Executive summary

Membranes for oxygen and hydrogen separation are expected to play a key-role in the development of CO_2 emission-free coal or natural gas power plants. Moreover, cost-effective oxygen and hydrogen production processes are needed in gas supply industry. Therefore world-wide R&D activities are focused on the development of cost-effective membranes, with higher permeability and long-term stability in the operating environment. In this frame the main objective of DEMOYS is the development of thin mixed conducting membranes for O_2 and H_2 separation by using a new deposition technique "Low Pressure Plasma Spray – Thin Film" (**PS-TF**) in combination with nano-porous, highly catalytic layers. PS-TF is a proprietary technology developed by Sulzer-Metco, which stands between the conventional thin film technologies, such as Physical Vapour Deposition (PVD) and Chemical Vapour Deposition (CVD), and the conventional thermal spray technologies. The PS-TF process, by operating at pressures below 2 mbar, allows the cost-effective production of thin, dense coatings on large areas at low substrate temperatures.

The first part of the project has been mainly focused on material and process development, in order to evaluate the feasibility of preparing dense membranes by using the **PS-TF** process, while in the second part membranes were tested in laboratory pilot loop and their potential for integration in power plant with CCS has been assessed.

More in detail, Lanthanum-Strontium-Cobalt-Iron oxide **(LSCF)** and Lanthanum Wolfram Oxide **(LWO)** have been selected as reference materials for O_2 and H_2 separation membranes, respectively. Several batches of powders of these materials with physico-chemical characteristics suitable for the PS-TF process have been manufactured. Deposition tests with these powders have been performed on planar ceramic and metallic porous support materials. Best results have been obtained with LSCF powders on metallic supports and, therefore, development has been focused on such a type of membrane. Moreover membrane testing evidenced that the development of a support with proper characteristics is a key issue in order to obtain a dense and stable membrane. To this purpose a porous material based on a NiCoCrAlY-alloy has been developed and manufactured by gravity sintering. Dense and stable LSCF membranes, 50 micron thick, have been obtained on such a support, properly modified with a LSCF functional porous layer. These membranes have been tested at lab level and, in addition to high selectivity and stability at temperature, showed remarkably high permeation rates: **a maximum oxygen flux of 5.29 ml·min^{-1}·cm^{-2} was obtained at 1000 ºC, establishing an outstanding result within the field of LSCF supported membranes.**

A modelling study concerning the integration of the developed membranes in power generation and/or hydrogen production plants has been performed. This study has provided inputs for process scale-up and cost evaluation in selected plant configurations in order to approach zero CO_2 emission and minimize CO_2 capture cost. More in detail the cost estimate of electricity and CO_2 capture has been focused on oxygen transport membranes (OTM) in coal-based power plants. The primary conclusion is that their integration in power plants with low carbon emissions has the potential to be more cost effective than benchmark plants using the leading CO_2 capture technologies. The capital cost of an OTM-based unit is from about 20% to 35% lower than the equivalent cost of standard cryogenic Air Separation Unit, respectively for IGCC and CFB power plants. The Levelized Cost of Electricity (LCOE) and the CO_2 avoidance cost (CAC) of the OTM-based plants are lower than those of plants using benchmark CO_2 capture technologies. This is particularly evident for the CFB-based plants, for which the LCOE and the CAC are respectively 12% and 27% lower than the reference oxy-combustion plant with CO_2 cryogenic purification unit. Additionally, the use of OTM in niche applications, i.e. oxygen and electric power co-production in plants with micro-gas turbine generators, has been assessed. Results indicates that OTM-based plants have the potential to be more cost effective than benchmark Pressure Swing Adsorption (PSA) or Vacuum Swing Adsorption (VSA) plants.

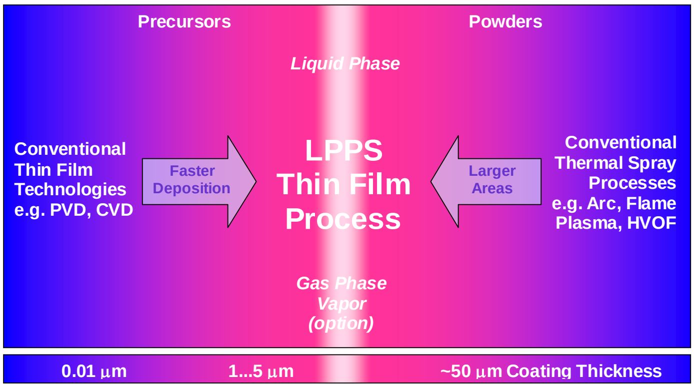
Summary description of project context and objectives

Membranes for oxygen and hydrogen separation are expected to play a key-role in the development of CO_2 emission-free coal or natural gas power plants. In addition, cost-effective oxygen and hydrogen production processes are needed in gas supply industry.
The most promising oxygen membranes are based on mixed ionic electronic conducting oxides such as perovskites which give sufficiently high oxygen fluxes only at high temperatures (>750°C). Similarly ceramic-metal materials (cermets) have been recently studied in order to obtain H_2 separation from CO_2 in reforming and Water Gas Shift (WGS) reactors. However the above membranes, which are usually produced by sintering techniques using ceramic cylindrical porous substrates, are not able to meet the requirements for an economical use because of the high costs in combination with limited permeability values and long-term stability in the operating environment. Hence, world-wide activities are focused on the development of more efficient membranes in combination with cost-effective supporting concepts.

More specifically, an increase in membrane permeation can be achieved by two routes:

- reduction of the membrane thickness;
- improvement of the catalytic performance of the membrane surface where adsorption, dissociation, and reduction of oxygen (hydrogen) and the charge transfer takes place and become rate limiting.

The main objective of this project is, therefore, the development of thin mixed conducting membranes for O_2 and H_2 separation by using a new deposition technique “Low Pressure Plasma Spray – Thin Film” (PS-TF) in combination with nano-porous, highly catalytic layers.



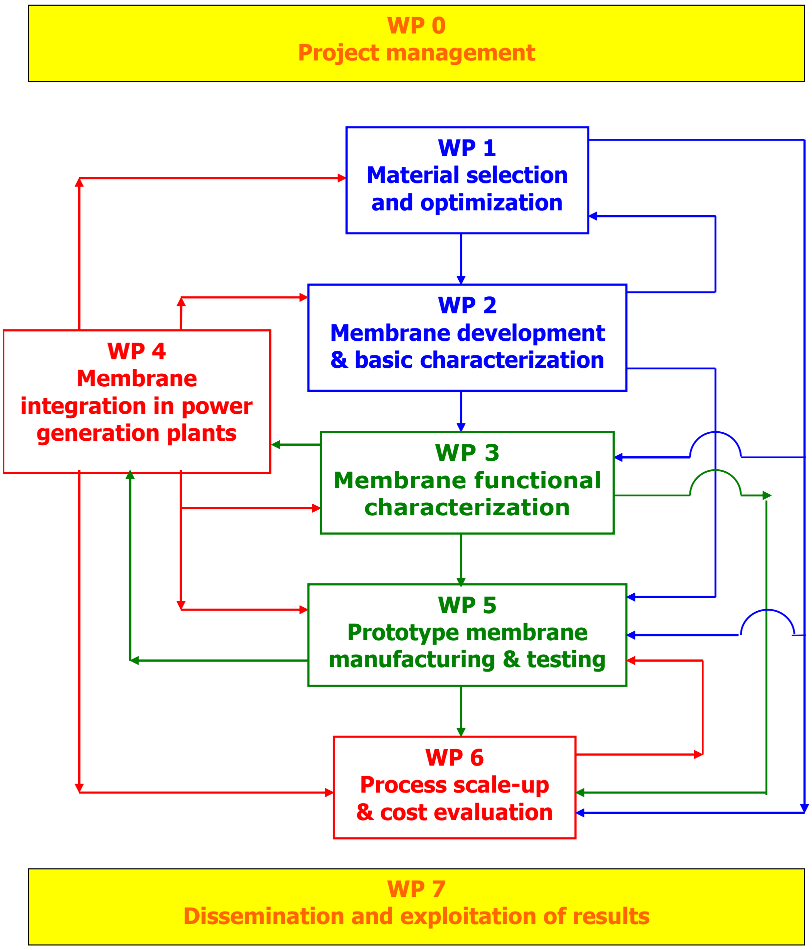
PS-TF is a proprietary technology developed by Sulzer, which stands between the conventional thin film technologies, such as PVD and CVD, and the conventional thermal spray technologies.
The PS-TF process, by operating at pressures below 2 mbar, allows the cost-effective production of **thin and dense ceramic or metallic coatings.** Furthermore, the lower working pressure of PS-TF allows **covering large areas** with relatively thin and homogenous layers resulting from the broad spray pattern and fast sweeping gun motion. Typically, an area of 1 m^2 can be coated with 10 µm thick ceramic layer in about 1 minute.
By using the PS-TF process, a dense, stable deposit with thickness lower than 50 micron can be obtained. This would allow increasing membrane performances while decreasing their manufacturing costs. Catalytic layers will be also applied to enhance the surface reactions becoming rate limiting for thin membranes.
Membrane performances will be assessed in pilot loops in order to meet specific targets in terms of permeability and stability at high temperature. A modelling study concerning the integration of the developed membranes in power generation and/or hydrogen production plants will be also performed. This will provide inputs for process scale-up and cost evaluation in the selected plant configurations in order to approach zero CO_2 emission and a CO_2 capture cost of 15 €/ton.

The development of DEMOYS membranes can lead to following main impacts:

- **A remarkable reduction of the cost of carbon capture in power and/or H_2 generation plants.** Compared to the technologies currently adoptable, a cut in the cost of CO_2 capture can be achieved by membranes because of a simultaneous increase of plant energy efficiency and a reduction of plant capital investment.

- **Increase the competitiveness of European Industry**. Low Pressure Plasma Spray – Thin Film (PS-TF) is a proprietary technology developed by a European company (Sulzer Metco). Therefore the successful development of O_2 and H_2 membranes by the PS-TF process can be an important step in reducing the gap with the USA industry which has a leading position in this field.

R&D activities of DEMOYS are developed in six work packages as shown in the diagram below.



The first part of the project (WP1-4) is mainly focused on development of materials and process, in order to evaluate the feasibility of preparing dense membranes for O_2 and H_2 separation by using the Low Pressure Plasma Spray – Thin Film (**PS-TF**) process and evaluating their integration in power generation and/or hydrogen production plants

The second phase is more focused on application in operating environment and on process scale-up and cost evaluation.

Specific WP's for dissemination and exploitation of project results **(WP7)** and for project management and coordination (WP0) are also foreseen.

Description of main S&T results and foreground

Material selection and optimization (WP1)

The objective of this WP is the selection, manufacture and characterization of powders and porous membrane supports to be used for deposition with PS-TF process.
$La_{0.58}Sr_{0.40}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) and $La_{5.5}WO_{12}$ (LWO) have been selected as reference materials for O_2 and H_2 separation membranes, respectively.
Several batches of LSCF and LWO powders have been manufactured by Sulzer in a prototype plant (up to 50 kg for a single batch). The main steps of the manufacturing process are shown in fig. 1.
The raw materials were sourced using the usual supply chain of Sulzer Metco and specifications were kept within conventional industry standards, to ensure that any developed material can be successfully up-scaled for viable industrial production.

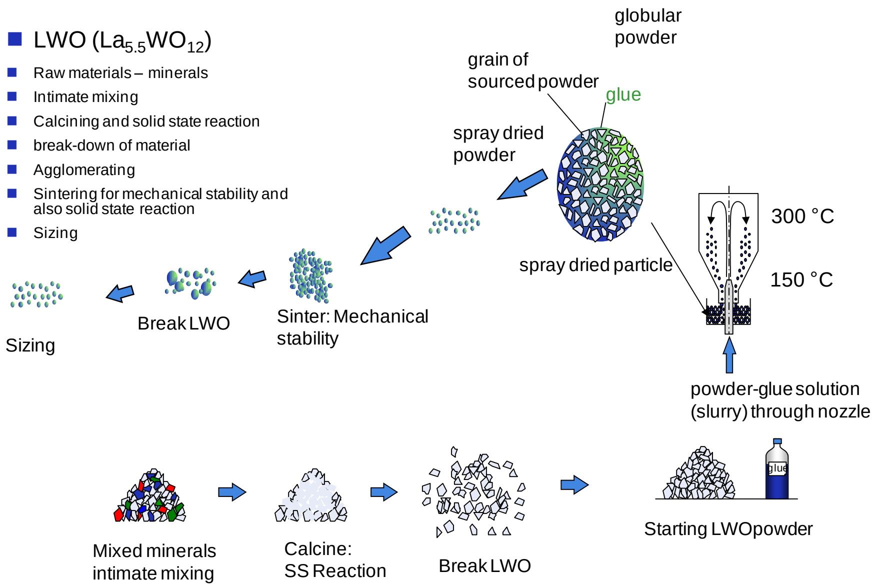
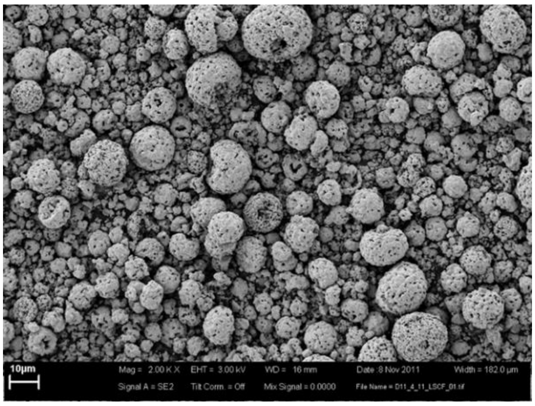


Fig. 1 Main step of the manufacturing process of powders suitable for PS-TF process.

ICP and XFS have been used to determine the elemental composition of the powders, while structural and morphological characterization has been carried out by XRD and SEM analysis. Results indicate that synthesized powders meet specification requirements for the PS-TF process in terms of average particle size and particle size distribution, and show sufficient phase purity (fig. 2).



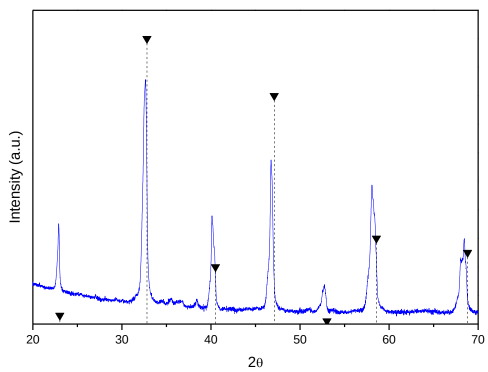


Fig. 2 SEM micrograph (left) and XRD pattern (right) of LSCF powders manufactured by Sulzer. Triangle symbols show the reported diffraction peaks in the reference LSCF pattern.

An improved formulation for LSCF powders (selective doping with Cu) has been defined and synthetized by ETHZ. The introduction of Cu in the LSCF helps to get a more stable perovskite with cubic phase (beneficial to avoid crack formation in heating/cooling cycles). Moreover, Cu^{2+} substitution on the B-site of the perovsikte (instead of Co and Fe that exhibit effective charge between 4+ and 2+) is expected to generate oxygen vacancies and be beneficial for the oxygen transport through the membrane.
Concerning LWO, DC conductivity measurements using the 4-probe bar configuration have been also performed in hydrogen as a function of temperature, at CSIC laboratories. Results indicate that the synthesized powders are good proton conductors and present certain electronic conductivity while they remain structurally stable in wet CO_2 at high temperatures.

Regarding membrane supports, a planar geometry has been chosen: porous disks up to 11 cm in diameter have been manufactured and used for deposition tests. Both metallic and ceramic materials have been initially considered.

Several porous ceramic materials (magnesium oxide, alumina, two compositions of zirconia yttria with a top layer of cerium gadolinium oxide[1]) have been manufactured by CTIsa. Deposition tests, however, haven't been successful since cracks developed in the support and/or coating exhibit poor adhesion, despite the development of appropriate spraying procedures which included a better heat management. Moreover a porous LSCF support has been also manufactured and used for deposition, to avoid any problem due to differential thermal expansion. Although cracking did not occur in the support during deposition process, pinhole and cracking were still present in the LSCF deposited layer, thus preventing to obtain gas tight coating.
Porous Hastelloy X, has been first selected as reference material for metallic supports. Hastelloy X has been manufactured by GKN according to its standard production route (powder blending, powder compaction, sintering, secondary operations). Dense and stable deposits has been obtained on such a support. Permeation tests, however, indicate a lack of O_2 permeation, due to a densification of the metallic support which occurs, during spraying process, in the region underneath the LSCF layer. For this reason a new porous support material based on NiCoCrAlY-alloys has been prepared at Julich laboratories. Such a material exhibits an higher creep resistance and stability in oxygen atmosphere under spraying conditions. Moreover it exhibits a much higher interconnected porosity, in order to reduce mass transfer resistance of the support (see fig. 3).

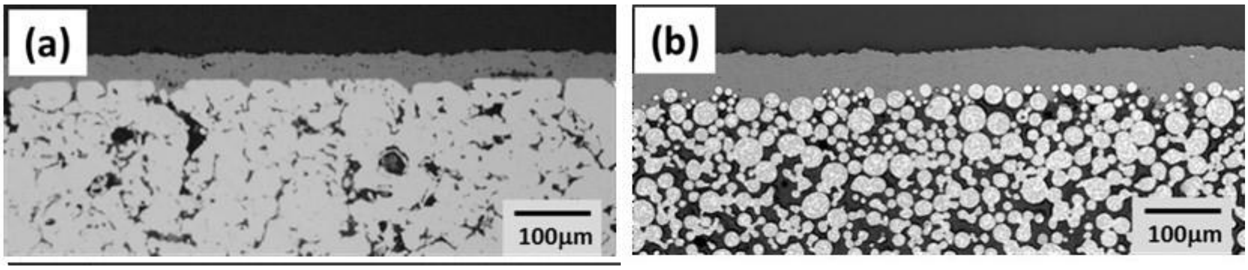


Fig. 3 Micrograph of LSCF deposited on porous Hastelloy X (a) and NiCoCrAlY (b) supports

The membranes sprayed on these substrates showed a promising permeation rate (see WP2 results for details).
In contrast to Hastelloy X, NiCoCrAlY alloy is not suitable for powder compaction due to its hard and brittle behavior. Therefore a new manufacturing strategy for the substrates has been established and optimized by GKN. Porous supports have been manufactured by gravity sintering by using powders supplied by Sulzer-Metco. In order to improve surface quality and flatness, the discs could be sized by subsequent axial compaction. Disks up to 110 mm in diameter and 2 mm thick have

[1] CGO are applied in order to limit inter-diffusion problem between zirconia and the dense conductive membrane.

been manufactured (see fig. 4). They can stand spraying conditions and LSCF and LWO deposit are sticking on the support.

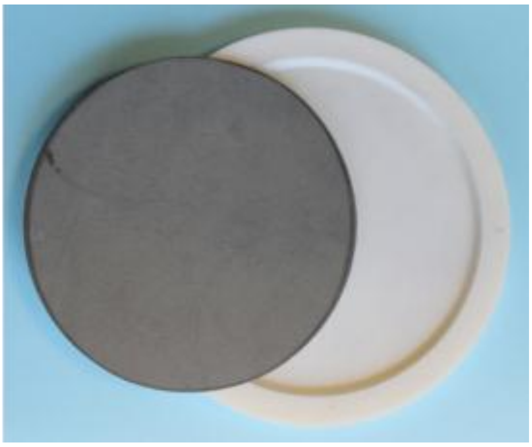


Fig. 4 Cross-section and sintering dies of gravity sintered NiCoCrAlY discs

Porous NiCoCrAlY manufactured by gravity sintering at GKN, was therefore selected as reference material for membranes to be tested in WP 3 and 5.

Membrane development and basic characterization (WP2)

The WP activity has been mainly addressed to obtain dense membranes for O_2 and H_2 separation by the PS-TF process.
Several spray sessions have been performed both at Jülich and at Sulzer Metco. Jülich performed spray trials using Sulzer Multicoat facility and intensive activities were conducted to determine the best process parameters, such as torch power, carrier gas, plasma jet velocity as well as understanding of the dominant deposition mechanisms. Sulzer also made deposition tests in a prototype plant (see fig. 5) , where large samples can be sprayed.

Fig. 5 Prototype plant for PS-TF at Sulzer Metco.

Both LSCF and LWO have been deposited on NICoCrAlY porous supports developed in WP1. Process parameters have been optimized in order to obtain target composition and crack-free structure. Metallographic characterization has been performed both at UNIGE and at CSIC. Deposited layers show good adhesion to the supports and their thicknesses typically range from 30 to 70 microns.

Permeation tests have been performed at CSIC and UNIGE with small membranes samples (1.5 mm disks in diameter) in a quartz cell at atmospheric pressure under different temperature and operational conditions.

Typical oxygen permeations obtained for LSCF membranes are shown in figure 6. In this case an air stream was fed on the dense membrane side, while Ar was used as a sweep gas on the porous substrate side.

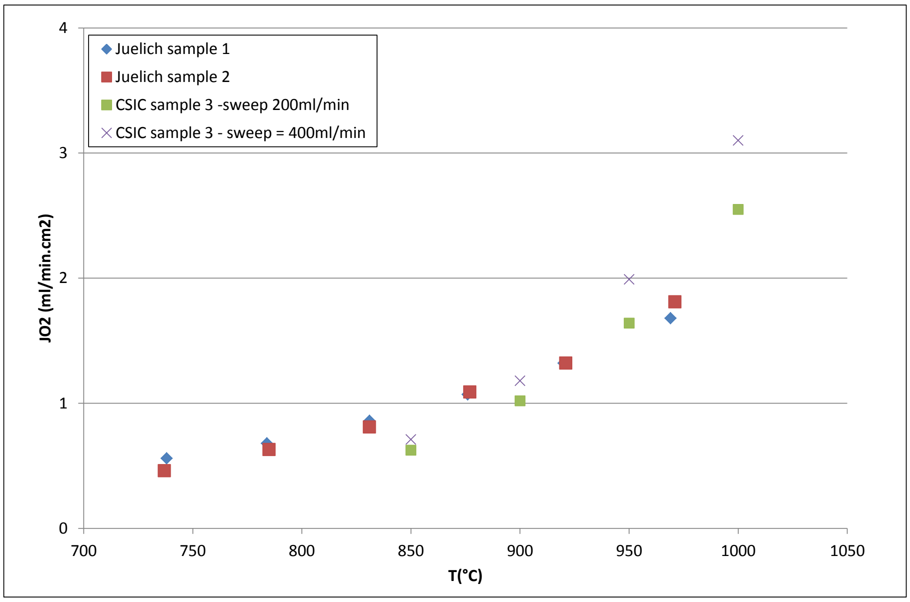


Fig. 6 O_2 flux as a function of the temperature measured with LSCF membranes

Catalytic layers have been also applied on both sides of LSCF membranes in order to enhance the surface reactions becoming rate determining for thin membranes.
A peak value of 6 ml/min-cm^2 at 1000°C has been obtained at CSIC laboratories (see fig. 7), thus approaching the target permeation established among the objectives of the project. In this case a porous BSCF layer was deposited by screen printing on the dense membrane layer and, subsequently, infiltrated palladium. Moreover the addition of methane in Ar sweep gas increases oxygen partial pressure gradient across the membrane, so determining an enhanced permeation.

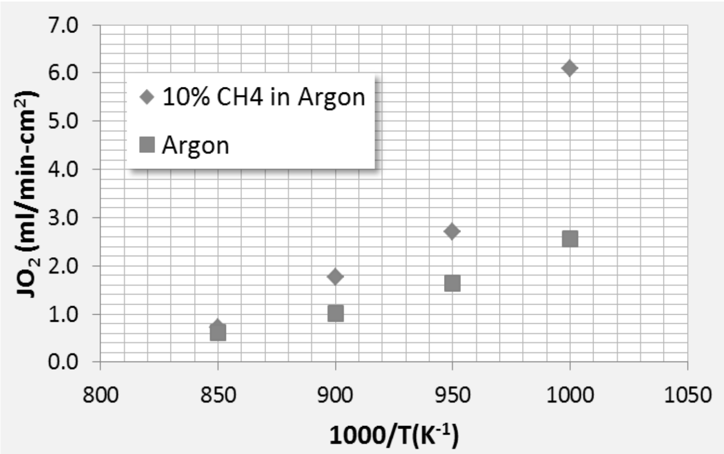


Fig. 7 O_2 permeation of activated LSCF membranes while using a mixture of argon an methane as sweep gas

Concerning hydrogen separation membranes, a very low permeation rate was achieved (fig. 8), in particular when taking into account the much higher values expected for thin supported LWO membranes.

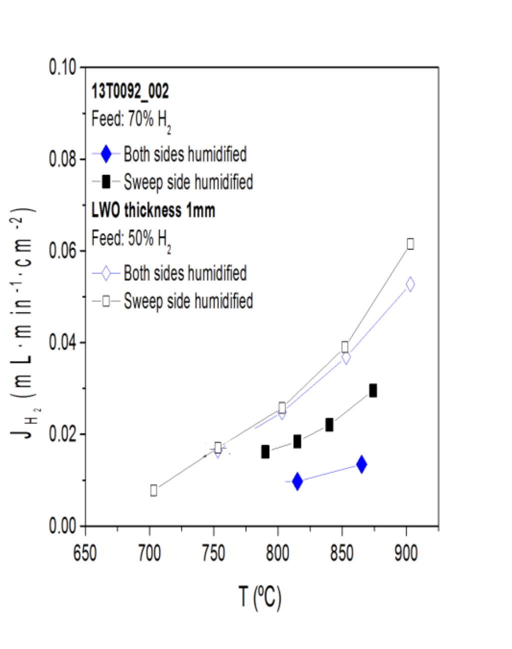


Fig. 8 H_2 flux as a function of the temperature measured with LWO membranes

Metallographic investigation (SEM and XRD) evidenced the presence of phase segregations inside the LaWO coating layer. In respect to the expected ratio La/W 5.5, values such as 2.5 or 14 have been detected. The phases with lower or higher La/W ratio are much less conductive than $La_{5.5}WO_{12}$ and this can explain the low membrane permeation.

A three-dimensional finite element method (FEM) model for mixed ionic/electronic conducting materials has been developed by KIT-U. The model is based on the commercial software package COMSOL Multiphysics® which includes a representation for the actual microstructure of a multiphase material. The model is able to predict the performance of a dense mixed conducting membrane with an (optional) porous functional layer on the top. The model considers gas diffusion (in porous support structures and functional layers), surface exchange at the solid–gas interfaces including the impact of functional/catalytic layers and protective coatings and the ion diffusion in the membrane material (see fig. 9) The model enables to differentiate between material properties (surface exchange coefficient k^{δ}, diffusion coefficient D^{δ}) and microstructural influences of the functional layer on the performance.

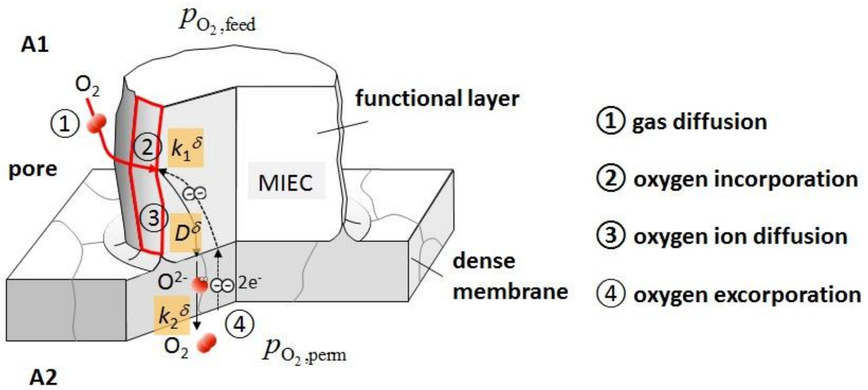


Fig. 9 Illustration of the permeation process for a LSCF membrane with a top functional layer

Validation of the model has been achieved by using both literature values from permeation measurements on LSCF thin-film membranes, as well as results achieved within the DEMOYS project (see Fig. 10). Despite the partly different temperature ranges, a good agreement between measured and simulated data can be observed.

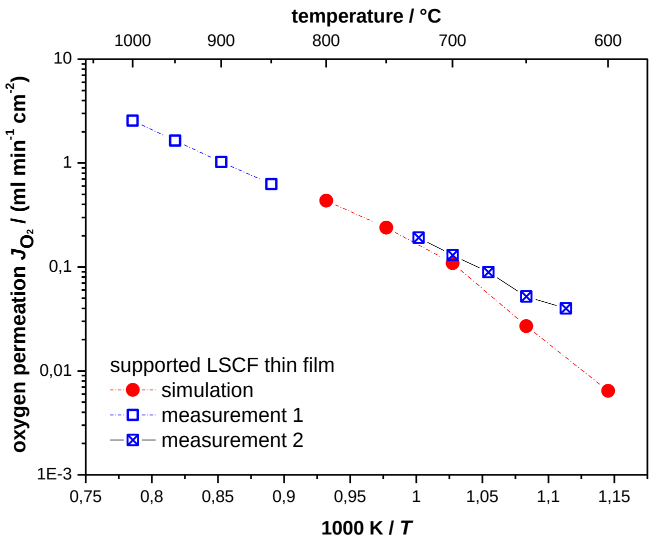


Fig.10 Comparison of simulation results (red circles) with permeation data measured in synthetic air (feed) within the DEMOYS project by partner CSIC

The model has also been used to identify the slowest reaction steps for various membrane configurations and address membrane development, particularly for catalytic/functional layer application . The simulation results clearly show that the performance of a thin-layer OTM made of LSCF is predominantly limited by the excorporation of oxygen and, thus, predict a significant performance enhancement by a suitable custom-made porous functional layer applied to the permeate side of the LSCF membrane. Optimum parameters of the functional layer have been estimated: e.g. active thickness < 10 µm, porosity (~ 30 %) and particle size as small as possible, less than 600 nm.

The functional layer has been successfully deposited on porous metal support following a powder-processing route at Julich laboratories. This layer is shown in Fig. 11 together with the dense membrane deposited on top. These samples are gas-tight after spraying. With the introduction of a functional interlayer, the dense layer can be reduced in thickness, typically from 50 to 30 µm.

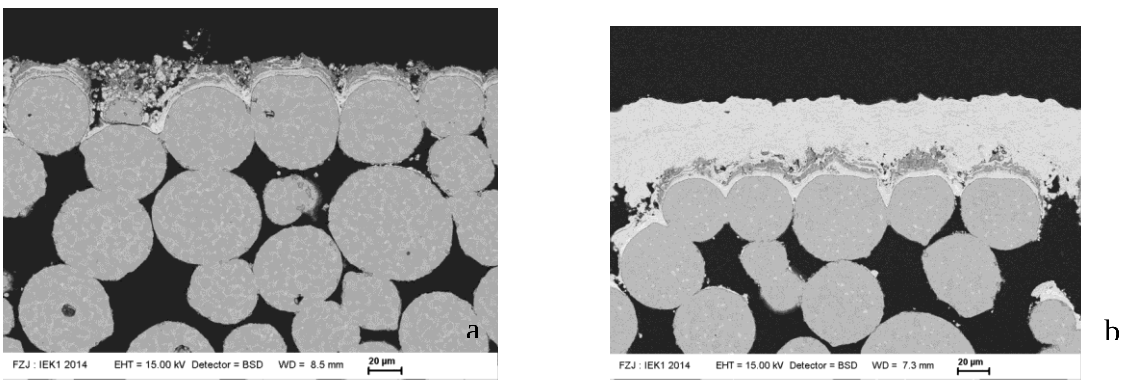


Fig 11. Scanning electron microscope images of a) the functional interlayer and b) dense membrane deposited on top

Membrane functional characterization (WP3)

WP3 activities have been focused on the performance evaluation of LWO and LSCF membranes.
Permeation tests of membranes have been performed on samples of bigger size (32 -64 mm in diameter) in lab a pilot loop able to operate up to 1000°C and 10 MPa (see fig. 12).
Tests were also addressed to evaluate technological problems such as mechanical stability and sealing system in order to provide a feed-back and properly address prototype membrane manufacturing and testing in WP 5.

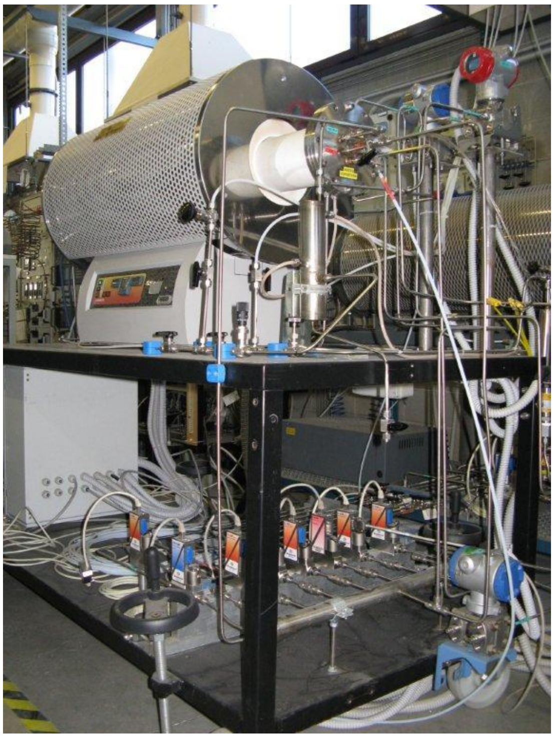


Fig. 12 Laboratory pilot loop for membrane permeation tests

Permeation tests of LSCF membrane samples have been performed at IEn premises.
Membrane sealing in the test section was achieved with a ceramic paste in addition to a golden ring sealing. Specifically ceramic glass sealant has been used to cover the surface of the porous support, while the golden ring ensures proper sealing of the membrane surface.
Permeation test have been carried out in the temperature range 700-950^{o}C at ambient pressure, by feeding air and helium on the permeate side. However during permeation tests an high amount of nitrogen has been detected in the permeate stream indicating gas leakage, due to the formation of cracks in the LSCF layer. Despite of the gas leakage, O_2 measurements in the permeate have been performed. Measured oxygen flux is in the same range as obtained in WP2.
In order to confirm cracking of the membranes during heating up procedure and exclude sealing and system influence, sample was exposed to high temperature treatment without mounting it into the test section. SEM analysis performed before and after heat treatment reveled appearance of big cracks (fig. 13) on the whole LSCF layer, due to the difference in thermal expansion coefficients of support.

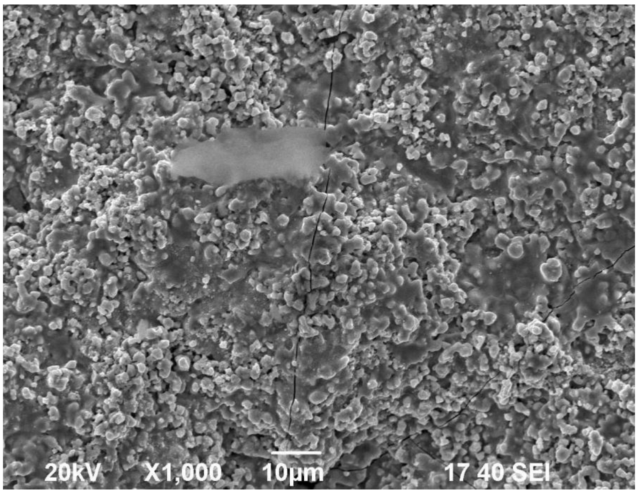


Fig. 13 SEM image of LSCF membrane surface after high temperature treatment.

Concerning LWO , similar result have been obtained, by RSE, e.g. membranes are leak tight at room temperature, while leakages develop at high temperature.

Moreover, in view of the development of industrial modules, RSE performed an experimental study concerning weldability of the new NiCoCrAlY alloy, based on the Electron Beam Welding (**EBW**) process. Welding tests between rectangular samples of porous NiCoCrAlY and Hastelloy solid material have been carried out in cooperation with the Italian Welding Institute. Welding parameters have been defined and the quality of the welding has been proved with metallographic examination performed by GKN (see fig. 14).

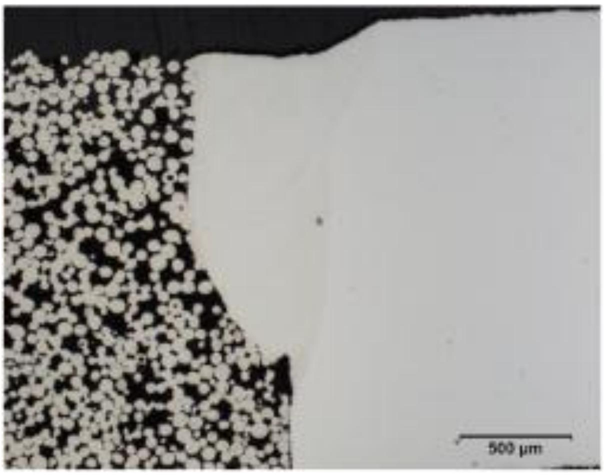


Fig. 14 SEM image of a EBW sample

Membrane integration in power generation plants (WP4)

Activities of this work package have been devoted to the opportunity of integrating the membranes developed in WP2 to actual industrial processes. A wide spectrum of applications has been considered and four classes of plants have been identified for further investigations. For each class, a significant number (up to 10) of different plant configurations has been considered, including plants without membranes assumed as reference. Each plant configuration has then been modellized by means of proper simulation tools to evaluate mass and balance and predict performance. The most important results achieved during this activities are summarized in the following for the four classes considered:

- **Reforming plants for pure H_2 production from natural gas**
  Application of H_2 separation membranes to reforming plants for pure hydrogen production from natural gas appears moderately attractive. It leads to a slight increase of the H_2 production efficiency and to a simplification of the plant flow diagram with a reduction of the number of components, but the necessity of compressing H_2 permeated across the membrane represents however a significant drawback for applications where high pressure H_2 is required. Application of oxygen transport membranes for the separation of pure O_2 required in Auto Thermal Reforming (ATR) plants for H_2 production doesn't lead to an appreciable advantages due to a poor thermodynamic matching with the power section.

- **Natural gas fired plants for power generation with CO_2 capture and sequestration**
  Application of membranes in natural gas fired power generation plants with CO_2 capture is very promising. The presence of a large gas turbine, offers the possibility to integrate in the plant a O_2 separation membrane Catalytic Partial Oxidation (CPO) reactor instead of a oxygen blown ATR. This saves a lot of work for oxygen separation resulting in an efficiency gain of about 3 point over a plant based on a conventional cryogenic air separation unit (ASU).
  H_2 compression is no more required given that a significant flow rate of sweep stream is used to dilute the H_2 permeated across the membrane. This allows to achieve an adequate hydrogen separation efficiency with a backpressure on the permeate side high enough to directly feed the gas turbine. The configuration featuring a two stage, oxygen blown ATR (where the second stage is integrated with a H_2 separation membrane) achieves an efficiency gain of about 4 percentage points over a combined cycle with pre-combustion CO_2 capture based on commercially ready technologies.
  The best performance can be achieved by combining the previous features in a single plant (i.e. by including an oxygen transport membrane CPO reactor followed by a second reforming reactor integrated with a H_2 separation membrane). **This configuration is shown in the figure below and reaches an outstanding 52.4 LHV efficiency, about 6.5 higher than comparable plants based on commercial technologies.**

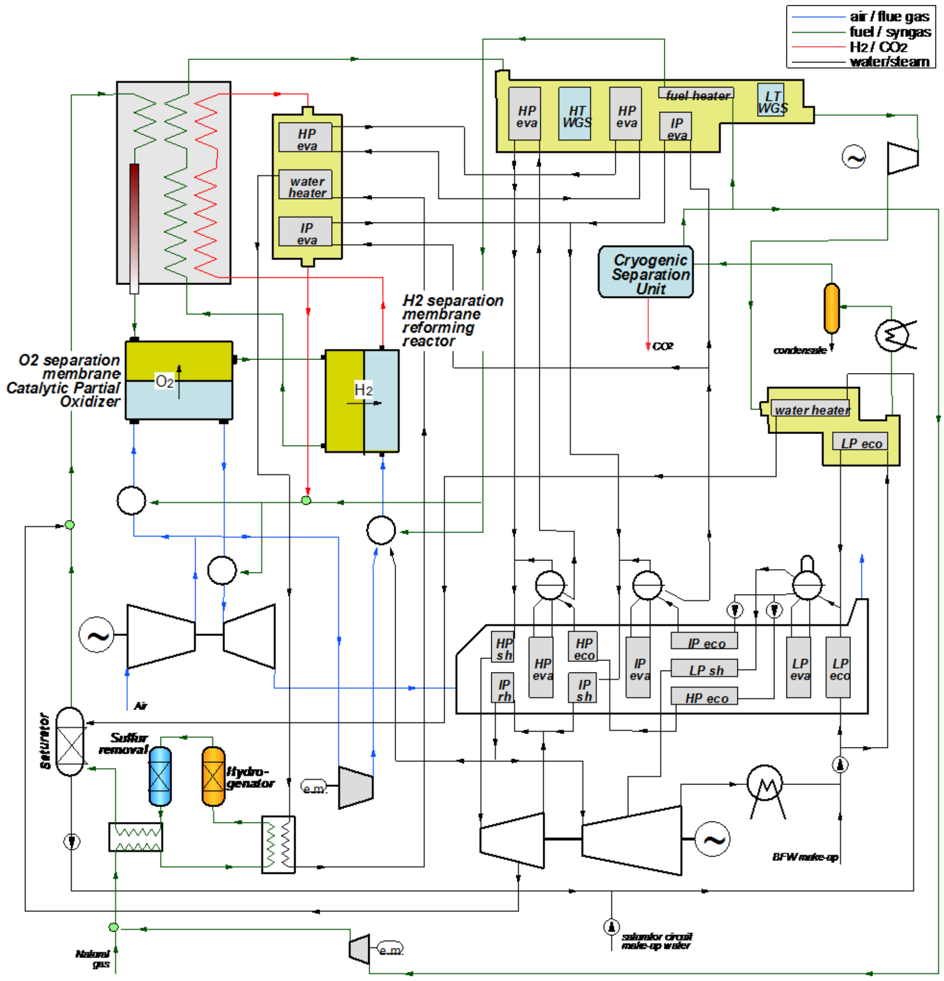


Fig. 15 Scheme of the plant with a CPO reactor followed by a second reforming reactor integrated with a H_2 separation membrane

- **Coal fired plants for power generation**
  Two different power plants fall in this category: Integrated Gasification Combined Cycles (IGCC) and Fluidized Circulating Bed Boiler (FCBB) Ultra Super Critical (USC) steam cycles.
  In **the IGCC case** the O_2 membrane module is integrated in the plant essentially to replace the cryogenic ASU and produce a pure oxygen stream to feed the gasifier. Such O_2 membrane can be indifferently applied to plants with and without CO_2 capture and it allows an efficiency increase between 0.6 to 1 point depending on the backpressure on the oxygen side. The higher the backpressure the higher the efficiency is, but it results in a larger and more expansive membrane area. To solve this trade-off, an economic model and the evaluation of the membrane area are necessary. Since this evaluation has been performed before meaningful permeation data of membranes developed in DEMOYS become available , O_2 permeability was assumed equal to that experimentally measured for a membrane, made of the same active material (LSCF) and the same thickness (30 µm) but obtained by tape casting on a ceramic support [2].
  Resulting membrane area are between 18'000 and 47'000 m^2 as the backpressure varies from 0.5 to 1.4 bar for a plant with a net electric output of about 335 MW. The economic model shows a little advantage to decrease the pressure on the permeate side in order to reduce the membrane cost.

[2] J. M. Serra, J. Garcia-Fayos, S. Baumann, F. Schulze-Küppers, and W.A. Meulenberg: "Oxygen permeation through tape-cast asymmetric all-$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ membranes", J. Memb. Sci., vol. 447, pp. 297–305, Nov. 2013.

A broader investigation has been carried out to evaluate the potential of O_2 transport membranes **in oxyfuel combustion FCBB-USC** steam cycles with CO_2 capture. The plant flow diagram of this plant is reported in the figure below. The analysis showed that the plant thermodynamic and economic performance is significantly affected by four design parameters:

- The mass flow rate of the air stream sent to the feed side of the membrane module to separate the oxygen flow rate required to burn the coal
- The temperature of air stream at the membrane feed side inlet
- The air compressor pressure ratio (i.e. pressure of the air stream at the membrane feed side inlet)
- The mass flow rate of the stream recirculated on the membrane module permeate side.

A full optimization of these four design parameters has been performed aiming at determining the lowest cost of the electricity produced. The area of the O_2 membrane has been evaluated on the basis of the permeability mentioned above. It is about 114'000 m^2 for a plant rated at 646 MW net power output.

The optimized plant shows an LHV efficiency of 40.5%, 3.8 percentage points below the reference, air blown plant without CO_2 capture but also 3.8 points higher than the plant with CO_2 capture based on a cryogenic ASU. In practice the oxygen membrane allows to halve the efficiency losses related to CO_2 capture.

This is an outstanding efficiency improvement that could lead to a significant reduction of the cost of the CO_2 avoided, provided that reliable and efficient membrane modules can be manufactured.

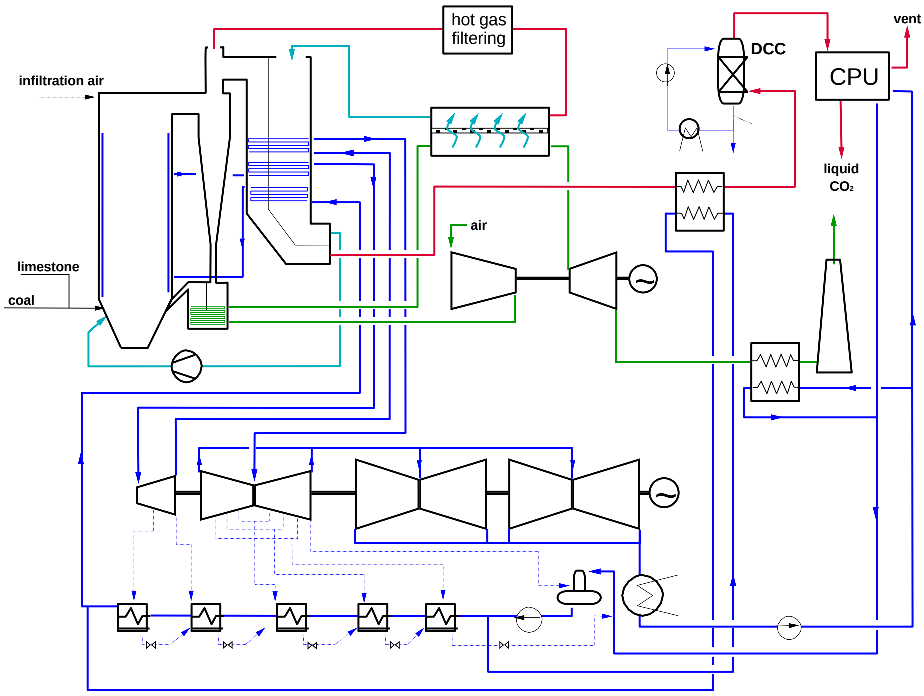


Fig. 16 Scheme of the oxyfuel combustion FCBB-USC steam cycle with CO_2 capture

- **Devices for small scale O_2 production**

This activity has been carried out in response to two emerging requirements:

- finding applications of economic interest where the O_2 membrane modules could be deployed on small scale, in order to demonstrate their technological feasibility;
- finding applications in industrial fields different from Carbon Capture and Sequestration.

The figure below shows the plant flow diagram of a device for production of pure oxygen based originated by integrating a membrane module in a micro gas turbine. Micro gas turbines are

commercial units for combined heat and power generation available from different manufacturers with a power output in a range from 30 to 200 kW. Typical conditions at the combustor outlet of the micro gas turbines are favorable for coupling with membrane modules. Temperature of the stream (in the range 900-950°C, set by the resistance of materials of the expander) is particularly favorable to operate the membrane, whose permeability is significantly affected by temperature. Oxygen concentration in the combustion gases to the membrane module is still high (~18%) because of the limited temperature drop of the air stream entering the combustor, which is pre-heated to almost 600°C in the recuperator. Pressurized hot gases at 4 to 5 bar enters the membrane module which separates a significant fraction (about 50%) of the O_2 contained in the stream. The backpressure on the permeate side is kept at 0.25 bar to reduce the membrane area. A compressor is required to take the O_2 separated to ambient pressure.
The study focused on a unit with a nominal electric net output of 200 kW and an inlet air flow rate of 1.29 kg/s.
The introduction of the membrane module allows to separate about 300 Nm^3/h of pure oxygen as the power output reduces to 130 kW, mainly due to the lower flow rate in the expander and the consumption of the oxygen compressor. The resulting membrane area (calculated according to the previous procedure) is in order of 200 m^2.
Since this plant co-produces oxygen, power and heat is difficult to define unambiguous efficiency indexes. An effort in this direction has been made by assuming reference natural gas to electricity LHV conversion efficiency (55%) and natural gas to heat LHV conversion efficiency (90%). The resulting specific electric consumption for O_2 production is about 0.5 kWh/Nm^3, approximately the same value achieved by vacuum swing adsorption (VSA) units, a technology commonly used for on-site production of O_2 at flow rate higher than 250 Nm^3/h. In this case an advantage of the membrane technology is the higher purity of the separated oxygen. In principle 100% O_2 can be separated as VSA typically gives purity in the range 90-93%. Much higher benefit can be achieved at smaller scale. The micro gas turbine can be downscaled of about one order of magnitude (approximately 50 Nm^3/h) at about the same efficiency, while at such low requirement rates current reference technology is represented by pressure swing adsorption, which has a typical consumption of 1.5 kWh/Nm^3.

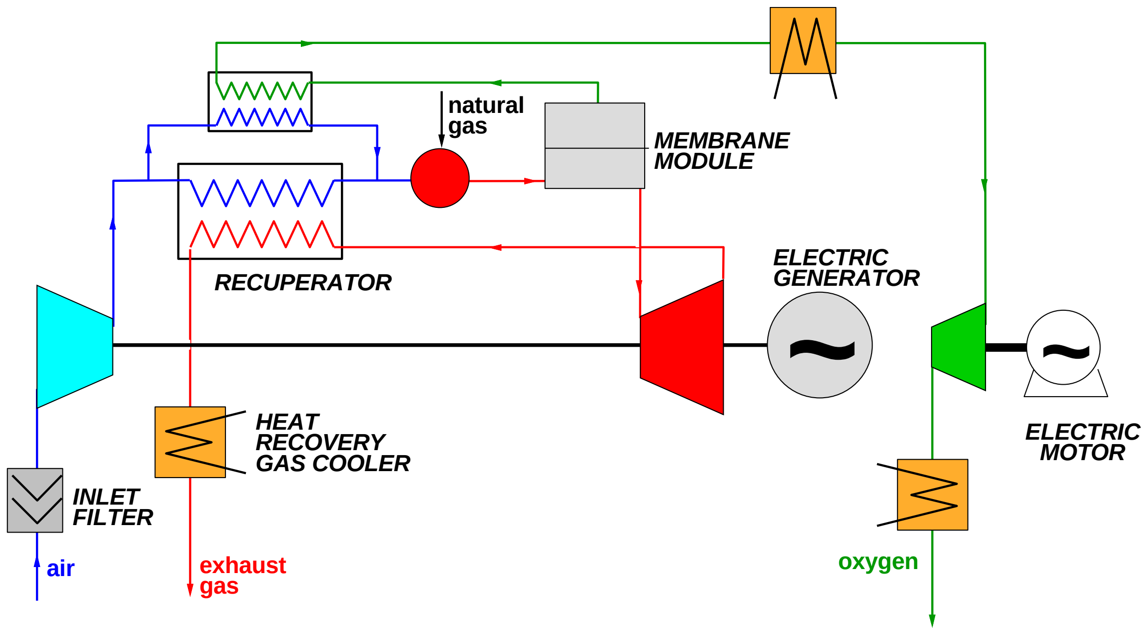


Fig. 17 Plant flow diagram of the micro-gas turbine integrated with a O_2 membrane module

Prototype membrane manufacturing and testing (WP5)

The manufacturing process of the supports and membranes has been optimized by GKN and Sulzer Metco, respectively.
Specifically, in order to overcome problems evidenced in WP3, different heat treatments of the substrate were performed before coating or even between dual layers coatings. With the objective to reduce the deformation of the support and relieve the internal stresses of the membrane layer. The heat treatment successfully reduced the deformation of the substrate.
The cost of membrane manufacturing was also estimated both for large scale applications (CCS related) and small scale application (not CCS related). The cost for large scale applications (100.000 m^2 of membrane) is about 1050 €/m^2. For small scale applications (1000 m^2) the cost increases up to 1900 €/m^2. The largest part of the cost derives from the support manufacturing rather than from the deposition of the dense thin layer (LSCF or LWO) with the PS-TF process and the subsequent application of a catalytic top layer.

Membranes samples up to 100 cm in diameter have been delivered both to Sol and to IEn for testing in pilot installation. The pilot loop allows to:

- test membranes from 700 °C to 1000 °C with a pressure difference of 10 MPa (1-11 MPa) between the sides of the membranes;
- control and acquisition of the main process parameters as gas temperature, pressure and flowrate.

Fig. 18 Pilot loop for membrane testing built at SOL premises

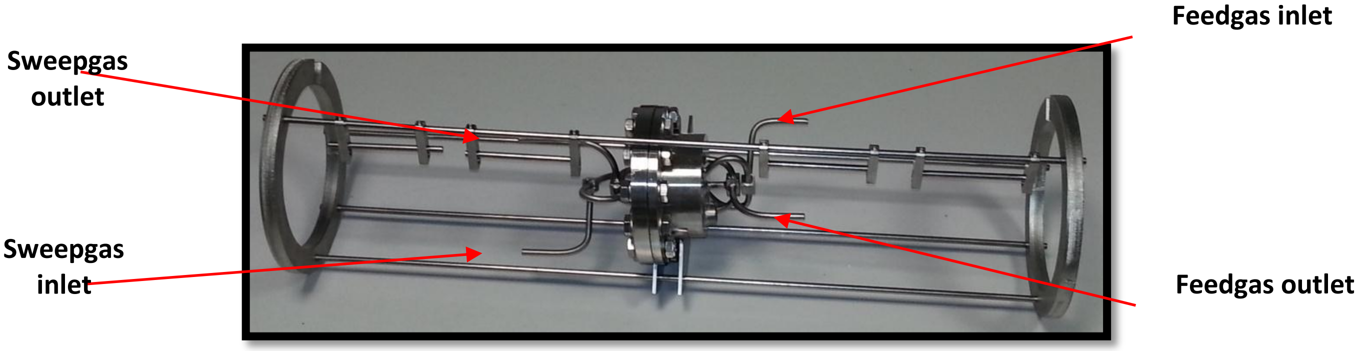


Fig. 19 As built test section + Hastelloy X support system

However, as already evidenced in WP 3, during membrane testing at high temperature, cracks developed in the LSCF deposited layer, thus preventing to obtain a feed-back on membrane performance in the long term. Further tests proved that crack development was determined by the difference in thermal expansion coefficients between the support and the deposited membrane layer. during the permeation test, the support experiences an increase in volume, leading to tensile stress levels in the membrane. The stress in the membrane leads to the appearance of vertical cracks and therefore to leakage during these tests.
As a consequence a lot of efforts have been made in order to fully assess and overcome such a problem. Various and complementary approaches have been tried by Partners, including modification of the GKN manufactured support, deposition of an intermediate porous layer between the support and membrane, modification of the process parameters during the PS-TF process, heat treatment of the composite membrane for stress relief, sintering of new MCrAlY supports.
Finally, both a proper modification of the GKN support and a sintering of new MCrAlY supports were successful in obtaining a dense and leak tight membrane, which do not exhibit cracking of the LSCF layer during heating-up procedure.
In Fig. 20, pictures of LSCF coated samples with “modified GKN” and “sintered at FZJ” support are shown. The samples are gas-tight after annealing in Argon at 900°C and air-tight after annealing in Air at 900°C. Even after 2 consecutive heat treatments, the surfaces of the samples remain crack-free. During permeation tests performed in a quartz lab-scale reactor with a 15 mm membrane sample, no N_2 was detected in the permeate for all the testing period (two weeks), so infinite selectivity of the membrane towards O_2 separation was confirmed.

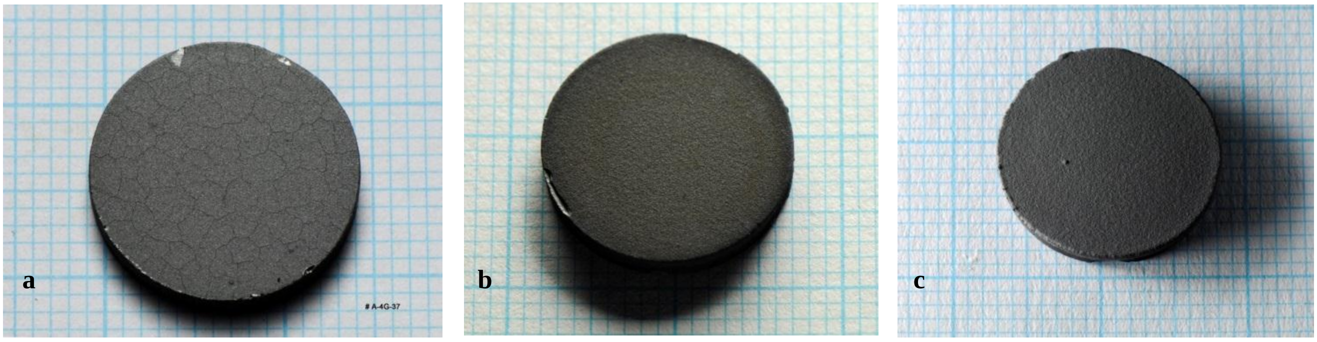


Fig.20 LSCF membranes on MCrAlY: a) On unmodified GKN support. b) On modified GKN support; c) On MCrAlY sintered at FZJ support. All samples were annealed in air at 900°C for 3H.

Larger crack-free LSCF membranes, up to 110 mm in diameter, have been prepared, accordingly.

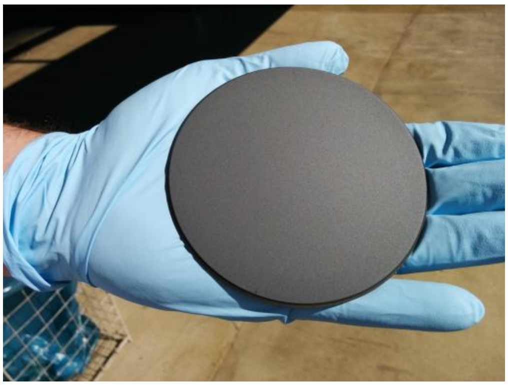


Fig. 21 LSCF membranes on NiCoCrAlY support manufactured by GKN

Moreover the optimization of the spraying parameters and catalytic activation of both membrane sides allowed to significantly increase the O_2 flux. As shown in fig. 22, the membranes prepared at the end of the project (5th generation membranes), in addition to high selectivity and stability at temperature, exhibit, at all temperatures, an increase in oxygen permeation by more than two times respect to the membranes prepared at the mid-term review (1st generation). **With the 5G-33 membrane a maximum oxygen flux of 5.29 ml·min^{-1}·cm^{-2} was obtained at 1000 ºC, establishing an outstanding result within the field of LSCF supported membranes. DEMOYS membranes, in fact, are now matching permeation flux of benchmark membranes (LSCF obtained by inverse tape casting).**

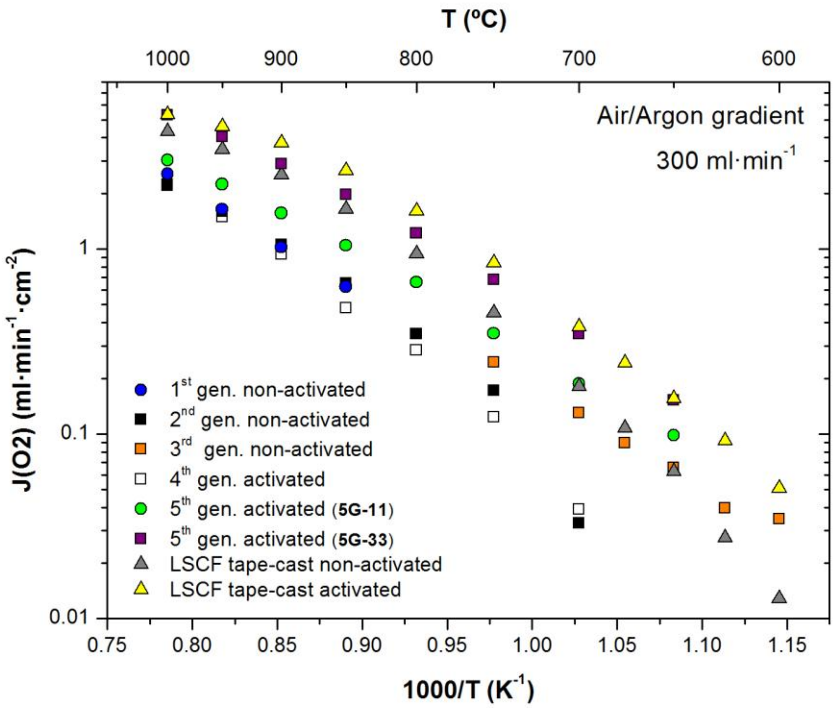


Fig. 22 Improvement **of o**xygen flux measured with DEMOYS membranes: comparison with benchmark membranes (LSCF tape-casted, *ref. J. Serra et al., JMS 447 (2013)297-305*)

Process scale-up and cost evaluation (WP6)

WP6 activities have focused on the evaluation of the potential economical attractiveness of large-scale production plants for power generation with carbon capture and storage, adopting the novel membranes developed in the DEMOYS project. Therefore, techno-economic assessments of selected large-scale membrane-integrated plants, designed to produce power with a low carbon footprint have been performed in this work package and the economic results have been used to evaluate, on a comparative basis, the potential economic advantage of membrane-integrated plants with respect to alternatives adopting the leading CO_2 capture technologies.
More specifically, the economic assessment has been initially aimed at estimating the Levelized Cost of Electricity (**LCOE**) production in coal-based power plants with CCS. Subsequently, these costs have been used to estimate the CO_2 avoidance cost (**CAC**), expressed as Euro per tonne of

avoided CO_2, for comparison to that of competing configurations, adopting current state-of-the-art technologies.

It is pointed out that cost data developed throughout the work package are defined in general accordance with the White paper "*Toward a common method of cost estimation for CO_2 capture and storage at fossil fuel power plants*" (March 2013), produced collaboratively by authors from EPRI, IEAGHG, Carnegie Mellon University, MIT, IEA, GCCSI and Vattenfall[3].

Making reference to the results of work package 4, the following table lists the main features of the plants selected for the final economic assessment of the DEMOYS project.

Case	Feedstock	Technology	Main product	CCS	Membrane
1	Coal	IGCC	Power	No	-
2	Coal	IGCC	Power	Yes	-
3	Coal	IGCC	Power	Yes	O_2
4	Coal	Air-CFB	Power	No	-
5	Coal	Oxy-CFB	Power	Yes	-
6	Coal	Oxy-CFB	Power	Yes	O_2
7	NG	MGT	O_2, Power & Heat	No	O_2

Some relevant results are summarized in Fig. 23 and Fig.24 where the LCOE and CAC for all power production cases are reported; and in Fig. 25 where the Levelized cost of Oxygen (LCOO) for the micro gas turbine-based case is shown.

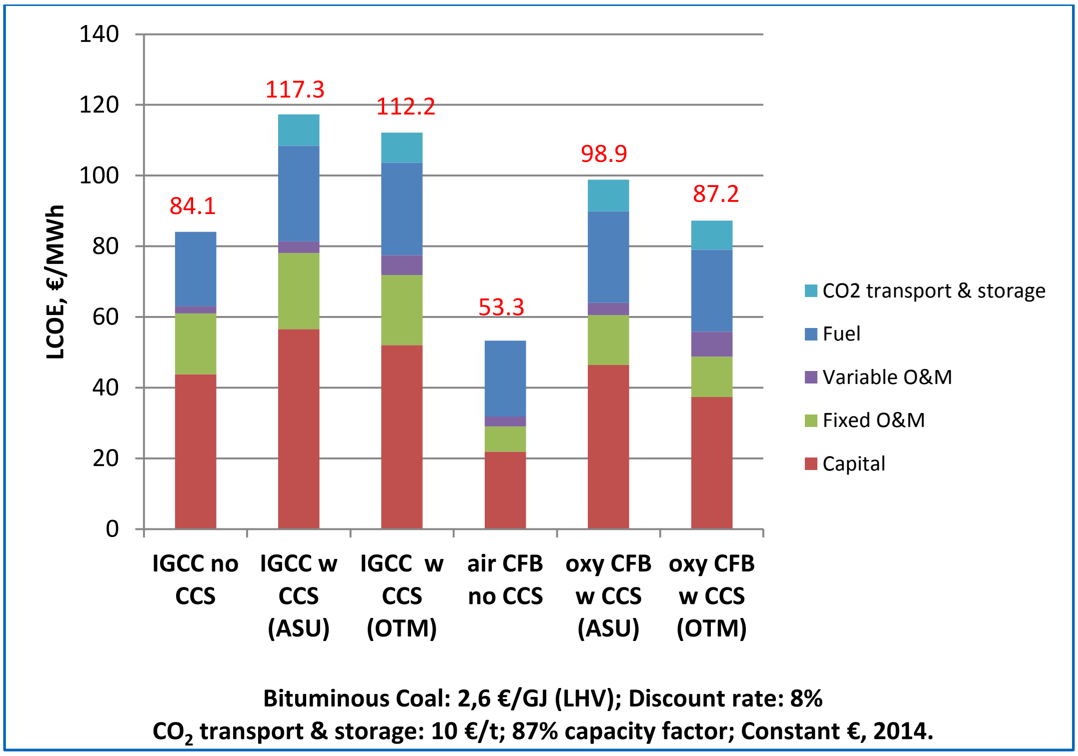


Fig. 23 Levelized Cost of Electricity (LCOE) production (Case 1-6)

[3] IEAGHG report 2013/TR2: http://www.ieaghg.org/publications/technical-reports

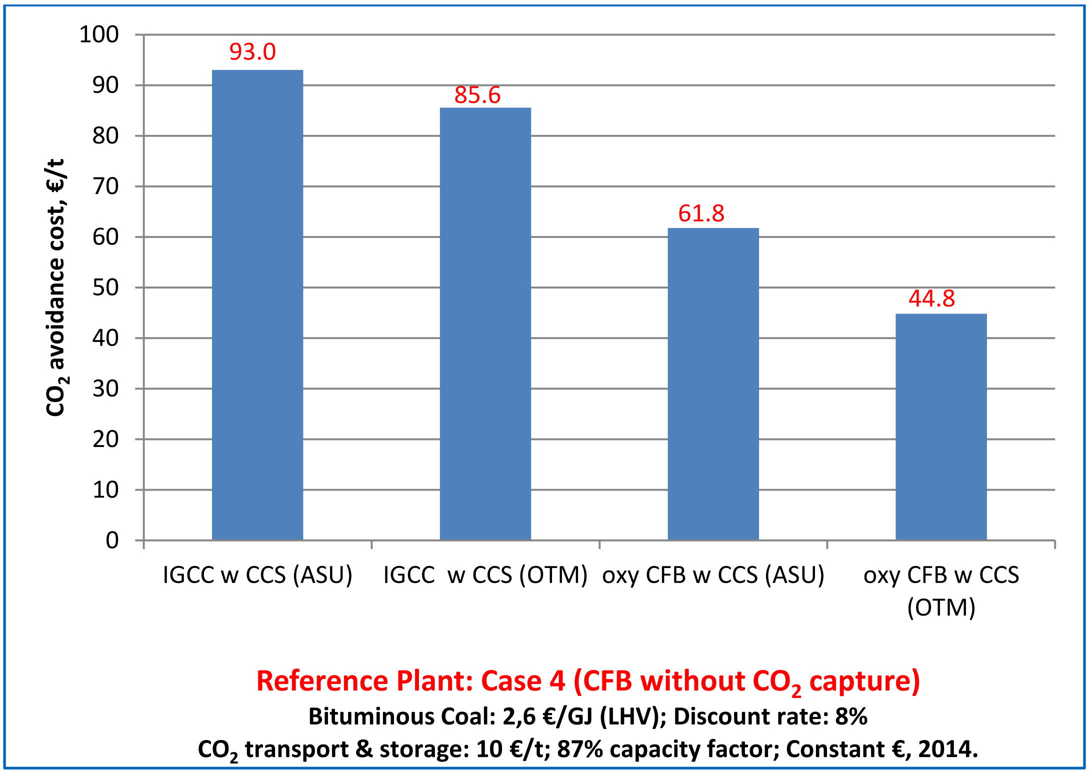


Fig. 24 CO_2 avoidance cost (CAC) of cases with CO_2 capture (Case 2, 3, 5, 6)

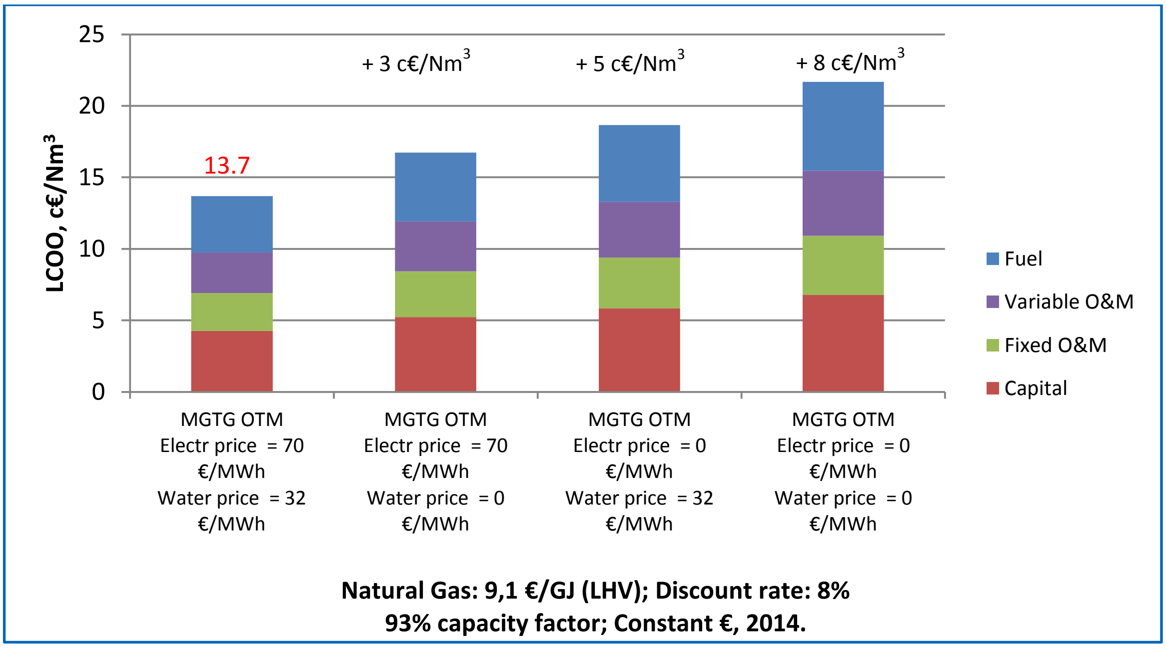


Fig. 25 Levelized cost of Oxygen (LCOO) production (Case 7)

As shown in the above figures, the primary conclusion that can be drawn from the assessments made in WP 6 is that the use of oxygen transport membranes in power plants with low carbon emissions has the potential to be more cost effective than benchmark plants using the leading CO_2 capture technologies. With respect to the benchmark technologies, the use of membranes improves the overall plant performance, while reducing also the total capital requirement for the investment.

More specifically on the economic aspect, the capital cost of an OTM-based unit is from about 20% to 35% lower than the equivalent cost of standard cryogenic Air Separation Unit, respectively for IGCC and CFB power plants. Nevertheless, it is noted also that the operating and maintenance costs of the OTM-based plants is about 10% higher than the benchmark plants, mainly due to the variable cost required for the replacement of the membranes at the end of their operating life.

Taking into account the above, the financial modelling of the different plants has shown that the LCOE and the CAC of the OTM-based plants are lower than those of plants using benchmark CO_2 capture technologies. This is particularly evident for the CFB-based plants, for which the LCOE and the CAC are respectively 12% and 27% lower than the reference oxy-combustion plant with CO_2 cryogenic purification unit.

The economical attractiveness of the membrane integrated plants strongly depends on key factors like permeability, specific cost and lifetime of the membranes. However, various sensitivity analyses have clearly demonstrated that there are still ample margins for each of the key membrane factors considered in the DEMOYS project to continue to be more economically attractive than plants with benchmark technologies (e.g. 60% lower permeability, 3 times cost or half lifetime).

Finally, the assessments shown in this report have demonstrated also that the use of OTM in niche applications, like the oxygen production in plants with micro gas turbine generators, have the potential to be more cost effective than benchmark PSA or VSA plants. Results indicates that OTM-based plants have the potential to be more cost effective than benchmark PSA or VSA plants, by reducing the oxygen selling price from 15 to 13.7 c€/Nm^3.

Potential impact and main dissemination activities and exploitation results

Dissemination activities

The results of DEMOYS have been disseminated by several channels, including project web-site, publications in scientific journals, presentations to conferences/workshops, press release and organization of specific events. More in detail the following actions have been made:

- a leaflet with description of project structure and objectives has been prepared. 2000 copies have been printed and distributed;
- the project web site (**http://demoys.rse-web.it**) has been established at the beginning of the project and regularly updated;
- Nineteen oral presentations have been delivered and five posters have been displayed at several conferences/workshops.
- eight peer-reviewed papers have been published on scientific journals. Moreover four papers will be submitted after the end of the project.

Networking activities with other 7th FP co-financed projects included the organization of one workshop and a summer school on membranes.
A focused workshop has been organized by RSE in Milano on 2011 H_2 and O_2-selective membranes to address activities of EERA-CCS project in this specific field . Participants included representative from the following organization: CSIC, ECN, Imperial College, Juelich, Politecnico di Milano, Riso DTU, Sintef, Edinburgh University, Vito. Discussion covered, among others, objectives, approaches, and open results concerning 7th FP projects on membranes where the above Organization are involved (Cachet II, DECARBit, DEMOYS, HETMOC, Nasa-OTM).
The summer school *"Inorganic Membranes for Green Chemical Production and Clean Power Generation"* has been organized in Valencia by CSIC on September 2013, in cooperation with other 7th Framework projects (CARENA, HETMOC, NASA-OTM).
The school tackled from transport fundamentals through synthesis/manufacturing to final applications of gas separation membranes. Specifically the topics addressed along the different sessions were: (1) oxygen transport membranes; (2) hydrogen permeable membranes; (3) theoretical modeling and characterization of transport and surface chemistry; (4) advanced manufacturing techniques; (5) European research projects and consortia; (6) microporous membranes; and (7) application to chemical processes and advanced separations.
More in detail 42 oral presentations have been delivered and 39 posters have been displayed.
A special session for students has been allocated in order to give the opportunity to several students to show a brief summary of their PhD research work. 130 persons attended the school, coming from 16 European countries and from 5 overseas countries (8 persons Korea, China ,USA, India, Australia). A book of abstract has been published and charged on DEMOYS site.

Main impacts and exploitation of results

The foreground generated in DEMOYS which has a potential for commercial exploitation can be summarized as follows:

- CoNiCrAlY metallic powders for the production of porous supports of gas separation membranes.

- Manufacturing process by gravity sintering of porous NiCoCrAlY alloy supports for the deposition of thermally sprayed membrane layers.

- LaWO powders suitable for the manufacture of hydrogen separation membranes with the Plasma Spray Thin-Film (PS-TF) process

- LSCF powders suitable for the manufacture of Oxygen separation membranes with the Plasma Spray Thin-Film (PS-TF) process .

- Plasma Spray Thin-Film (PS-TF) process for deposition of thin and dense ceramic layers on porous supports for the production of oxygen and hydrogen separation membranes.

- Oxygen separation membranes (OTM) for oxygen production in industrial applications.

Four patent applications have been filed in order to protect know how generated in the project.

Mainly exploitation will focus on O_2 membranes which, according to the analysis of WP4 and 6, exhibit a higher potential attractiveness for market penetration.

Provided that further development is required to fully develop O_2 separation membranes and bring them to the commercial stage for application in large-scale industrial plants, their development can be addressed to the following applications:

- **Integration in coal based Oxy-combustion steam power plants**
- **Integrated Gasification Combined Cycle (IGCC) with or without pre-combustion CO_2 capture.**

Significant technological, economic and environmental benefits can be foreseen by the integration of DEMOYS membranes in these plants.
From a technological point of view, the main result of DEMOYS is that the technical feasibility of manufacturing O_2 separation membranes on a porous metallic support by the Plasma Spray Thin-Film (PS-TF) process has been demonstrated. Their performance, in terms of permeating flux, are comparable to fully ceramic asymmetric LSCF membranes obtained by a different (and more expensive) manufacturing process (inverse tape casting).
Moreover it should be stressed that, among asymmetric oxygen separation membranes, DEMOYS membranes exhibit the unique characteristic of a porous metallic support. Their weldability to other solid metallic materials has been demonstrated and this can determine, as a perspective, a significant advantage compared to fully ceramic membranes where obtaining leak tight ceramic-metallic joints is a critical issue. This aspect, in fact, is particularly important for the technology scale-up, once the assembly of membranes in a module is addressed.
The integration of DEMOYS membranes in oxy-combustion and IGCC plants can be beneficial in terms of **energy efficiency**. An increase of the 3.8% and 1%, respectively, has been estimated respect to plants adopting the benchmark technology (Air Separation Unit with cryogenic distillation).
In addition, the higher purity of the oxygen output (compared to a cryogenic ASU) allows increasing the carbon capture ratio (from 91.6 to 95) so as to achieve an **environmental benefit.** The resulting CO_2 emissions of a circulating fluidized bed boiler supercritical steam plant, are 42.9 kg_{CO2}/MWh_{EL} for a plant based on O_2 separation membrane module vs. 80.1 of the benchmark.

Another important aspect is the rather **low cost of membrane manufacturing**. For large production capability, it has been estimated as 1070 €/m^2. The low manufacturing cost and rather high permeation flux determines that their integration in oxy-combustion and IGCC plants has the potential for being **economically more attractive** with respect to plants adopting cryogenic ASU. As described in WP 6 results, the LCOE is reduced by 13.4 % and 4.3%, respectively; moreover the CO_2 avoidance cost is reduced of the 27. 3% and of the 8.3%, respectively.
The corresponding **cost of carbon capture** is about 29.4 and 34 €/ton CO_2, for membrane based IGCC and oxy-combustion plants, respectively. These values are the 20% and the 24% lower than plants which make use of cryogenic ASU.

Results obtained in DEMOYS can be further evaluated by considering recent technological developments in the field of oxygen separation membranes, particularly in USA.
The most important efforts to develop commercial oxygen separation membrane based on mixed conducting materials have been undertaken in USA by Praxair and Air Products & Chemicals, respectively, in the frame of DOE co-funded projects. Both companies are developing asymmetric ceramic membranes; Praxair is focused on tubular membrane modules to be integrated in a boiler for oxy-fuel combustion, while Air Products has developed a planar module for three end operation for air separation to be integrated in a IGCC plant in substitution of a cryogenic ASU. More in detail, Air Product started membrane development in 1998. Commercial planar modules able to deliver 1 TPD (Ton/ day) O_2 have been successfully demonstrated. The construction of a prototype 100 TPD oxygen production plant has been completed at Convent in Louisiana and is ready to be operated. Little information about membrane characteristics and performances is available in literature and so a direct comparison with DEMOYS membrane performances is not possible.
An indirect comparison can be made, however, by considering the expected impact.
Recent evaluation performed by EPRI with Air Products and Worley Parson[4], indicate that in a 765 MWth IGCC plan designed for a 87 % CO_2 capture, the use of oxygen membranes can provide an efficiency increase of 1.8% and a LCOE reduction of the 10%, as regards benchmark technology (cryogenic ASU). Similarly for a 800 MWth oxy-combustion plant (SuperCritical Pulverized Coal boiler) designed for a 90% CO_2 capture, a 2.5% efficiency increase and a 5% LCOE reduction has been estimated.

Although these results were obtained for plants of slightly different size and features, it can be noted that DEMOYS membranes, once integrated in power plants, can provide benefits comparable to the ones obtained with Air Products membranes, as described previously in this chapter.

A sensitivity analysis concerning specific cost, permeability and lifetime of oxygen membranes has been also performed. Results clearly indicate that there are still ample margins for each of the key membrane factors considered in the DEMOYS project to continue to be more economically attractive than plants with benchmark technologies. As an example, Fig. 26 shows the variation of the CO_2 avoidance cost for the IGCC with OTM versus the specific cost of the membrane, at different values of permeation factors (K). It can be drawn the following:

- ✓ With current permeation, use of membrane is attractive vs. benchmark, even with membrane cost three times greater than reference one (1,060 €/m^2);
- ✓ With current cost, use of membrane is attractive vs. benchmark even with permeation 60% lower than the reference one.

[4] J.M. Repasky e tal, Ceramic and Coal: ITM Oxygen for Power Generation with Reduced CO_2-Emissions, Detailed Engineering Study Results, Proc . of 2013 AIChE Spring Meeting,

Similarly, Fig. 27 shows the variation of the CO_2 avoidance cost versus the expected operating life of the membranes, at different values of permeation factors (K). It can be drawn the following:

- ✓ With current permeation, use of membrane is attractive vs. benchmark down to a membrane lifetime of 2 years (reference is 5 years);
- ✓ With current lifetime, use of membrane is attractive vs. benchmark even with permeation 60% lower than the reference one.

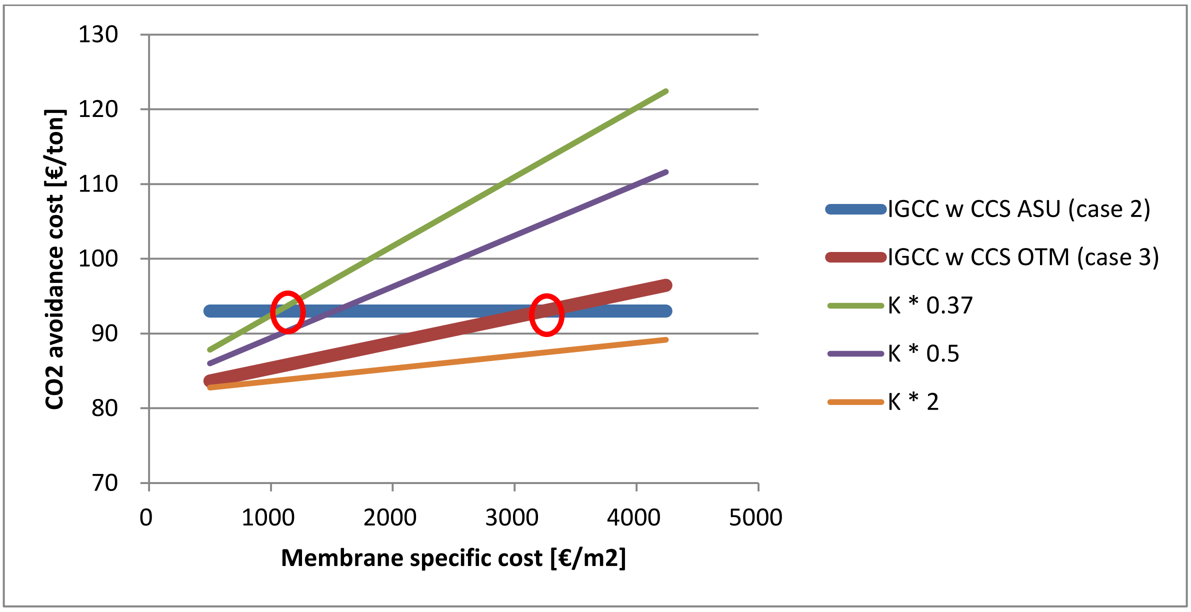


Fig. 26 CO_2 Avoidance Cost vs. membrane specific cost (IGCC with OTM)

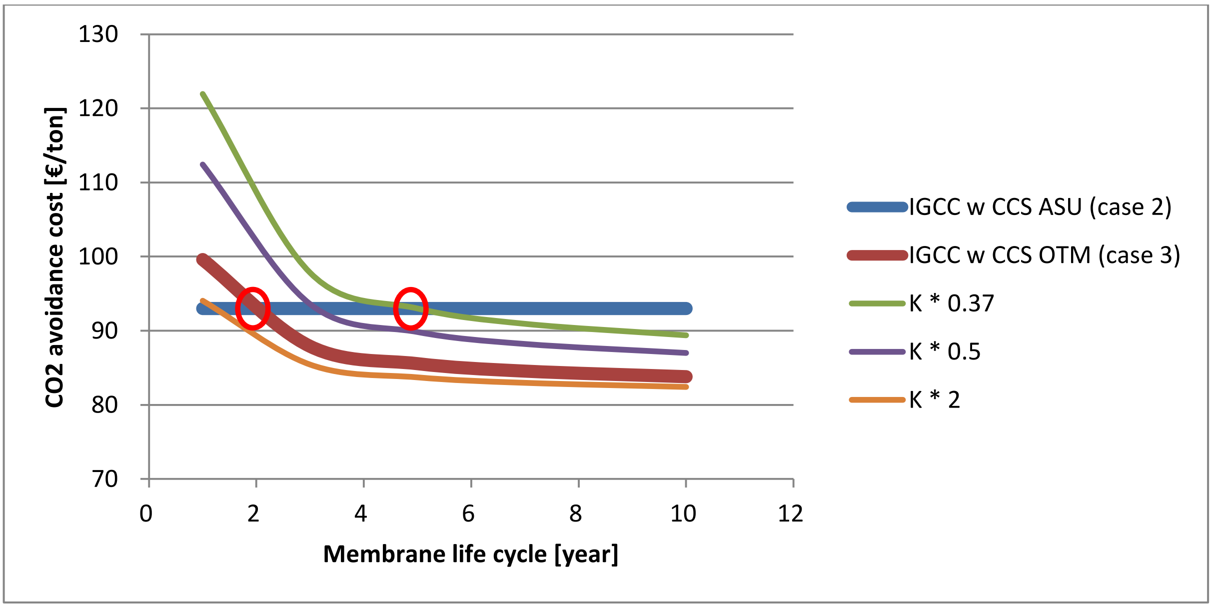


Fig. 27 CO_2 Avoidance Cost vs. membrane life cycle (IGCC with OTM)

Integration of membranes in power plants, however, requires large membrane surfaces; typically 17,700 m^2 and 114,000 m^2 have been estimated for IGCC and CFB plants, respectively. Consequently large investment costs are requested to establish production lines. For this reason integration of O_2 membranes in power plants for pre-combustion capture can be regarded **as a long-term business.** Its implementation can be also related to political and socio-economic factors which could lead to the introduction of carbon emission tax.

As the membrane development for CCS activities is a long-term option, it is essential to identify a **niche market and related small-medium size applications** which, as a perspective, could drive the technology development.
In this frame, the analysis developed in WP6, show that O_2 separation membranes (OTM) can be conveniently integrated in micro-gas turbine for on-site generation of oxygen and power for small-medium size applications (100-500 Nm^3/h), such as foundries (aluminium and cast iron smelting), fish breeding, medicinal uses. These applications require rather low membrane area (in the range of hundreds of square meters) and therefore, can be regarded **as short–medium term business.**
Furthermore OTM can be competitive both in terms of energy efficiency and cost with benchmark technologies, e.g. Pressure Swing Adsorption (PSA) and Vacuum Swing Adsorption (VSA).

The reference applications identified and their market perspectives are summarized in the table below.

Plant/application	**Market perspective**	**Production capability**	**Benchmark technology**
Integrated Gasification Combined Cycle (IGCC) with pre-combustion CO2 capture	Long-term	Large scale	Cryogenic ASU
Oxy-combustion with a Circulating Fluidized Bed (CFB) with CO_2 capture	Long-term	Large scale	Cryogenic ASU
Micro gas turbine (micro GT)/ oxygen on-site production for industrial uses	Short-medium term	Small scale	PSA or VSA

Accordingly, a business plan which outlines the main steps to reach commercial stage and identify the complementary role of industrial partners of DEMOYS along the whole supply chain has been defined. The business plan focus primarily on delivery of oxygen for small-medium size applications, which appears quite attractive and feasible in the short medium term. In this frame Sulzer Metco is in discussion for technology transfer to **a spin-off company established by CSIC (academic Partner of DEMOYS),** whose objective is the manufacture of oxygen membrane modules for small-medium scale applications.

This approach to the market has the advantage that it doesn’t require large investments and could help to progressively reduce the gap with USA industry by promoting a product manufactured by means of a proprietary technology of an European industrial company.
Moreover **social benefits** can be foreseen in term of employment by creating new high qualified jobs and supporting the consolidation of a SME which could be seen as a distinctive feature of the European economy in a globalized competitive market.

Address of project public web-site and relevant contact details

http://demoys.rse-web.it/

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