DEMOYS Publishable Summary

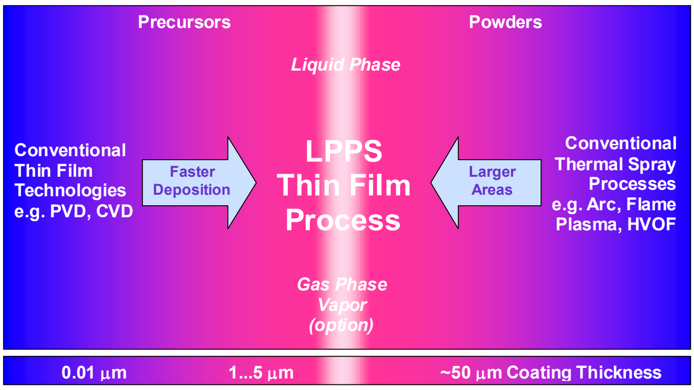
Reporting period: 1 November 2011 – 30 April 2013

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 urgently 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 (>800°C). Similarly ceramic-metal materials (cermets) have been recently studied in order to obtain H_2 separation from CO_2 in 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 Spraying – 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, dense coatings on large areas at low substrate temperatures and has been already successfully used to deposit membranes for the solid oxide fuel cells.

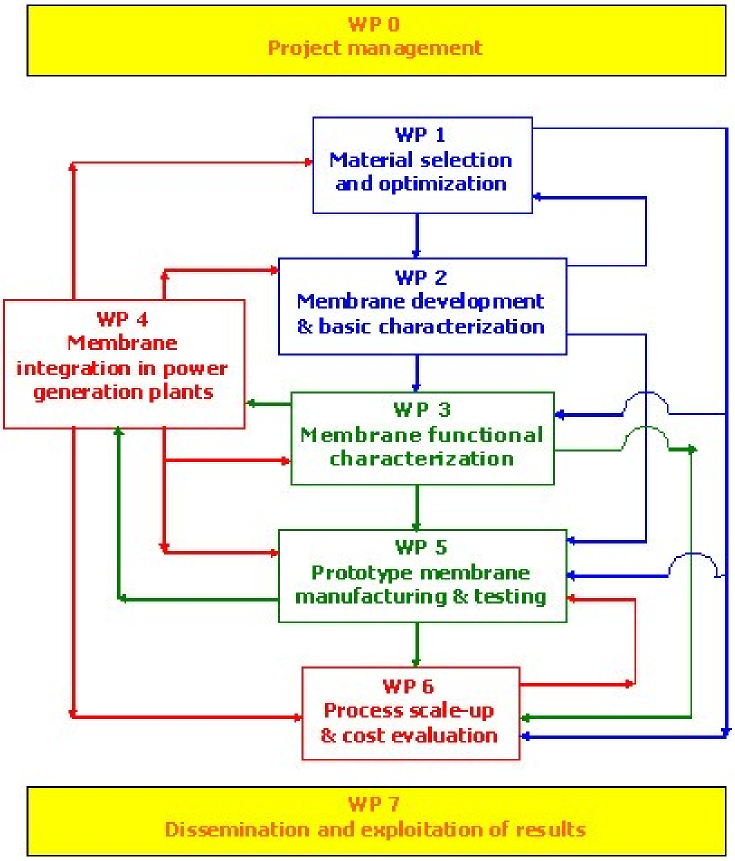


It is expected that, by using the PS-TF process, a dense, stable deposit with thickness lower than 20 micron can be obtained. This would allow increasing membrane performances while decreasing their manufacturing costs. Catalytic layers will be also applied to enhance the surface reactions becoming rate 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.

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

A summary of the main activities and results obtained from month 19 up to month 36 follows.



Description of work performed and main results

$La_{0.58}Sr_{0.40}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) and a proton conducting ceramic (patent to be submitted) have been selected as reference materials for O_2 and H_2 separation membranes, respectively. Several batches of both powders have been manufactured by Sulzer in a prototype plant. 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. Both porous ceramic and metallic supports have been manufactured by Ctisa and GKN, respectively. Deposition tests with LSCF powders have been performed on several ceramic materials (yttria stabilized zirconia, alumina, LSCF); however, they haven't been successful since cracks developed in the support and/or coatings exhibit poor adhesion. Concerning metallic supports, porous Hastelloy X has been first selected as reference material. Dense and stable LSCF layers deposited on such a support; permeation tests, however, indicate a lack of O_2 permeation, due to a densification of the porous support underneath the LSCF layer which occurs during spraying process.

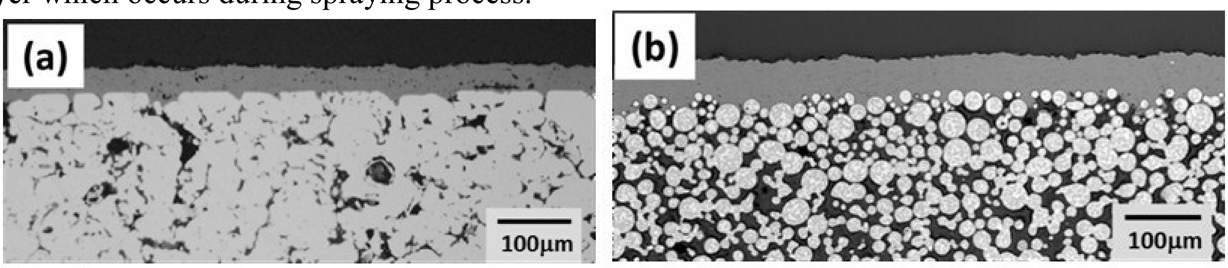


Fig. 1 Micrograph of LSCF coating deposited on porous Hastelloy X (a) and NiCoCrAlY (b) supports

Consequently a new porous support material based on a NiCoCrAlY-alloy has been developed at Juelich. The membranes sprayed on these substrates showed a promising permeation rate, although below project targets, and led to filing two patent applications. Porous supports were then manufactured by gravity sintering at GKN, and used for deposition of both LSCF and proton conducting ceramic dense layer, either by Sulzer or by Juelich.

Permeation tests are in progress, with 15 mm samples (CSIC, Unige, see fig. 2), in a quartz cell and 50 mm samples (Ien and RSE) in laboratory pilot loop designed to operate up to 1000°C and 10 bar.

Application of catalytic layers on both sides of membranes is in progress at CSIC and at Unige, in order to enhance permeation flux of membranes.

The development of a porous LSCF functional layer is in progress at Juelich to achieve maximum surface area contact between the support and the dense membrane layer.

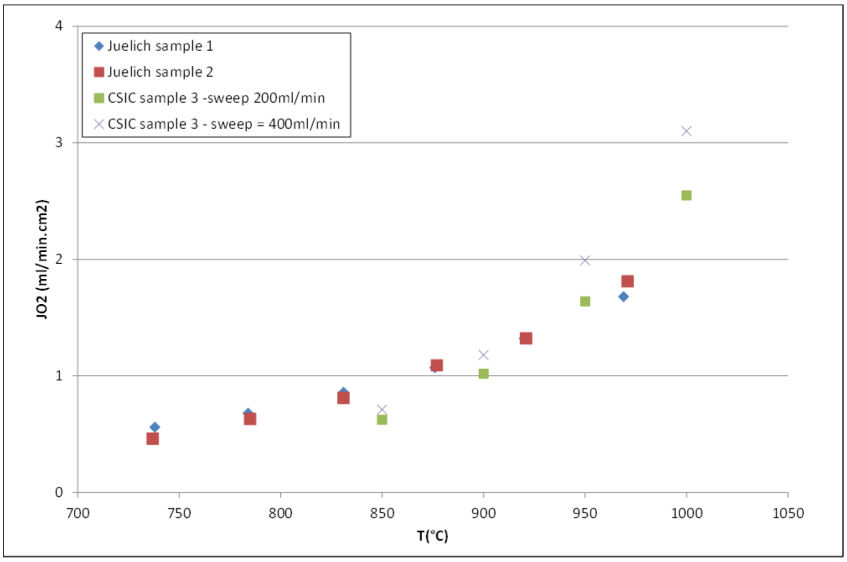


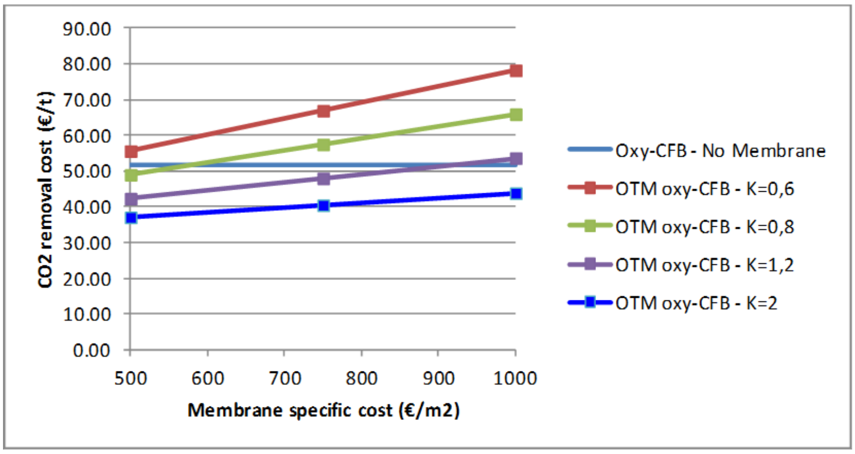
Fig. 2 Permeation tests with LSCF membranes (feed: air; sweep: argon; at atmospheric pressure)

A three-dimensional finite element method (FEM) model for mixed ionic/electronic conducting materials has been developed by KIT-U. The model is able to predict the performance of a dense mixed conducting membrane with an (optional) porous functional layer functional layer on the top.

Specifications for prototype membranes manufacturing have been defined by Sulzer. Test specifications and design of the pilot test installation for prototype H_2 and O_2 membranes have been defined by Sol and Ien, respectively. The construction of pilot installations is in progress.

Detailed mass and energy balances simulations and performance analysis have been performed by Polimi for selected plant configurations. For coal fired power plants, results obtained show that clear advantage can be obtained from O_2 membrane implementation in term of electric efficiency, especially for the CFB-USC configuration. As far as ATR based, natural gas fired plants with pre-combustion CO_2 capture are concerned, significant efficiency gains are expected by integration of both H_2 and O_2 separation membranes. The configuration including an OTM integrated membrane catalytic partial oxidation reactor followed by a second stage reforming reactor integrated with a H_2 separation membrane, reaches an outstanding 52.4 LHV efficiency, about 6.5 higher than comparable plants based on commercial technologies.

Cost estimate of electricity and CO_2 capture has been performed by FWI by means of an in-house developed economic model, for the following plant configurations: IGCC and CFB-USC for power generation, FTR for hydrogen production. A sensitivity analysis concerning specific cost and permeability of membranes indicate that, for each plant arrangement, the membrane integration in the process has the potential for being more economically



attractive than benchmark technologies.

Expected final results and potential impact

The project is now entering in the final phase where performances of both H_2 and O_2 membranes will be evaluated in laboratory pilot loops.

The expected final result of the project is to **prove the technical feasibility of dense, stable O_2 and H_2 separation membranes, obtained by using the PS-TF process.** Specific goals are the following:

- development of O_2 membranes with a flux > 8 ml/cm^2/min and a selectivity > 99% at 950°C;
- development of H_2 membranes with a flux > 10 ml/cm^2/min and a selectivity >99.5% at 950°C;
- remove more than 90% of CO_2 emissions by integration of the developed membranes in power generation and/or hydrogen production plants;
- lower the manufacturing cost of membranes down to 1000 €/m^2.

Accordingly the main expected impacts of the project are:

- **Approach the CO_2 capture cost of 15 €/ton** in power and/or H_2 generation plants. Compared to the technologies currently adoptable, a remarkable cut in the cost of CO_2 capture can be achieved by membranes because of a simultaneous increase of the conversion efficiency and a reduction of the 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). If the project is successful, it will be an important step in reducing the gap with the USA industry which has a leading position in the development of such a type of membranes.