

Document downloaded from:

<http://hdl.handle.net/10251/65865>

This paper must be cited as:

García Fayos, J.; Vert Belenguer, VB.; Balaguer Ramirez, M.; Solis Díaz, C.; Gaudillere, CC.; Serra Alfaro, JM. (2015). Oxygen transport membranes in a biomass/coal combined strategy for reducing CO₂ emissions: Permeation study of selected membranes under different CO₂-rich atmospheres. *Catalysis Today*. 257(2):221-228.
doi:10.1016/j.cattod.2015.04.019.



The final publication is available at

<http://dx.doi.org/10.1016/j.cattod.2015.04.019>

Copyright Elsevier

Additional Information

Oxygen Transport Membranes in a biomass/coal combined strategy for reducing CO₂ emissions: Permeation study of selected membranes under different CO₂-rich atmospheres

Julio Garcia-Fayos, Vicente B. Vert, María Balaguer, Cecilia Solís, Cyril Gaudillere, Jose M. Serra*

Instituto de Tecnología Química (Universitat Politècnica de València – Consejo Superior de Investigaciones Científicas), Av. Los Naranjos, s/n, 46022 Valencia (SPAIN)

Abstract

This contribution introduces how the integration of biomass as fuel in power plants would balance CO₂ emissions and the related role of oxygen transport membranes (OTM) on it. CO₂ capture techniques could be introduced to minimize CO₂ emissions at the cost of a substantial energy penalty in the overall process. Among the different approaches, the use of pure O₂ and/or N₂-free oxidation gases for combustion and/or for gasification leads to promising energy efficiencies. Ceramic OTM membranes could be successfully integrated in such thermal processes, which enable to increase the net plant efficiency when CO₂ capture is implemented. Further, this work reviews how selected ceramic materials and membrane architectures behave under CO₂ containing atmospheres at high temperatures above 700 °C. These conditions have been selected for checking the viability of these compositions and configurations to fit in an oxy-co-gasification process, involving coal and biomass. The tested asymmetric membranes present promising oxygen fluxes in the range 0.6-1.2 ml·min⁻¹·cm⁻² when using 100% CO₂ as sweep gas at 850 °C (optimal membrane operation conditions in oxy-fuel power plant) and stable oxygen production up to 100 hours of continuous operation in similar conditions. Specifically, La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} and NiFe₂O₄ - Ce_{0.8}Tb_{0.2}O_{2-δ} composite materials showed the best results for oxygen permeation and time stability under CO₂-rich atmospheres.

Keywords: oxygen transport membrane; biomass gasification; perovskite; air separation; oxyfuel; CCS; oxy-co-gasification

*corresponding author: jmserra@itq.upv.es, Tel. +34.963879448

1. Introduction and technology survey

Energy consumption will increase significantly in the next decades [1, 2] and it is expected to be produced mainly by coal/natural gas power plants (both summing up around 60% [1] of the world total production). This fact implies that anthropogenic CO₂ will contribute, even more, to the global greenhouse gases concentration in the atmosphere.

The Zero Emission Platform (ZEP) has challenged the reduction of CO₂ emissions on three concepts: (i) the increase in renewable sources utilization, as it is expected to occur [2], (ii) the application of new processes or technologies to enable more efficient energy production, and (iii) the integration of Carbon Capture and Sequestration and Utilization (CCSU), as the only technology to effectively reduce the CO₂ emissions produced by the largest producers.

CCS is an energy intensive approach in which CO₂ is separated using one of the three models presented in Figure 1 for power plants: (i) after the fuel is burnt (post-combustion), (ii) before burning the fuel (pre-combustion), by means of a gasification and hydrogen separation process or (iii) by means of avoiding the use of air but pure oxygen for the combustion (oxyfuel).

Carbon-based power plants are well established and new ones are being built up in non-OECD countries, i.e. China, where carbon is abundantly available. Co-firing biomass on active coal-fuelled power plants could reduce CO₂ footprint by means of using this renewable energy source (first point of ZEP concept). However, the lower specific heat capacity of biomass compared to coal must be increased by combusting this coal/biomass feedstock with pure O₂ instead of air. An analogous oxyfuel approach is currently used in cement plants, where the use of alternative fuels such as biomass, or other residues with lower specific combustion heat, requires the use of O₂-enriched air [3]. Apart from this energetic consideration that involves a reduction in the overall fuel consumption of the plant, the exhaust gases from an oxyfuel coal/biomass fed power plant contain mainly water and CO₂ so the CCS process is

straightforward (Figure 1). Then second and third ZEP's concepts are also satisfied within oxyfuel approaches in these co-fed power plants as several studies suggest [4-8].

On the contrary, biomass and coal could also be gasified into syngas prior to enter to the boiler, in order to increase the specific heating capacity of the raw fuel. Then pre-combustion process is straightforward for CCS (Figure 1), and the three ZEP concepts for reducing CO₂ emission are fulfilled too. Indeed, the combined use of biomass with fossil fuels in oxy-co-gasification [9] power plants could lead to a power plant with an overall theoretically negative CO₂ emission.

Besides the oxyfuel technology, there are other alternatives to implement CCS strategies in thermal power plants, as presented in Figure 1. Post-combustion involves huge CO₂-separation plants, typically amine washing or calcium looping process, in which CO₂ is absorbed on the amines or calcium and then thermally desorbed to regenerate amine/calcium carrier and produce CO₂. In the pre-combustion approach, fuel is gasified and the gasification gases are equilibrated in water gas shifting (WGS) reactors to form a mixture comprising principally H₂ and CO₂, the latter being separated previously to a combustion process. The most efficient gasification plant for power generation is the so-called Integrated Gasification Combined Cycle (IGCC) plant.

In both pre-combustion and oxyfuel approaches (Figure 1) an oxygen source is required, i.e., an Air Separation Unit (ASU) should be installed nearby of such big plants. State-of-the-art technologies for on-site O₂ production are based on (i) cryogenic distillation of air and (ii) (vacuum) pressure swing adsorption – (V)PSA – from air, but only cryogenic distillation could supply the required oxygen needs of a power plant involving zeolites as adsorbents. However, these two conventional O₂ separation processes are very energy intensive and they are only used when they are mandatory in the process. Developing alternatives to these state-of-the-art ASU technologies with reduced energy consumption would be the key for an intensive

integration in power plants and related gasification processes, in order to effectively proceed with CCS. In this scenario, oxygen transport membranes (OTM), based on ceramic materials, should provide the perfect balance between energy consumption and overall plant efficiency due to the proper thermal integration in fuel fired power plants [10]. Besides all the research groups that are currently investigating on the integration of OTMs in gasification processes, main advanced developments are those performed by Praxair and Air Products. These two companies are working in the field of ceramic membranes for O₂ separation for more than 20 years, developing industrial OTM modules and systems for IGCC and related applications. Praxair is focused on developing OTMs for oxycombustion and syngas applications through a U.S. DoE granted project (DE-FC26-07NT43088), by means of the use of advanced boilers and heaters using OTM technology in combustion processes. Several U.S. Patents have been resulted from these developments [11, 12], specially an OTM boiler that enables steam generation and power cycle with CCS [13-15], and an OTM syngas system for autothermal reforming of NG enabling downstream synthesis and oxycombustion power cycle [16]. Praxair's OTM technology consists in tubular membrane modules that are integrated in an Advanced Power Cycle layout as Partial Oxidation equipments and OTM boiler. After completing phases I and II, which comprised the development of materials, design of an OTM-enabled coal power cycle, single tube testing and basic engineering of OTM modules, Praxair has achieved in phase III a successful integration of membranes into systems, what is leading the way to the scale-up to systems including 1 TPD O₂ OTMs.

Air Products started its R&D activities on OTMs in 1988, since then, more than 90 U.S. Patents related to materials, catalysts, membrane and modules structures, process cycles, applications and integrations have been produced [17]. Furthermore, Air Products and the U.S. DoE entered into a Cooperative Agreement in 1998 to develop oxygen membrane technology to the point of pre-commercialization. Currently, an intermediate scale testing with a capacity of 100 TPD O₂ (corresponding to an IGCC output of 12 MW) is being developed. Simultaneously, a

2000 TPD O₂ module is also under development. Once completed, next phase will comprise the construction of energy installations yielding power outputs of 250 MW (IGCC) and 110 MW (oxycombustion). Air Products OTM modules present a planar wafer design as described in [18, 19]. Air Products developments are the most advanced in terms of facilities size, oxygen production and proximity to commercialization.

In the scientific field, research groups are focused mainly in the characterization of materials for OTM membranes, aiming to improve the performance and the stability under operational conditions. Among other research institutes, Instituto de Tecnología Química (ITQ) has developed advanced ceramic materials for high temperature oxygen separation purposes since 2006, and novel materials and configurations have been discovered. Some of them are presented in this work.

Membrane technology for O₂ separation

Ceramic materials exhibiting both ionic and electronic conductivity are known for their good properties in oxygen separation since the 1970 decade. These ceramic materials consist of dense layer(s) of multi-metallic oxides presenting alkali, alkali-earth, rare-earth or transition metals together in the same crystalline structure. The solid-state permeation of oxygen through these materials is possible due to the presence of oxygen vacancies in the crystalline lattice since they are non-porous membranes. At high temperatures (>500 °C), oxygen is transported through the ceramic crystalline material hopping from vacancy to vacancy and, in parallel to ionic diffusion, the counter-diffusion of electronic carriers for charge compensation takes place. In other words, mixed ionic and electronic conductivity (MIEC) is required for these membrane materials to allow oxygen transport. Further and deeper details for MIEC and ceramic dense membrane applications can be found in [20].

The main drawbacks of OTM technology are the high temperatures needed for practical operation, typically between 700 and 1000 °C, and the presumably modest chemical and

mechanical stability of the materials. As a rule of thumb, the higher the temperature the higher the oxygen permeation is but the more expensive the ancillary materials are. The chemical and mechanical behavior of these OTMs is influenced by the nature of the gas environment in contact with both sides of the membrane. Specifically, environments with low O_2 partial pressure (p_{O_2}) and/or containing CO_2 , SO_2 gases and reducing species (i.e. light hydrocarbons, hydrogen, water, etc.) affect the membrane performance and the material integrity, even causing the membrane mechanical failure [21-24]. Within the objective to overcome these operational limitations, a large number of research groups have made great efforts in OTM development and new materials have been formulated with improved O_2 flux at lower temperatures and under harsh atmospheres, approaching the conditions of industrial target applications as oxyfuel, gasification and chemical and petrochemical reactions [10, 25-34].

Integration of OTM modules in gasification processes

OTM modules can be operated according to two different concepts, known as 3-end and 4-end modes, depending on how many stream are connected with the membrane module (Figure 2). In both configuration modes, pressurized air is fed into the module, forcing O_2 to permeate due to the O_2 partial pressure gradient across the membrane. In the 4-end operation, sweeping of the permeated O_2 is made by means of a gas stream. In the case of power plants or gasification units, part of the hot flue gas mainly consisting of CO_2 and H_2O , when properly cleaned, can be recirculated and fed into the membrane module, thus exploiting the gas waste heat for conducting oxygen separation. The recirculation of hot (>1000 °C) gases facilitates the thermal integration of the membrane in the process, especially considering the high temperature (ca. 850 °C) required for the OTM operation. In the 3-end mode, vacuum is used to achieve the desired driving force, then obtaining a pure O_2 stream and avoiding the membrane to come in contact with the flue gases, which typically promote the membrane

degradation. However, high-temperature oxygen stream should be cooled down before entering into the vacuum pump, so an extra heat exchanger (non-commercial for pure oxygen) should be proposed. Regarding the needed membrane area, and keeping the pressure in the air side of the membrane, vacuum in the permeate side increases the driving force for oxygen permeation thus reducing the active area for the same oxygen demand in the 3-end mode. Nevertheless, temperature and pressure conditioning of the oxygen stream is also a challenge for this operation mode. In the specific case of co-gasification processes, water, CO₂ and oxygen are introduced to carry out all the gasification reactions [9, 35]. Therefore, in 4-end mode, flue gases from the boiler or gasification unit (Figure 3) could be used as sweep to achieve a high OTM integration degree in the co-gasification process. A work carried out by Engels et al. [31] on BSCF tubular membranes module concluded a higher net-efficiency for a OTM-based power plant together with a lower estimated membrane area for the 4-end concept compared to the 3-end concept. The latter is applied to a tubular architecture. Issues like thermal integration, needing of additional equipment, membrane area... probably are more dependent on the specific technology considered for the systems and on the membrane architecture (planar or tubular) than in the choice of operating mode. As an example of this, the two major OTM developers are using different approaches regarding operation mode. Praxair system considers tubular membranes modules in a 4-end mode [36], whereas Air Products plant works in a 3-end configuration with planar stack modules [17]. Taking into account that both systems present substantial differences, the choice of the operating mode has to be done according to the specific characteristics of a given layout.

Two simplified layout examples of the OTM module industrial integration in a 4-end mode are shown in Figure 3, for an oxyfuel/co-gasification process (Figure 3a) or a pre-combustion/co-gasification process (Figure 3b). Both schemes differ in the origin of the membrane sweep gas and how the CO₂ separation is accomplished. The permeate gas comprises O₂ and the recirculated gases, generally steam and CO₂ and is fed in the coal/biomass gasifier. The ratio

H₂O/CO₂ should be adjusted to reach the target composition of the treated gasification gases, e.g. the H₂/CO syngas ratio [37]. In general, O₂-steam gasification of biomass based on OTM technology is regarded as a highly efficient process [38]. Other minor components are produced in the gasification, depending on the used fuel, i.e., light hydrocarbons (C₁,C₂), H₂S, SO_x, other acids and ashes and may require an intermediate gas purification (not tackled with this paper).

The highest oxygen permeation fluxes are reported for Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} (BSCF) material [39]. However, this material is specially unstable in CO₂ and SO₂ containing atmospheres due to the formation of carbonates and sulfates leading to a dramatic drop in O₂ flux and loss of membrane integrity [40]. Alternatives to BSCF come from La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-δ} (LSFC) perovskites [41, 42] or alternative NiFe₂O₄ (NFO) - Ce_{0.8}Tb_{0.2}O_{2-δ} (CTO) composites [43], showing better stability to CO₂ and SO₂. Thus, current research focuses on the investigation of different membrane materials and architectures under realistic oxyfuel/gasification conditions and for other target applications.

The experimental part of the present work aims to show different materials and membrane architectures under operating conditions fitting to 4-end mode configuration integrated in oxy-co-gasification processes, i.e., with CO₂ containing sweep gas. Specifically, six different membranes, comprising different materials and architectures, have been selected:

- (i) bulk/monolithic dense Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} (BSCF) self-supported membrane
- (ii) thin dense La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-δ} (LSFC) bare membrane supported on porous freeze-casted LSFC support
- (iii) thin dense La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-δ} (LSFC) activated membrane supported on porous freeze-casted LSFC support
- (iv) thin dense 60% vol. NiFe₂O₄ (NFO) - 40%vol. Ce_{0.8}Tb_{0.2}O_{2-δ} (CTO) (6NF4CT) membrane over a porous freeze-casted LSCF support

- (v) bulk/monolithic dense 60% vol. NiFe_2O_4 - 40%vol. $\text{Ce}_{0.8}\text{Tb}_{0.2}\text{O}_{2-6}$ (6NF4CT) dual-phase self-supported membrane
- (vi) bulk/monolithic dense 40% vol. NiFe_2O_4 - 60%vol. $\text{Ce}_{0.8}\text{Tb}_{0.2}\text{O}_{2-6}$ (4NF6CT) dual-phase self-supported membrane

2. Experimental

Membrane preparation

All membrane samples consisted of gastight 15 mm in diameter disk-shaped specimens. BSCF membrane was obtained by means of powder uniaxial pressing and then sintering at 1100 °C during 2 hours as explained in [28]. As sintered BSCF membrane was then sputter-coated with a 400nm-thick $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ (GDC) protective layer to avoid well known surface carbonation and the possible membrane breakage during the tests.

LSCF thin and $\text{NiFe}_2\text{O}_4\text{-Ce}_{0.8}\text{Tb}_{0.2}\text{O}_{2-6}$ thin dense membranes were deposited over a freeze-casted LSCF monolith following the procedure in [44]. One of the LSCF thin-film supported membrane was subsequently covered by a top catalytic layer of porous screen-printed LSCF for enhancing oxygen electrochemical reaction.

Dual-phase powder compositions $\text{NiFe}_2\text{O}_4\text{-Ce}_{0.8}\text{Tb}_{0.2}\text{O}_{2-6}$ (NFCT) and bulk membranes were obtained following Pechini method as described elsewhere [43]. In addition, both sides of bulk NFCT self-supported membranes were coated with a 30 μm thick screen-printed porous layer of $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}\text{-La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-6}$ (CGO-LSM), infiltrated with Pd nitrate solution, for improving the surface oxygen activation. All membrane specifications are depicted in Table 1, in which the different experimental tests are also described for each membrane.

Oxygen flux measurements

Oxygen permeation studies were carried out in a lab-scale quartz reactor. Synthetic air (21%, vol. O_2 in the feed stream) was fed into the O_2 -rich chamber, while different mixtures of Ar and

CO₂ were used as the sweep gas on the permeate side in a 4-end mode configuration. Both gases were fed at atmospheric pressure. Inlet gases were preheated in order to ensure the correct gas temperature for contact with the membrane surface. The samples consisted of gastight 15 mm diameter disk-shaped membranes and membrane gas leak-free conditions were achieved using gold rings on both sides of the membrane, which were heated to 970 °C for 4 h immediately prior to the measurement. The permeate was analyzed at steady state by online gas chromatography using a micro-GC Varian CP-4900 equipped with Molsieve5A, Poraplot-Q glass capillary, and CP-Sil modules. Membrane gas leak-free conditions were ensured by continuously monitoring the nitrogen concentration in the product gas stream. The data reported here were achieved at steady state after 1 h in the reaction stream. Each test was repeated three times to minimize the analysis error. The experimental analytical error was below 0.5%, whereas the error due to reproduction of experiments is below 3%.

3. Results and discussion.

One of the most critical points for the integration of an OTM module in an oxy-co-gasification power plant, fed with coal/biomass, is the use of the flue gas coming from the gasification unit as sweep stream (Figure 3). Since the main and more critical component of this flue gas is the CO₂ (after proper gas cleaning/drying of the flue gas), it is necessary to evaluate the membrane materials performance and stability under these conditions (i.e. high CO₂ percentages at high temperatures in the range 850-950 °C). Thus, the influence of CO₂ presence in the sweep gas on the permeation behavior through distinct ceramic membranes is investigated. It includes (1) the variation of the CO₂ partial pressure and (2) the study of the time stability under fixed CO₂ content and fixed operation conditions.

Oxygen permeation evolution with temperature

The effect of temperature variation (700-1000 °C) on the oxygen flux for the 6FN4CT_bu membrane (see Table 1 for details), for two sweep gas compositions (Ar and pure CO₂) is

presented in Figure 4. This material has been selected as a promising candidate for 4-end mode OTMs. The flux of oxygen – $J(O_2)$ – is thermally activated (Figure 4) and fits a single Arrhenius behavior. This is the expected trend since $J(O_2)$ in dense bulk MIEC membranes follows Wagner’s equation¹, stating that O_2 permeation is thermally activated. The use of CO_2 as sweep gas improves O_2 separation above 900 °C, whereas the oxygen flux diminished below this temperature. This different behavior depending on the temperature when sweeping with CO_2 can be explained by two phenomena: (i) CO_2 competes with O_2 to adsorb on surface active sites [41, 42, 45], and (ii) CO_2 presents higher thermal emissivity and better sweeping properties than Ar at high temperatures [41, 43, 44, 46, 47]. CO_2 adsorption is exothermic and therefore surface coverage increased with decreasing temperatures. Then a larger active area keeps blocked. At high temperatures, surface exchange, i.e., CO_2 - O_2 competitive adsorption becomes less limiting while CO_2 seems to alleviate polarization concentration in a better way than Ar, thus enhancing oxygen flux values as seen in Figure 4. Taking into account the good performance under pure CO_2 atmosphere, 6NF4CT composite can be considered as a suitable material for its integration in OTM units for oxy-co-gasification process, although $J(O_2)$ optimization is still needed by means of, for instance, decreasing the dense membrane thickness.

Carbon dioxide content variation in sweep gas stream

According to Wagner’s equation, another way to optimize O_2 separation, apart from material selection, involves decreasing membrane thickness. Here, standard membranes present thicknesses of about 1 mm. Membranes in the range of 20-60 μm can also be obtained. This fact implies theoretically an improvement in $J(O_2)$ up to 50-fold when bulk diffusion limits oxygen permeation, i.e., typically at temperatures above 700 °C as it is the case. Thin-film (less

¹ $J_{O_2} = \frac{RT}{16F^2L} \int_{P''_{O_2}}^{P'_{O_2}} \sigma_{amb}(p_{O_2}) d \ln p_{O_2}$, where J_{O_2} is the oxygen permeation flux in $mol \cdot m^{-2} \cdot s^{-1}$, R is the gas constant, F is the Faraday constant, L is the membrane thickness, σ_{amb} is the ambipolar conductivity, and P'_{O_2} and P''_{O_2} are the oxygen partial pressures at the feed side and the permeate side, respectively. Note that typically σ_{amb} is thermally activated following typically an Arrhenius behavior.

than 100 μm) self-supported membranes are very fragile structures. Consequently, thin-film membranes are generally fabricated over porous supports thus resulting in mechanically more stable assemblies when thermo-chemical compatibility is ensured. Therefore, three thin-film membranes were prepared: a 10 μm thick 6NF4CT (6NF4CT_ba) membrane and two 30 μm thick LSCF membranes, one of them with a porous catalytic layer (LSCF_ac) for promoting O_2 permeation. All of these three thin membranes were obtained over porous LSCF supports obtained by means of freeze casting technology[44, 46, 47]. The performance of these membranes under different CO_2 -containing atmospheres was studied at 850 $^\circ\text{C}$ in order to evaluate material behavior in dependence of carbon dioxide content in the sweep gas stream. Thus, different dilutions of CO_2 in Ar were employed in the range 0-100% vol. CO_2 . Figure 5 shows $J(\text{O}_2)$ dependence on CO_2 content in sweep gas at 850 $^\circ\text{C}$ for the three aforementioned thin-film membranes. Moreover, an 800 μm BSCF membrane (BSCF_bu) was added for comparison, as an example of highly CO_2 sensitive material. Under CO_2 -free conditions, BSCF_bu presents a $J(\text{O}_2)$ value of 5 $\text{mL}\cdot\text{min}^{-1}\cdot\text{cm}^{-2}$ at 900 $^\circ\text{C}$, but this rate falls down to 0.07 $\text{mL}\cdot\text{min}^{-1}\cdot\text{cm}^{-2}$ by just adding a 20% CO_2 . For the rest of the materials, O_2 flux drops when increasing CO_2 content at 850 $^\circ\text{C}$, but $J(\text{O}_2)$ is still in the range of 0.6-1.2 $\text{mL}\cdot\text{min}^{-1}\cdot\text{cm}^{-2}$ even under pure CO_2 , which reveals the adequate performance of this material for OTM integration. Furthermore, after testing permeation under 100% CO_2 in sweep, tests under initial conditions (pure Argon as sweep) were repeated resulting in the fact that the initial $J(\text{O}_2)$ value was recovered for all the membranes excepting BSCF_bu, thus proving the stability of these materials in presence of CO_2 but not for the BSCF_bu as previously stated.

Comparing results in Figures 4 and 5 it is possible to analyze the influence of thickness reduction over the oxygen permeation for 6NF4CT membrane. By reducing thickness from 680 μm to 10 μm , O_2 fluxes rise at 850 $^\circ\text{C}$ from 0.071 to 2.46 $\text{mL}\cdot\text{min}^{-1}\cdot\text{cm}^{-2}$ using a CO_2 -free sweep gas, and from 0.063 to 0.64 $\text{mL}\cdot\text{min}^{-1}\cdot\text{cm}^{-2}$ when sweeping with pure CO_2 . This flux

enhancement represents a 35- and 10-fold improvement when reducing the thickness of a stable membrane, when using a CO₂-free or pure CO₂ sweep gas respectively.

CO₂ stability tests

As well as for O₂ flux values under determined conditions, time stability is essential for a suitable material validation. For this purpose, stability tests lasting up to 100 hours were conducted on some membrane architectures. Figure 6 shows the O₂ permeation evolution with time for three different monolithic membranes: BSCF_bu, 6NF4CT_bu and 4NF6NF_bu. The tests were performed at 900 °C and with pure CO₂ as sweep gas for the NFO-CTO composite membranes. BSCF membrane was tested with only 15% CO₂ for a better observation of J(O₂) evolution, since O₂ flux drop at higher CO₂ percentages laid practically within the experimental error, as seen in the evolution of Figure 5. As it can be seen in Figure 6, O₂ flux corresponding to the BSCF_bu membrane drops significantly from 5 to 0.09 mL·min⁻¹·cm⁻², whereas J(O₂) presents only slight variations for the 6NF4CT_bu and 4NF6CT_bu membranes, with a positive change of 1.125·10⁻⁴ (mL·min⁻¹·cm⁻²)·h⁻¹ for the first, and a decay rate of 0.0014 (m·min⁻¹·cm⁻²)·h⁻¹ for the second.

Figure 7 represents the J(O₂) response with time for three thin-film membranes deposited over LSCF porous support when using a 50% CO₂ content stream as sweep. Different temperatures in the range 950-850 °C were considered in order to study CO₂ adsorption dynamics with time and its influence on O₂ permeation. 6NF4CT_ba membrane presents a J(O₂) stabilization at 4.3 mL·min⁻¹·cm⁻² after 100 h of continuous operation at 950 °C. LSCF_ac membrane, with an activation layer, suffers a J(O₂) drop when switching to 50% CO₂ from 4.65 to 2.4 mL·min⁻¹·cm⁻² at 900 °C and after 52 hours. Finally, the non-activated asymmetric LSCF_ba membrane keeps an O₂ flux of 1.26 mL·min⁻¹·cm⁻² after 92 hours, after an initial flux of 2.82 mL·min⁻¹·cm⁻² under CO₂-free conditions.

For all the studied cases, excepting BSCF_bu, it is confirmed that the oxygen permeation remains stable under CO₂-containing environment despite a substantial drop for the LSCF material at 850°C is observed (Figure 7). Furthermore, the high permeation fluxes reached for the thin-film membranes under this harsh environment represent an important step towards the practical application of these membranes in oxy-co-gasification processes.

4. Conclusions

A survey on the integration of oxygen transport membranes (OTM) in different biomass gasification and combustion processes was presented, illustrating the large potential of this technology to increase energy efficiency and to limit CO₂ emissions. OTM are proposed as an alternative for oxygen generation in power plants for adopting carbon capture and sequestration approaches. For coal or biomass gasification purposes, oxygen is needed together with CO₂ and water. This means that flue gas from the gasification unit (or boiler) could serve as a sweep gas for a 4-end ceramic membrane integration, exploiting this waste heat in the OTM module and thus improving thermal efficiency of the process. For that reason, membrane materials should be stable under different CO₂ containing environments and temperatures. Indeed, several advances are still needed regarding materials development, upscaling and module design to achieve sufficient technological and market readiness.

This kind of ceramic materials has been developed for more than 20 years. Promising fluxes and time stability under gasification-like conditions have been achieved and presented in this work with La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} and NiFe₂O₄ - Ce_{0.8}Tb_{0.2}O_{2-δ} membranes. These materials seem suitable for a proper test in an oxy-co-gasification of coal/biomass for power plants. Nevertheless, further work is necessary for the industrial implementation, i.e., the improvement of the O₂ permeation rates through surface promotion, longer term stability evaluation and realistic thermal/stream integration among others. Despite these aspects to

overcome, results presented in this work point a promising milestone on the materials development for OTM technology in the frame of its integration in gasification/combustion processes to increase energy efficiency and minimize CO₂ emissions.

Acknowledgments

Financial support by the Spanish Government (ENE2011-24761 and SEV-2012-0267 grants), by the EU through FP7 GREEN-CC Project (GA 608524), and by the Helmholtz Association of German Research Centers through the Helmholtz Portfolio MEM-BRAIN is gratefully acknowledged.

References

- [1] U.S. Energy-Information-Administration, International Energy Outlook 2013 with Projections to 2040, International Energy Outlook 2013 with Projections to 2040, 2013.
- [2] E.-T.-P.-f.-Z.-E.-.-. Fossil-Fuel-Power-Plants-<http://www.zeroemissionsplatform.eu/carbon-capture-and-storage.html>, <http://www.zeroemissionsplatform.eu/carbon-capture-and-storage.html>, 2014.
- [3] O. Marin, O. Charon, J. Dugue, S. Dukhan, W. Zhou, Simulating the impact of oxygen enrichment in a cement rotary kiln using advanced computational methods, Combust. Sci. Technol., 164 (2001) 193-+.
- [4] E. Amirabedin, D. McIlveen-Wright, A Feasibility Study of Co-Firing Biomass in the Thermal Power Plant at Soma in order to Reduce Emissions: an Exergy Approach, International Journal of Environmental Research, 7 (2013) 139-154.
- [5] S.C. Pickard, S.S. Daood, M. Pourkashanian, W. Nimmo, Co-firing coal with biomass in oxygen- and carbon dioxide-enriched atmospheres for CCS applications, Fuel, 137 (2014) 185-192.
- [6] V. Bertrand, B. Dequiedt, E. Le Cadre, Biomass for electricity in the EU-27: Potential demand, CO₂ abatements and breakeven prices for co-firing, Energy Policy, 73 (2014) 631-644.
- [7] E. Karampinis, P. Grammelis, M. Agraniotis, I. Violidakis, E. Kakaras, Co-firing of biomass with coal in thermal power plants: technology schemes, impacts, and future perspectives, Wiley Interdisciplinary Reviews-Energy and Environment, 3 (2014) 384-399.
- [8] D. Loeffler, N. Anderson, Emissions tradeoffs associated with cofiring forest biomass with coal: A case study in Colorado, USA, Applied Energy, 113 (2014) 67-77.
- [9] A. Valero, S. Usón, Oxy-co-gasification of coal and biomass in an integrated gasification combined cycle (IGCC) power plant, Energy, 31 (2006) 1643-1655.
- [10] R. Castillo, Thermodynamic analysis of a hard coal oxyfuel power plant with high temperature three-end membrane for air separation, Applied Energy, 88 (2011) 1480-1493.
- [11] L.E. Bool, H. Kobayashi, Oxygen separation and combustion apparatus and method. U.S. Patent 6,394,043, 2002.
- [12] L.E. Bool, H. Kobayashi, Method and system for combusting a fuel. U.S. Patent 6,562,104, 2003.
- [13] L. Rosen, N. Degenstein, M. Shah, J. Wilson, S. Kelly, J. Peck, M. Christie, Development of Oxygen Transport Membranes for Coal-Based Power Generation, 10th International Conference on Greenhouse Gas Control Technologies, 4 (2011) 750-755.

- [14] B.R. Kromer, M.M. Litwin, S.M. Kelly, Oxygen transport membrane based advanced power cycle with low pressure synthesis gas slip stream. U.S. Patent 7,856,829, 2014.
- [15] M.M. Shah, A. Jamal, R.F. Dmevich, A. van Hassel, G.M. Christie, H. Kobayashi, L.E. Bool, Electrical power generation apparatus: U.S. Patent 8,196,387, 2012.
- [16] S.M. Kelly, B.R. Kromer, M.M. Litwin, L.J. Rosen, G.M. Christie, J.R. Wilson, L.W. Kosowski, C. Robinson, Synthesis gas method and apparatus. U.S. Patent 8,349,214, 2013.
- [17] D.M. John Repasky, Phillip Armstrong, Michael Carolan, ITM Technology for Carbon Capture on Natural Gas and Hybrid Power Systems, Workshop on Technology Pathways Forward for Carbon Capture & Storage on Natural Gas Power Systems Washington DC, 2014.
- [18] A.L.L. Repasky J.M., Stein V.E., Armstrong P.A., Foster E.P., ITM Oxygen technology: scale-up toward clean energy applications, International Pittsburgh Coal Conference 2012, 2012.
- [19] W.E.W. John M. Repasky, Christopher F. Miller, Michael F. Carolan, David W. Studer, Clifford M. Lowe, Karl F. Gerdes, Joris Smit. , ITM Syngas: Ceramic Membrane Technology for Lower Cost Conversion of Natural Gas, AIChE Spring National Meeting San Antonio, TX, 2010.
- [20] M. Balaguer Ramirez, New solid state oxygen and hydrogen conducting materials. Towards their applications as high temperature electrochemical devices and gas separation membranes, Instituto de Tecnología Química, Universitat Politècnica de València, 2013.
- [21] S. McIntosh, J.F. Vente, W.G. Haije, D.H.A. Blank, H.J.M. Bouwmeester, Oxygen stoichiometry and chemical expansion of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ measured by in situ neutron diffraction, *Chemistry of Materials*, 18 (2006) 2187-2193.
- [22] S. McIntosh, J.F. Vente, W.G. Haije, D.H.A. Blank, H.J.M. Bouwmeester, Structure and oxygen stoichiometry of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$, *Solid State Ionics*, 177 (2006) 1737-1742.
- [23] S. McIntosh, J.F. Vente, W.G. Haije, D.H.A. Blank, H.J.M. Bouwmeester, Phase stability and oxygen non-stoichiometry of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ measured by in situ neutron diffraction, *Solid State Ionics*, 177 (2006) 833-842.
- [24] D.N. Mueller, R.A. De Souza, T.E. Weirich, D. Roehrens, J. Mayer, M. Martin, A kinetic study of the decomposition of the cubic perovskite-type oxide $Ba_xSr_{1-x}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) ($x=0.1$ and 0.5), *Physical Chemistry Chemical Physics*, 12 (2010) 10320-10328.
- [25] M.P. Lobera, J.M. Serra, S.P. Foghmoes, M. Søggaard, A. Kaiser, On the use of supported ceria membranes for oxyfuel process/syngas production, *Journal of Membrane Science*, 385–386 (2011) 154-161.
- [26] I. Garcia-Torregrosa, M.P. Lobera, C. Solis, P. Atienzar, J.M. Serra, Development of CO₂ Protective Layers by Spray Pyrolysis for Ceramic Oxygen Transport Membranes, *Advanced Energy Materials*, 1 (2011) 618-625.
- [27] M. Pilar Lobera, S. Escolastico, J.M. Serra, High Ethylene Production through Oxidative Dehydrogenation of Ethane Membrane Reactors Based on Fast Oxygen-Ion Conductors, *Chemcatchem*, 3 (2011) 1503-1508.
- [28] M. Pilar Lobera, S. Escolastico, J. Garcia-Fayos, J.M. Serra, Ethylene Production by ODHE in Catalytically Modified $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ Membrane Reactors, *Chemsuschem*, 5 (2012) 1587-1596.
- [29] M.P. Lobera, M. Balaguer, J. Garcia-Fayos, J.M. Serra, Rare Earth-doped Ceria Catalysts for ODHE Reaction in a Catalytic Modified MIEC Membrane Reactor, *Chemcatchem*, 4 (2012) 2102-2111.
- [30] W.G. Haije, S.C. Kluiters, R.W. van den Brink, D. Jansen, Systems and materials for mixed ionic electronic conducting membranes in integrated oxyfuel combustion systems, in: J. Gale, C. Hendriks, W. Turkenberg (Eds.) 10th International Conference on Greenhouse Gas Control Technologies 2011, pp. 996-1001.
- [31] S. Engels, F. Beggel, M. Modigell, H. Stadler, Simulation of a membrane unit for oxyfuel power plants under consideration of realistic BSCF membrane properties, *Journal of Membrane Science*, 359 (2010) 93-101.

- [32] S. Engels, T. Markus, M. Modigell, L. Singheiser, Oxygen permeation and stability investigations on MIEC membrane materials under operating conditions for power plant processes, *Journal of Membrane Science*, 370 (2011) 58-69.
- [33] X. Zhu, H. Liu, Y. Cong, W. Yang, Novel dual-phase membranes for CO₂ capture via an oxyfuel route, *Chemical Communications*, 48 (2012) 251-253.
- [34] A. Julbe, D. Farrusseng, C. Guizard, Limitations and potentials of oxygen transport dense and porous ceramic membranes for oxidation reactions, *Catalysis Today*, 104 (2005) 102-113.
- [35] J.S. Brar, K. Singh, J. Wang, S. Kumar, Cogasification of Coal and Biomass: A Review, *International Journal of Forestry Research*, 2012 (2012) 10.
- [36] S.M. Kelly, Praxair's Oxygen Transport Membranes for Oxycombustion and Syngas Applications, 2014.
- [37] C.V. Huynh, S.C. Kong, Performance characteristics of a pilot-scale biomass gasifier using oxygen-enriched air and steam, *Fuel*, 103 (2013) 987-996.
- [38] M. Puig-Arnavat, S. Soprani, M. Sogaard, K. Engelbrecht, J. Ahrenfeldt, U.B. Henriksen, P.V. Hendriksen, Integration of mixed conducting membranes in an oxygen-steam biomass gasification process, *RSC Advances*, 3 (2013) 20843-20854.
- [39] S. Baumann, J.M. Serra, M.P. Lobera, S. Escolastico, F. Schulze-Kueppers, W.A. Meulenbergh, Ultrahigh oxygen permeation flux through supported Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} membranes, *Journal of Membrane Science*, 377 (2011) 198-205.
- [40] J. Yi, M. Schroeder, High temperature degradation of Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} membranes in atmospheres containing concentrated carbon dioxide, *Journal of Membrane Science*, 378 (2011) 163-170.
- [41] J.M. Serra, J. Garcia-Fayos, S. Baumann, F. Schulze-Kueppers, W.A. Meulenbergh, Oxygen permeation through tape-cast asymmetric all-La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} membranes, *Journal of Membrane Science*, 447 (2013) 297-305.
- [42] X. Tan, N. Liu, B. Meng, J. Sunarso, K. Zhang, S. Liu, Oxygen permeation behavior of La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O₃ hollow fibre membranes with highly concentrated CO₂ exposure, *Journal of Membrane Science*, 389 (2012) 216-222.
- [43] M. Balaguer, J. Garcia-Fayos, C. Solis, J.M. Serra, Fast Oxygen Separation Through SO₂- and CO₂-Stable Dual-Phase Membrane Based on NiFe₂O₄-Ce_{0.8}Tb_{0.2}O_{2-δ}, *Chemistry of Materials*, 25 (2013) 4986-4993.
- [44] C. Gaudillere, J. Garcia-Fayos, J. Serra, Enhancing oxygen permeation through hierarchically-structured perovskite membranes elaborated by freeze-casting, *Journal of Materials Chemistry A*, (2013).
- [45] V.B. Vert, J.M. Serra, Study of CO₂ stability and electrochemical oxygen activation of mixed conductors with low thermal expansion coefficient based on the TbBaCo₃ZnO_{7+δ} system, *Journal of Power Sources*, 196 (2011) 4270-4276.
- [46] C. Gaudillere, J. Garcia-Fayos, M. Balaguer, J.M. Serra, Enhanced Oxygen Separation through Robust Freeze-Cast Bilayered Dual-Phase Membranes, *Chemsuschem*, 7 (2014) 2554-2561.
- [47] C. Gaudillere, J. Garcia-Fayos, J.M. Serra, Oxygen Permeation Improvement under CO₂-Rich Environments through Catalytic Activation of Hierarchically Structured Perovskite Membranes, *ChemPlusChem*, (2014) n/a-n/a.

Tables

Table 1. List of the selected membranes and the experimental tests performed on them

Membrane	Dense layer Thickness (μm)	Extra layer	Support	T ($^{\circ}\text{C}$)		t (h) / % CO_2 900 $^{\circ}\text{C}$	T ($^{\circ}\text{C}$) / t (h) 50 % CO_2
				0%, 100% CO_2	0-100 % CO_2		
BSFC_bu	BSCF 800	GDC protective	---	---	900	24 / 15	---
LSCF_ba	LSCF 30	---	LSCF freeze-cast	---	850	---	850 / 92
LSCF_ac	LSCF 30	LSCF porous	LSCF freeze-cast	---	850	---	900 / 52
6NF40CT_ba	60%NFO-40%CTO 10	---	LSCF freeze-cast	---	850	---	950 / 100
6NF40CT_bu	60%NFO-40%CTO 680	---	---	700 - 1000	---	80 / 100	---
4NF6CT_bu	40%NFO-60%CTO 770	---	---	---	--	100 / 100	---

Figure captions

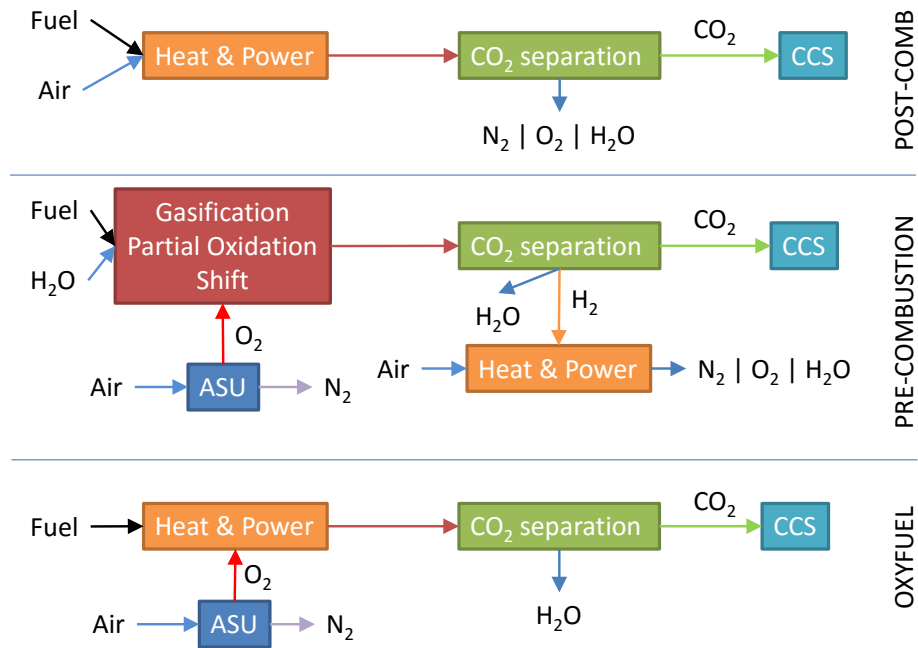


Figure 1. Different approaches for the implementation of Carbon Capture and Sequestration (CCS) in a power plant.

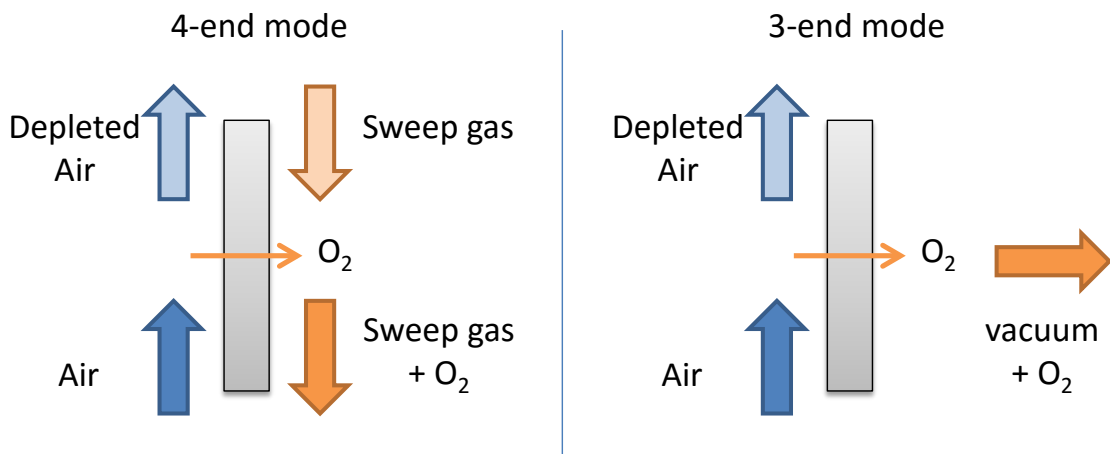


Figure 2. Schematic diagrams of the two different modes of operation for oxygen transport membranes: (left) 4-end and (right) 3-end modes.

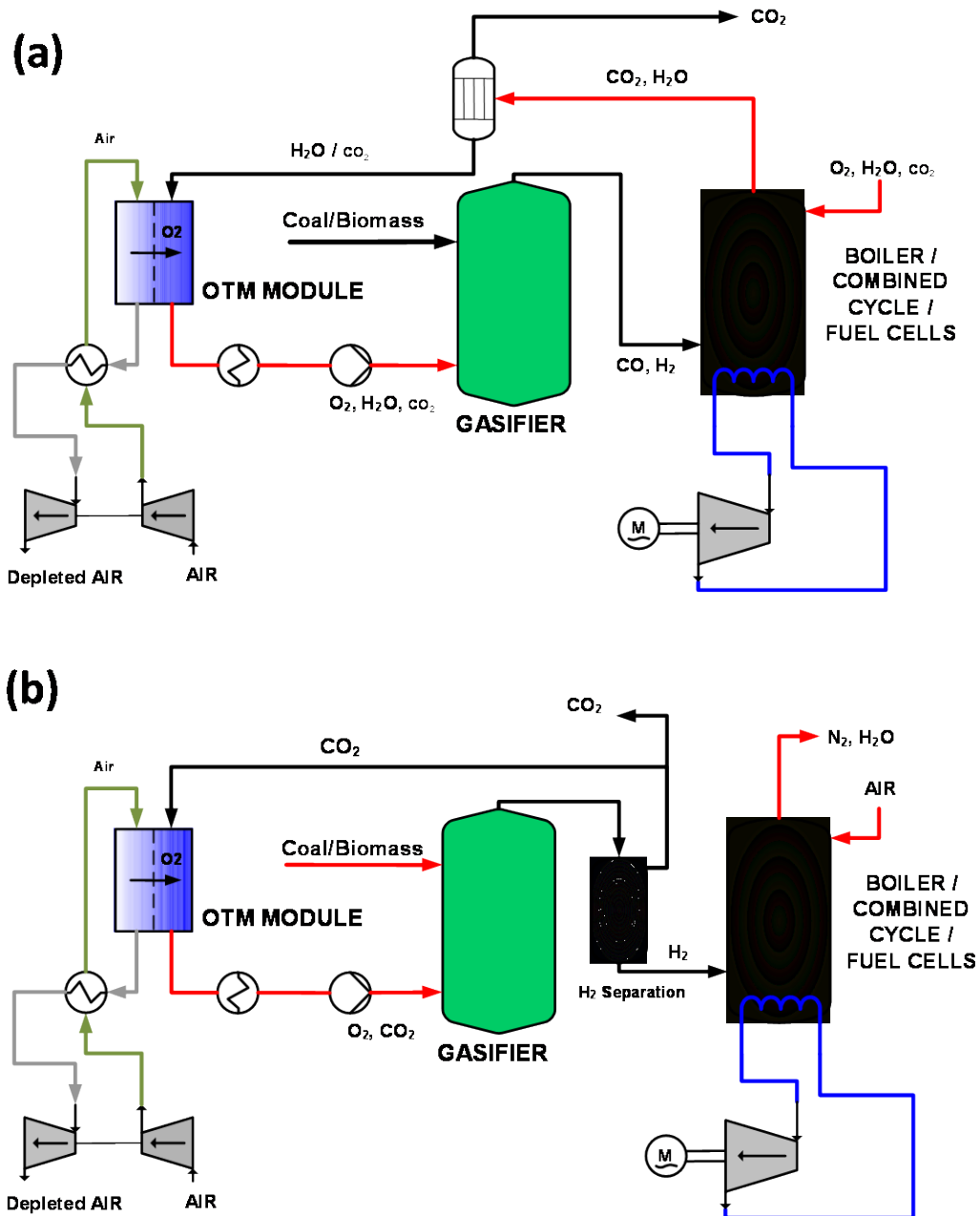


Figure 3. Simplified process layouts for oxygen permeating membrane module integrated in a biomass/coal oxy-co-gasification power plant with CCS: (a) based on oxyfuel or (b) pre-combustion approach.

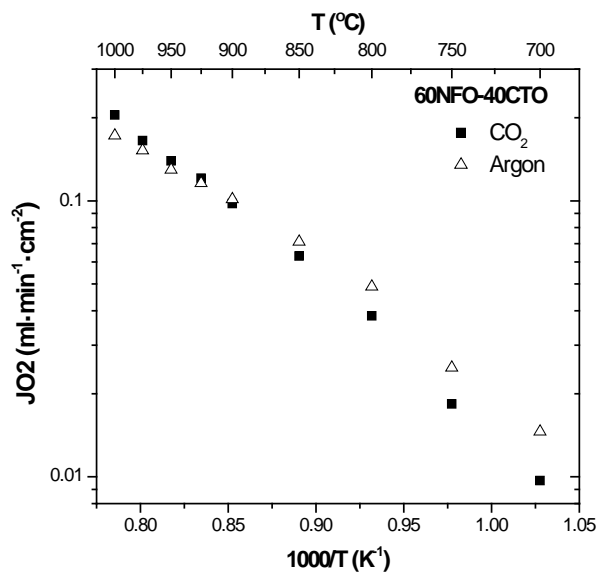


Figure 4. Variation of O₂ flux as a function of temperature for different sweep stream compositions for the 6NF4CT_bu membrane.

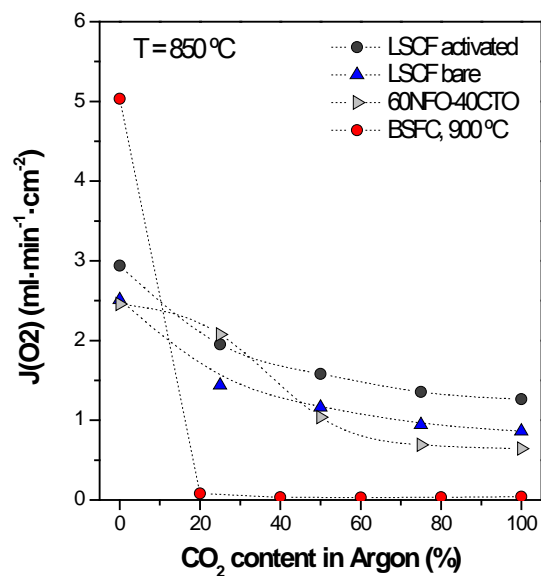


Figure 5. Oxygen flux of different supported membranes depending on the CO₂ content in the sweep gas at 850 °C. BSFC_bu membrane at 900 °C is plot for comparison.

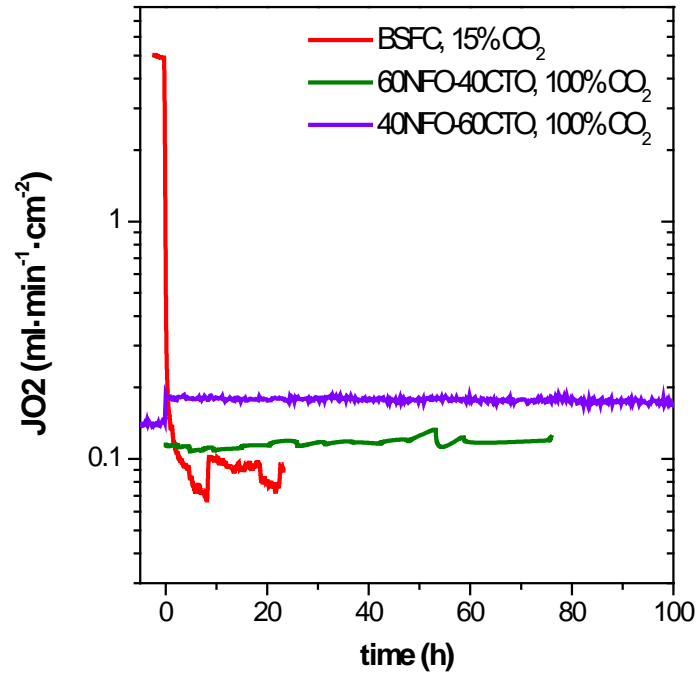


Figure 6. Time stability for selected monolithic membranes at 900 °C under CO₂rich gas environments.

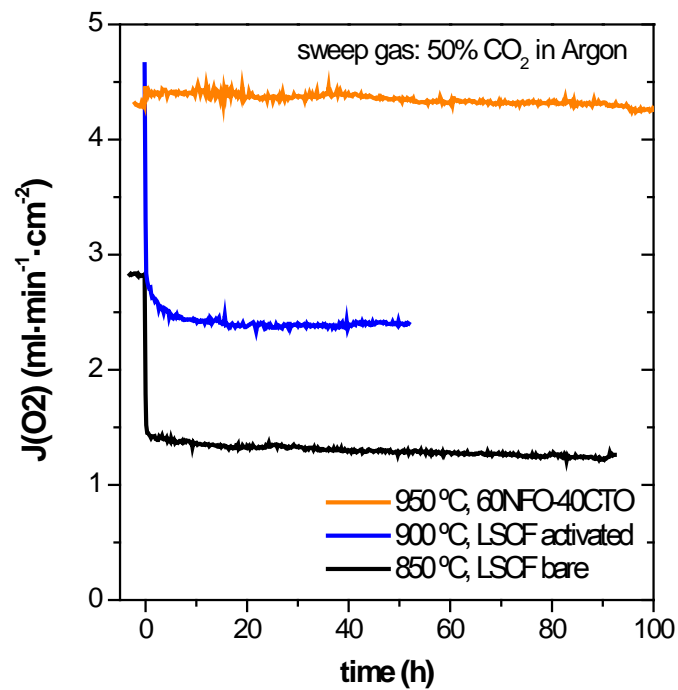


Figure 7. Time stability for thin-film membranes at different temperatures under 50% CO₂ containing sweep gas.