

Chapter 2

Viability of ITM Technology for Oxygen Production and Oxidation Processes: Material, System, and Process Aspects

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Abstract This chapter is devoted to the state of the art of the most important aspects of high temperature ceramic air separation membranes for oxygen production and oxidation processes. Alternative technologies, operational principle, fields of application, energy efficiency and cost aspects, materials science, module design, and sealing will be discussed.

Introduction

The threat of global warming due to increasing carbon dioxide (CO_2) concentrations has been recognized as one of the main environmental challenges of this century. To limit atmospheric CO_2 concentrations to acceptable levels of about 550 ppm [1] major changes in energy consumption are required in the coming decades. Still, fossil fuels are widely expected to remain the world's major source of energy for well into the twenty-first century. Although supply of oil and gas is under threat due to political instability and uncertainties on reserves, the use of coal is increasing, with concomitant higher CO_2 emissions [2]. To meet this target set for atmospheric CO_2 concentrations, the development of breakthrough technologies is essential. Otherwise, it will prove to be impossible to reach the dramatic decrease of the CO_2 emission into the atmosphere during the conversion of fossil fuels to other forms of energy, for example, electricity or hydrogen. The three main routes for mitigation of CO_2 emissions in electricity plants can be defined as:

1. Post-combustion processes: CO_2 is captured from the flue gases.
2. Pre-combustion processes: The fuel (natural gas or coal) is converted into hydrogen and CO_2 . The CO_2 is separated and hydrogen is combusted in a gas turbine.
3. Oxyfuel processes: Combustion is carried out using pure oxygen, resulting in a flue gas that mainly contains water (H_2O) and CO_2 .

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These routes are connected with carbon capture with subsequent sequestration. Another approach is to avoid the production of CO₂ emissions altogether through increased industrial energy efficiency and thus a lower energy consumption. The topic of this chapter, oxygen production, is related to the last two points. In the first three routes mentioned above, three different methods can be used for the separation of CO₂ and the other gases: absorption in solvents, separation by membranes and adsorption or absorption on or in a sorbent.

This chapter is devoted to the state of the art of the most important aspects of high temperature ceramic air separation membranes for oxygen production and oxidation processes. Alternative technologies, operational principle, fields of application, energy efficiency and cost aspects, materials science, module design, and sealing will be discussed.

Alternative Technologies

Polymeric membranes are used for oxygen enrichment or depletion of air. Not only are large-scale applications of the oxygen enrichment found in the industry but also small-scale applications are possible which are much closer to the individual consumer, such as for wellness and health branch. Oxygen depletion is often related to safety as fire prevention in buildings and future blanketing over airplane fuel tanks. The polymers are commonly based on among others polyphenyloxide (Parker Gas Separation) and polyimides (Air Products). The separation is based on preferred dissolution and diffusion of oxygen over nitrogen in these materials. Operating temperature is limited by the thermal stability of the polymers used. The membrane unit consists of bundles of hollow fibers, a porous polymer support with a dense polymer separating layer, or spiral wounds. The technology is mature and due to its modular nature applicable both for small and large production volumes. Pressure Swing Adsorption (PSA) and Vacuum Swing Adsorption (VSA) technologies are based on the preferred absorption of nitrogen in, for example, zeolite beds. Purities of oxygen of about 90–94 percent are obtainable. Plant size is up to about 1,500 Nm³ per hr. Cryogenics is currently the most developed mature large-scale oxygen production technology, with a typical plant size being 30,000–50,000 Nm³ per hr or 9,000–15,000 tons per day. The produced oxygen is of very high purity > 99%. In addition, this technology can also be used to produce nitrogen and argon. However, oxygen is believed to be the main incentive for the separation. Relatively new developments that are currently being investigated are the chemical looping combustion [3, 4] cycle and the so-called Ceramic Autothermal Recovery (CAR) [5] process originally devised by British Oxygen Company (BOC), now a part of Linde Gas. These processes are very similar. In CLC a metal or metal oxide is oxidized by air in one reactor and transferred to a reduction reactor that is fed with, for example, syngas. The reduced material is transferred back to the oxidation reactor. The CAR concept uses a set of two or more batch reactors alternating between oxidation and reduction cycles, containing a perovskite material ABO_{3-δ} that is cycled between two oxygen contents δ_1 and δ_2 .

General Aspects of ITM Technology

The process that is the subject of this article consists of the use of high temperature ceramic membranes that selectively transport oxygen. They are referred to with several acronyms of which ITM (Ion Transport Membranes), OTM (Oxygen Transport Membranes) and MIEC (Mixed Ionic Electronic Conducting) membranes prevail. We will use ITM throughout this article.

ITM technology can be used as a replacement of energy-demanding cryogenic distillations or PSA/VPSA plants. ITM technology in ASU's can result in high purity oxygen streams provided that defect-free membranes can be prepared on industrial scales and high quality sealing technology can be developed. The main drawback of the ITM technology is that it does not produce nitrogen. Advantages can be found in local decentralized production of oxygen to small-scale on-demand production in places where oxygen is actually needed in chemical processes. This would result in abandoning transport of oxygen over public roads, while storage facilities and associated safety measures are no longer required.

PSA/VPSA technology provides oxygen ranging from small-scale (e.g., small portable devices) to large-scale plants. It is anticipated that ITM technology can be introduced in the medium to large-scale production range following normal economical considerations while introduction in the "portable" sector requires comparison of module sizes as a function of oxygen output, additionally.

A schematic representation of the air separation process using ITM as a whole is presented in Fig. 2.1. The driving force for the transport of oxygen is a difference in partial oxygen pressure (pO_2) between the feed and permeate side of the membrane. As a result, oxygen permeates from the side with the high pO_2 to the side with the

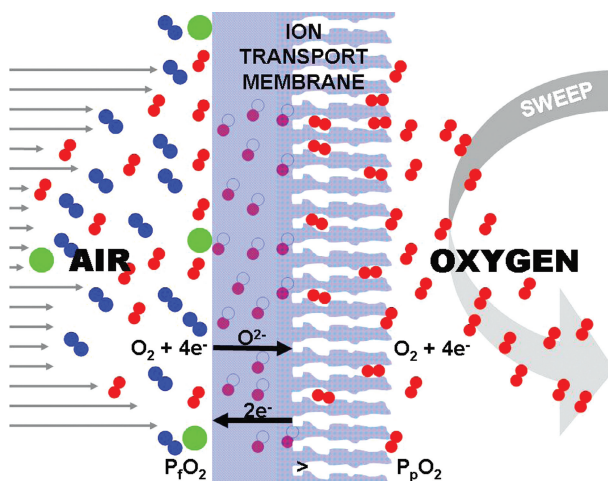


Fig. 2.1 Schematic representation of the transport of oxygen through an ion transport membrane consisting of a dense (*left*) and porous (*right*) part. The sweep can be either “inert,” for example, CO_2 or H_2O , or “fuel,” for example, CH_4

low pO_2 . On the feed side the oxygen molecules reduce to two oxide ions (O^{2-}). This pair of oxide ions permeate through a thermally activated hopping mechanism to the permeate side and recombine. Simultaneously, two pairs of electrons move from the permeate side to the feed side.

The majority of the ITM compounds showing mixed ionic electronic conductivity belong to the structural family of Ruddlesden–Popper compounds [6] $A_{n+1}B_nO_{3n+1}$. The end members of this family are the cubic perovskite $SrTiO_3$ for $n = \infty$ and the layered K_2NiF_4 structure for $n = 1$. These end members form two very versatile families of compounds and are generally referred to as ABO_3 and A_2BO_4 . The A cations are typically relatively large cations from trivalent lanthanide series or divalent earth metals (large spheres in Fig. 2.2), the smaller B cations are in general transition metals and are found in octahedral coordination. Ionic conduction in cubic perovskites is achieved when oxygen vacancies are formed as a result of a too low total formal valence on the cations. In the formed $ABO_{3-\delta}$ compounds oxygen vacancies can move from one site to another through a thermally assisted hopping mechanism. Typically this movement is quenched at temperatures below $\sim 450^\circ\text{C}$, and it becomes significant in terms of technical applicability at temperatures well above 700°C . In A_2BO_4 compounds, the oxide conduction can be quite different from that of the perovskites. One option is similar to perovskites and leads to sub-stoichiometric oxygen content. In the second option extra oxide ions are intercalated in between the subsequent perovskite-like layers resulting in an over-oxidized state ($A_2BO_{4+\delta}$), which may eventually lead to higher reduction stability. $ABO_{3-\delta}$ is clearly an isotropic oxide conductor whereas $A_2BO_{4+\delta}$ is a 2D anisotropic oxide conductor. Depending on the composition, both types can show high electronic conductivity, and even super conductivity [7–9]. Well-known examples of perovskites with a high oxygen conductivity are $La_{1-x}SrCo_{1-y}Fe_yO_{3-\delta}$ [10], and for the layered systems $La_2Ni_{0.9}Co_{0.1}O_{4-\delta}$ [11] can be mentioned.

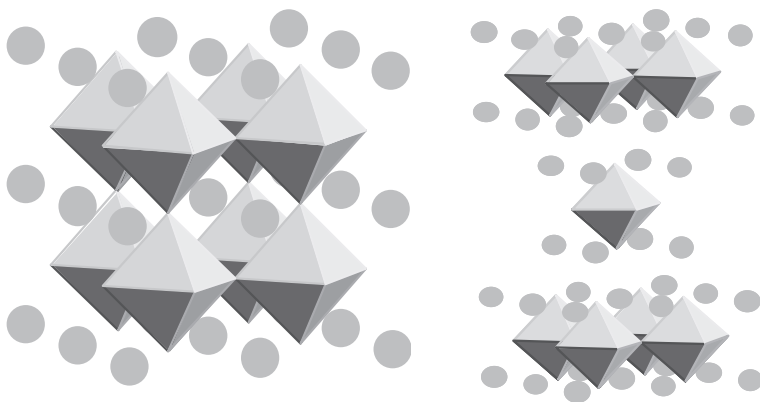


Fig. 2.2 Archetypical structures of the cubic perovskite, ABO_3 , (left) and K_2NiF_4 , A_2BO_4 , (right). Green balls: large A cations, blue octahedra of small B cation in the center surrounded by six oxide ions

Techno-economic evaluations [12] have shown that oxygen selective membranes are required that can deliver oxygen at a rate of over $10 \text{ ml/cm}^2\text{min}$. This value will be used as a base case for all our considerations.

Applications

The two main applications of high temperature membrane technology are the production of high purity oxygen as valuable chemical and as a reactant for various (partial) oxidation processes such as methane conversion [13]. For the first application, this technology is in direct competition with the well established and energy intensive cryogenic distillation. For the second application this, in comparison, is much less clear. Now the (partial) oxidation and the separation of air take place within the same unit operation, leading to a membrane reactor. These applications may look very similar at first sight, but difference start to appear on closer inspection. The most important ones are the necessity of catalysts and the very different demands that are being put on the membrane materials. For the production of pure oxygen a partial oxygen pressure of about 0.3 bar is anticipated on the permeate side. In the case of partial oxidations this value can be as low as 10^{-18} bar. In the chemical industry, oxygen is used in a large number of processes. In Table 2.1 the main chemical processes are listed where air and/or pure oxygen is used, divided into worldwide production figures in megaton per year.

The main use of oxygen in industry is for production of ethylene oxide, ethylene dichloride, propylene oxide, and acetic acid. Notice that the sequence of product production quantities is slightly different since different amounts of oxygen are required for each ton of product. This especially applies for polyethylene, requiring only a small oxygen quantity per ton of product. Most of these production processes are carried out in plants making use of oxygen but sometimes air is used as oxygen source as well. Additionally, many chemical processes are carried out using oxygen in the form of air only. Examples are the production of nitric acid, formaldehyde, terephthalic acid, and carbon black as the main air-consuming production processes. Production of these 4 compounds consumes an additional 106.5 Mton/a of oxygen, 74% of the total oxygen consumption (129.5 Mton/a) of the full range of air consuming production processes.

Huge oxygen consumers outside the chemical industry are the steel producers. The oxygen consumption for primary steel production being six times the sum of the major oxygen consuming chemicals mentioned in Table 2.1. The relative contributions to oxygen consumption in the steel industry can be found in blast furnace enrichment (32%), basic oxygen furnaces (43%), electric arc furnaces (19%), and cutting and burning activities (6%).

Next to bulk production of chemicals and steel, other applications exist where oxygen is required. For instance, air enriched with oxygen is used for bleaching purposes in the pulp and paper industry, not putting strains on the purity of the oxygen used. Finally, a market that is likely to show a fast growth over the coming years is that of oxygen of gas-to-liquid (GTL) plants. In this case natural gas is first transformed into syngas, which in turn is used in a Fischer-Tropsch process for

Table 2.1 World use of gaseous oxygen (GOX) in bulk production of chemicals and steel in 2004

Product	Production [Mt/a]	O ₂ use [Mt/a]	Process Description
Ethylene oxide	15.1	7.2	Oxidation of ethylene. Air is sometimes used but O ₂ preferred in new and larger plants.
Ethylene dichloride	49.1	4.0	Oxichlorination of ethylene. Air is sometimes used
Propylene oxide	5.8	2.0	Epoxidation of propylene: PO/TBA-route. Air is sometimes used
Acetic acid	8.1	1.6	Oxidation of naphtha/n-butane (35 %) or acetaldehyde (5 %). Air is sometimes used
Titanium oxide	4.3	0.9	From the ore: chlorination (in presence of O ₂) to TiCl ₄ , subsequent oxidation to TiO ₂
Vinyl acetate	5.0	0.8	From ethylene, acetic acid and O ₂ .
Acetaldehyde	2.4	0.7	Oxidation of ethylene (Wacker-Hoechst process). The 1-step process uses O ₂ ; the 2-step process uses air
Perchloroethylene	0.7	0.1	Oxychlorination of ethylene dichloride (PPG process)
Acetic anhydride	1.9	0.1	Oxidation of acetaldehyde. Air is sometimes used
Polyethylene (LDPE)	18.7	0.01	Polymerisation of ethylene in a high pressure tubular reactor. Oxygen is used as initiator (radical formation)
Cyclododecanol Cyclododecanone Crotonic acid	0.01	0.02	Oxidation of cyclododecane. Air is sometimes used
Subtotal		17.4	
Steel [14]	1241.0	104.0	
Total		121.4	

the preparation of highly linear hydrocarbons. The air separation unit (cryogenic distillation) on its own is responsible for about 30–40% of the total capital costs. A similar costing figure can be put on the running cost.

Oxygen is put into the market as gaseous oxygen (GOX) by pipelines and liquefied oxygen (LOX) in bottles or tanks. Despite supplying both forms, most of the oxygen in chemical processes is used in the gaseous form. Membrane technology directly supplies gaseous oxygen that, depending on the process, only needs to be pressurized for use whereas the temperature level allows for easy integration in high temperature processes.

Pure Oxygen Production

A typical process flow diagram for oxygen production is presented in Fig. 2.3. Our in-house assessments have shown that, if no high temperature thermal integration is possible, the co-generation of oxygen and electric power is required to render this system to be energetically more efficient than conventional cryogenic distillation.

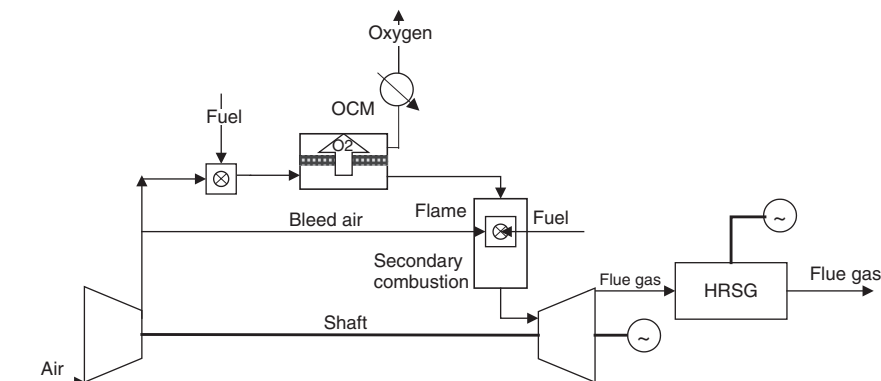


Fig. 2.3 Large-scale oxygen production ($30,000 \text{ Nm}^3/\text{hr}$) using ITM technology. For small-scale systems ($1,500 \text{ Nm}^3/\text{hr}$) the Heat Recovery Steam Generator (HRSG) cannot be applied

One specific process scheme, as depicted in Fig. 2.3, consists of first compressing the incoming process air followed by internal combustion of natural gas. The hot air is depleted of oxygen in the following separation module, and the retentate is fed to a secondary combustion chamber. The hot off-gas is used to power the turbine, and the flue gas is fed to a HRSG unit. If the energy efficiency of such a process is compared with that of a cryogenic distillation unit in co-junction with the average efficiency of the Dutch electricity park, an energy saving of over 20% can be achieved (Fig. 2.4). However, if the base case includes a state-of-the-art STAG (steam and gas turbine), then the efficiency improvement is limited to $\sim 8\%$.

This comparison can also be made with PSA- and VPSA-based system, as presented in Fig. 2.5. For this case, depending on the purity of the oxygen required, the energy savings can range from -4% (so a small penalty!) to over 50%. It is clear that the production of oxygen using ITM is most promising for small-scale applications where very high purity oxygen is required.

Costs

We have made a rough estimate of the costs for both a large and a small-scale system (Table 2.2). The difference between *Total process equipment* and *Total fixed capital* is caused by including percentages, for example, piping, installation, and engineering, following standard cost engineering procedures [15].

In order to determine the economic viability the running costs and revenues have been estimated (Table 2.3) as well. The main contribution to the fixed costs can be found in the membrane overhaul that is supposed to take place every three years. The oxygen price for large-scale production is taken to be equal to the price for gaseous oxygen from a cryogenic plant. The small-scale price is taken to be equal to that of a PSA plant.

For economic viability the simple pay out time (SPOT) should be smaller than five years. This gap can be reduced by several factors: cheaper membranes, higher

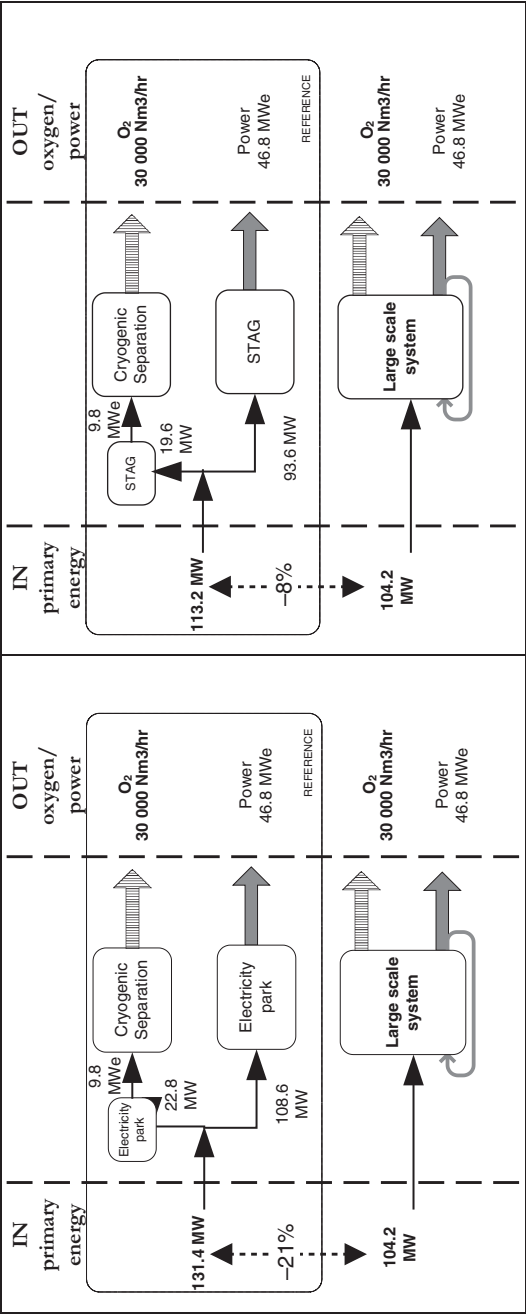


Fig. 2.4 Comparison of cryogenic and ITC technology as energy use for average power plant (*left*) and modern STAG based power plant (*right*)

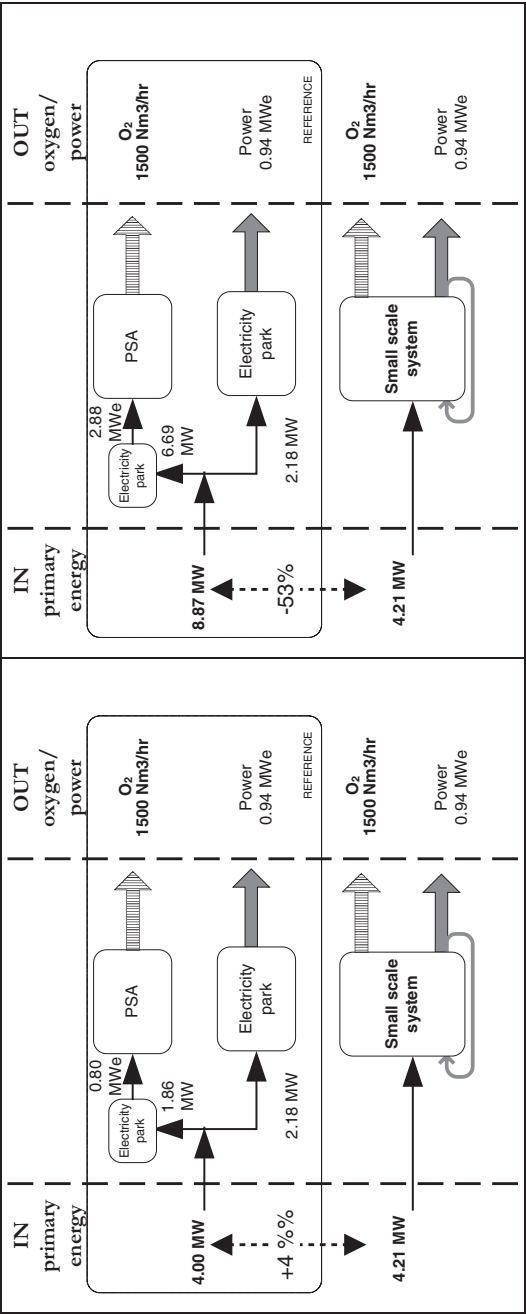


Fig. 2.5 Comparison PSA and ITC technologies for small-scale systems for 90–94% Oxygen purity (*left*) and 100% purity (*right*)

Table 2.2 Breakdown of total fixed capital for large and small-scale ITM systems (the HRSG is not used in the latter system)

	#	k€	#	k€
Investments	Large-scale		Small-scale	
Process equipment				
Heat exchangers	3	362	2	112
Oxygen compressor	1	1530	1	18
Membrane module shells	38	7692	1	385
Burners (or modification)	2	200	2	60
Gas turbine + HRSG	1	33724	1	1100
Membrane tubes*		7500		375
Total process equipment		50809		2050
Total fixed capital		101949		4695

*Oxygen flux taken: 10 ml/cm²min

Table 2.3 Economic evaluation of the large and small-scale systems

	M€/year	
Costs	Large-scale	Small-scale
Variable costs	12.3	0.490
Fixed costs	9.2	0.460
Admn. and sales	0.2	0.040
Total	21.5	0.970
Revenues		
Oxygen	13.5	1.09
Electricity	13.6	0.280
Total	27.1	1.360
Cash Flow	5.5	0.400
Simple Pay Out Time	16.8 years	11.0 years

flux through the membranes, longer lifetime of the membranes, higher energy prices and CO₂ trading. Fluxes will have to be at least two to three times higher if this were the only option. We do not believe that this is feasible.

Oxidation Reactions

The processes to be discussed under this topic are all designed to maintain a strict separation between N₂ and carbon containing streams in the generation of electricity. Four different system configurations in which ITM provides the pure oxygen can be distinguished:

- Systems in which all fuel is combusted in the membrane reactor (MR) at the permeate side.
- Systems with partial oxidation in the membrane reactor at the permeate side.
- Systems without combustion anywhere near the membrane, but in a separate unit.
- Systems for afterburning of flue gasses from, for example, fuel cells.

Table 2.4 Viability of ITM based membrane process options in power production

Oxidation Process	Feed Coal, biomass, waste, slurry, etc.	Natural gas, gasoline, syngas, etc.
Full oxidation in membrane reactor	Not viable, mechanical deterioration of membrane	Viable but temperature control difficult and expensive
Partial oxidation in membrane reactor	Not viable, mechanical deterioration of membrane	Viable as a nitrogen free syngas generator
Oxidation and separation not integrated	Viable in principle, but techno-economic uncertainties; not really a membrane reactor For coal gasification it is viable and proven (replaces ASU)	Viable, systems being under investigation by several groups [16–19] (replaces ASU)
Post-oxidation in membrane reactor	Viable if flue gas is N ₂ lean, ASU is competitor	Viable, especially in SOFC applications (flue gas N ₂ lean)

In summary: the lighter the color of the cells in the table the more viable the option is.

When a distinction is made between fuels that can be present in the form of gas or vapor and those that will be present as solids or liquids, the applicability of an ITM based membrane reactor is found to be limited to a few cases (Table 2.4).

Quite a number of system layouts have been proposed for Zero Emission Power Plants (ZEPP) [16–23]). From these specific systems a general scheme as depicted in Fig. 2.6 can be constructed. The main issue is to keep the nitrogen and carbon side of the system strictly separated. On the carbon side all conversions of the fuel take place in the end leading to predominantly water and CO₂ as combustion products and the production of electricity by single or combined cycle processes. On the nitrogen side air is separated at high temperature and pressure. The oxygen lean hot retentate is expanded in a gas turbine combined cycle. In a few cases fuel is burned on the nitrogen side to adjust the turbine entrance temperature to the optimum value, in which case we have low emission power plants.

Costs

For the ZEPP system presented in Fig. 2.7 the allowable installed costs for the capture plant have been estimated to be in between 80 and 120 M€ for a 1.4 GW_{thermal input} natural gas combined cycle (NGCC) plant. To meet the cost targets, an ITM based ZEPP power plant should have an electric efficiency of at least 52%. Capture ratios (carbon captured/carbon fed to the process) of 100% result in plant efficiencies lower than 50%. Capture ratios of the order of 85% are accompanied with plant efficiencies of about 52%. The allowable installed costs window is satisfied when the oxygen flux is at least 20 ml/cm²min⁻¹ and the costs of the ITM tubes should be less than 1,500 €/m². This clearly sets the targets for materials and turbine development in order for the system to be economically viable within the capture cost boundary conditions.

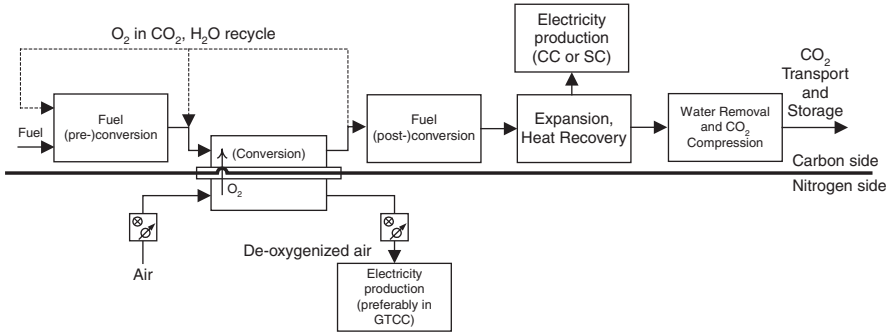


Fig. 2.6 General building blocks for power/ITM /carbon capture systems in which carbon and nitrogen sides are strictly separated (ZEPP)

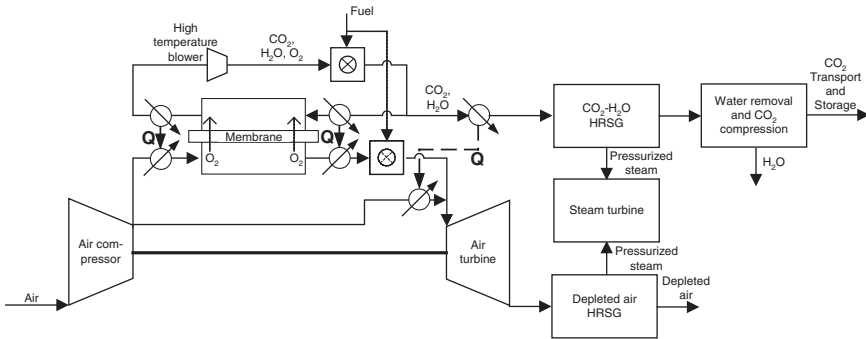


Fig. 2.7 ZEPP using ITM technology [16, 17]

Membrane Materials and Sealing Aspects

Membrane Materials

As mentioned earlier oxygen fluxes of at least $10 \text{ ml/cm}^2\text{min}$ are needed for economic viability of the membrane process. This value is equivalent to an electron current density of $\sim 3 \text{ A/cm}^2$. From this flux, we can also calculate the time it takes for all the oxide ions in the perovskite layer to be replaced by fresh oxide ions. Depending on the thickness of the selective layer, this value is of the order of a few minutes. It is clear that these values put very large demands on the stability of the membrane material. It also means that in one minute all the oxygen has to be removed from an air layer with an equivalent thickness of $\sim 50 \text{ cm}$. We believe that that can only be achieved if the air on the feed side is compressed. The selectivity demands of over 1,000 are likely to be met with defect-free membranes. Further demands include stable performance under real industrial conditions (presence of CO_2 , H_2O). As shown in Fig. 2.8, the required flux ($> 10 \text{ ml/cm}^2\text{min}$) can be reached by at least 2 different perovskites $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (SCF) and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) in

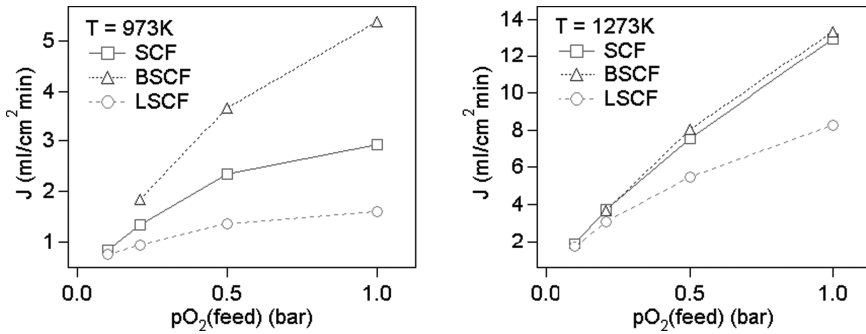


Fig. 2.8 Oxygen fluxes for SCF, BSCF, and LSCF at 973 K and 1273 K for a $5 \times 5 \text{ cm}^2$ and $200 \mu\text{m}$ thick dense membrane as a function of oxygen feed partial pressure

contrast to, for example, the lanthanum containing $\text{La}_{0.2}\text{Sr}_{0.8}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (LSCF) for which lower flux values are measured [24].

The two compositions, SCF and BSCF, have very similar oxygen fluxes at high temperature, but at lower temperature, BSCF has a much higher oxygen flux than SCF. This has been ascribed to the occurrence of a low temperature phase with the brownmillerite (see Fig. 2.9) structure in which the oxygen vacancies are ordered in rows [25]. Such ordered phases tend to have a lower permeability for oxygen [26].

Concomitant with the phase transition from brownmillerite to perovskite, SCF shows a negative thermal expansion coefficient over a limited temperature range [24]. This phase transition is present up to a remarkably high partial oxygen pressure of ~ 0.1 bar [25]. Such a phase transitions may cause stress and enhance degradation of the membrane upon start-up and shut-down cycling. In contrast to SCF, BSCF [27] was shown not to have transitions to brownmillerite and may therefore be preferred over SCF. However, BSCF is believed to be susceptible to kinetic demixing [28] under the influence of a gradient in the oxygen chemical potential, and phase separation may also play a critical role as life time determining factor [24].

SCF or BSCF are suitable candidates for the production of pure oxygen. For more reducing conditions like using syngas as a combustile at the permeate size the high content of Co is detrimental. Based on observations by [29–32] $\text{Sr}_{0.97}\text{Ce}_{0.03}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$ (SCFC) and $\text{La}_2\text{Ni}_{0.9}\text{Co}_{0.1}\text{O}_{4-\delta}$ (LNC) were selected as promising candidates for operation under reducing conditions and are at present under scrutiny in our laboratories.

In Fig. 2.10, the oxygen flux through LNC and SCFC between 1,073 and 1,173 K is presented. Both LNC and SCFC are measured as a $200 \mu\text{m}$ thick self-supporting membrane of $5 \times 5 \text{ cm}^2$ surface area, denoted D. The feed is one bar of air and the permeate side is swept with one bar of helium. Both materials have similar fluxes up to about 1,100 K. At higher temperature, SCFC shows a strong increase of oxygen permeation. Asymmetric SCFC membranes have also been made, consisting of a porous support of about $200 \mu\text{m}$ thickness and a dense top layer of about $10 \mu\text{m}$ thickness, denoted P-D, the porous part being on the air feed side.

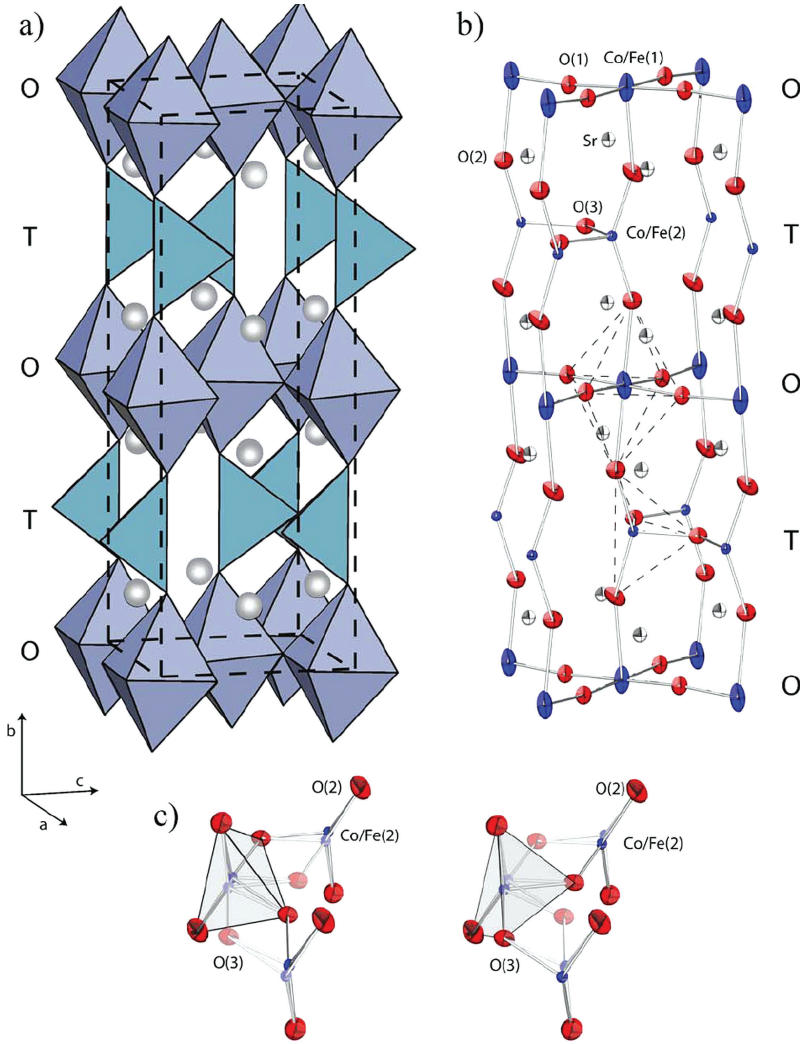


Fig. 2.9 The structure of $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{2.5}$ in the brownmillerite structure

In one measurement He is used as a sweep gas and in the other a gas with a typical composition of SOFC off gas (SOFC o.g.), for example, $\text{CO} : \text{CO}_2 : \text{H}_2 = 1 : 2 : 2$ and a relative humidity of about 40% that is clearly a reducing composition. The oxygen flux is usually given by the following expression:

$$J_{\text{O}_2} = \frac{RT\sigma_e\sigma_i}{16F^2(\sigma_e + \sigma_i)L} \ln\left(\frac{p_h}{p_l}\right) \quad (2.1)$$

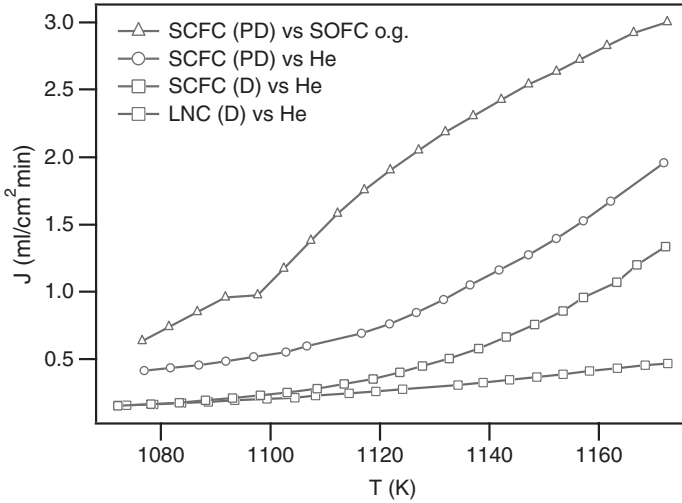


Fig. 2.10 Oxygen flux between 800 and 900°C of a dense LNC membrane and dense and supported SCFC membranes with 1 bar air on the feed side and different sweep gasses on the permeate side (see text)

Here J_{O_2} is the oxygen permeation rate, R gas constant, T the absolute temperature, σ_e and σ_i the electronic and oxide ionic conductivities, F the Faraday constant, L the thickness, and p_h and p_l the partial oxygen pressures on feed and permeate side respectively. Here it is assumed that the bulk diffusion is rate limiting. From this equation, it is clear that for high fluxes, high feed or very low permeate pressures are benevolent as well as small membrane thicknesses. Purely based on thermodynamics, values for the partial oxygen pressure at the permeate side can be as low as 10^{-18} when partial or complete combustion of fuel takes place. Referring to the measurements shown on SCFC it is clear that a thinner membrane gives a higher flux as well as a lower oxygen partial pressure in the case of the reducing SOFC off gas composition. Differences in temperature dependence between He and SOFC off gas stem from the fact that the shift equilibriums also change drastically as a function of temperature whereas in the case of He the exponential behavior of an activated diffusion process is reflected. Clearly the transport in LNC is more difficult than in SCFC at these temperatures.

Membrane Architecture

In order to obtain sufficiently high oxygen flux, a thin (10–40 μm) and dense perovskite layer is required that must be strong and robust enough to withstand typical pressure differences of ~ 15 bar at elevated temperatures (800–1,000°C). Therefore, a support is needed on which the perovskite layer is deposited. The main advantage

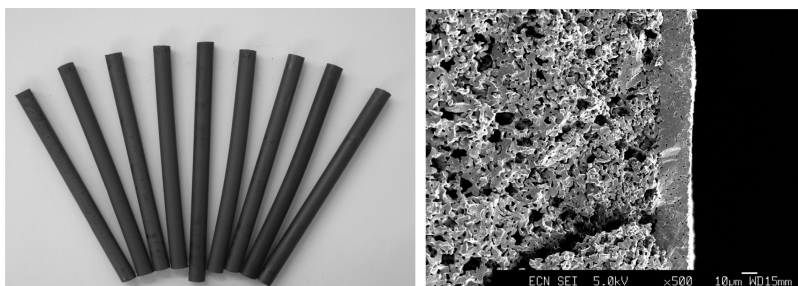


Fig. 2.11 Oxygen-conducting membranes consisting of a porous support and a dense top layer; both parts consist of the same perovskite

of a membrane configuration where the support material is identical to the dense top layer is that the build up of undesirable tensions resulting from differences in the thermal expansion coefficient can be prevented. Furthermore, solid state reactions between the support and top layer are prevented, and no interlayer with a negative effect on the oxygen flux will be formed. Tubular membranes can be prepared by first extrusion of a porous perovskite support. Subsequently, a thin dense selective perovskite layer is deposited. Challenges are still found in the preparation of a defect free top layer that would otherwise reduce the selectivity. At the same time the underlying support must remain porous. Fine tuning of the recipes for the extrusion paste and the dense top layer, in terms of composition, viscosity, and so on. together with appropriate drying and sinter protocols can result in supported tubular membranes as depicted in Fig. 2.11. Our choice for a tubular membrane system has been made on the basis of a conceptual module design as detailed below.

Sealing

A proper sealing system to link the ceramic membranes tubes to the steel module is required.

High demands exist with respect to the seal materials since they have to operate under rather extreme conditions in terms of an oxidizing environment in combination with a high temperature. It is not anticipated that low temperature sealing is a viable option since this would create major temperature differences over the membrane causing stress while parts of the membranes that are present in the low temperature zones are not functional with respect to oxygen conductance, decreasing the economics of the module. Many other aspects of concern affect the choice of material:

- chemical inert towards the perovskite and the steel module;
- physical compatibility such as matching expansion coefficients, low creep rate;
- high temperature resistance;

- resistance against oxidation;
- possibility of adaptation to un-roundness of the membrane tube (e.g. ductility);
- industrial producibility; ease of handling/manifolding.
- economical viability such as cost prize/automation

Apart from materials issues, the engineering aspects have to be addressed. Different type of seal principles can be distinguished such as compression seal, ceramic glue like, and, for example, glasses. Solid state reactions between one of the more promising type of seal, a glass that crystallizes at the operating temperature are rather common [33]. A proper choice of thermal expansion coefficients (TEC) of the sealing materials is a prerequisite for success. The thermal expansions of SCF and BSCF are known from neutron diffraction data [25, 27] and dilatometry [24]. The values are rather high and are similar to that of commonly used stainless steel (e.g. 316). For a compression seal [34] the TEC of the sealing material should, preferably, be just a little higher than that of both the steel parts and the membrane material as it will be able to close the gap between both materials. For seal materials with a lower TEC, end-cap materials are required with a smaller TEC. Different steel types with lower TEC's exist such as 410S, 430, and 444 or materials like Monel or Inconel. The required oxygen resistance is, however, limiting the choice of steel types.

In Fig. 2.12, the principle of compression sealing of membranes with a tubular configuration is depicted. The membrane tube is mounted in a metal end-cap and the space in between end-cap and membrane filled by the sealing material. Compressive forces are obtained upon increasing the temperature and the magnitude of these forces can be tuned by proper selection of the metal type and sealing material, based

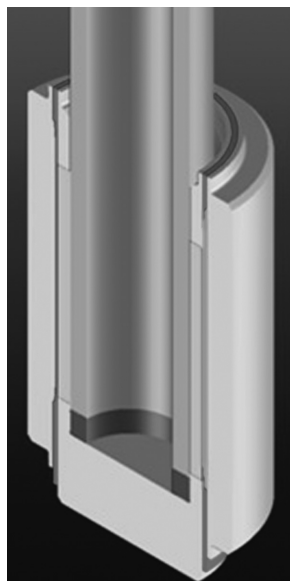


Fig. 2.12 Principle of compression sealing of tubular membranes

on their TEC's. This tunable principle is beneficial since the perovskite membranes will likely have moderate strength compared to steel.

Other sealing material options can be found in ceramic glues with tunable TEC, SCF-melt or SCF/binder systems. Last two options have the advantage of a proper TEC but are less preferred from an economical point of view since manifolding will be more complicated.

Module Concepts

The design of an adequate air separation unit highly depends on the type of membrane configuration chosen. Several conceptual options are available: hollow fibers [35], multi-channel monoliths [36], single tube [37], and tube-and-plate [38] configurations. Each membrane configuration has its advantages and disadvantages when taking reachable surface area, sealing technology and possible use of a sweep gas into account. Hollow fibers provide the highest membrane surface area but are relatively fragile and difficult to seal. Sealing of multichannel monoliths, especially when small channels are used for maximizing the amount of surface area, is also difficult. Single tube configurations, on the other hand, are less difficult to seal while up-scaling principles to one meter length has already been proven for other tubular membrane systems.

The use of a sweep gas is, in contrast to the other configurations, very complicated in the case of a tube-plate configuration since the space in between the plates can be poorly reached.

A conceptual design study of a full-scale plant with an oxygen production capacity of $3 \times 10^4 \text{ Nm}^3/\text{hr}$ or 9,000 tonnes per day, values comparable to a normal sized cryogenic distillation plant, was carried out. In this numerical study, the merits of these membrane geometries were compared in terms of packing density, expressed as surface area to module volume ratio (m^2/m^3) manufacturability and so on, leaving influences of pressure drops and presuming a constant oxygen flux. The maximum allowable gas velocity (25 m/s) has also been taken into account here since higher gas velocities would result in resonances that might result in damaging of the membranes, especially for fragile hollow fibers. The study reveals that the tubular membrane with an outer diameter of $\sim 20 \text{ mm}$ leads to the optimal configuration [39] despite the fact that hollow fibers provide more membrane surface area. The maximum allowable gas velocity restricts the membrane length severely. With a decrease of diameter of single-hole tubes, the maximum allowable length when reaching the maximum gas velocity also decreases rapidly. This argument is especially valid for thin hollow fibers and results in a high amount of small separation units that are needlessly costly. Tubular configurations with dimensions of $\sim 20 \text{ mm}$ diameter allow membrane lengths exceeding 2.5 meter. Since the cost price of the stainless steel vessel will make up $\sim 50\%$ of the total cost price of the module, minimized use of steel is to be preferred.

Dimensional limitations contribute to the design of an air separation unit. Only parts of the volume of the module can be used because of the arrangement of the membranes. In this respect, hexagonal packed volumes are most desirable since they allow for the highest module space-filling. In case of monoliths, the same argument is valid, but additionally, a choice can be made with respect to the outer monolith dimensions. Minimization of the lost space in between the monoliths by the use of square monoliths rather than tubular one's is to be preferred but, as can be seen from Fig. 2.13, lost space at the boundary of module vessel and monolith will still exist. Square monoliths will only increase the m^2/m^3 ratio with $\sim 10\%$.

Additionally, space is required for manifolding and heat insulation while space is also required at the top and bottom of the module so as to gain maximal profit of the available membrane surface area, Fig. 2.14. A module vessel consisting of an insulated double wall has the advantage of minimization of expensive heat- and oxygen-resistant stainless steel, used for relatively thin inner walls, and therefore reduction of the total costs of the module. Accommodation of the pressure inside the module is reached by a thick cold external wall that can be manufactured from cheap steel.

Based on the tubular configuration, and presuming a total module diameter of about 2 meter including the space required for insulation, the module of Fig. 2.15 can be designed with a height of about 4.5 meter which contains $\sim 160 \text{ m}^2$ of membrane surface area. In order to meet an oxygen production of $30.000 \text{ Nm}^3/\text{hr}$, 32 of these module units will be needed.

For reaching the same oxygen production, single-hole tubes of 10 mm diameter would increase the amount of units to 41, comparable to multi-channel monoliths (39 units). The extreme restriction in membrane length of hollow fiber systems would result in $\sim 1,800$ modules. The difference in expansion behavior of vessel wall and membrane tubes can be compensated by mounting the tubes in a

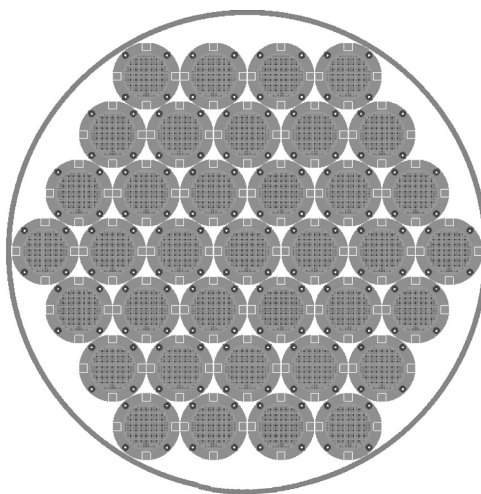


Fig. 2.13 Hexagonal packing of multi-channel tubular monoliths

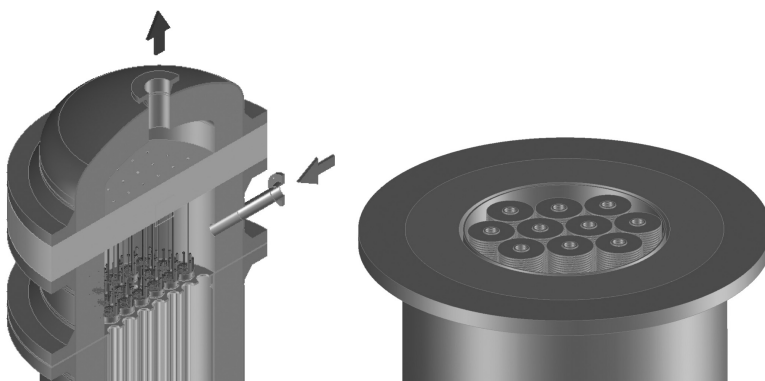


Fig. 2.14 Schematic view of the insulated double wall vessels filled with tubes (*left*) and tube-and-plate assemblies (*right*), showing the space lost due to the manifolding and insulation

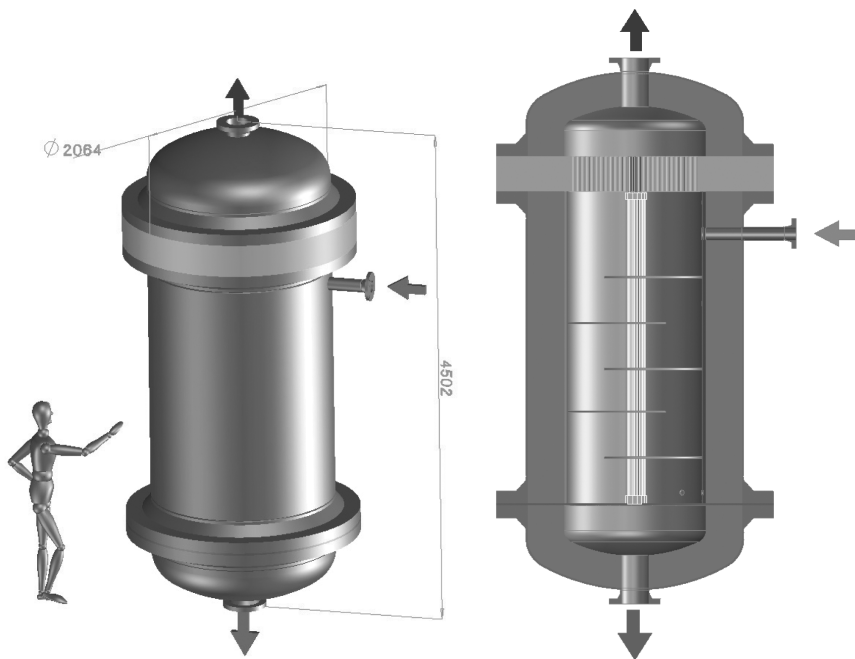


Fig. 2.15 Representation of a full scale module containing about 160 m^2 of membrane area

“pipe-plate” at the top side of the vessel and a “centre-plate” at the bottom of the vessel, keeping the membrane tubes centered while maintaining the possibility of moving, see Fig. 2.16. In order to make use of a sweep gas, sweep gas supply tubes with a diameter much smaller than the membrane tube diameter are connected to the upper plate and stuck through each membrane tube over nearly the full length of the membranes.

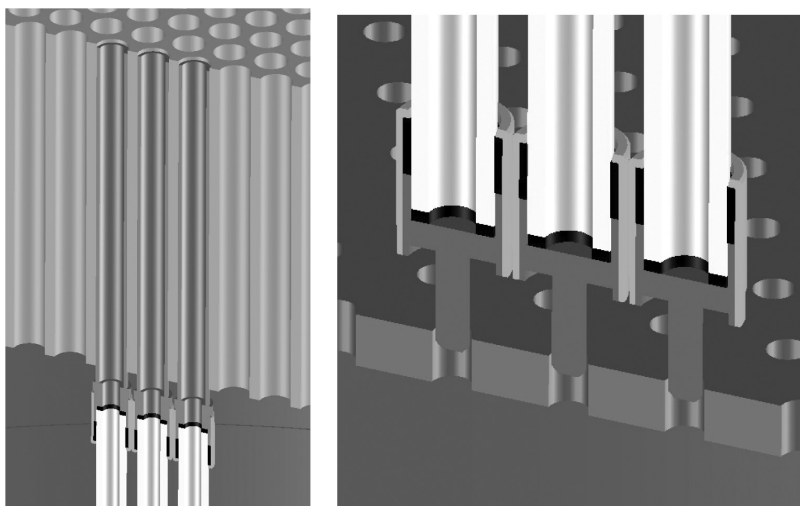


Fig. 2.16 The pipe-plate from where the membrane tubes are suspended (*left*) and the centre-plate at the bottom of the module (*right*)

This reasoning leading to the best option being tubular membranes in a module does not necessarily apply for membrane reactors in which (partial) combustion takes place. The necessity of catalysts also sets extreme demands as to bed permeability.

Concluding Remarks

From the discussion in this chapter, the conclusion can be drawn that the actual implementation of ITM technology cannot be expected in the short term. We believe that there is a number of technology challenges that still needs to be met. However, the small amount of public information from two large leading consortia in the US, led by Air Products and Praxair, hampers a thorough and reliable assessment of the current state-of-the-art ITM technology. Our vision on the viability of high-temperature ITM technology can thus be unnecessarily pessimistic. From our viewpoint, we can point at the following barriers that have to be removed before this technology will be successfully applied

Economic Viability

This is one of the main issues for the implementation of any breakthrough technology. We believe that external factors like energy price, CO₂ penalty and legislation will play a decisive role in this respect. Our economic calculations are still not exact enough for the determination of the maximum allowable membrane in

module price. Significantly, increased membrane fluxes will lead to lower surface areas and smaller number of modules. However, we do not anticipate a flux increase of a factor 2–3 is likely with any material that is stable under the given conditions. However, the inclusion of heat integration options in our assessments may result in a much more optimistic view. Those options are certainly available when an ITM air separation unit is combined with a partial oxidation reactor, for example, in coal gasification, natural gas reforming, and iron ore reduction.

Technological Viability

One of the first assumptions in our economic considerations was that all the technological challenges were met. This remains, at the moment of writing, uncertain. In the above discussion, a number of issues have passed, such as sealing technology, thermodynamic phase stability of the cubic perovskite versus brownmillerite, and kinetic demixing. In relation to this, we have not mentioned creep resistance as yet. For SCF, this was shown to be very low [40], which is likely to be the case for BSCF as well.

Acceptability

Before this technology can be applied on a full-scale as envisaged in our conceptual module design, the end-users should gain sufficient trust in long term performance and reliability of this membrane solution. We believe that to achieve this, first, a number of smaller on-site production facilities must be set up. Only through wide publication of the information obtained in those demonstration plants can significant industrial application be expected.

Oxygen Production or Partial Oxidation?

At this moment, it is uncertain which of the two major possible applications will be first on the market. The production of oxygen puts a much smaller demand on the material properties. The change of oxygen partial pressure will be limited to about one order of magnitude. The amount of impurities that may cause membrane degradation in the feed is likely to be limited to H_2O and CO_2 . When a membrane reactor is considered, the change in oxygen partial pressure over the membrane is expected to be much larger; up to 20 orders of magnitude can be envisaged. This will put significant constraints on the membrane materials as they have to be stable under a wide range of reducing conditions. However, thanks to the large driving force, the demands on the intrinsic transport properties of the materials can be much relaxed. As a result, materials with a larger creep resistance can be chosen. In this case

of partial oxidation, catalyzed chemical reactions take place that are exothermic. Precautions to prevent the occurrence of hot spots and runaways have to be in place.

Finally

Despite the fact that the current class of Co/Fe perovskites has been under investigation for over 20 years [10], there are still a large number of uncertainties in getting this technology towards implementation. A joint research agenda combining the worldwide activities directed at achieving this implementation is likely to be required. The involvement of public and private funding appears to be also prerequisite.

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