Preparation and characterization of thin Pd-Ag-Au supported membranes for hydrogen separation

Jon Meléndez[1,2] , D. A. Pacheco Tanaka[1] , Alba Arratibel[1,3], Niek de Nooijer, Ekain Fernandez[1], M. van Sint Annaland[3], Pedro L. Arias[2], Fausto Gallucci[3].

[1] TECNALIA, Materials for Energy & Environment Department, Mikeletegi Pasealekua, 2, 20009 Donostia-San Sebastian, Spain
[2] University of the Basque Country (UPV-EHU), Chemical Engineering and Environmental Department, Spain.
[3] Eindhoven University of Technology, Department of Chemical Engineering and Chemistry, Multiphase Reactors Group.

Contact us at:

jon.melendez@tecnalia.com
f.gallucci@tue.nl

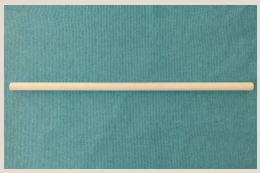
Introduction

- Among the membrane materials for hydrogen separation, Pd membranes present the highest hydrogen flux and exclusive perm-selectivity due to their mechanism of hydrogen transport. Hydrogen molecule is chemisorbed on the Pd surface; dissociated in hydrogen atoms and diffused through the membrane driven by the difference in the partial pressure between both sides.
- Pure palladium membranes have some drawbacks, in terms of stability, that can be solved by alloying with other metals. The addition of Ag increases the hydrogen permeation [1] and prevents from hydrogen embrittlement when working at lower temperatures (below 573 K and 2 MPa).
- However, the presence of few ppm of sulphur in the gas mixture (typical in bio-based feedstock) deteriorates the performance of palladium based membranes due to its strong surface adsorption.
- It is reported that the addition of gold to palladium based membranes improves the tolerance to sulfur compounds, improves the hydrogen embrittlement resistance, and, for certain compositions, could also improve the hydrogen permeability [2].
- In this work, a Pd-Ag supported membrane was prepared by electroless plating (ELP). In order to have better comparison of the properties of the membrane after the addition of Au, half of the membrane was covered with teflon and gold was deposited by ELP onto the other half. The effect of the addition of Au on the hydrogen permeation properties are presented.

Experimental Procedure

MEMBRANE PROCEDURE FABRICATION by ELP

Step 1:
Support fabrication



Step 2:
Support activation [3]

Step 3:
Simultaneous deposition of Pd and Ag [4]

Step 4:
Au deposition [5] and annealing

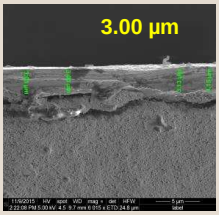
Step 5:
Sealing [6]

Pd88Ag12

Pd79Ag12Au9

PERMEATION TEST OF THIN PALLADIUM-SILVER-GOLD MEMBRANES

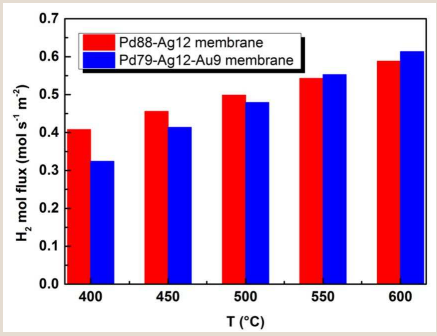
Hydrogen and nitrogen permeation single gas tests were carried out for Pd88-Ag12 and Pd79-Ag12-Au9 membranes in a temperature range between 673 K and 873 K. Long term test for 150 hours at 873K was performed too for Pd79-Ag12-Au9 membrane.

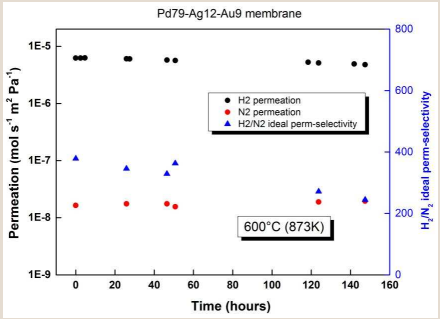


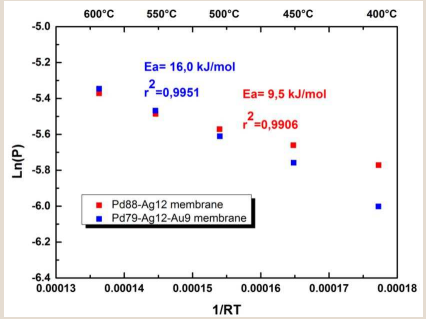
SEM characterization before Au addition in order to determine its thickness.

Code	% Pd	% Ag	% Au
Membrane #2. Pd-Ag	87,7	12,3	-
Membrane #2. Pd-Ag-Au	79,3	11,4	9,3

•The membranes alloy composition was determined by SEM (PerkinElmer OPTIMA 2000 DV)







	Thickness (µm)	H_2 permeance [mol s^{-1} m^{-2} $Pa^{0.5}$] at 450°C (723K)	H_2/N_2 ideal perm-selectivity at 450°C (723K)	Ref.
Membrane Pd88-Ag12	3.0	3.64E-03	1294	This work
Membrane Pd79-Ag12-Au9	3.0	3.16E-03	1222	This work
Membrane Pd75-Ag22-Au3	1.9	4.89E-03 (90%-10% N2)	6825	[7]
Membrane Pd75-Au29	5.0	2.23E-03 (at 755K)	-	[8]

Conclusions

- A Pd-Ag-Au membrane showed higher hydrogen permeation than the Pd-Ag membrane at temperatures ≥ 550 ºC (823 K).
- Addition of gold to a palladium-silver membranes increases the activation energy of hydrogen permeation.
- The hydrogen permeation of Pd-Ag-Au membrane was stable for 150 hours at 600 ºC (873 K), but H_2/N_2 ideal perm-selectivity decreased.

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