Membranes Targeting Industrial O_2 Production from Air – A Short Review

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Abstract: Some of the most promising membranes for O_2/N_2 gas separation (air separation) mentioned in literature so far are selected, in terms of meeting a O_2-gas-production breakeven cost that is lower than that of competing air separation unit (ASU) technologies, based on latest reported technoeconomic studies. An overview regarding most important applications of O_2 and N_2 gases is first given, in respect with the demanded purity limits for each case, since the purity parameter is crucial in defining the minimum breakeven cost.

Keywords: oxygen production; air separation technologies; membrane technology; industrial O_2 production processes.

1. INTRODUCTION

Industrial gas market had a size of 80.1 billion $ in 2020 and is expected to reach 118.9 billion $ by 2026, according to recent forecasts [1]. Half of this market is equally shared by two gases: O_2 and N_2, from which only N_2 is produced by membrane-based gas separation today (Figure **1**), a fact mainly attributed to the already high concentration of N_2 in air and its wide applicability, even at purities as low as 90% for certain applications (*e.g*., preservation of particular kinds of food [2]). On the contrary, O_2 production by membranes still remains at research level, because most applications demand high purity, a requirement met by the competing mature air separation technologies of cryogenic distillation and adsorbent-based separation (PSA, VSA). Recent advances regarding O_2/N_2 gas separation with various kinds of membranes are opening new prospects towards industrial O_2 production, with membranes showing a strong potential to compete with mature technologies at low-, mid- and even large scale of production. However, construction and testing of these novel membranes is still at laboratory level. Only a few pilot-level examples with all-membrane ASUs for O_2-production are known today, mainly concerning OTMs (Oxygen ion Transport Membranes), such as the 16 TPD (tons per day) production rate module constructed and tested by Anderson *et al*. [3] and the BSCF-tube module presented by Nauels *et al*. [4]. At the same time, regarding industrial level, there are mainly reported simulation studies which examine incorporation of membranes in ASUs of oxy-fuel plants. For example, in the recent study of Alqaheem *et al*. it is claimed that a membrane-based ASU providing 30% oxygen to a gas-fuel power production plant could have the technoeconomic advantage over other ASU technologies, if membrane cost is lower than 10$ per m^2 [5]. This low membrane cost could only be met by membranes other than OTMs. Here a concise description of hand-picked, exceptional reported membrane technology findings is given, in respect with application-defined O_2 purity targets and limitations set by recent technoeconomic studies, aiming to underline the most promising research directions in this field.

2. APPLICATIONS AND REQUIRED PURITIES

Main O_2 and N_2 gas applications and respective, usually required, gas purity levels are summed up in Table **1**. Among the various applications, today the major market share (about 1/3 of total) goes for metal production and processing for both gases [6, 7], which are also highest purity-demanding applications (>99%). Nonetheless, in the O_2 production case there is significant market space for lower purity O_2, in the very important application sectors of medicine (>82%), wastewater treatment (>90%) and oxyfuel combustion (>90%), as well as for mid-purity O_2 in other applications, such as oxyfuel gasification (>95%), for future IGCC (integrated gasification combined cycle) electricity production from biomass and waste (Figure **2**), fish-farming (>95%) and delignification & bleaching of pulp and paper (>95%), where harmful active chlorine is replaced with O_2. It should be noted that, in particular, medical O_2 use has a COVID-19 pandemic-driven rapidly increasing demand [8], mainly in form of portable units for home care and less for fixed units at hospitals [9-11].

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Table 1: Important Applications and Typical Demanded Purities for Gaseous Air Separation Products O_2 and N_2

Gas	Application	Required Purity (% v/v)	Reference
O_2	Oxyfuel gasification	95	[12]
	Medical sector	82	[13]
	Steelmaking (basic oxygen furnace, electric arc furnace, CAS-OB process and AOD process)	99.5	[14]
	Metal Gas-cutting	99.5	-
	Metal welding	99.2	-
	Wastewater treatment	90	[15]
	Fish farming	95	-
	Biogas upgrading (microbial H_2S oxidation)	92	[16]
	Paper industry (delignification & bleaching)	92	[17]
	Fluid catalytic cracking (catalyst regeneration)	95	[18]
	Sulfur recovery unit (O_2-based Claus process)	28	[19]
	Glass and ceramic furnace (oxyfuel combustion)	90	[20]
	Nitrox I&II OEA mixtures for minimizing risk for diver's decompression illness	32 & 36	[2]
	Limestone flue gas desulfurization ($CaSO_3$ to $CaSO_4$ oxidation)		[21]
	Plasma cleaning of organic contaminants on surfaces		[22]
	Plasma surface modification of polymers		[23]
	H_2O_2 production		[24]
	HNO_3 production production (NH_3 to NO & NO to NO_2 oxidation in Ostwald process)		[25]
N_2	Inerting for food maintenance	98	
	Inerting for maintenance of drugs	97	
	Use in chemical reactors	95	
	Power plant boiler maintenance	95	
	Storage of petrochemicals (incl. pipelines, tankers)	95	
	Metal working	97	
	Laser cutting	99.9	
	Soldering, cleaning and storage of electronics	95	
	Storage, extrusion & molding of molten plastics	95	

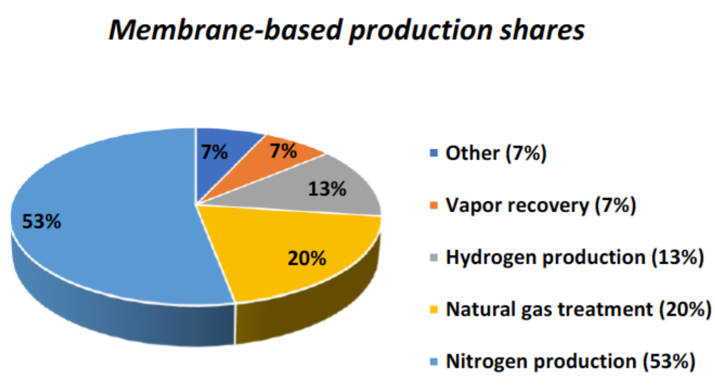

Figure 1: Membrane-based gas separation market shares for various applications in 2017 [26].

3. TECHNOECONOMIC COMPARISON WITH MATURE AIR SEPARATION TECHNOLOGIES

A usual gas separation membrane system has the form of a cascade, consisting of one or more membrane stages, with one or more compressors for pressurizing feed streams and/or vacuum pumps for applying vacuum to permeate sides. Typical setups of such staged systems are given for example by

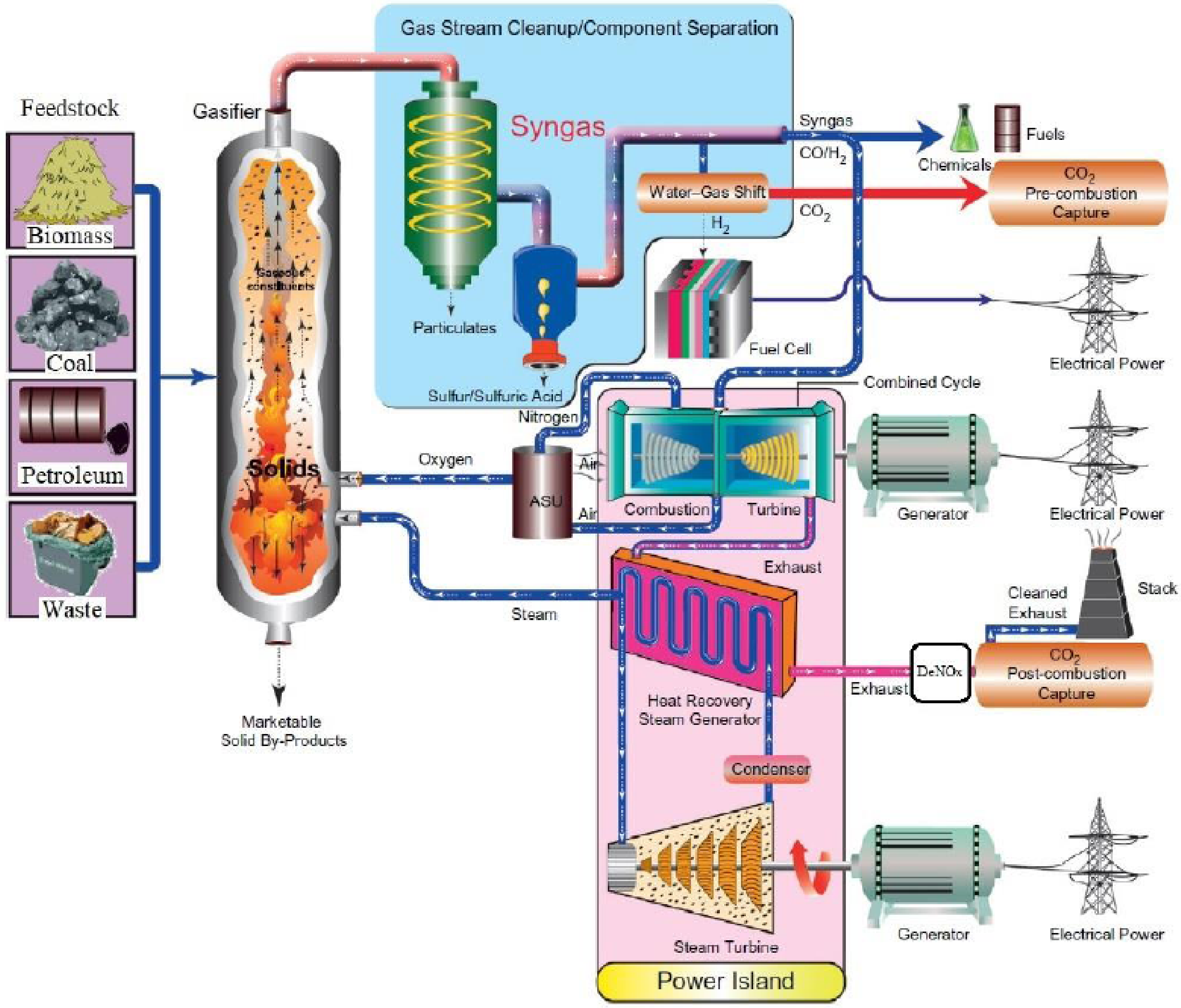

Figure 2: IGCC Scheme (Reproduced with minor changes, with permission from Ref. [27]).

Harlacher and Wessling [28]. For any such system, a tradeoff exists between flux enhancement and energy consumption when increasing transmembrane pressure, or any other driving force, such as temperature in the case of OTMs. At the same time, in particular for polymeric membranes, selectivity sees a drop beyond an applied pressure difference limit, which is reflected as a drop in product purity with flux beyond that limit. In this case, the decisive OPEX-defining parameter of specific energy consumption is reduced with transmembrane pressure, as its denominator (flux) increases more rapidly than its numerator (power consumption), but beyond the said pressure difference limit this happens at the expense of product purity. The result is the curved, vertical lines depicted in the diagram of Figure **3** for polymeric membranes of different selectivities α [29]. When these lines lie below respective lines of competing technologies (lines with symbols), then polymeric membranes are most probably the preferred option, in terms of a lower OPEX. Additional literature data regarding specific energy consumption of competing technologies are given in Table **2**.

Furthermore, based on the diagrams of Figure **3**, in order to reach an O_2 purity level of at least 90%, which meets the requirements of some important O_2 applications mentioned in Table **1**, with a typical gas separation membrane of 40 GPU O_2 permeance and O_2/N_2 selectivity less than 15, a membrane system of more than one stages is definitely needed. For a 2-staged system, the added purification stage (2nd stage) can make the desired 90% purity reachable, but on the other hand, it adds to the specific power consumption. Therefore, process design aiming the minimum number of stages for reaching a given purity is advisable. At the

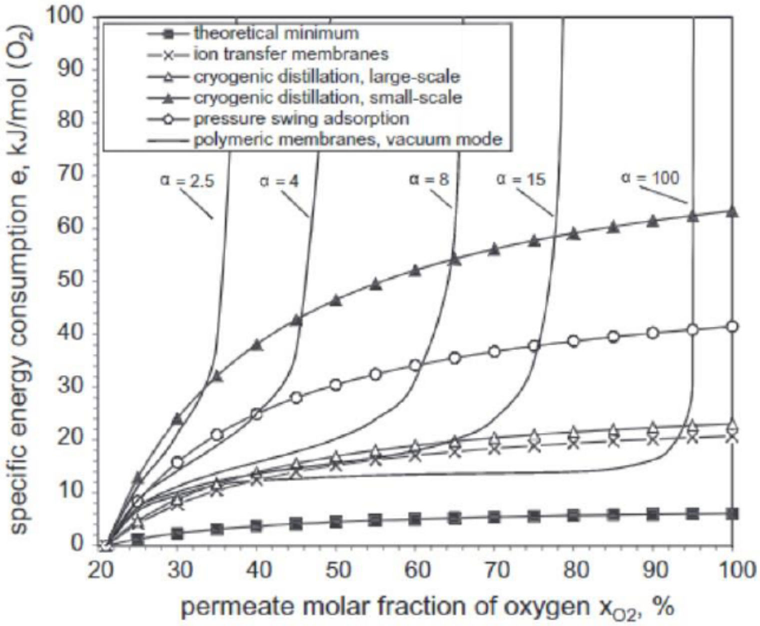

Figure 3: Calculated specific energy consumption of membrane vs. competing technologies, assuming a 1-stage membrane with 400 Barrer (40 GPU, 10 μm thickness) O_2 permeability and O_2/N_2 selectivity *α* (Reproduced with permission from Ref. [29]).

Table 2: Specific Energy Consumption of Competing Technologies

Technology	Production Rate	O_2 Purity (% v/v)	Specific Energy Consumption (kWh/ton_{EPO2})	Reference
OTM	Small scale (0.34 TPD)	96.3	140 (16.13 kJ/mol)	[30]
Cryogenic distillation	Large scale	99	220-325	[31-34]
Cryogenic distillation	Large scale	95	159	[35]
Cryogenic distillation	Small scale (25 TPD)	99	550	[2, 26]
PSA	Medium scale	99	280-340	[37]

same time, for a given selectivity (it defines the maximum reachable purity), a membrane with higher permeance has an increased denominator of specific power consumption and therefore needs less power consumption for producing a given volume of product. As shown in the work of Adhikari *et al*. [38], this results in a steep drop of breakeven cost with increasing membrane permeance. However, it should be noted that, when specific cost of production is calculated for gas separation membrane systems, both CAPEX and OPEX are included. CAPEX consists mainly of the system component cost and the installation cost and is distributed over the system's expected lifetime, while OPEX mainly regards energy expenses. In Figure **4** a typical cost analysis of a 2-stage membrane system for O_2/N_2 separation is given, according to Adhikari *et al*. [38].

It must be noted that membrane cost, which is typically estimated to be 30% of CAPEX, is the product of membrane material cost (in $\$/m^2$) and needed membrane area (membrane life-time expectancy is also crucial in determining the latter). For a certain (single-stage) membrane, in order to increase the amount of product per day (if feed rate is given, then this corresponds to a higher O_2 recovery), without dropping product purity, the membrane area must be increased. For example, Gilassi *et al*. have calculated that a membrane with 9.3 GPU O_2 permeance and O_2/N_2 selectivity of 40, needs an active permeation area of 9000 m^2, in order to reach 35% recovery for a O_2 product with 70% v/v purity [39], while Haider *et al*. estimated that for a carbon membrane with 10 Barrer O_2 permeability and selectivity of 18, the same recovery and 78% v/v purity need an membrane area of 50000 m^2 [40].

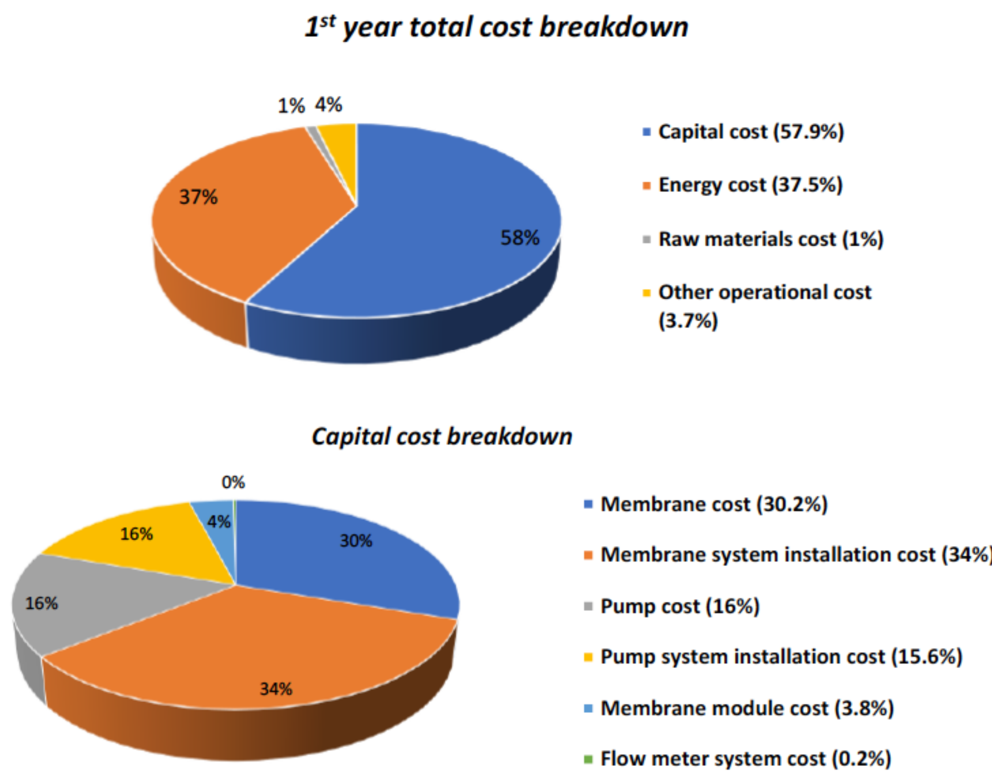

Figure 4: The breakdown of first year total cost (**a**) and capital cost (**b**) for a two-staged gas separation membrane system (Reproduced with permission from Ref. [38]).

When competing air separation technologies are compared, in terms of better product purity and specific cost of production, a very important parameter to take into account is scale of production, expressed as the production rate in TPD. Usually, as far as specific cost of production is concerned, its denominator sees a steeper rise with production rate, than its numerator and, overall, all technologies reach their best performance at large scale. For example, for cryogenic distillation, specific production costs for 25, 50, 100 and 300 TPD are approx. 75, 50, 35 and 25 $\$/ton_{EPO2}$, respectively [40-42], while in the case of VPSA, this decline is less pronounced and for 10, 50, 100 and 300 TPD, the specific production costs are approx. 40, 35, 35 and 35 $\$/ton_{EPO2}$, respectively [41]. Such data are still very scarce for gas separation membranes. One such work is the reported technoeconomic study of Micari *et al*. [43], where for a 2-stage system using membranes with 1000 GPU O_2 permeance and O_2/N_2 selectivity of 20 (membrane cost is 100 $\$/m^2$) for producing 95% purity O_2, specific production costs of 29 and 32 $\$/ton_{EPO2}$ are calculated for 10 and 50 TPD production rates, respectively. If such membranes become a reality, a clear advantage over other technologies arises at low scale. Data for higher scales of production have still not been reported in literature, as far as we know. According to the same work, a 2-stage system with membranes of 1000 GPU O_2 permeance and only 5.5 O_2/N_2 selectivity, at a small production rate of 25 TPD, has a specific O_2 production cost as low as 50 $\$/ton_{EPO2}$, which is less than the respective cost of 75$\$/ton_{EPO2}$ for cryogenic distillation [40-42], but still higher than 40 $\$/ton_{EPO2}$ of VPSA [41]. To underline the importance of high permeance, one further reported technoeconomic analysis is mentioned, regarding a carbon membrane with high selectivity of 18, but O_2-permeance of only 300 GPU. This membrane system was found to have a specific production cost as high as 80$\$/ton_{EPO2}$ for a O_2-purity of 73% [44].

4. PROMISING MEMBRANES FOR COMPETING WITH MATURE TECHNOLOGIES

Unfortunately, only simulated results have reached an O_2/N_2 selectivity of 20 for a membrane of high permeance (>1000 GPU) so far, in particular for a few metal organic framework (MOF) membranes of certain types [45]. However, if selectivities lower than 20 are taken into consideration, various types of membranes with O_2 permeances far exceeding 1000 GPU are available today, as has been shown in recent experimental works. For example, a carbonized polyimide/MOF mixed matrix membrane, namely of carbonized 6FDA-DAM with UiO-66-NH_2 filler on porous Al_2O_3 substrate, has been found to reach 2616 GPU O_2 permeance with O_2/N_2 selectivity of 5.3 [46]. This membrane is expected to drop specific production cost below the 50 \$/ton$_{EPO2}$, as predicted by Adhikari *et al*. for a 2-stage system with 1000 GPU permeance, 5.5 selectivity and 90% purity, and maybe even below the competing 40 \$/ton$_{EPO2}$ of VPSA. Similar results were also obtained by numerous triptycene- and spiro-PIMs (polymers of intrinsic microporosity), as is presented in the detailed reviews of Wang *et al*. [47, 26], but the bottleneck of significant ageing effect is still hindering application of such membranes (Figure **5**). Ye *et al*. [48] also reported a high O_2 permeance of 2568 GPU and ideal O_2/N_2 selectivity of 5 for a thin film MFI zeolite membrane supported on porous alumina. In this case measurements took place at the cryogenic temperature of 67 K, while both feed and permeate pressures were set to 100 mbar. At 100 mbar the dew point of air is 65.9 K, so that keeping the temperature at 67K assures pores are not blocked by liquefied air, which would in turn drop permeance, while, according to the authors, formation of a thin layer of LOX at pore walls is still enhancing O_2/N_2 selectivity.

Furthermore, a ZIF-71 in PIM-1 mixed matrix membrane presented by Hao *et al*. [49], that reached 8010 GPU with a selectivity of 3.5, or a 2D-polymer membrane prepared by Qu *et al*. [50] reaching 5034 GPU with 3.86 selectivity, would both significantly drop the 71 \$/ton$_{EPO2}$ predicted by Adhikari *et al*. for a 3-stage membrane system with 1000GPU, 3.1 selectivity and 90% purity. This drop might possibly reach a specific cost below the competing 40 \$/ton$_{EPO2}$ of VPSA. The same goal could also be reached by a pure ZIF-8 membrane grown on PIM-1 substrate, with 6435 GPU and selectivity 3.7 according to Liu *et al*. [51], as well as by other very promising membranes which have been tested for various gases, but not for O_2/N_2 separation yet. One such example is membranes of metal-induced ordered microporous polymers (MMPs), which were introduced by Qiao *et al*. in 2019 [52] and were shown to easily form ultrathin layers on porous supports, covering a relatively large active membrane area, while their exceptional performance was proven for CO_2/N_2 separation, giving 3000 GPU CO_2 permeance and real gas mixture selectivity of 78. However, testing of these membranes for O_2/N_2 gas separation has still not been reported.

In a different approach for obtaining 90% O_2 purity, based on the diagram of Figure **3**, a membrane with a selectivity of 100 and O_2 permeance of 40 GPU would be more efficient than competing technologies. Therefore, a few existing membranes with extremely high O_2/N_2 selectivity, exceeding 100, could gain attention regarding applications utilizing 90% O_2 purity, even if their permeance is lower than 40 GPU. One example of such a membrane is the porous a-Al_2O_3-supported liquid (facilitated transport) membrane with a 50/50 liquid mixture of ionic liquid (IL) [EMIM][BF_4] and the highly O_2 absorbing perfluorocarbon (PFC)

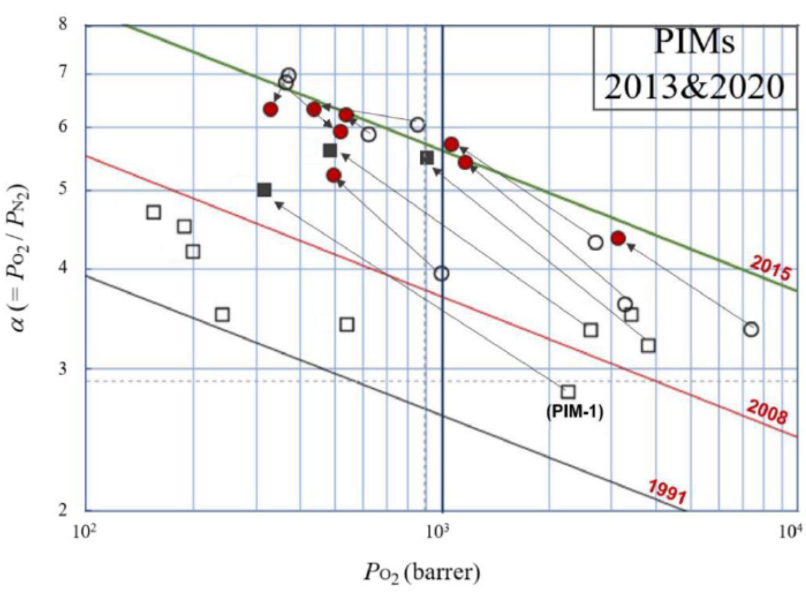

Figure 5: Ageing of PIMs and comparison with Robeson upper bounds. Plots of oxygen permselectivity for polymers of intrinsic porosities (PIMs), showing the highest α at each permeability P_{O2} reported in literature until 2013 and 2020. ●○: Trip-PIM, ■□: Spiro-PIM, ●■: aged values, □○: none-aged values [47].

perfluorotributylamine (PFTBA), as reported by Castro-Domínguez *et al*. [53]. A very high O_2/N_2 selectivity of 370 was measured at 40°C, but with an O_2 permeance of only 2.4 GPU. Notably, this selectivity further increased with temperature (660 at 50°C), but at the expense of permeance. Also, gradual mass loss by PFTBA evaporation led authors to suggest a future examination of the same liquid in a different setup, such as a membrane contactor. Future examination of more mixtures, having as constituents various ILs and highly O_2-selective PFCs, could reveal that enhanced permeance combined with very high selectivity is possible. Other high selectivity membranes, but with very low O_2 permeance, are carbon molecular sieve membranes (CMSMs), such as cellulose-based CMSMs with very high O_2/N_2 selectivities, up to 800 [54], or polyimide-derived CMSMs [55, 56] and PIM-PI-derived CMSMs [57], as is summed up in the review of Wang *et al*. [47]. Such membranes could gain prospects to become usable in applications only if the selective layer thickness is significantly reduced, below 1.5 μm, as was achieved in the aforementioned work of Lee *et al*. [46].

The strategy of reducing selective layer thickness, in order to enhance permeance, comes to an extreme in the case of ultrathin membranes, which refer to thicknesses below 50 nm [58, 59]. A characteristic example of the kind is nanoporous single layer graphene (N-SLG) membranes, *i.e*., one single graphene veil of relatively large dimensions with a high number of defects in form of atomic-scale holes in its 2D structure. A recent example, reported by Huang *et al*., refers to SLG pore-opening treatment by localized pyrolysis in oxygen-ozone atmosphere, resulting in N-SLG membranes with O_2 permeance of 1314 GPU and O_2/N_2 selectivity of 3.4 [60]. In parallel, simulation studies of Vallejos-Burgos *et al*. predict that, with proper hole dimension and rim-chemistry adjustment, O_2/N_2 separation performance could be further enhanced, reaching the extraordinary level of 60500 GPU combined with a selectivity of 5 [61]. Additional recent experimental findings have shown that gas separation performance can also be improved, in terms of selectivity, by drop casting an ultrathin IL layer on top of these membranes [62]. However, tests for O_2/N_2 are still missing. Finally, computational studies are also showing very promising prospects for gas separation with other defected 2D materials, such as 2D metal chalcogenides, but unfortunately without providing data for O_2/N_2 [63].

In parallel to low temperature gas separation membranes, significant improvements have been recently reported for high operational temperature (>600°C) Oxygen ion Transport Membranes (OTMs), which are considered as the most promising air separation technology today for high purity O_2 production, since it could be integrated into industrial processes with excessive amounts of waste heat, such as thermoelectric power plants. Specific energy consumption of 16.13 kJ/mol_{EPO2} (140 kWh/ton_{EPO2}), measured for Zr-stabilized BSCF OTM in the work of Hu *et al*. [30] is lower than that of competing mature technologies, as is shown in Figure **3**, and high purities of >99% are easily achievable without the compromise of reducing flux for OTMs. In addition, if produced O_2 is also consumed at the same power plant, such as in the IGCC process depicted in Figure **2**, or any other industry with excessive waste heat, this would definitely constitute one major driver for industrial OTM integration in the form of an ASU. However, significant ageing problems have to be tackled first for these membranes, in cases where they come into contact with CO_2, H_2O, SO_2 and CH_4 gases. Mid- and long-term stability tests for continuous operation in such environments are still needed to prove industrial applicability. Proposed stabilization methods include covering with protective coating [64, 65], modifying composition [66] and using two phases, one focused on electron conduction and one focused on ion conduction (dual-phase OTMs [67, 68]). Most promising dual-phase OTMs so far are listed in the detailed review of Kiebach *et al*. [69], with CGO-LSCF having the highest flux (6.23 $ml(STP)/cm^2/min$ at 1173K, corresponding to 6590 GPU with “infinite” selectivity of an equivalent polymeric membrane) so far with a 200 h tested stability [70]. Typical performances of stable reported OTMs are given in Table **3**.

Finally, it should be noted that OTMs find also many other applications beyond air separation, such as: Solid oxide fuel cells (SOFCs) [71], aiming for energy production, or reverse-mode SOFCs, for H_2 & O_2 co-production and CO_2 reduction (*e.g*., O_2 production on Mars [72]), as well as coupling to other chemical reactions [73, 74], as in the case of simultaneous reduction of CO_2 and H_2O at the feed interface, combined with exothermic partial CH_4 oxidation at the permeate interface (reactive sweep gas), aiming to form syngas at both membrane sides [75, 76] in a process with high potential to replace the usually applied method of CH_4 steam reforming.

Table 3: Experimental O_2/N_2 Gas Separation Data for Different OTMs

Membrane	Δ*P* (bar(a)), *T*(K)	O_2 Flux (ml(STP)/cm^2/min)	O_2 Purity (% v/v)	Stability Tested for (hrs)	Reference
CGO-LSCF	0.21, 1173	6.23 (He sweep) 4 (CO_2 sweep)	99	< 200	[70]
BSCF3Zr	5.2, 1123	6.2 (vacuum, no sweep gas)	96.3	120	[30]
LSCF	0, 1223	3 (He sweep)	-	720	[77]
SCFN181	0, 1173	0.9 (He sweep) 0.6 (CO_2 sweep)	-	< 100	[78]

5. CONCLUSIONS

Overall, room (and cryogenic) temperature membrane-based O_2 production can be the best technology in terms of lowest specific cost of production, if applications of 90% O_2 purity are considered. Several reported promising membranes towards this target are mentioned in this review. On the other hand, high temperature OTM-based O_2 production has already been proven to be the best performing technology, in terms of lowest specific energy consumption, for applications requiring high O_2 purities of >95%. As is shown by latest technoeconomic studies, mature technologies of cryogenic distillation and VPSA are outperformed by these membrane technologies at low- and possibly also mid- and large- scale production rates. However, proof of concept experiments regarding mid- and long- term stability, as well as ease of upscaling, combined with technoeconomic studies predicting breakeven costs at high scales of production, are main subjects that still need to be addressed in literature for both low- and high- operational temperature membranes.

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