National Research Council of Italy - CNR
Institute of Condensed Matter Chemistry and Technologies for Energy - ICMATE

# HiPIMS deposition of dense Palladium-Silver films for hydrogen separation

S. Fasolin, S. Barison, S. Boldrini, F. Montagner,
M. Romano, A. Ferrario, M. Fabrizio, L. Armelao

CNR-ICMATE, Corso Stati uniti 4, 35127, Padova - Italy

**e-mail:** stefano.fasolin@cnr.it

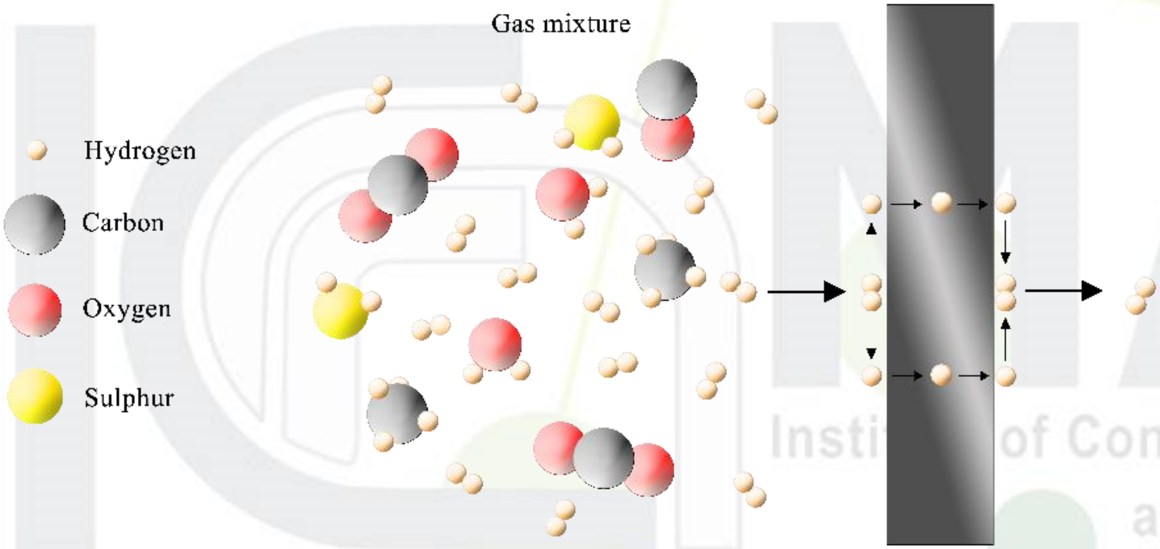
EERA
European Energy Research Alliance

AMPEA Advanced Materials and Processes for Energy Applications

# Palladium-based membranes

**Pure Palladium exhibit the ability to adsorb hydrogen and to catalyse dehydrogenation from hydrocarbons.**

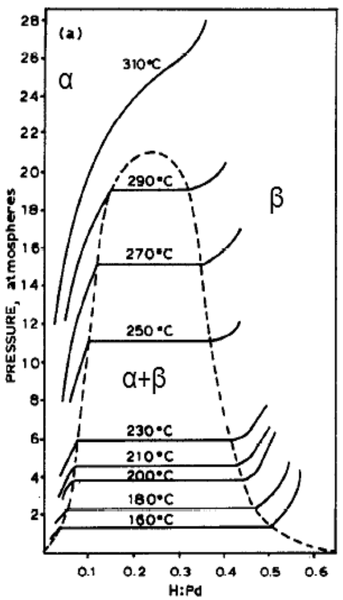
**Membrane development started with self standing palladium membranes for hydrogen purification (mostly tubular).**




**Pd - FCC**
**a = 0.3890 nm**

**Pd(H) α - FCC**
**a = 0.3895 nm**

**Pd(H) β - FCC**
**a = 0.4100 nm**




**PROS**
- **High selectivity/permeability to hydrogen**
- **Working temperature**

**CONS**
- **Embrittlement**
- **Costs**

# Palladium-based membranes

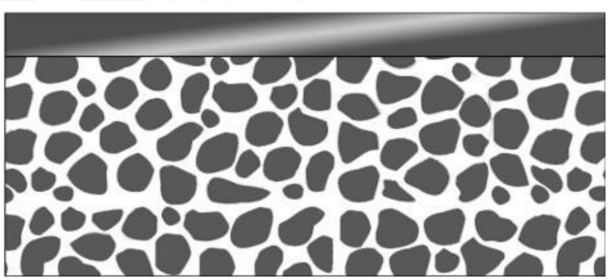
**Hydrogen membrane costs are strictly related to Pd amount.**

**European limits for critical raw materials + US Dep. of Energy cost target -> 1000$/m$^2$**
**(film of pure Pd thinner than 3µm)**

**How to reduce Pd amount and improve stability?**

1. **Thinner membranes supported onto porous substrates**
2. **Improve stability and reduce Pd amount, introducing elements (Pd alloys or alternatives)**

**$Pd_{77}Ag_{23}$** → **Silver stabilize lattice, promoting hydrogen adsorption and diffusion, and lowering the embrittlement temperature.**



**$Al_2O_3$** → **Alumina is a common and cheap oxide, easy to use to obtain porous substrate.**

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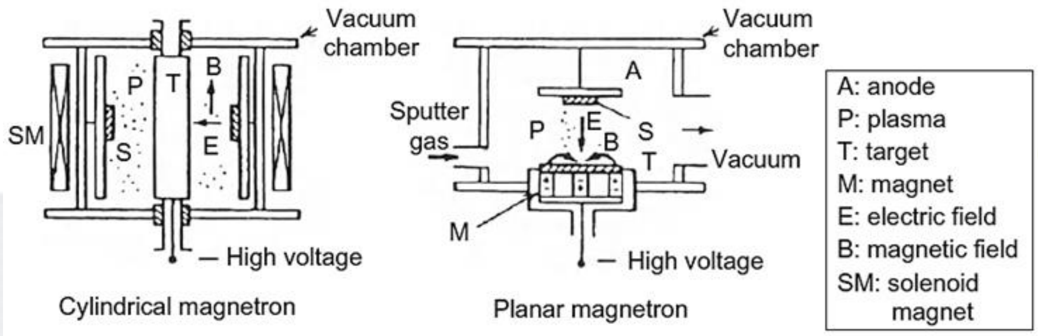
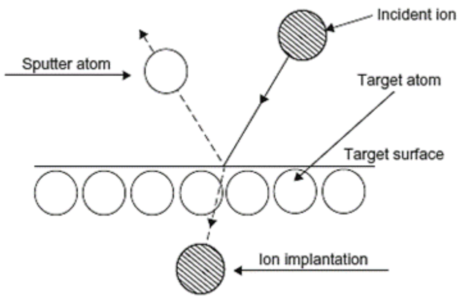
# Hi-PIMS: High-Power Impulse Magnetron Sputtering

**It is a Physical Vapour Deposition technique derived from Magnetron Sputtering (MS).**



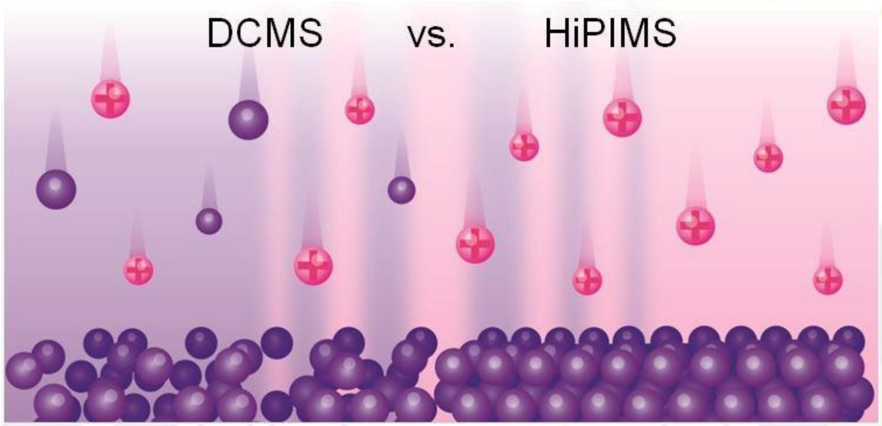

| Parameter | HIPIMS | DC MS |
|---|---|---|
| **Working Pressure** | 0.001 – 0.1 mbar | 0.001 – 0.1 mbar |
| **Cathode Current Density** | $J_{MAX} \leq 10$ A/cm$^2$ | $J_{MAX} \leq 0.1$ A/cm$^2$ |
| **Discharge Voltage** | 0.5 – 1.5 kV | 0.3 – 0.6 kV |
| **Plasma Density** | $\leq 10^{13}$ cm$^{-3}$ | $\leq 10^{11}$ cm$^{-3}$ |
| **Cathode Power Density** | 1 – 3 kW/cm$^2$ | < 0.1 kW/cm$^2$ |
| **Ionization Fraction** | 30% – 90% | < 1% |

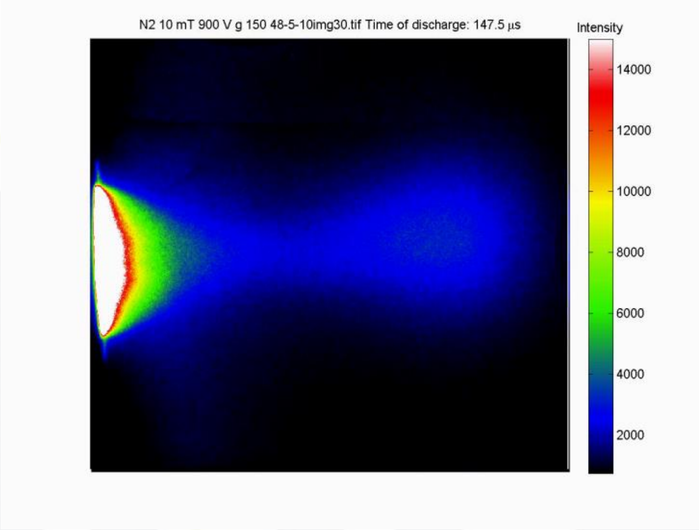
**By using pulse mode (target current pulsed from 1μs to 1s) the target current density can be increased with formation of ultra dense plasma.**

# Hi-PIMS: High-Power Impulse Magnetron Sputtering

**Features:**

- High power densities ($kW/cm^2$) in short pulses (µs)
- High degree of ionization (sputtered species)




Target material ions can be accelerated towards the substrate along the field lines

**Benefits:**

- Film quality: better adhesion and density, lower defectivity and roughness.
- Homogenous deposition onto complex shapes.
- Easily scalable for industrial application.

# Hi-PIMS: High-Power Impulse Magnetron Sputtering

DC unit

HiPIMS Pulse unit

- Arc Suppression
- droplet-free sputtering
- T pulse and frequency

Bias unit

- Designed to work with generators Hi-pulse
- Arc Management

DC Pulse unit

# Hi-PIMS parameters

## Which parameters affect deposition rate and film quality?

- Pressure (mainly affect the ions free medium path)
- Gas (inert, reactive…)
- Type of target (metallic, non metallic, magnetic…)
- Type of substrate (conductive, insulating, smooth, rough…)
- Power, current, pulses applied to the target
- Distance between target and substrate
- Bias (acceleration of ions from target to substrate)
- Substrate temperature
- Deposition time
- Sample holder rotation (homogenization)

…

# Porous support

$\alpha$-$Al_2O_3$ + pore former

Pore former tested: **starch, graphite, poly methyl methacrylate** (round shape, average size 1,5 – 3 – 7 µm)

Ball milling

Uniaxial pressure

Sintering

Surface polishing

Cleaning

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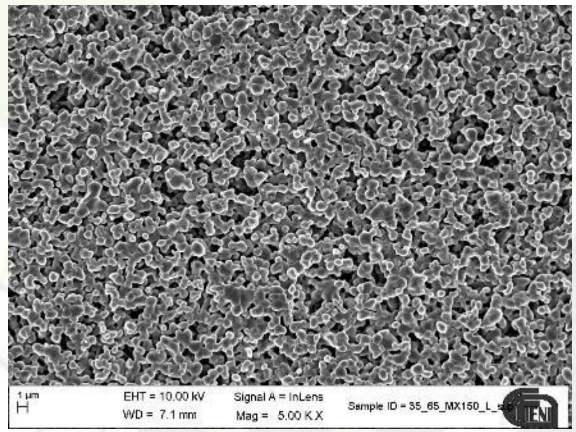
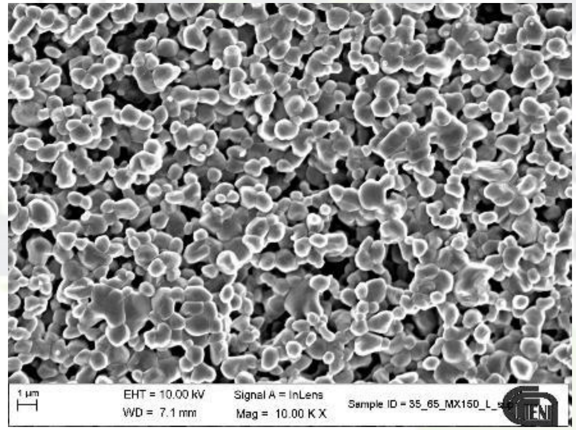
# Porous support

Best result:
α-$Al_2O_3$ + PMMA (1,5 µm average size)

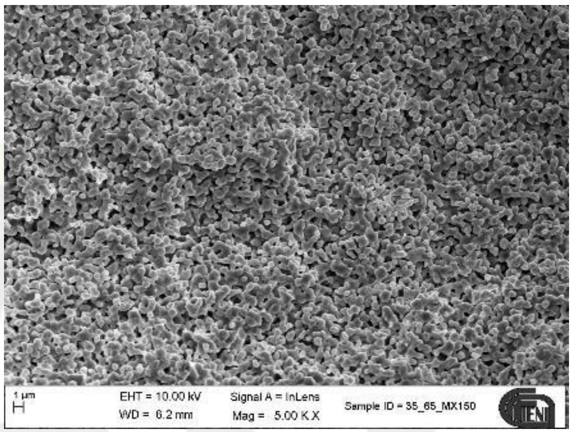
Open porosity (40 vol%)
Maximum pore size about 1 µm

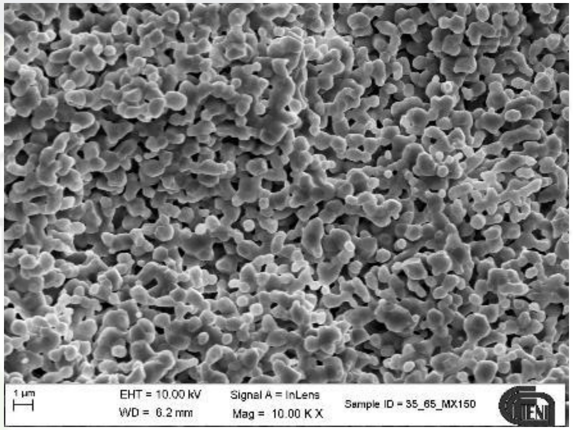
**Surface**



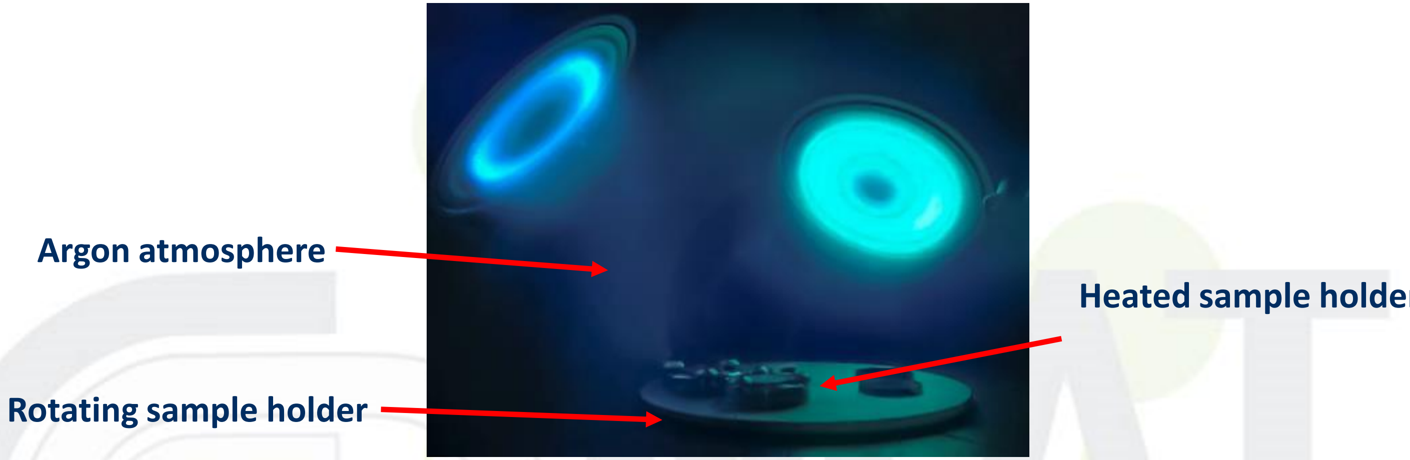



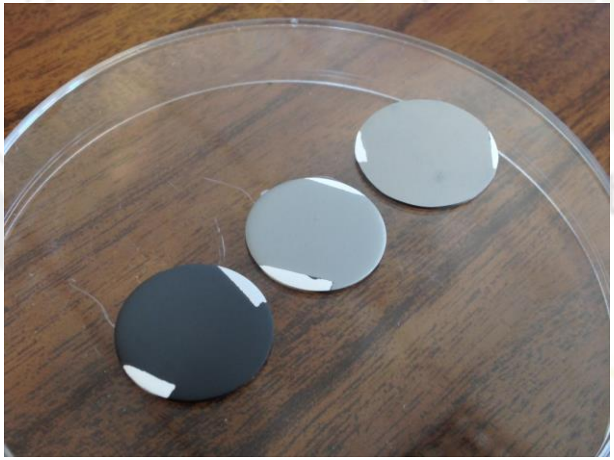

**Cross section**



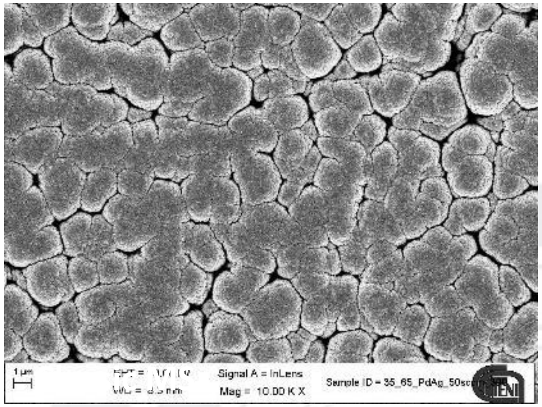
# Hi-PIMS: planar membranes deposition

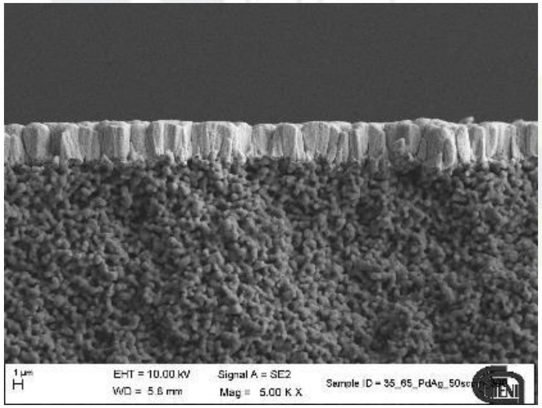


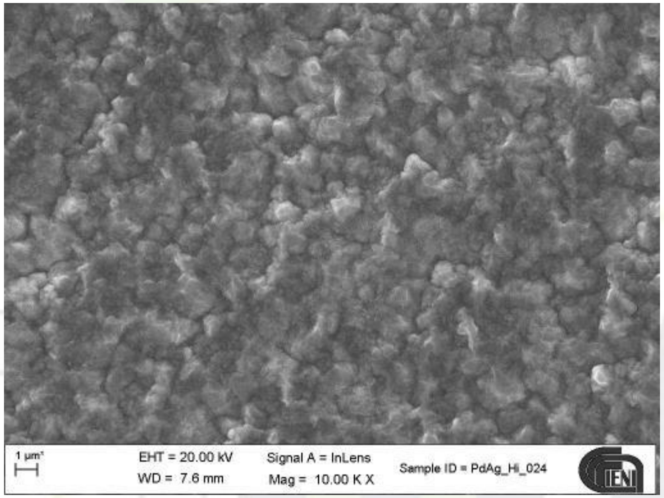
# $Pd_{77}Ag_{23}$ membranes: SEM analyses

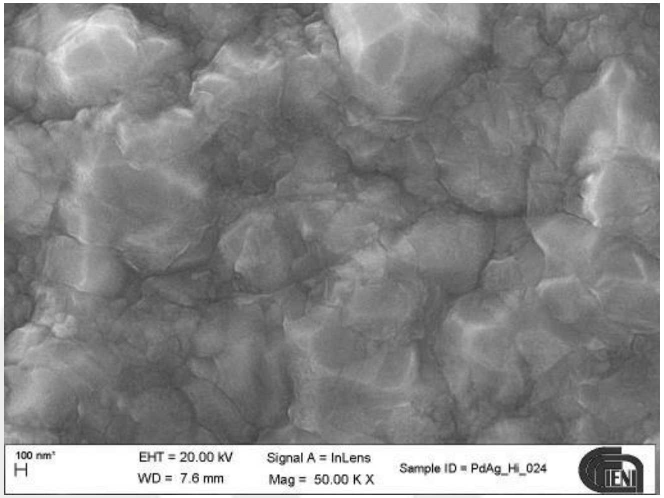
**Classic MS**

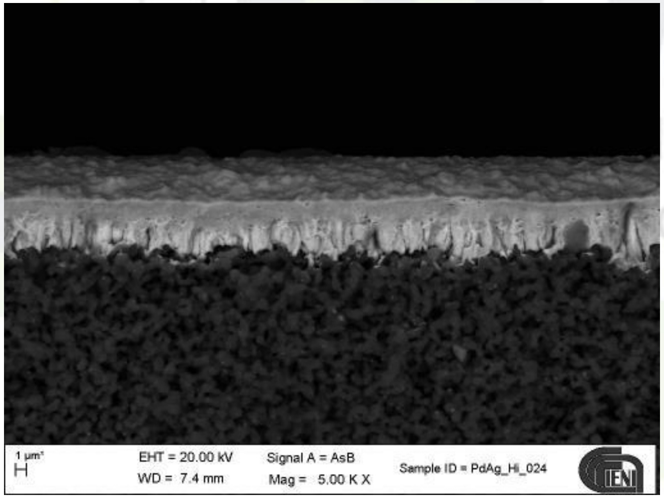


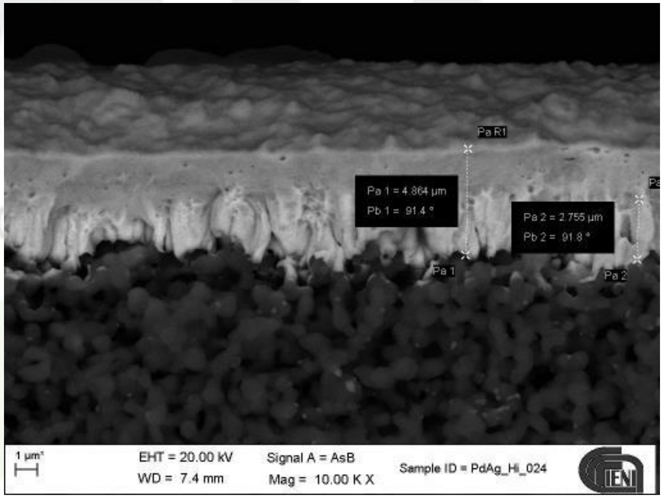




**Hi-PIMS**

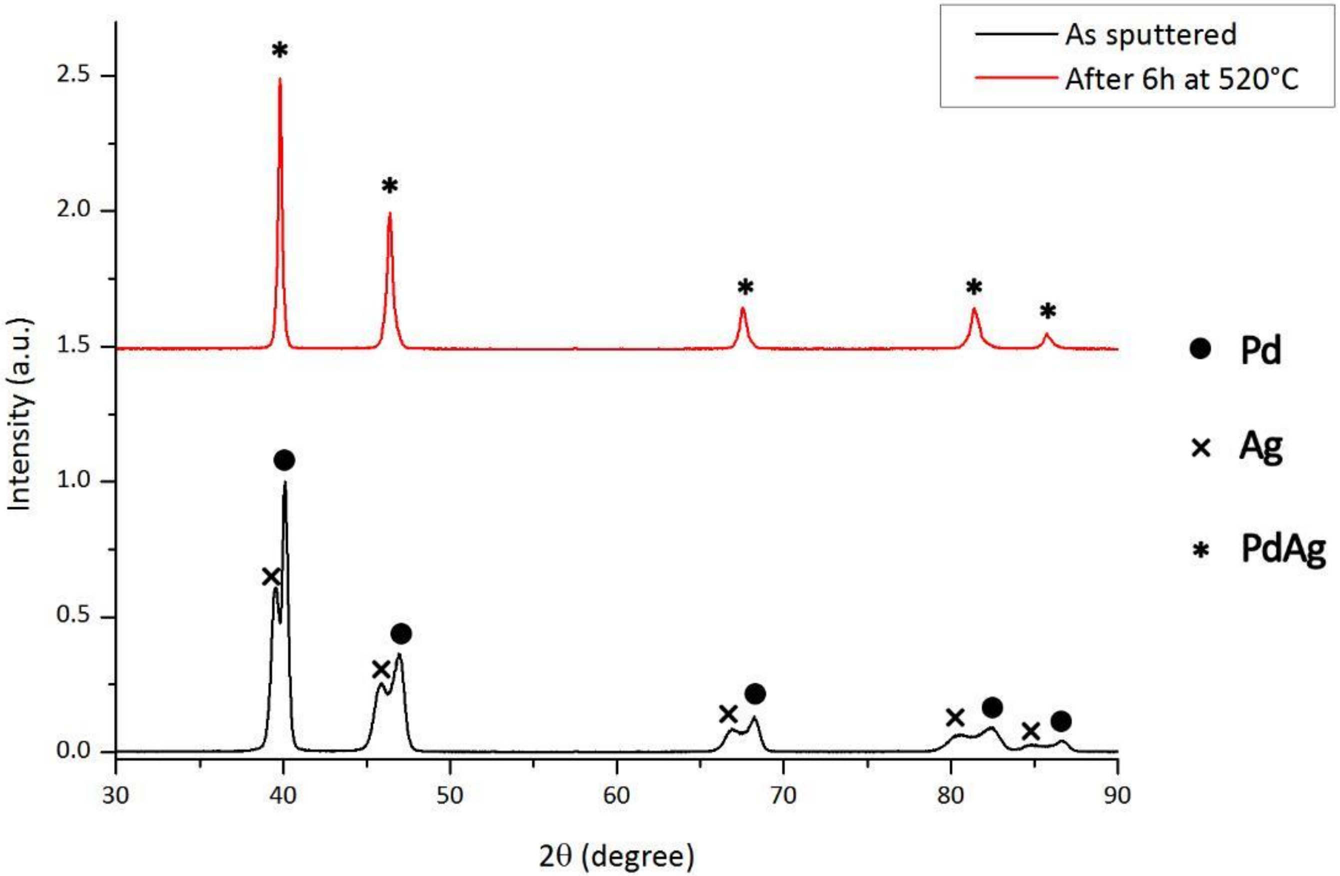


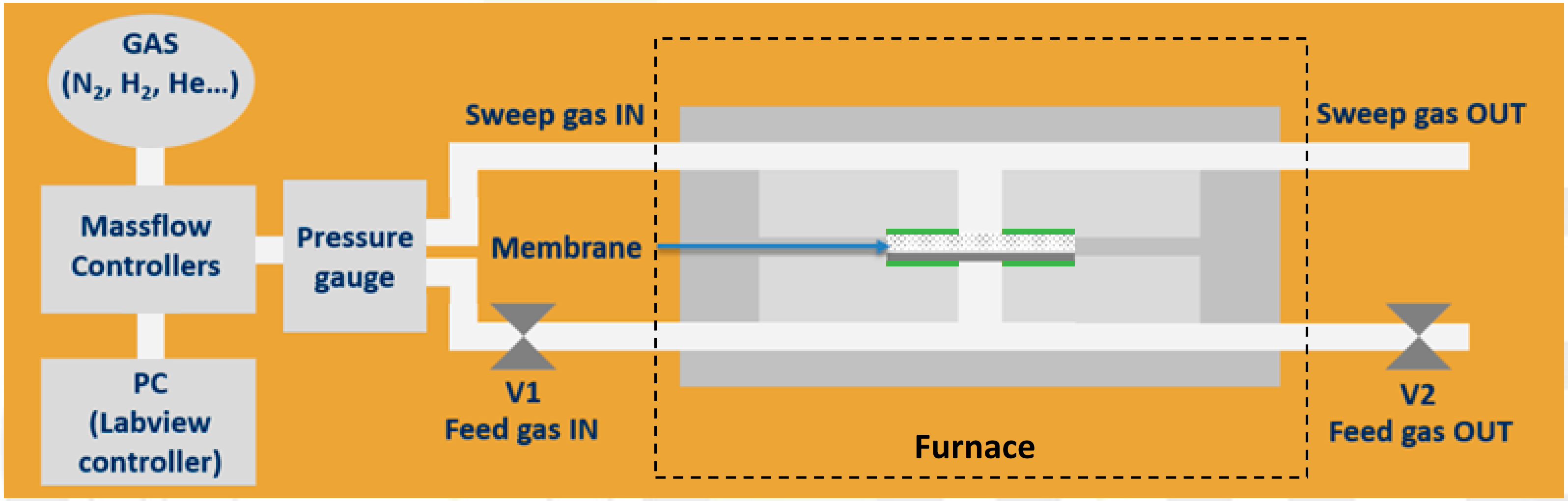
# PdAg membranes: XRD and EDS analyses



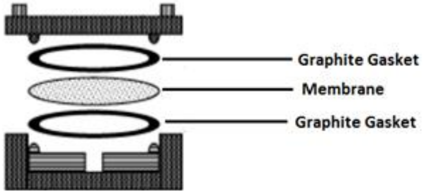

**EDS**

**Pd 77% ± 2%    Ag 23%± 2%**

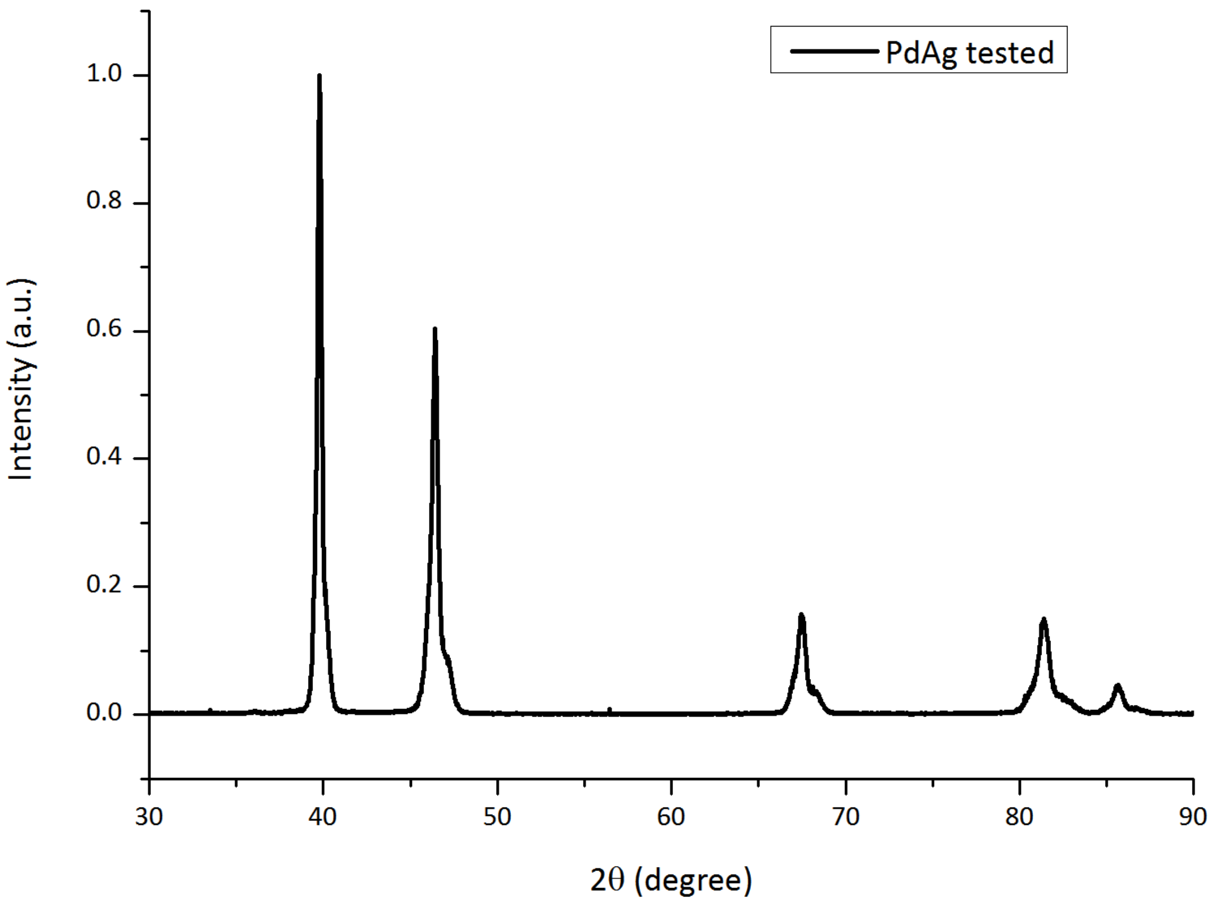
# PdAg membranes: permeability test



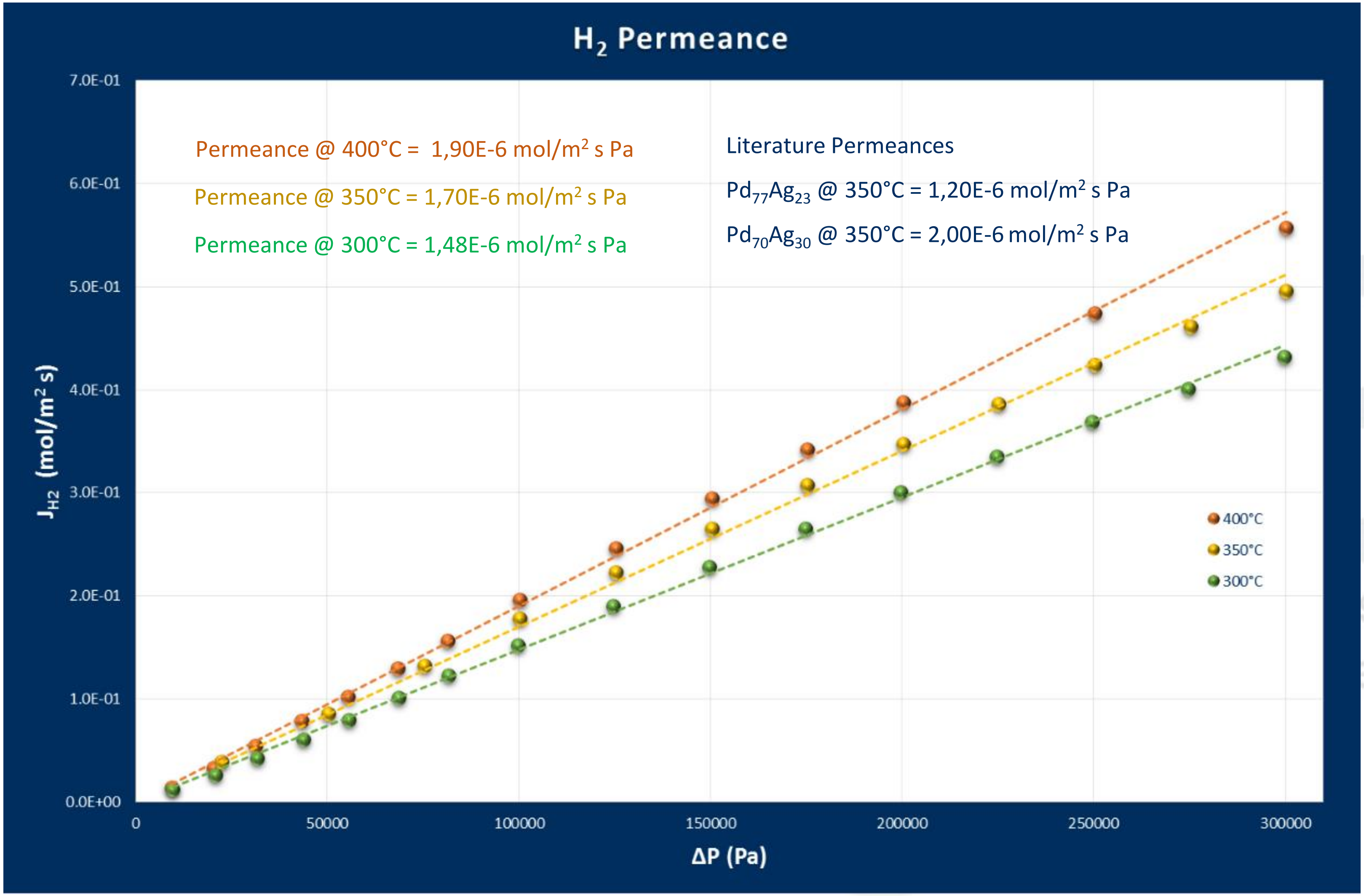

- Gas: nitrogen, helium, hydrogen, argon, syngas.
- Pressure range: from 0,1 to 3 bar over atmospheric pressure;
- Temperature range: RT-450ºC;
- PC with Labview controller



# PdAg membranes: XRD analyses



# $Pd_{77}Ag_{23}$ membranes: permeance



# Conclusions and perspectives

## Conclusions

- A fine tuning of HiPIMS parameters for insulating and porous substrate coverage were achieved.
- Thin and dense $Pd_{77}Ag_{23}$ films have been deposited onto porous alumina by means of HiPIMS.
- PdAg phase were detected after annealing and after test conditions.
- High permeance values were obtained for membranes with 2 µm dense layer.

## Perspectives

- Investigation of other alloys (other Pd-alloy, V-based…)
- Investigation on $H_2$/gases selectivity.
- Set up of PdAg membranes (thickness, sealing…).
- Evaluation of porous metallic supports.
- Scale up in membranes size.

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