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Additional Information

## **Oxygen Transport Membranes in a biomass/coal combined strategy for reducing CO<sub>2</sub> emissions: Permeation study of selected membranes under different CO<sub>2</sub>-rich atmospheres**

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### **Abstract**

This contribution introduces how the integration of biomass as fuel in power plants would balance CO<sub>2</sub> emissions and the related role of oxygen transport membranes (OTM) on it. CO<sub>2</sub> capture techniques could be introduced to minimize CO<sub>2</sub> emissions at the cost of a substantial energy penalty in the overall process. Among the different approaches, the use of pure O<sub>2</sub> and/or N<sub>2</sub>-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 CO<sub>2</sub> capture is implemented. Further, this work reviews how selected ceramic materials and membrane architectures behave under CO<sub>2</sub> 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<sup>-1</sup>·cm<sup>-2</sup> when using 100% CO<sub>2</sub> 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<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub> and NiFe<sub>2</sub>O<sub>4</sub> - Ce<sub>0.8</sub>Tb<sub>0.2</sub>O<sub>2-δ</sub> composite materials showed the best results for oxygen permeation and time stability under CO<sub>2</sub>-rich atmospheres.

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

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## 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 CO<sub>2</sub> will contribute, even more, to the global greenhouse gases concentration in the atmosphere.

The Zero Emission Platform (ZEP) has challenged the reduction of CO<sub>2</sub> 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 CO<sub>2</sub> emissions produced by the largest producers.

CCS is an energy intensive approach in which CO<sub>2</sub> 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 CO<sub>2</sub> 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 O<sub>2</sub> 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 O<sub>2</sub>-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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub>-separation plants, typically amine washing or calcium looping process, in which CO<sub>2</sub> is absorbed on the amines or calcium and then thermally desorbed to regenerate amine/calcium carrier and produce CO<sub>2</sub>. 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 H<sub>2</sub> and CO<sub>2</sub>, 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 O<sub>2</sub> 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 O<sub>2</sub> 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 O<sub>2</sub> 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 O<sub>2</sub> 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 O<sub>2</sub> (corresponding to an IGCC output of 12 MW) is being developed. Simultaneously, a

2000 TPD O<sub>2</sub> 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 O<sub>2</sub> 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, CO<sub>2</sub> 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 CO<sub>2</sub> separation is accomplished. The permeate gas comprises O<sub>2</sub> and the recirculated gases, generally steam and CO<sub>2</sub> and is fed in the coal/biomass gasifier. The ratio

H<sub>2</sub>O/CO<sub>2</sub> should be adjusted to reach the target composition of the treated gasification gases, e.g. the H<sub>2</sub>/CO syngas ratio [37]. In general, O<sub>2</sub>-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 (C<sub>1</sub>,C<sub>2</sub>), H<sub>2</sub>S, SO<sub>x</sub>, 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<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3-δ</sub> (BSCF) material [39]. However, this material is specially unstable in CO<sub>2</sub> and SO<sub>2</sub> containing atmospheres due to the formation of carbonates and sulfates leading to a dramatic drop in O<sub>2</sub> flux and loss of membrane integrity [40]. Alternatives to BSCF come from La<sub>0.6</sub>Sr<sub>0.4</sub>Fe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3-δ</sub> (LSFC) perovskites [41, 42] or alternative NiFe<sub>2</sub>O<sub>4</sub> (NFO) - Ce<sub>0.8</sub>Tb<sub>0.2</sub>O<sub>2-δ</sub> (CTO) composites [43], showing better stability to CO<sub>2</sub> and SO<sub>2</sub>. 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 CO<sub>2</sub> containing sweep gas. Specifically, six different membranes, comprising different materials and architectures, have been selected:

- (i) bulk/monolithic dense Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3-δ</sub> (BSCF) self-supported membrane
- (ii) thin dense La<sub>0.6</sub>Sr<sub>0.4</sub>Fe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3-δ</sub> (LSFC) bare membrane supported on porous freeze-casted LSFC support
- (iii) thin dense La<sub>0.6</sub>Sr<sub>0.4</sub>Fe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3-δ</sub> (LSFC) activated membrane supported on porous freeze-casted LSFC support
- (iv) thin dense 60% vol. NiFe<sub>2</sub>O<sub>4</sub> (NFO) - 40%vol. Ce<sub>0.8</sub>Tb<sub>0.2</sub>O<sub>2-δ</sub> (CTO) (6NF4CT) membrane over a porous freeze-casted LSCF support

- (v) bulk/monolithic dense 60% vol.  $\text{NiFe}_2\text{O}_4$  - 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.  $\text{NiFe}_2\text{O}_4$  - 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  $\mu\text{m}$  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.  $\text{O}_2$  in the feed stream) was fed into the  $\text{O}_2$ -rich chamber, while different mixtures of Ar and

CO<sub>2</sub> 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, Pora-Plot-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 CO<sub>2</sub> (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 CO<sub>2</sub> percentages at high temperatures in the range 850-950 °C). Thus, the influence of CO<sub>2</sub> presence in the sweep gas on the permeation behavior through distinct ceramic membranes is investigated. It includes (1) the variation of the CO<sub>2</sub> partial pressure and (2) the study of the time stability under fixed CO<sub>2</sub> 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 CO<sub>2</sub>) 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 equation<sup>1</sup>, 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  $\mu m$  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

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<sup>1</sup>  $J_{O_2} = \frac{RT}{16F^2L} \int_{P''_{O_2}}^{P'_{O_2}} \sigma_{amb}(p_{O_2}) d \ln p_{O_2}$ , 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,  $\sigma_{amb}$  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  $\sigma_{amb}$  is thermally activated following typically an Arrhenius behavior.

than 100  $\mu\text{m}$ ) 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  $\mu\text{m}$  thick 6NF4CT (6NF4CT\_ba) membrane and two 30  $\mu\text{m}$  thick LSCF membranes, one of them with a porous catalytic layer (LSCF\_ac) for promoting  $\text{O}_2$  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  $\text{CO}_2$ -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  $\text{CO}_2$  in Ar were employed in the range 0-100% vol.  $\text{CO}_2$ . Figure 5 shows  $J(\text{O}_2)$  dependence on  $\text{CO}_2$  content in sweep gas at 850  $^\circ\text{C}$  for the three aforementioned thin-film membranes. Moreover, an 800  $\mu\text{m}$  BSCF membrane (BSCF\_bu) was added for comparison, as an example of highly  $\text{CO}_2$  sensitive material. Under  $\text{CO}_2$ -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%  $\text{CO}_2$ . For the rest of the materials,  $\text{O}_2$  flux drops when increasing  $\text{CO}_2$  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  $\text{CO}_2$ , which reveals the adequate performance of this material for OTM integration. Furthermore, after testing permeation under 100%  $\text{CO}_2$  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  $\text{CO}_2$  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  $\mu\text{m}$  to 10  $\mu\text{m}$ ,  $\text{O}_2$  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  $\text{CO}_2$ -free sweep gas, and from 0.063 to 0.64  $\text{mL}\cdot\text{min}^{-1}\cdot\text{cm}^{-2}$  when sweeping with pure  $\text{CO}_2$ . This flux

enhancement represents a 35- and 10-fold improvement when reducing the thickness of a stable membrane, when using a CO<sub>2</sub>-free or pure CO<sub>2</sub> sweep gas respectively.

### **CO<sub>2</sub> stability tests**

As well as for O<sub>2</sub> 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 O<sub>2</sub> 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 CO<sub>2</sub> as sweep gas for the NFO-CTO composite membranes. BSCF membrane was tested with only 15% CO<sub>2</sub> for a better observation of J(O<sub>2</sub>) evolution, since O<sub>2</sub> flux drop at higher CO<sub>2</sub> percentages laid practically within the experimental error, as seen in the evolution of Figure 5. As it can be seen in Figure 6, O<sub>2</sub> flux corresponding to the BSCF\_bu membrane drops significantly from 5 to 0.09 mL·min<sup>-1</sup>·cm<sup>-2</sup>, whereas J(O<sub>2</sub>) presents only slight variations for the 6NF4CT\_bu and 4NF6CT\_bu membranes, with a positive change of 1.125·10<sup>-4</sup> (mL·min<sup>-1</sup>·cm<sup>-2</sup>)·h<sup>-1</sup> for the first, and a decay rate of 0.0014 (m·min<sup>-1</sup>·cm<sup>-2</sup>)·h<sup>-1</sup> for the second.

Figure 7 represents the J(O<sub>2</sub>) response with time for three thin-film membranes deposited over LSCF porous support when using a 50% CO<sub>2</sub> content stream as sweep. Different temperatures in the range 950-850 °C were considered in order to study CO<sub>2</sub> adsorption dynamics with time and its influence on O<sub>2</sub> permeation. 6NF4CT\_ba membrane presents a J(O<sub>2</sub>) stabilization at 4.3 mL·min<sup>-1</sup>·cm<sup>-2</sup> after 100 h of continuous operation at 950 °C. LSCF\_ac membrane, with an activation layer, suffers a J(O<sub>2</sub>) drop when switching to 50% CO<sub>2</sub> from 4.65 to 2.4 mL·min<sup>-1</sup>·cm<sup>-2</sup> at 900 °C and after 52 hours. Finally, the non-activated asymmetric LSCF\_ba membrane keeps an O<sub>2</sub> flux of 1.26 mL·min<sup>-1</sup>·cm<sup>-2</sup> after 92 hours, after an initial flux of 2.82 mL·min<sup>-1</sup>·cm<sup>-2</sup> under CO<sub>2</sub>-free conditions.

For all the studied cases, excepting BSCF\_bu, it is confirmed that the oxygen permeation remains stable under CO<sub>2</sub>-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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub> and NiFe<sub>2</sub>O<sub>4</sub> - Ce<sub>0.8</sub>Tb<sub>0.2</sub>O<sub>2-δ</sub> 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 O<sub>2</sub> 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 CO<sub>2</sub> emissions.

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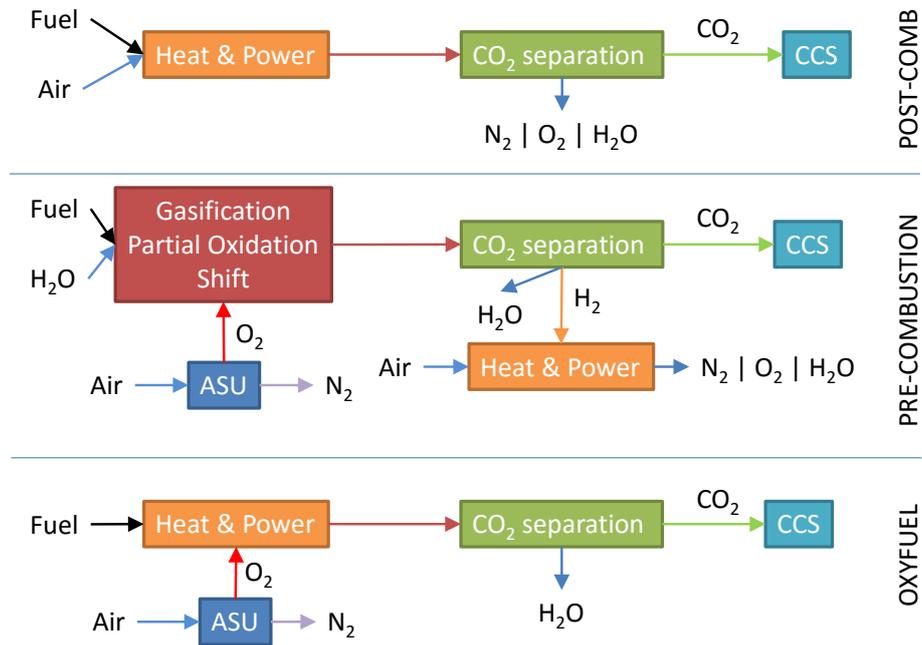
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## Tables

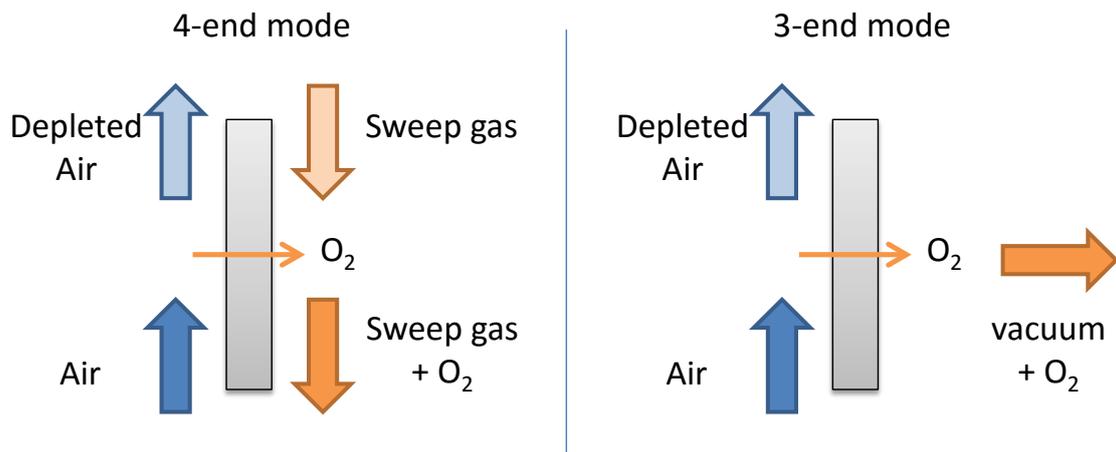
Table 1. List of the selected membranes and the experimental tests performed on them

Membrane	Dense layer Thickness ( $\mu\text{m}$ )	Extra layer	Support	T ( $^{\circ}\text{C}$ )		t (h) / % $\text{CO}_2$ 900 $^{\circ}\text{C}$	T ( $^{\circ}\text{C}$ ) / t (h) 50 % $\text{CO}_2$
				0%, 100% $\text{CO}_2$	0-100 % $\text{CO}_2$		
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	---

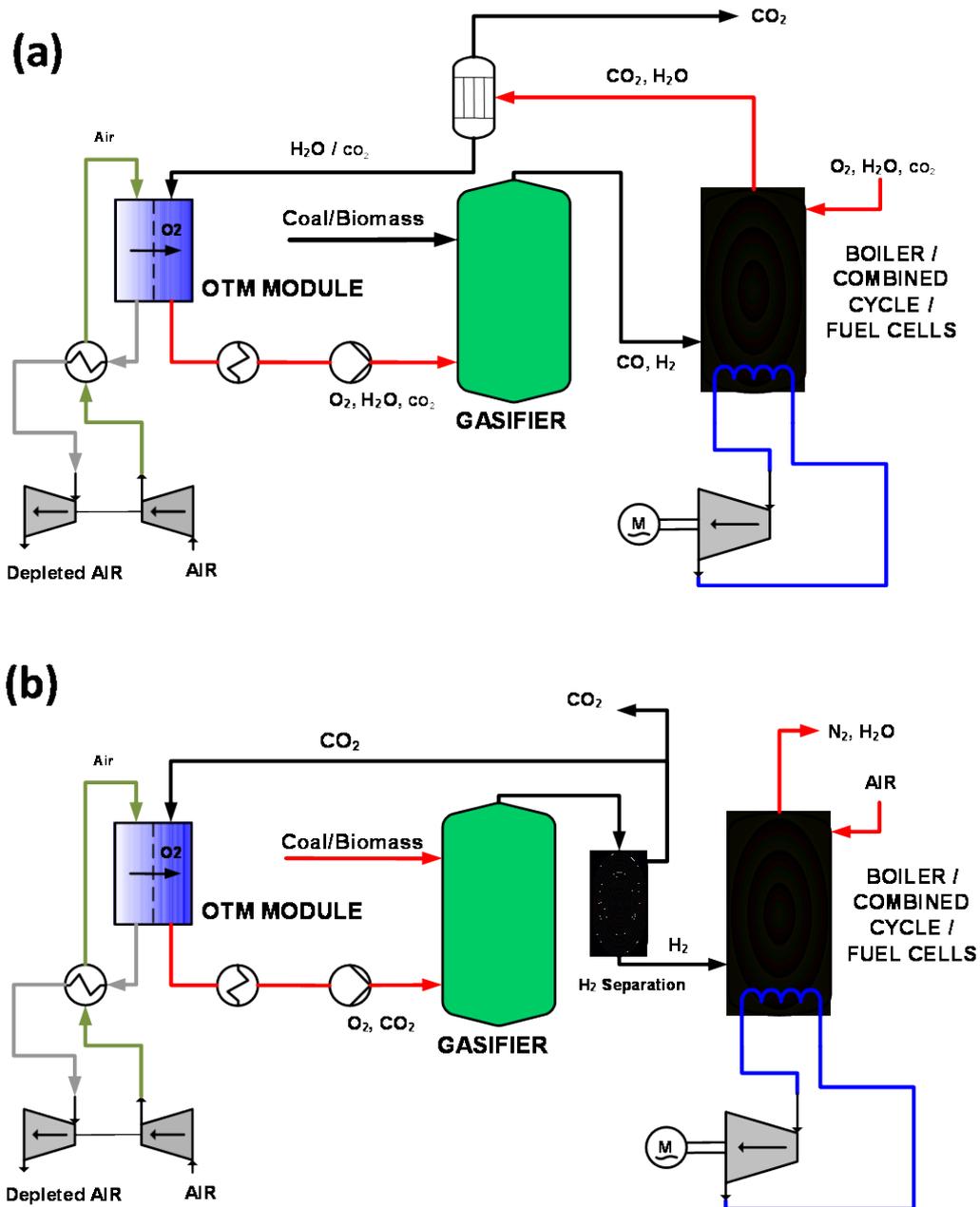
**Figure captions**



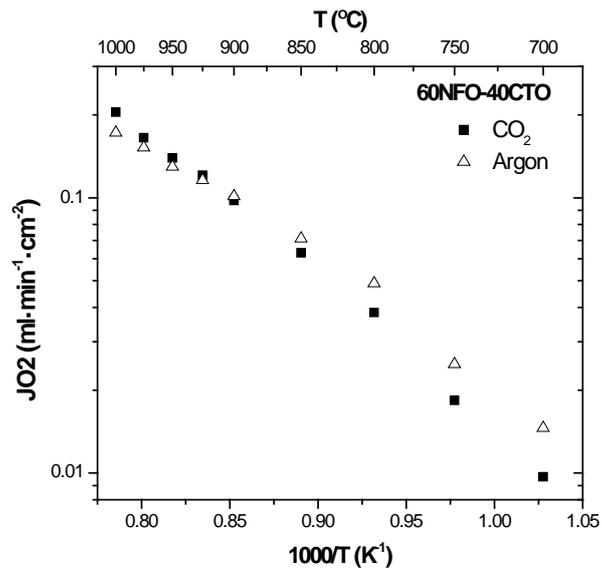
**Figure 1.** Different approaches for the implementation of Carbon Capture and Sequestration (CCS) in a power plant.



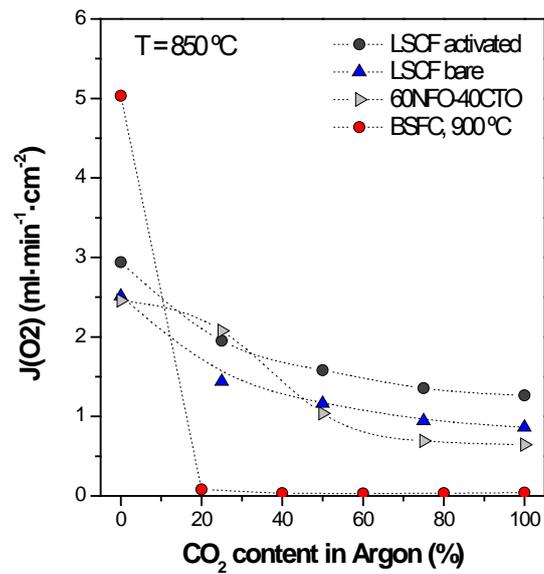
**Figure 2.** Schematic diagrams of the two different modes of operation for oxygen transport membranes: (left) 4-end and (right) 3-end modes.



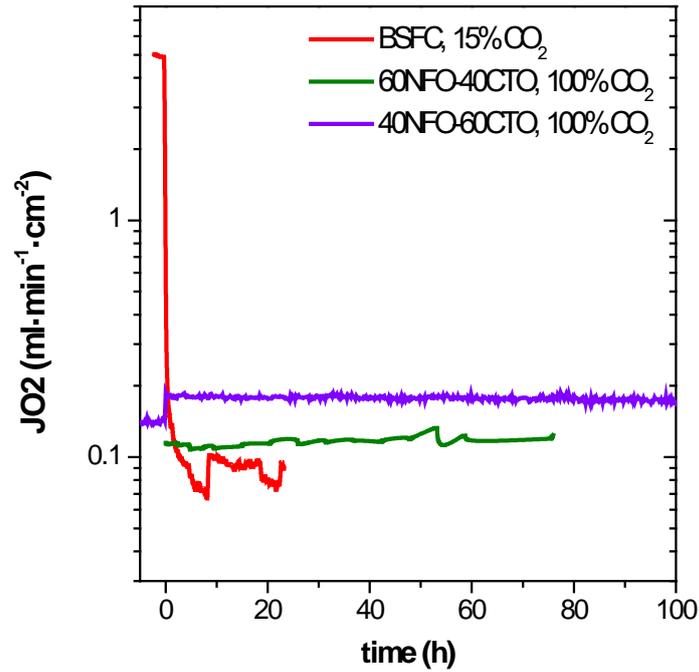
**Figure 3.** Simplified process layouts for oxygen permeating membrane module integrated in a biomass/coal oxy-co-gasification power plant with CCS: (a) based on oxyfuel or (b) pre-combustion approach.



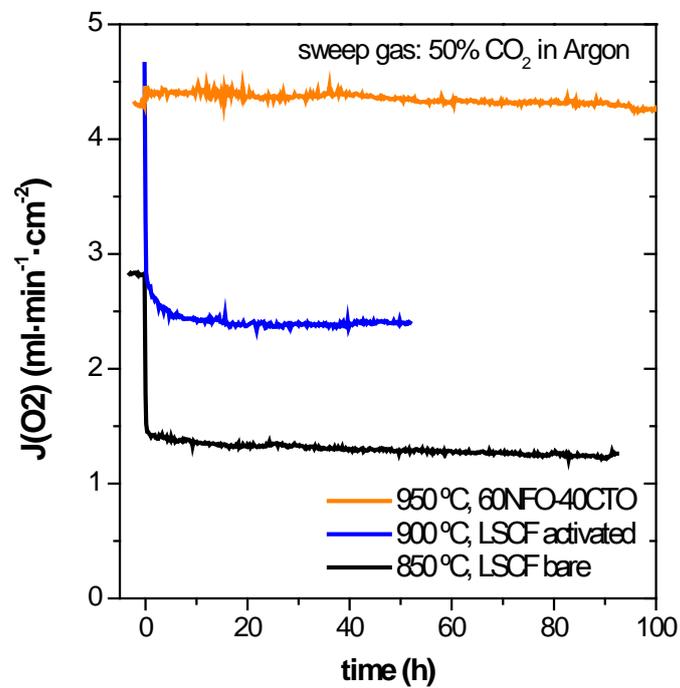
**Figure 4.** Variation of O<sub>2</sub> flux as a function of temperature for different sweep stream compositions for the 6NF4CT\_bu membrane.



**Figure 5.** Oxygen flux of different supported membranes depending on the CO<sub>2</sub> 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 CO<sub>2</sub>rich gas environments.



**Figure 7.** Time stability for thin-film membranes at different temperatures under 50% CO<sub>2</sub> containing sweep gas.