membranes capillaries ($1 < \varnothing < 10$ mm) or tubes ($\varnothing > 10$ mm) and replace hollow fibres as state of the art. Indeed, recent work at both The Fraunhofer Institute of Ceramic Technologies and Systems (IKTS) and RWTH Aachen have seen both groups independently produce larger scale membrane modules (up to 1m^2 in membrane area) utilising tubular geometries²⁵. Flat geometries are typically problematic to handle due to the inherent brittle nature and increased sealing requirements and so have typically only been constructed in laboratory settings at very small dimensions. However, it must be noted that the most successful demonstration of ITM technology has been the Air Products design which utilises a variation of flat sheet technology in its 5 TPD plant.

To increase the mechanical robustness of dense ceramic membranes, there have been several attempts to coat a dense perovskite layer on more mechanically robust porous tubular supports. The theory being that the porous support would allow oxygen to access the perovskite layer which also provide the mechanical stability for the thin perovskite layer. However, the thermal expansion coefficient of perovskites is highly material specific and frequently non-linear and the membranes fabricated generally suffer from high air leakage. This problem has been tackled by several groups around the world, but remains to be solved. In the case of some fluorites²⁶, the thermal coefficient expansion tends to be linear. Hence, fluorites could be more attractive for coating on porous structures of mechanically robust materials. Currently, the state of the art regarding mechanical strength is produce membranes from a single material only, with thicker membrane dimensions, which has the natural trade-off of reducing oxygen production.

4.3 Membrane Module Engineering Challenges

One of the great advantages of membrane systems is their traditional modularity which reduces process complexity and enables relatively simple expansion (or reduction) of production capacity. It is expected therefore, that an air separation unit utilising ITM technology would be modular in design and will likely contain a large number of membrane modules. Until membrane fluxes of the more stable perovskites are improved this will likely represent a significant capital investment, but on the other hand it should enable operational flexibility which may decrease operational costs. The major engineering problem is sealing membranes in such a way as to allow continuous operation at high temperature (up to $1000\text{ }^\circ\text{C}$) with leakage rates of $<10\%$. The primary engineering focus to reduce the leakage rates has been to reduce the sealing area. In this case, hollow fibres, capillaries and tubes are preferred over flat geometries.

²⁵ X. Dong, W. Jin, Mixed conducting ceramic membranes for high efficiency power generation with CO_2 capture. *Current Opinion in Chemical Engineering*, 1 (2012) 163-170.

²⁶ S. Smart, J.C. Diniz da Costa, S. Baumann, W.A. Meulenber, Oxygen transport membranes: dense ceramic membranes for power plant applications, in: A. Basile, S.P. Nunes (Eds.) *Advance membrane science and technology for sustainable energy and environmental applications*, Woodhead Publishing Ltd, Cambridge, 2011, pp. 255-294.

The primary concern here is again related to matching the thermal expansion coefficient of the sealant with the dense ceramic membranes and the module itself. To address this problem, either special sealing compounds are required or the membrane/seal interface must be designed outside the high temperature region (~1000°C) region of the membrane module. This allows for the membrane / seal interface to be kept relatively cooler, at temperatures <600°C, where engineering sealing solutions become more technically and economically feasible. This has the added benefit of reducing any potential chemical interactions at the membrane / seal interface, favouring long term operation. At the moment there are no state of the art seals for dense ceramic membranes commercially available and research groups typically employ a combination of noble metals and heat reduction techniques. Proprietary seals, such as those used by Air Products target the dense ceramic material; much in the same manner as the seals in high temperature solid oxide fuel cells.

There is only one membrane module fully reported in the literature by Li's group based on hollow fibre geometry²⁷. The membrane module consisted of 889 hollow fibres totalling 9914 cm². One end of the hollow fibre was sealed by the same ceramic membrane material as the hollow fibre, while the other end was left open for the flow of oxygen. A low-temperature silicone sealant was used (maximum 350°C). Hence, the sealed area was isolated from the membrane module high temperature region. The membrane module operated at 1070 °C and delivered a maximum 3.1 l (STP) min⁻¹ with the purity of 99.9%. This design reduced the effective membrane area as only the hollow fibres were effective in oxygen air separation only at high temperatures. A similar approach has been shown in conferences by RWTH Aachen University (Germany) where a fundamental mechanical design is under development of perovskite tubes and seals. The German design includes a water cooling system around the sealing area of tubes.

5 Demonstration

The state of the art in demonstration of dense ceramic membranes for oxygen separation from air has been achieved by Air Products & Chemicals in the USA. This is the only demonstration plant at industrial scale with proof of concept for long term operation, delivering 5 TPD of oxygen for over 515 days²⁸. This major achievement by Air Products & Chemicals was significantly funded by the USA Department of Energy, on the order of \$148 million since 1999 to scale up the technology²⁹. The approach taken by Air Products involved an innovative module design. They developed flat membranes in a wafer configuration as depicted

²⁷ X. Tan, Z. Wang, B. Meng, X. Meng, K Li, Pilot-scale production of oxygen from air using perovskite hollow fibre membranes, *Journal of Membrane Science*, 352 (2010) 89–196.

²⁸ S. Smart, J.C. Diniz da Costa, S. Baumann, W.A. Meulenber, Oxygen transport membranes: dense ceramic membranes for power plant applications, in: A. Basile, S.P. Nunes (Eds.) *Advance membrane science and technology for sustainable energy and environmental applications*, Woodhead Publishing Ltd, Cambridge, 2011, pp. 255-294.

²⁹ P. Armstrong, K. Fogash, *Oxygen Production Technologies: Cryogenic and ITM*, 2nd Int'l Oxy-Combustion Workshop, Windsor, CT, USA, Jan 25-26, 2007.

in Figure 6, adapting concepts used in traditional spiral wound modules for polymeric membranes to the rigid, brittle BSCF material. The membrane wafers are assembled in stacks with a central oxygen collector tube which conducts the permeate stream. This design reduces the sealing area per membrane area, whilst also providing a large membrane packing density, which translates to high oxygen fluxes per unit volume. This perovskite membrane design currently represents the closest air separation unit to commercialisation. Air Products will take a significant step forward when they commission their newest oxygen production facility, designed to be 100 TPD, in 2013³⁰. The investment from Air Products & Chemicals is the first indication that this technology could be very close to overcoming the “cost hump” in the technology development cycle (see Figure 1) towards deployment and commercialisation. All the information about the perovskite materials, seals and module design are proprietary information of Air Products & Chemicals. None of this information has been divulged or published in the open literature.



Figure 6 – Planar wafer ITM ceramic membrane stacks from Air Products & Chemicals (USA).

The OXYCOAL-AC project sponsored by the German Federal Ministry of Economics and Technology (BMWi), the Ministry of Innovation and Technology of North-Rhine Westphalia (MIWFT), among others, was established to stimulate the commercialisation of oxyfuel technology. Within this project RWTH Aachen researchers designed a 120 kW oxyfuel pilot plant, operating with an ITM module. Here oxygen production volumes were on the order of 0.5 TPD with 15m² of membrane area³¹. Finally, the IKTS module was developed with the MEM-BRAIN in Europe as a portable solution, able to be moved to conferences and

³⁰ J.M Repasky, L. L. Anderson, V.E. E. Stein, P. A. Armstrong, E. P. Foster, ITM Oxygen technology: scale-up toward clean energy applications, International Pittsburgh Coal Conference, Pittsburgh, Pa., U.S.A. October 15–18, 2012

³¹ S. Baumann, W. A. Meulenber, H. P. Buchkremer, Manufacturing strategies for asymmetric ceramic membranes for efficient separation of oxygen from air. *Journal of the European Ceramic Society*, 33 (2013) 1251-1261.

trade shows in order to promote the technology and IKTS. Here, they utilised long membrane tubes in a three-point design with 1m² of membrane area with a feed of fresh air and a vacuum pump operating at 20 - 100 mbar. The researchers acknowledge that the design would be unfeasible for larger scale pilot plants, with the parasitic losses from vacuum pump prohibitive.

6 Conclusions

ITM technology represents the most promising alternative to cryogenic distillation for large scale, high purity oxygen production for use in the next generation of integrated CCS power plants based on gasification or oxy-fuel combustion. The state of the art here are dense ceramic membranes made from doped perovskite materials such as BSCF which exhibit fluxes on the order of 10 ml min⁻¹ cm⁻² at the laboratory scale. However, BSCF perovskites are not mechanically stable and LSCF is currently preferred for long term oxygen separation from air, though at lower fluxes. Fluorites are now showing good oxygen fluxes under water and CO₂ exposure, and could be considered for CCS applications due to their chemical stability. Currently, BSCF tubes are being tested at RWTH Aachen in Germany functioning pilot scale facility. Nevertheless, the demonstration state of art is the ITM plant developed by Air Products in the USA. Air Products is the industry leader with a 5 TPD facility operating in excess of 500 days, and a new 100 TPD facility due to be commissioned in 2013. Air Products wafer-like membrane modules arguably represent the state of the art in module design by virtue of these pilot facilities, although other researchers see future modules adopting tubular geometries. Regardless, the critical issues for adoption of ITM on a wider scale are the fabrication of mechanically and chemically robust membranes and the development of innovative sealing systems able to withstand the high operating temperatures required.