ECN-M--06-085

# Hydrogen transport through thin layer Pd alloy membranes: kinetics and gas permeation studies

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*Presented at the 9th International Conference on Inorganic Membranes - ICIM-9, 25-29 June 2006, Lillehammer, Norway*

| Revisions | | |
|---|---|---|
| A | Date, 1 August 2006 | |
| B | Date; 30 August 2006 | |
| Made by: Y.C. van Delft | Approved by: P.P.A.C. Pex | ECN Energy Efficiency in Industry |
| Checked by: L.A. Correia | Issued by: P.T. Alderliesten | Molecular Separation Technology |

August 2006

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Separating hydrogen with high selectivity from a gas mixture needs a dense membrane through which only hydrogen can penetrate. Transport of hydrogen from one side of a dense membrane to the other side of the membrane is a sequence of different processes, such as adsorption and dissociation of hydrogen, absorption and diffusion of protons, recombination and desorption of hydrogen. Probably the most important step in this transport is the dissociation of hydrogen molecules in atoms at the membrane surface. This dissociation is necessary for absorption and diffusion to occur and can be realised with a catalytic metal such as palladium. Furthermore, both the solubility and the diffusivity of hydrogen in palladium are relatively very high, which makes palladium a good candidate material for hydrogen selective membrane films. However, palladium suffers from embrittlement by hydrogen that leads to deterioration of metal films. This phenomenon is caused by the formation of palladium hydride that can exist in an alpha and beta phase that co-exist at temperatures lower than about 310°C. To increase the lifespan of membranes made of this material the co-existence of alpha and beta palladium hydride has to be suppressed. One way of doing this is to alloy palladium with e.g. silver or copper that will hardly effect the migration of hydrogen through the membrane.

Thin palladium and palladium silver membranes with a thickness of approximately 3-5 micrometer have been manufactured at ECN on the outside of tubular asymmetric supports by a two step electroless plating process. To understand and improve the transport processes of hydrogen through these thin layer palladium alloy membranes, gas permeation tests were extended with kinetic studies. The present paper discusses the results of this study. The hydrogen permeance derived for these membranes is between 0.1 and 5 micromol/$m^2$.s.Pa. Pre-treatment of the membranes in hydrogen after alloying and before testing showed to be crucial for obtaining a high hydrogen flow. The apparent activation energy for hydrogen permeation is estimated to be 12.4 kJ/mol H for palladium and 4.8 - 14.0 kJ/mol H for palladium silver membranes. Additionally some of the membranes made show a deviating temperature dependency that suggests that two mechanisms, or activation energies, are operating. The temperature at which the transition occurs is about 250°C. This is the temperature at which palladium alpha- and beta-hydride coexists. The results suggest that these palladium silver membranes contain regions with pure palladium, which is verified with X-ray diffraction, that dominate hydrogen permeation at low temperature.

**Acknowledgement**
This work has been supported by the Dutch Ministry of Economic Affairs through the EDI program administered by SENTERNovem (project number EDI-03202).

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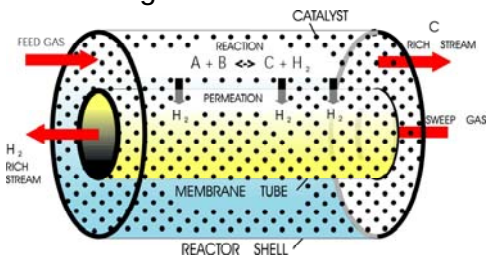
## Outline

- Introduction
- PdAg membrane preparation
- Performance testing
- Permeation characteristics
- Conclusions

## Introduction

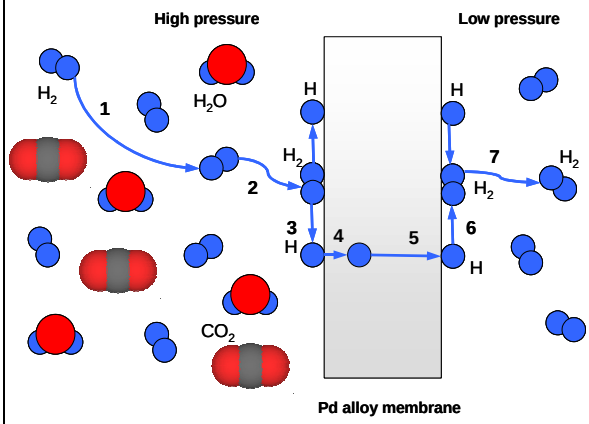
- Large energy savings by shifting the reforming reaction with a hydrogen membrane reactor
- For viable process further increase in flux and/or decrease in membrane price is needed.




- R&D issues:
  - New materials for increased diffusion
  - Fabrication of robust films with reduced film thickness
- Membrane development at ECN in cooperation with universities to support alloying and hydrogen transport studies



## $H_2$ transport in dense Pd alloy membranes




1. Bulk diffusion
2. Adsorption of hydrogen molecules
3. Dissociation into atoms
4. Absorption of atoms
5. Diffusion of atoms
6. Recombination
7. Desorption

**Temperature activated process**

**Layer thickness l**

**Activation energy $E_{act}$**

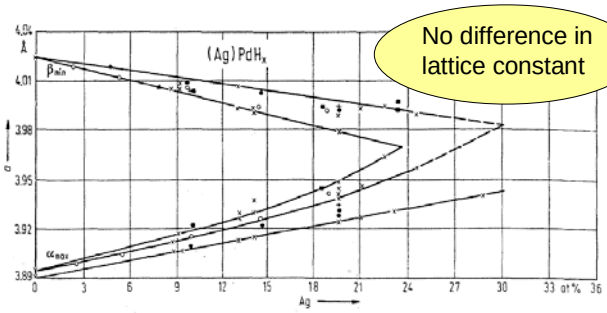
**Pressure exponent n**

**$H_2$ flux: $J_{H2} = (P_{oH2}/l).\exp(-E_{act}/RT).(P_{H2f}^{n}-P_{H2p}^{n})$**

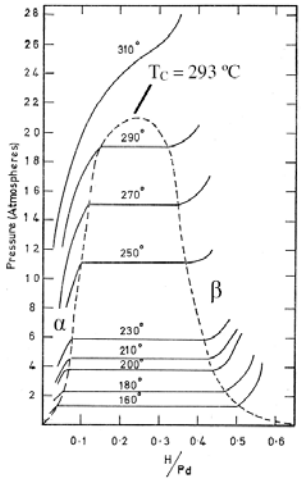
## Hydrogen embrittlement at low temperatures

T<300°C: co-existing region for α and β Pd hydride
Different lattice constants induce strain
⇒ cracks in Pd membrane

Solution: lowering the critical temperature for phase separation by alloying with Ag, Cu,….




Bruning and Sieverts (1933)



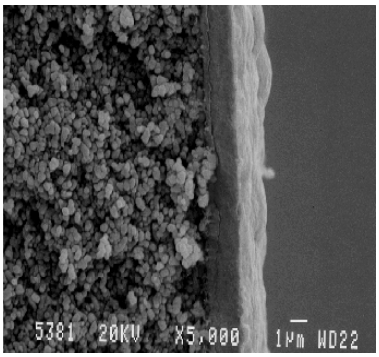



## Ceramic support tube

- Commercial low-cost alumina tubular supports (L= 1 meter, OD=14 mm and ID=10 mm)
- Film coating of suspensions on outside of tube

| Layer | Coating type | Name | Thickness (μm) | Porosity (%) | Pore diameter $d_{50}$ (nm) | Bubble point (μm) |
|---|---|---|---|---|---|---|
| 1 | Extrusion | Extruded tube | 3000 | 35 | 4000 | 4500 |
| 2 | Suspension-Filmcoating | alpha 1 | 30-50 | 35 | 180 | |
| 3 | Suspension-Filmcoating | alpha 2 | 30-40 | 34 | 170 | 350 |

## Thin layer Pd alloy membranes




Pd/23%Ag

Production procedure up to 80 cm tubes:

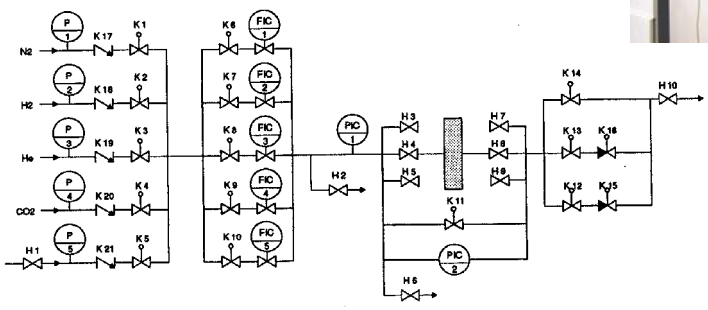
- Recipe development plate bath
- Controlled nucleation
- Sequential electroless plating
- Annealing/alloying

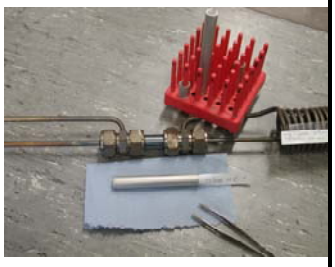
Thin layer defect free membrane 3-5 µm on tubular ceramic support



## Performance testing

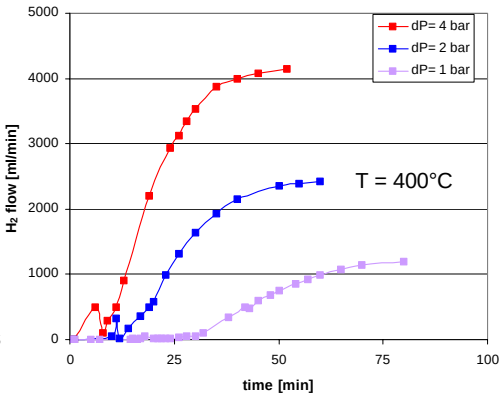
- Single gas permeation
- Kinetic studies
- Thermal cycling experiments
- Long term stability testing



## Permeation characteristics

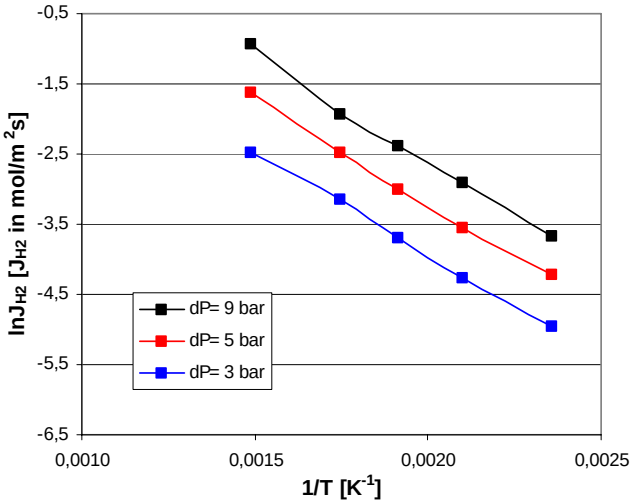
- Influence of measuring time on $H_2$ flow
- Prolonged treatment at high temperature in $H_2$ is needed to obtain high $H_2$ permeances




| PdAg sample | $H_2$ permeance [mol/m²sPa] | | $H_2/N_2$ permselectivity (dP= 9 bar) | | Layer thickness [μm] |
|---|---|---|---|---|---|
| | 350°C | 500°C | 350°C | 500°C | |
| 1 | $8.9\ 10^{-7}$ | $2.0\ 10^{-6}$ | - | 340 | 3.5 - 5.3 |
| 2 | $9.7\ 10^{-7}$ | $1.6\ 10^{-6}$ | - | 298 | 6.2 |
| 3 | $2.1\ 10^{-6}$ | $3.1\ 10^{-6}$ | - | 297 | 5.8 - 8.1 |
| 4 | $9.8\ 10^{-7}$ | - | 712 | - | - |



## Permeation characteristics Pd




150°C<T<400°C

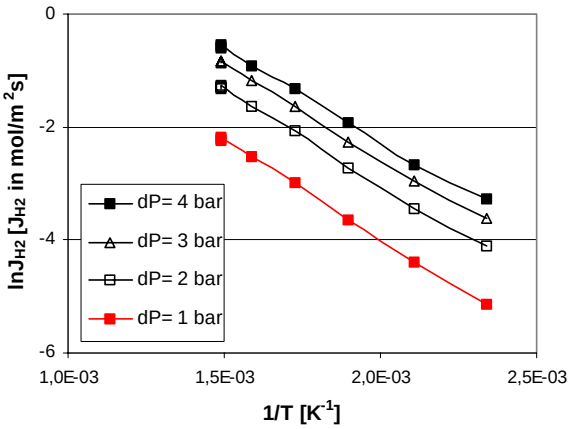
$E_{act}$ = 25 kJ/mol $H_2$
= 12.4 kJ/mol H
= 0.13 eV/at. H

| Pd Alloy | $E_{act}$ for H diffusion [eV/at.H] |
|---|---|
| Pure Pd | 0.23 |
| $PdH_{0.25}$ | **0.13** |
| $Pd_{0.75}Ag_{0.25}H_{0.25}$ | 0.32 |
| $Pd_{0.5}Ag_{0.5}H_{0.25}$ | 0.21 |

(Ke et al. 2002)

⇒ Activation energy consistent with model $E_{act}$ for H bulk diffusion

## Permeation characteristics PdAg




150°C<T<400°C

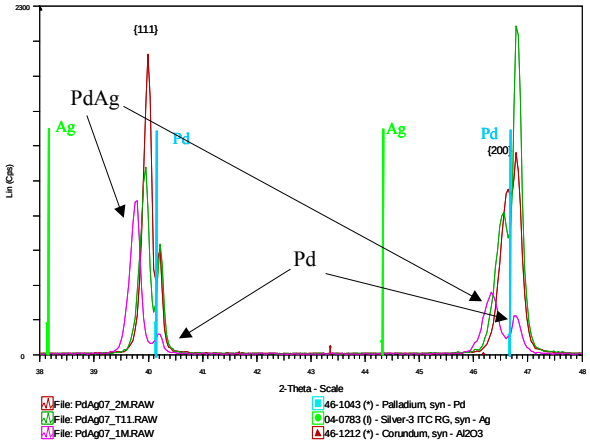
$E_{act}$ = 27.5 kJ/mol $H_2$
= 14 kJ/mol H
= 0.146 eV/at. H

Activation energy for H diffusion in $Pd_{0.75}Ag_{0.25}H_{0.25}$= 0.32 eV/at.H

⇒ Pd metal still present in PdAg membrane, incomplete alloying?



## Pure Pd regions in PdAg membrane?



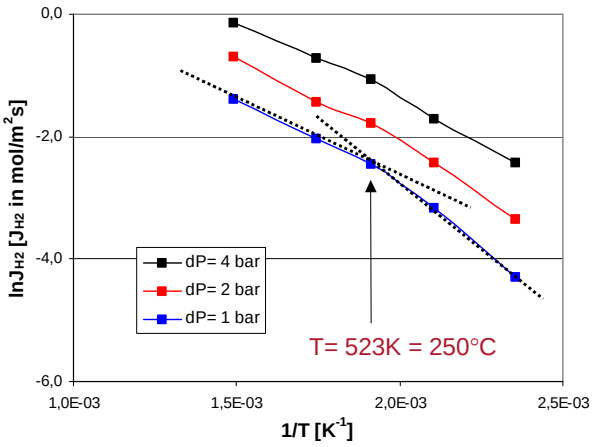

XRD
2 peaks: a small Pd peak and a large PdAg peak

⇒ Regions with pure Pd and > 25% Ag

$E_{act}$ for H diffusion = 0.13 – 0.21 eV/ at.H

⇒ Activation energy consistent with model $E_{act}$ for H bulk diffusion

## Deviating temperature dependency Pd




150°C<T<400°C

**Two activation energies!**

High T:

$E_{act}$ = 18.1 kJ/mol $H_2$
= 9.1 kJ/mol H
= 0.09 eV/at. H

Low T:

$E_{act}$ = 35.3 kJ/mol $H_2$
= 17.7 kJ/mol H
= 0.18 eV/at. H

⇒ change of activation energy because of hydride formation?

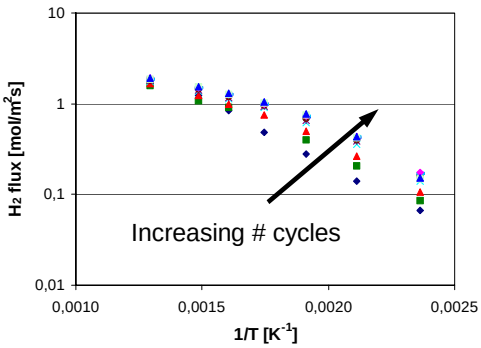


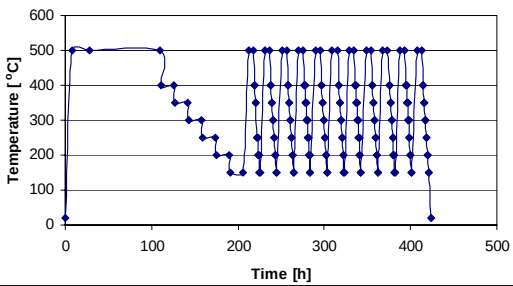
## Thermal Cycling

- $Pd_{75}Ag_{25}$ at $dP_{H2}$= 9 bar
- $H_2$ flux increases with # cycles

$J_{H2} = C \exp(-E_{act}/RT)$

- $P_{N2}$= 3.2 $10^{-8}$ mol/m²sPa (initial 500°C)
- $P_{N2}$= 2.4 $10^{-9}$ mol/m²sPa (cycle 5 150°C)




| Cycle # | $E_{act}$ apparent [kJ/molH] |
|---|---|
| 1 | 15.2 |
| 2 | 12.4 |
| 3 | 8.4 |
| 4 | 5.8 |
| 5 | 5.7 |
| 6-12 | 5.5 - 4.9 |

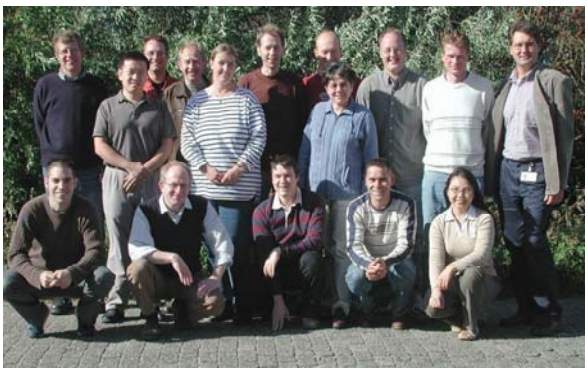
## Conclusions

- Thin Pd and PdAg membranes (l = 3-5 μm) have been manufactured with:
  - high $H_2$ permeances (1 - 3 $10^{-6}$ mol/$m^2$sPa)
  - maximum $H_2/N_2$ permselectivity of 700 (350°C, dP = 9 bar)
- Pre-treatment of the membranes in $H_2$ after alloying and before testing is crucial for high $H_2$ flux
- Arrhenius-type temperature dependency of $H_2$ flux is consistent with a bulk diffusion limited transport
- Some PdAg membranes contain regions with pure palladium because of incomplete alloying
- During measurements increase in $H_2$ flux due to further alloying



## Acknowledgements

Diana Nanu (TUDelft), colleagues and co-workers



Sponsors: Dutch ministry of Economic Affairs, EU, SenterNovem, a.o.

## Thank you for your attention!