Ternary alloy membranes for carbon-neutral hydrogen production from biomass gasification exhaust

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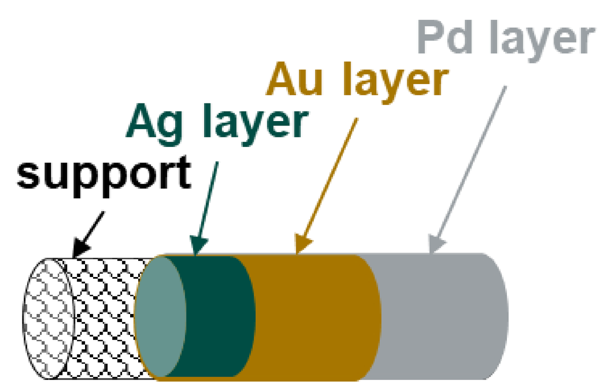
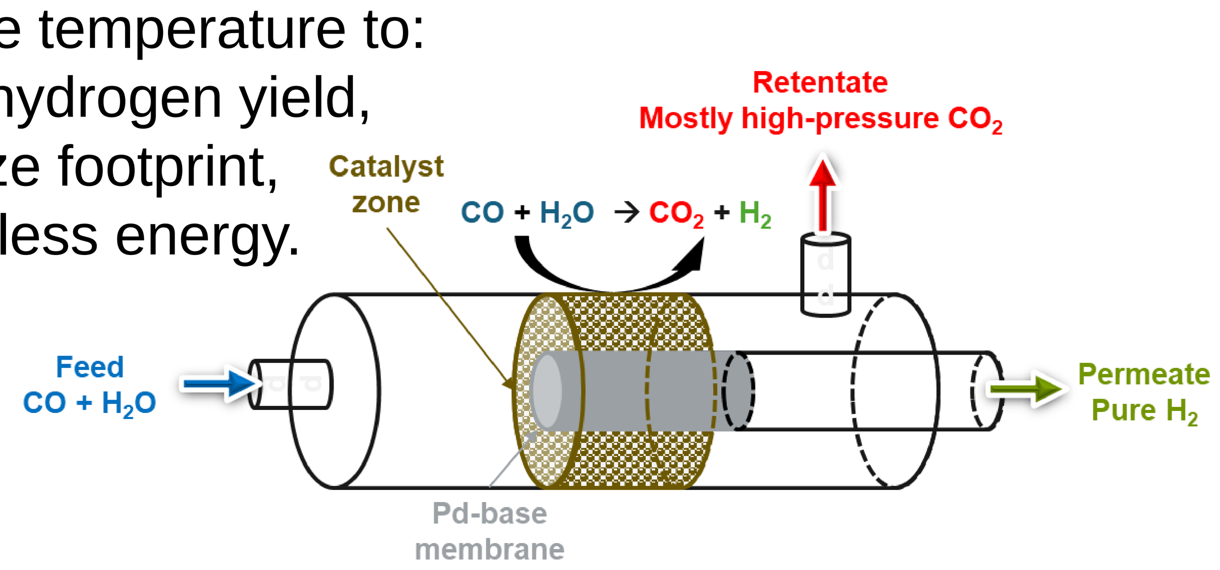
Objectives

- Synthesize ternary ($Pd_{(1-x-y)}$-Au_x-Ag_y) metallic membranes with:
  - ✓ high selectivity to hydrogen,
  - ✓ high surface area,
  - ✓ thermochemical stability.



- Integrate synthesized ternary membrane into membrane reactor and perform catalytic water-gas shift (WGS) reaction at intermediate temperature to:
  - ✓ enhance hydrogen yield,
  - ✓ reduce size footprint,
  - ✓ consume less energy.



Electroless Plating Method

Palladium (Pd):

$H_2NNH_2 + 4\,OH^- \rightarrow N_2 + 4\,H_2O + 4\,e^-$ (1)

$2\,Pd^{2+} + 4\,e^- \rightarrow 2\,Pd^0$ (2)

$2\,Pd^{2+} + H_2NNH_2 + 4\,OH^- \rightarrow 2\,Pd^0 + N_2 + 4\,H_2O$

Silver (Ag):

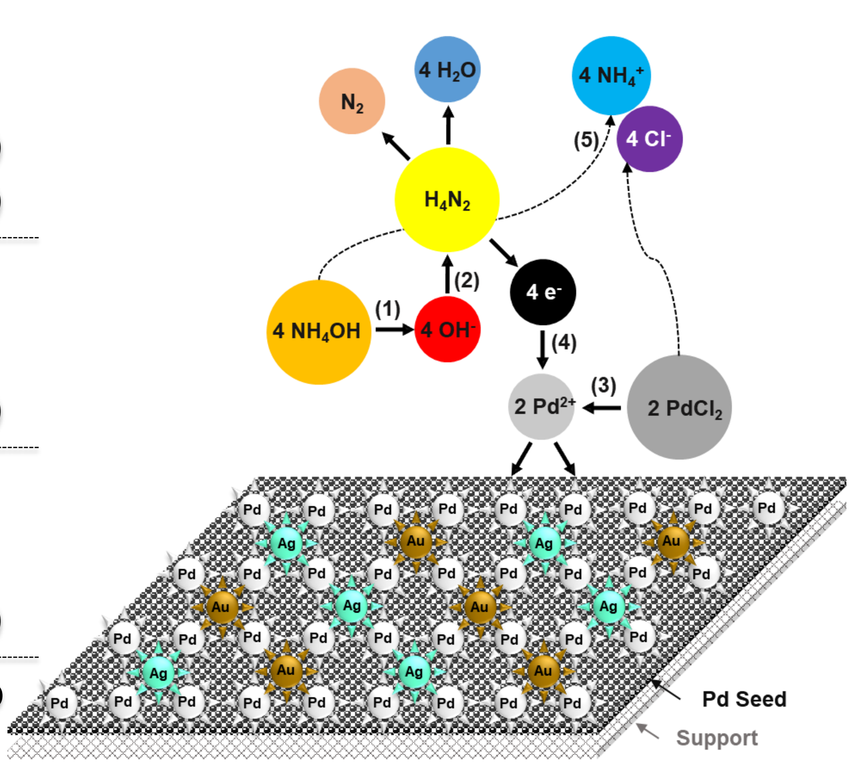
$4\,Ag^+ + 4\,e^- \rightarrow 4\,Ag^0$ (3)

$4\,Ag^+ + H_2NNH_2 + 4\,OH^- \rightarrow 4\,Ag^0 + N_2 + 4\,H_2O$

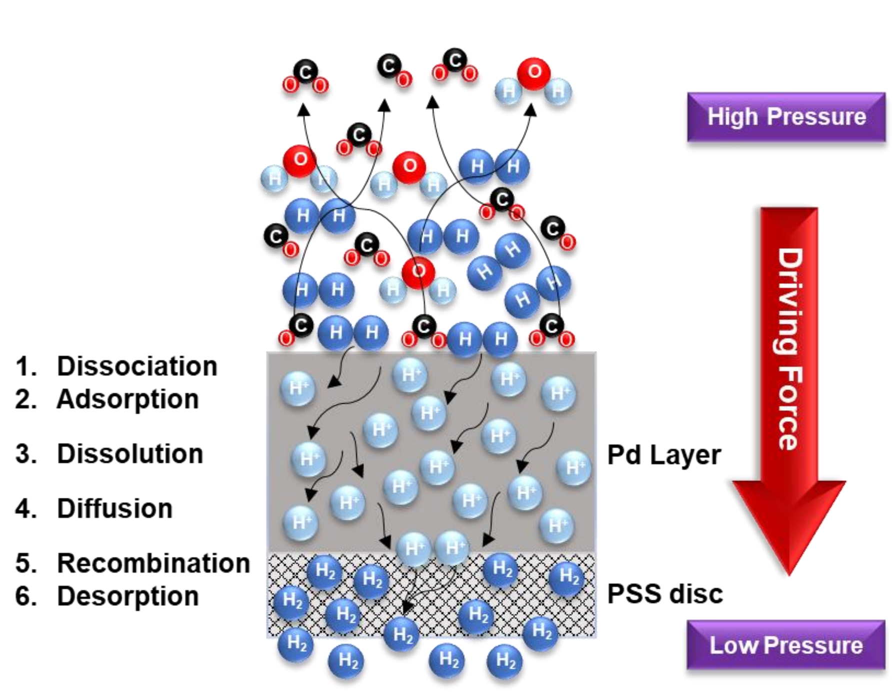
Gold (Au):

$Au^{3+} + 3\,e^- \rightarrow 3\,Au^0$ (4)

$Au^{+3} + \tfrac{3}{4}\,H_2NNH_2 + 3\,OH^- \rightarrow 3\,Au^0 + \tfrac{3}{4}\,N_2 + 3\,H_2O$



Solution-Diffusion Mechanism



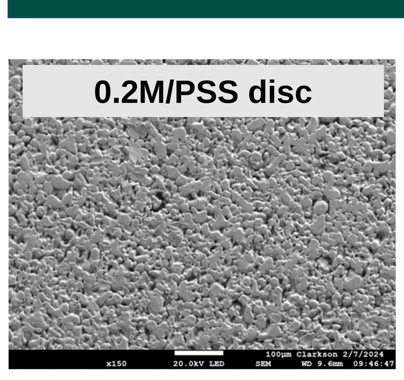
$$Flux\ (J_i) = P_i(p^n{}_{retentate} - p^n{}_{permeate})$$

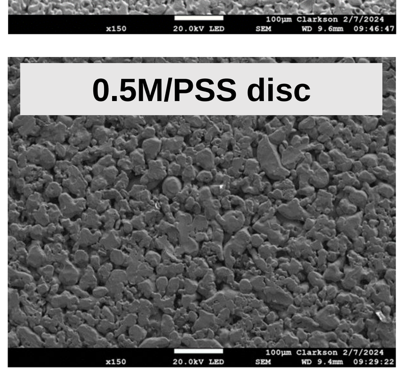
$$Ideal\ selectivity, \alpha(i/j) = \frac{P_i}{P_j}$$

$$Arrhenius, P_i = P^0{}_i\, exp\left(-\frac{E_a}{RT}\right)$$

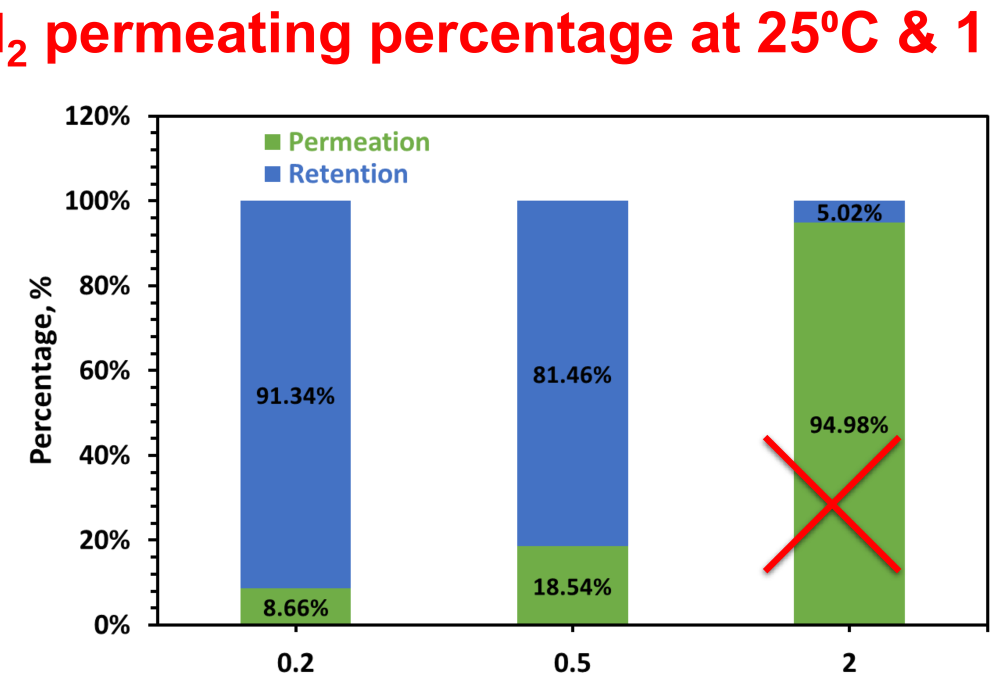
J_i = Permeation flux, mole/m²$.sec
P_i = Permeance, mole/m²$.sec.bar^n
$p^n{}_{retentate} - p^n{}_{permeate}$ = pressure difference, bar^n
n = Variable between 0.5 – 1,
$P^0{}_i$ = Pre-exponential factor,
E_a = Apparent activation energy, KJ/mole
R = Universal gas constant = 8.413 KJ/mole.K
T = Temperature, K

PSS Support Characterization



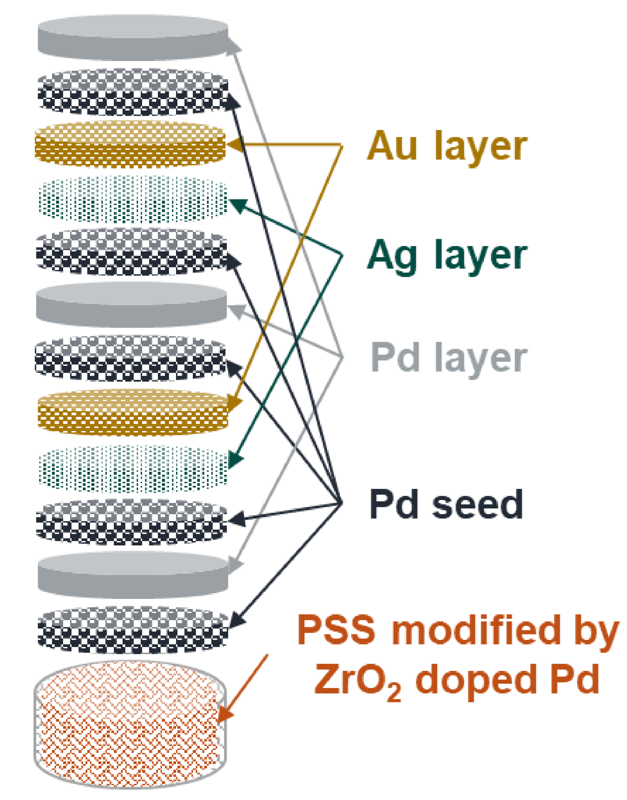


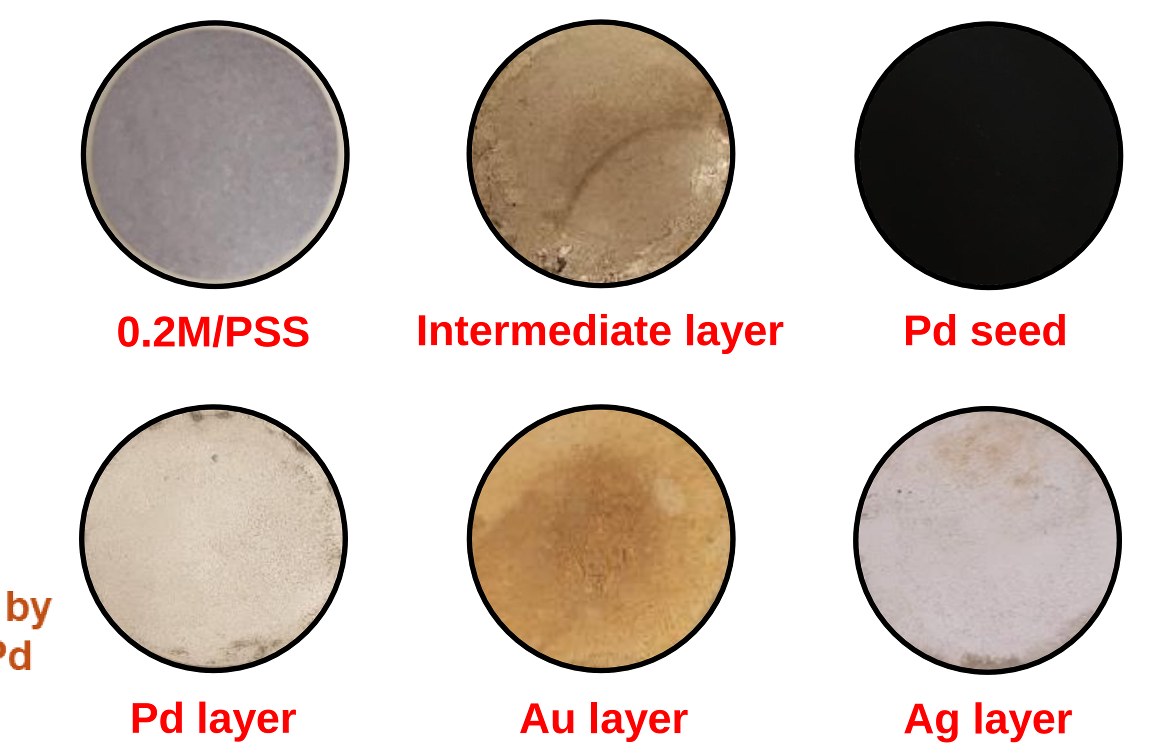
N_2 permeating percentage at 25°C & 1 bar



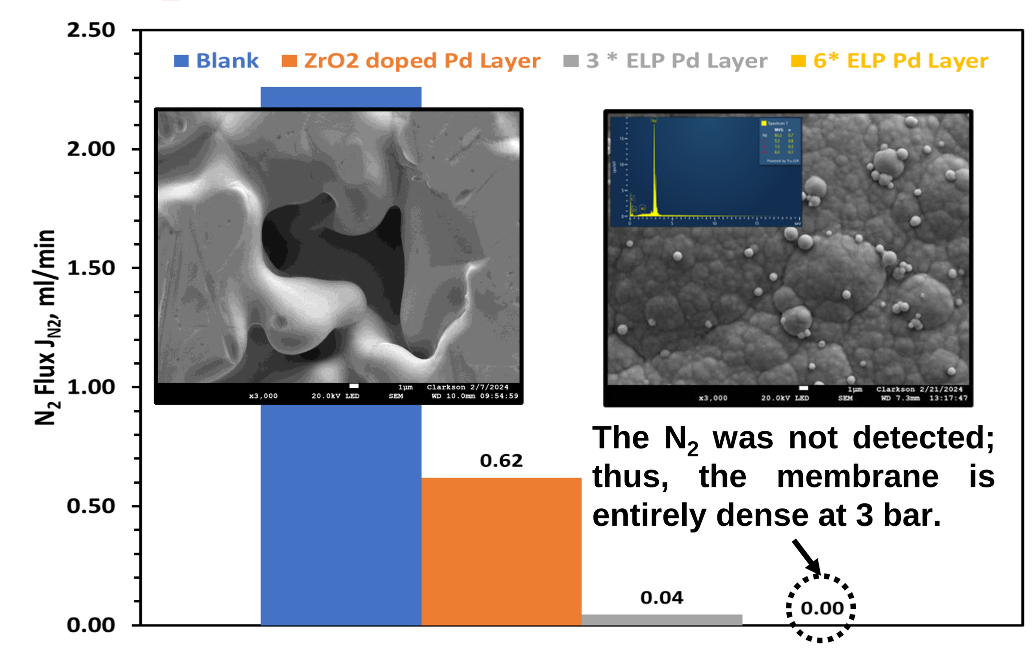
- The PSS with a 2 µm pore size was excluded due to the required amount of Pd, Au, and Ag to block its pores and fabricate a dense membrane.

Synthesis of Pd-based, Binary, and Ternary Membranes





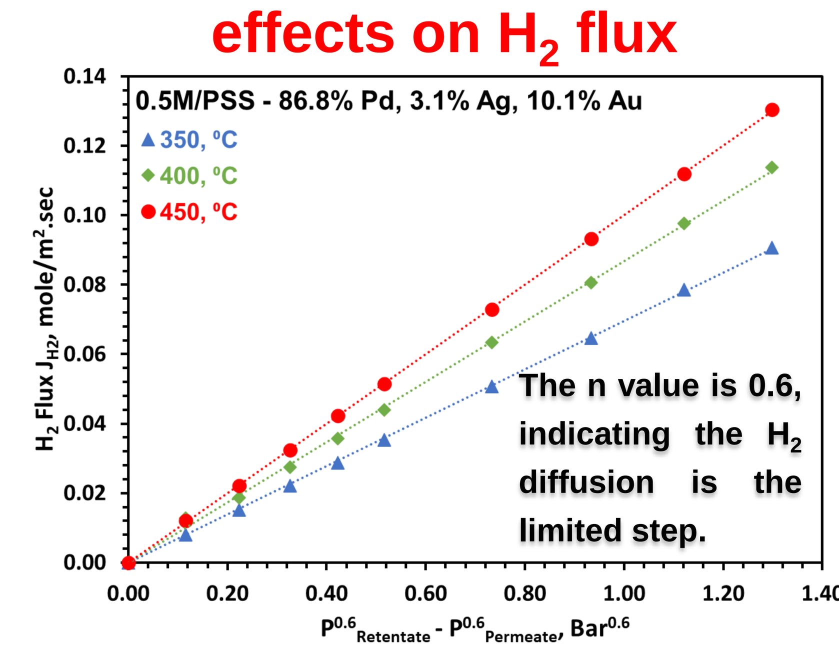
N_2 permeating flux at 25°C & 1 bar and SEM-EDX analysis



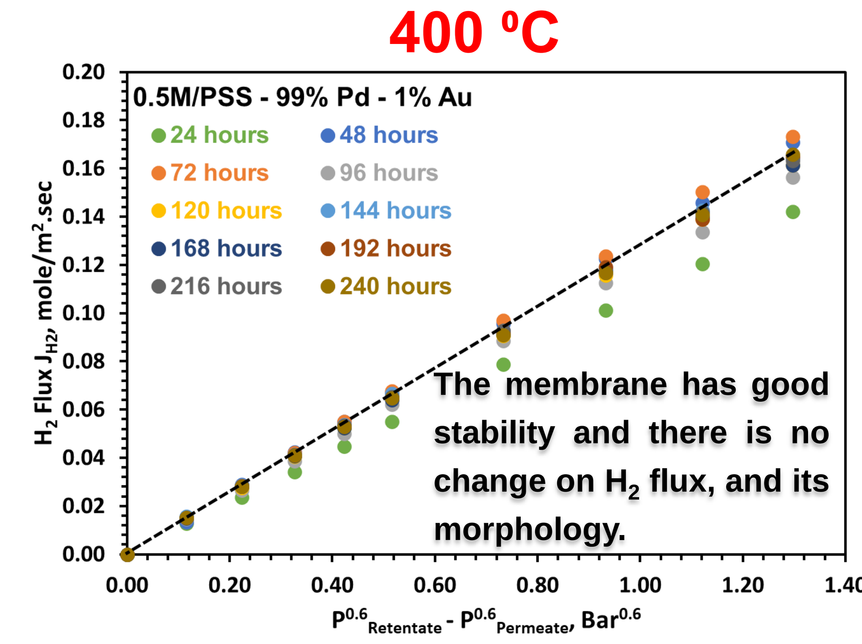
- A dense, uniform, defect-free Pd layer covered the entire PSS support pores.
- The ZrO_2-doped Pd layer decreased the N_2 permeating flux, indicating the blocking of the pores..

Performance of Fabricated Membranes

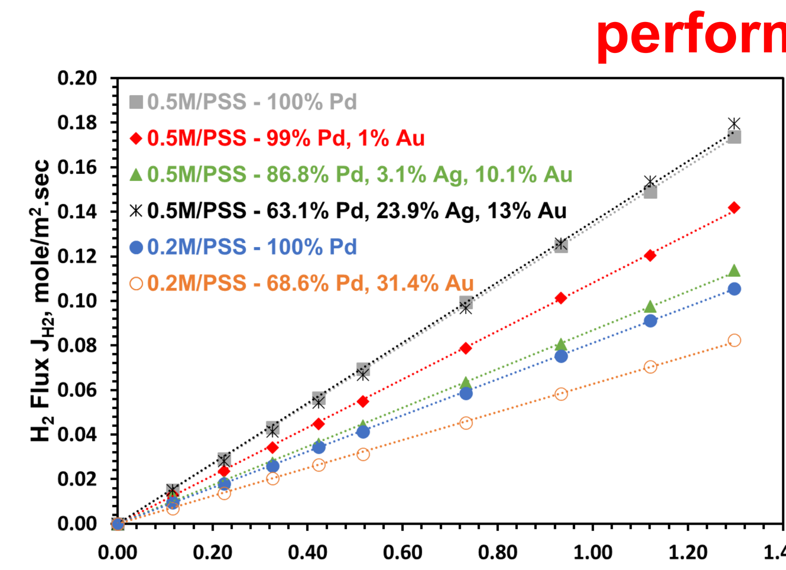
Temperature and pressure effects on H_2 flux



Long-term stability at 400 °C



Effect of pore size and alloy composition on membrane performance at 400 °C



Membrane	Permeance, mole/m²$.sec.Pa	E_0, kJ/mole	Thickness, µm	H_2 Flux, mole/m²$.sec	Ideal Selectivity
0.5M/PSS - 100% Pd	6.95E-07	12.41	17.43	0.0695	2550
0.5M/PSS - 99% Pd, 1% Au	5.49E-07	14.48	34.16	0.0549	infinite
0.5M/PSS - 86.8% Pd, 3.1% Ag, 10.1% Au	4.40E-07	13.99	54.02	0.0440	infinite
0.5M/PSS - 63.1% Pd, 23.9% Ag, 13% Au	6.68E-07	11.73	11.35	0.0668	infinite
0.2M/PSS - 100% Pd	4.14E-07	13.58	50.52	0.0414	infinite
0.2M/PSS - 68.6% Pd, 31.4% Au	3.14E-07	17.61	67.03	0.0314	infinite
0.2M/PSS – 70.3% Pd, 3.3% Ag, 26.4% Au	4.96E-07	11.95	90.87	0.0496	infinite

Adding Au and Ag positively impacts the H_2 flux and activation energy E_0 of the prepared membrane.

Conclusion

- Ternary alloy ($Pd_{(1-x-y)}$-Au_x-Ag_y) membranes were synthesized with an infinite ideal selectivity and highly selective toward hydrogen.
- Depending on the fabrication conditions, the ELP technique led to dense membranes with a 10 – 90 µm thickness range.
- PSS support plays a key role; although small pore sizes led to lower hydrogen flux, they also led to infinite ideal selectivity.

Acknowledgment

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