Optimization of porous metal support for Pd deposition

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Pd based membranes may be realized **self supported or supported on porous materials**.

**The self-supported membranes** require thickness greater than 50-100μm to assure a sufficient mechanical strength with a consequent reduction of the hydrogen flux being inversely proportional to Pd thickness.

**The composite membranes** consist of a porous support, providing the required mechanical strength, and of a thin Pd-based film (few microns) performing high H₂ flux. Porous supports may be realized of **ceramics (CS) or metallic (MPS) materials** according to different geometries.

The structure of a porous support strictly influences membrane manufacturing process and consequently final performance.
The composite membranes manufactured on metallic supports require an additional intermetallic layer to avoid that at high temperature metals such as Fe, Cr and Ni, migrate into the Pd lattice thereby negatively affecting the membrane H₂ permeance.

Depending from adopted operating conditions, MPS may be directly in contact with Pd film as well with the intermetallic barrier layer.
Features of metallic porous supports (MPS)

Porous metallic supports are obtained through a sintering process which allows that metallurgical bondings take place. Compared to a ceramic support a MPS allows for:

- **Better mechanical strength** making it well suited for differential pressure application
- **Higher resistance to cracking** due to a similar thermal expansion coefficients between metal and Pd
- **Higher adherence and stability** of the composite membrane during consecutive heating and cooling cycles
- **Easyness of sealing and module fabrication**

The latter is a very important aspect in view of a **full membrane industrialization** requiring methods of fabrication as cheap and simple as possible.
Porous metallic supports may be characterized according to:

- **Material of construction** (SS, Hastelloy, Inconel, Nickel and monel)
- **Shape** (tubular, flat)
- **Porosity** (20-25% is a measure of voids)
- **Media Grade** (0.1 μm, 0.2 μm, 0.5 μm; the “grade” of porous material means that 95% rejection of particles with a size greater than the grade is guaranteed)
- **End connections**

Commercial MPS supports are generally fabricated for other applications rather than for surface deposition of thin membranes thus showing a rough and non-standardized porous support surface.
The primary applications of MPS are relevant to filtration of solids from liquids and gases, flame and spark arrestors as well as gas distribution and sparging systems. Respect to ceramic ones, MPS show:

- Higher surface roughness
- Large mean pore size
- Higher pore size distribution
- Higher number of superficial defects

The structure of metallic support has a significant effect on the membrane performance and may be responsible for the membrane not being completely pinhole free.

In order to fabricate thin membranes on available commercial MPS supports, the general tendency is to adopt pre-treatment to increase surface finishing.
Main issues in using MPS

- ROUGHNESS AND SUPERFICIAL DEFECTS

The high dimension voids and holes of typical MPS make difficult to have continuity on the surface. By applying a coating the risk is that material fills cavities and holes in the surface without giving a uniform layer unless applying a very high thickness.

SEM of Commercial MPS (magnification 800)
Main issues in using MPS

PORE SIZE DISTRIBUTION

Commercial 0.1 μm grade: \( \rightarrow \) max pore size = 4-5 μm

Commercial 0.2 μm grade: \( \rightarrow \) max pore size = 6-7 μm

Commercial 0.5 μm grade: \( \rightarrow \) max pore size = 11-12 μm

To achieve a pinhole-free layer by electroless plating, Pd-thickness has to be approximately three times the diameter of the largest pores.
Main issues in using MPS

WELDED CONNECTIONS

Welding between porous material and solid connection is a crucial aspect. A not proper procedure may be responsible for damages in support structure. Under the heat of welding arc, voids present in the structure of MPS tend to collapse thus allowing for defect formation.

Transition region between sintered and cast material

Bubble test evidences defects caused by welding procedure

Broglia et al., (2011)
The roughness and the defects may be minimized by shrinking the pore size through a dispersion of submicron particle on the surface, through a mechanically alteration of upper layer or by applying sintering step at high temperature.

**SHRINKING THE PORE SIZE THROUGH A DISPERSION OF SUBMICRON PARTICLES** (1-3)

MPS may be modified by using particles with different dimensions to fill large pores on the surface thus decreasing surface pore entrance and to decrease surface roughness \((\text{Al}_2\text{O}_3, \text{CeO}_2, \text{ZrO}_2)\).

**MECHANICAL ALTERING OF THE SURFACE** (4-5)

Polishing and etching treatment, followed or not by two successive coatings with oxide sols (aluminium) of different particle sizes. The polishing considerably decreased surface roughness of the substrate, while the etching opened up pore entrances closed during polishing. The successive coatings reduced surface roughness and surface pore size.

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(2) Tong et al., (2005), Separation and Purification Technology 46, 1–10
(3) Wang et al., (2004), Catalysis Today 93–95, 689–693
Procedure to improve MPS finishing

The roughness and the defects may be minimized by shrinking the pore size through a dispersion of submicron particle on the surface, through a mechanically alteration of upper layer or by applying sintering step at high temperature.

- **SINTERING AT HIGH TEMPERATURE** (1)
  Dispersion of submicron metal powder on the substrate followed by sintering to allow bonding and to make the substrate surface smoother.

- **INTERMETALLIC BARRIER AS FINISHING LAYER** (2-3)
  Intermetallic barrier may act as finishing layer thus leveling superficial roughness and improve smoothness.

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(2) Damle, Pall Corporation (2011)
Efforts in the framework of Comhety Project

A CS generally shows an asymmetric structure consisting of graded layer with fine pore size deposited on a much coarser support. Moving from this consideration a similar approach has been adopted for MPS moving to **Asymmetric supports**

**ASYMMETRIC SUPPORTS**

- **SEM of asymmetric MPS (magnification 1000)**
  - Finished top layer
  - Coarse underlying layer

- **SEM of symmetric MPS (magnification 800)**
Efforts in the framework of Comhety Project

A CS generally shows an asymmetric structure consisting of graded layer with fine pore size deposited on a much coarser support. Moving from this consideration a similar approach has been adopted for MPS moving to **Asymmetric supports**

**ASYMMETRIC SUPPORTS**

SEM of asymmetric MPS (magnification 1000)
Efforts in the framework of Comhety Project

A CS generally shows an asymmetric structure consisting of graded layer with fine pore size deposited on a much coarser support. Moving from this consideration a similar approach has been adopted for MPS moving to **Asymmetric supports**

- **ASYMMETRIC SUPPORTS**
  - SEM of asymmetric MPS (magnification 2500)
  - SEM of asymmetric MPS (magnification 5000)

- Barrier layer
Under the scenario to use symmetric support thus characterized by only one synerization step, the manufacturing procedure based on isostatic compaction followed by syntering step has been modified in order to achieve higher smoothness.

- **SYMmetric SUPPORTS WITH REDUCED ROUGHNESS**
- Change in the manufacturing procedure allowing for higher smoothness

![New tool technology](image1)
![Previous tool technology](image2)
Conclusions

- **Metallic Porous Supports** appear to be the best candidates for a **full membrane industrialization allowing** for enhanced mechanical stability and adhesion as well as in easiness weldability and module assembly.

- The quality of currently commercial MPS shows a rough and non-standardized porous surface which may be responsible for non pinhole free membranes.

- Surface modification by mechanical treatment as well by addition material **by shrinking the pore size** and defects are required in order to obtain pinhole free membranes.

- Improvements in MPS manufacturing procedure has to be directed to reduce pore size distribution and superficial roughness as well as in reducing cost considering that membrane support cost is one of the dominant component.
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