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APPENDICES

APPENDIX A

APPENDIX A

Membrane characterization data

For palladium membrane characterization, there were 6 items like (1) the dense test of prepared palladium membrane using helium flux (J_{He})at room temperature with different pressure at 1 atm, (2) the hydrogen flux (J_{H_2}) testing at 350°C, 400°C, and 450°C with different pressure from 1-3 atm, respectively, (3) selectivity($\alpha_{H_2/He}$) calculated from flux ratio between hydrogen flux (J_{H_2}) and helium flux (J_{He}), (4) long term stability, (5) permeance test, and (6) determination of activation energy of hydrogen diffusing through palladium membrane layer.

From Sievert's equation

$$J = \frac{Q}{L} \cdot (P_{H_2h}^{0.5} - P_{H_2l}^{0.5})$$

or

$$J = F \cdot (P_{H_2h}^{0.5} - P_{H_2l}^{0.5})$$

Where J = Flux of permeated gas through the palladium membrane, m^3/m^2h

Q = Permeability, m^3cm/m^2 h $atm^{0.5}$

F = Permeance, m^3/m^2h $atm^{0.5}$

L = Palladium membrane length, cm

Therefore, the permeance (F) of prepared palladium membrane could be obtained from slope of the graphic plotted between H_2 flux (J_{H_2}) and $(P_{H_2h}^{0.5} - P_{H_2l}^{0.5})$.

Moreover, in order to investigate the activation energy of hydrogen permeating through the palladium membrane, the correlation between the permeance of prepared palladium membrane and temperature in Kelvin degree ($\frac{1}{T}$) was plotted. The raw data of prepared palladium membrane namely palladium membrane without intermetallic diffusion barrier (membrane-01 and membrane-02) and palladium membrane contained Chromium oxide layer as an intermetallic diffusion barrier (membrane-03) were exhibited as following.

Tube 01

Date: 04/03/03

Sample #: Membrane-01 (Wat73801-01)

Sample background:

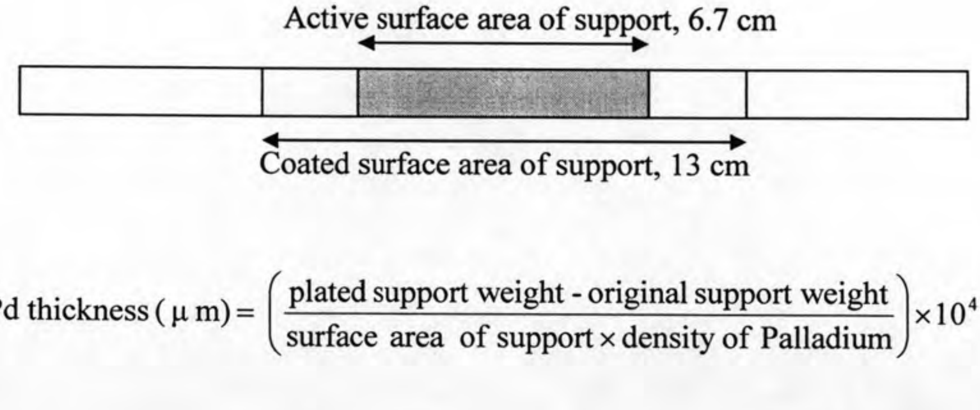
Porous stainless steel 0.1 µm

Coated surface area 38.8811 cm^2

Active surface area 20.0387 cm^2

Dense testing

	Weight (g)	ΔWt (g)	Pd Thickness (µm)	He flux (m^3/m^2h)
Before Pd plating	129.99	-	-	179.56
After Pd plating#1	130.27	0.28	5.99	115.10
After Pd plating#2	130.50	0.23	4.92	0.0021
After Pd plating#3	130.78	0.28	5.99	0.0007
After Pd plating#4	130.89	0.11	2.35	Dense
Palladium thickness total (µm)			19.26	



$$\text{Pd thickness}\ (\mu\text{m}) = \left(\frac{\text{plated support weight - original support weight}}{\text{surface area of support} \times \text{density of Palladium}}\right) \times 10^4$$

$$\text{Flux}\ (\text{m}^3/\text{m}^2\text{h}) = \left(\frac{\text{Flow rate of He on Tube side (ml/min)}}{\text{surface area of support}\ (\text{cm}^2)}\right) \times 0.6$$

Where Density of palladium = 12.02 g/ml

Coated surface area = $\pi \cdot d \cdot l$ = 3.14x0.9525x13 = 38.8811 cm^2

Active surface area = $\pi \cdot d \cdot l$ = 3.14x0.9525x6.7 = 20.0387 cm^2

Hydrogen flux test

Type of Gas: Helium

Temperature: Room temperature

#	ΔP	P_s	P_o	Flow rate (ml/min)								Flux
				1	2	3	4	5	Avg	SD	RSD	(m^3/m^2h)
0	0	764	764	0	0	0	0	0	0	0	-	0
1	0.25	942	764	0	0	0	0	0	0	0	-	0
2	0.50	1119	764	0	0	0	0	0	0	0	-	0
3	0.75	1297	764	0	0	0	0	0	0	0	-	0
4	1.00	1475	764	0	0	0	0	0	0	0	-	0
5	1.25	1653	764	0	0	0	0	0	0	0	-	0
6	1.50	1830	764	0	0	0	0	0	0	0	-	0
7	1.75	2008	764	0	0	0	0	0	0	0	-	0
8	2.00	2186	764	0	0	0	0	0	0	0	-	0
9	2.25	2364	764	0	0	0	0	0	0	0	-	0
10	2.50	2541	764	0	0	0	0	0	0	0	-	0
11	2.75	2719	764	0	0	0	0	0	0	0	-	0
12	3.00	2897	764	0	0	0	0	0	0	0	-	0
13	1.00	1475	764	0	0	0	0	0	0	0	-	0

Type of Gas:.......................Hydrogen gas..............................

Temperature:..........................350°C..................................

#	ΔP	P_s	P_o	Flow rate (ml/min)								Flux
				1	2	3	4	5	Avg	SD	RSD	(m^3/m^2h)
0	0	764	764	0	0	0	0	0	0	0	-	0
1	0.25	942	764	22	22	22	22	22	22	0	-	0.6650
2	0.50	1119	764	42	42	42	42	42	42	0	-	1.2629
3	0.75	1297	764	61	61	61	61	61	61	0	-	1.8190
4	1.00	1475	764	78	78	78	78	78	78	0	-	2.3481
5	1.25	1653	764	95	95	95	95	95	95	0	-	2.8574
6	1.50	1830	764	111	111	111	111	111	111	0	-	3.3279
7	1.75	2008	764	125	125	125	125	125	125	0	-	3.7349
8	2.00	2186	764	140	140	140	140	140	140	0	-	4.2017
9	2.25	2364	764	154	154	154	154	154	154	0	-	4.5968
10	2.50	2541	764	165	165	165	165	165	165	0	-	4.9439
11	2.75	2719	764	181	181	181	181	181	181	0	-	5.4108
12	3.00	2897	764	192	192	192	192	192	192	0	-	5.746
13	1.00	1475	764	78	78	78	78	78	78	0	-	2.3481

Type of Gas: Hydrogen gas

Temperature: 450°C

#	ΔP	P_s	P_o	Flow rate (ml/min)								Flux
				1	2	3	4	5	Avg	SD	RSD	(m^3/m^2h)
0	0	764	764	0	0	0	0	0	0	0	-	0
1	0.25	942	764	28	28	28	28	28	28	0	-	0.8439
2	0.50	1119	764	53	53	53	53	53	53	0	-	1.5843
3	0.75	1297	764	77	77	77	77	77	77	0	-	2.3169
4	1.00	1475	764	100	100	100	100	100	100	0	-	2.9969
5	1.25	1653	764	121	121	121	121	121	121	0	-	3.6211
6	1.50	1830	764	141	141	141	141	141	141	0	-	4.2197
7	1.75	2008	764	159	159	159	159	159	159	0	-	4.7703
8	2.00	2186	764	179	179	179	179	179	179	0	-	5.3569
9	2.25	2364	764	195	195	194	195	195	195	0	-	5.8238
10	2.50	2541	764	212	212	212	212	212	212	0	-	6.3445
11	2.75	2719	764	229	229	229	229	229	229	0	-	6.8592
12	3.00	2897	764	241	241	241	241	241	241	0	-	7.2184
13	1.00	1475	764	100	100	100	100	100	100	0	-	2.9969

Type of Gas: Hydrogen gas

Temperature: 450°C

#	ΔP	P_s	P_o	Flow rate (ml/min)								Flux
				1	2	3	4	5	Avg	SD	RSD	(m^3/m^2h)
0	0	764	764	0	0	0	0	0	0	0	-	0
1	0.25	942	764	32	32	32	32	32	32	0	-	0.9714
2	0.50	1119	764	61	61	61	61	61	61	0	-	1.8237
3	0.75	1297	764	89	89	89	89	89	89	0	-	2.6641
4	1.00	1475	764	115	115	115	115	115	115	0	-	3.4416
5	1.25	1653	764	139	139	139	139	139	139	0	-	4.1718
6	1.50	1830	764	161	161	161	161	161	161	0	-	4.8062
7	1.75	2008	764	183	183	183	183	183	183	0	-	5.4646
8	2.00	2186	764	205	205	205	205	205	205	0	-	6.1350
9	2.25	2364	764	224	224	224	224	224	224	0	-	6.6976
10	2.50	2541	764	243	243	243	243	243	243	0	-	7.2782
11	2.75	2719	764	264	264	264	264	264	264	0	-	7.9007
12	3.00	2897	764	280	280	280	280	280	280	0	-	8.3915
13	1.00	1475	764	115	115	115	115	115	115	0	-	3.4416

Selectivity test

From the above data, the selectivity ($\alpha_{H_2/He}$) of prepared palladium membrane was the ratio of H_2 flux (J_{H_2}) and He flux (J_{He}) at 350°C, 400 °C, and 450 °C at different pressure (ΔP) 1 atm.

Temperature (°C)	J_{H_2}	J_{He}	$\alpha_{H_2/He}$
350	2.3481	0.00000	Can not define
400	2.9969	0.00000	Can not define
450	3.4416	0.00000	Can not define

Long term stability test

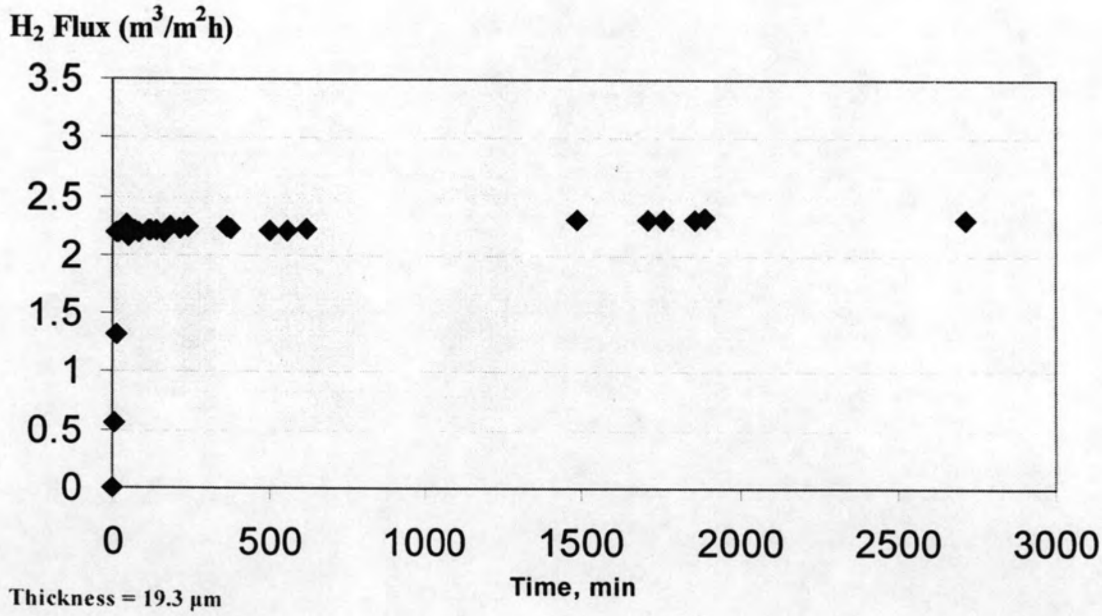


Figure A1 Hydrogen permeation flux as a function of time at 350°C, pressure 1 atm.

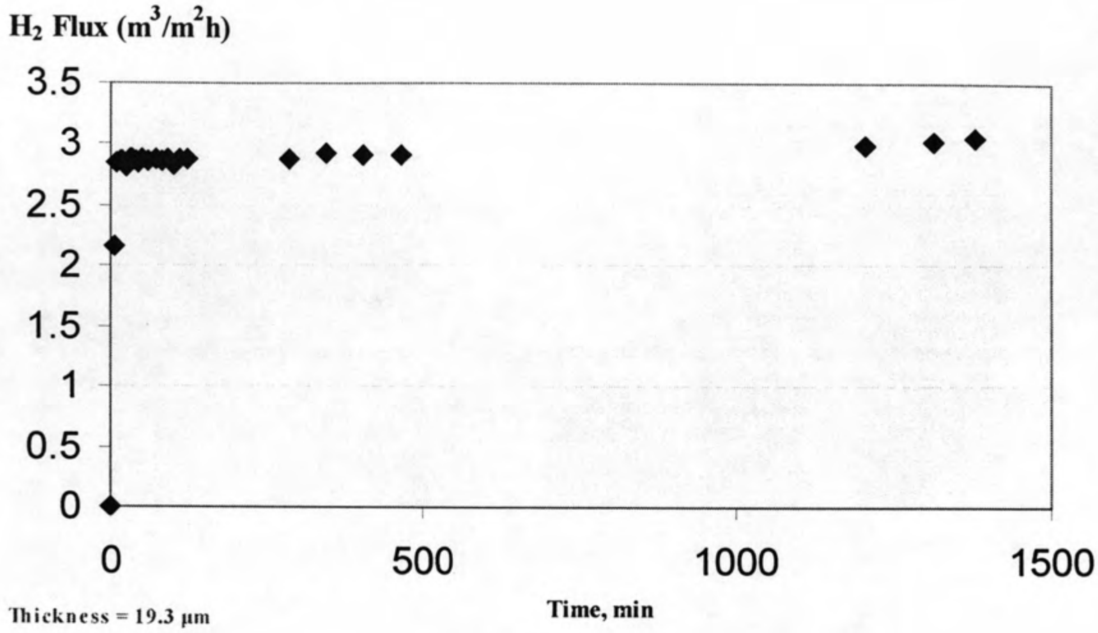


Figure A2 Hydrogen permeation flux as a function of time at 400°C, pressure 1 atm.

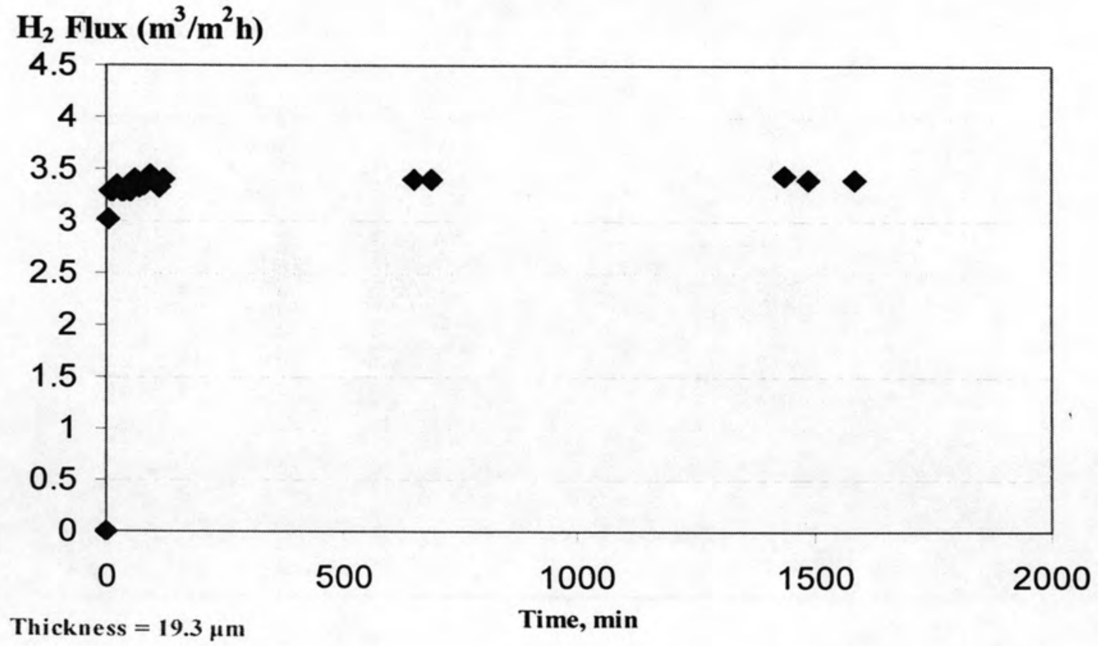


Figure A3 Hydrogen permeation flux as a function of time at 450°C, pressure 1 atm.

Permeance test

Temperature: 350°C

#	P_s	P_o	ΔP	$P_s^{0.5} - P_o^{0.5}$	Flux (m^3/m^2h)
0	764	764	0	0	0
1	942	764	0.25	0.1144	0.6650
2	1119	764	0.50	0.2179	1.2629
3	1297	764	0.75	0.3140	1.8190
4	1475	764	1.00	0.4037	2.3481
5	1653	764	1.25	0.4882	2.8574
6	1830	764	1.50	0.5677	3.3279
7	2008	764	1.75	0.6440	3.7349
8	2186	764	2.00	0.7169	4.2017
9	2364	764	2.25	0.7869	4.5968
10	2541	764	2.50	0.8539	4.9439
11	2719	764	2.75	0.9190	5.4108
12	2897	764	3.00	0.9820	5.746

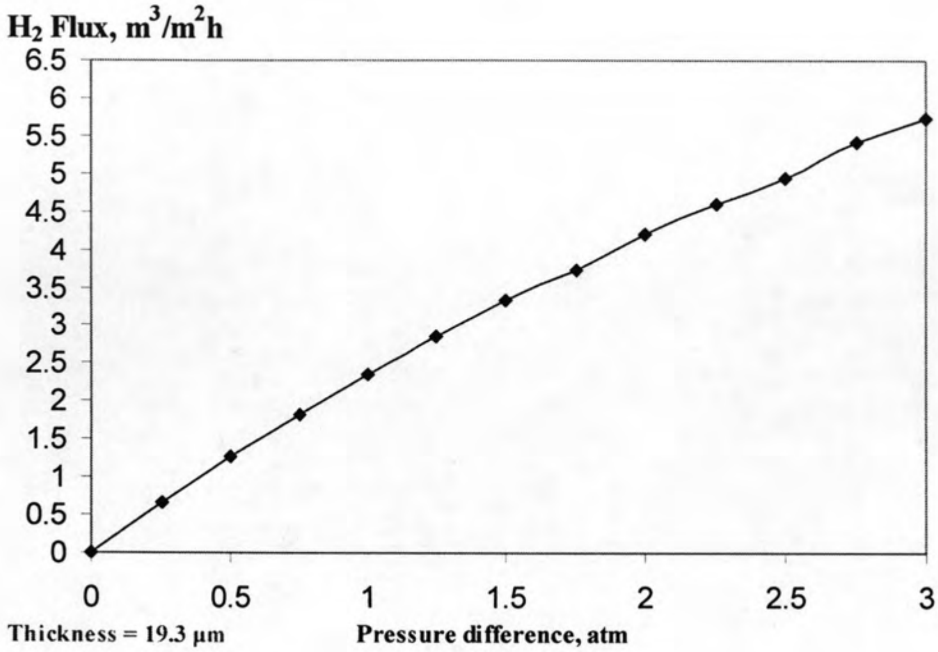


Figure A4 Hydrogen permeation flux of palladium membrane on porous stainless steel support as a function of pressure difference.

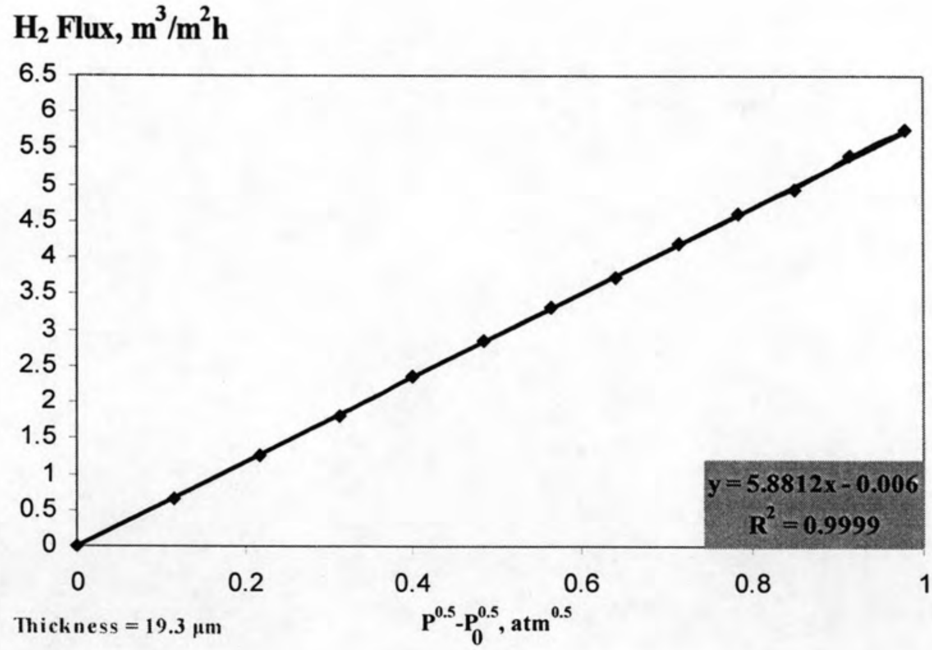


Figure A5 Hydrogen permeation flux of palladium membrane on porous stainless steel support as a function of the square roots of the pressure difference.

Temperature: 400 ºC

#	P_s	P_o	ΔP	$P_s^{0.5} - P_o^{0.5}$	Flux (m^3/m^2h)
0	764	764	0	0	0
1	942	764	0.25	0.1144	0.8439
2	1119	764	0.50	0.2179	1.5843
3	1297	764	0.75	0.3140	2.3169
4	1475	764	1.00	0.4037	2.9969
5	1653	764	1.25	0.4882	3.6211
6	1830	764	1.50	0.5677	4.2197
7	2008	764	1.75	0.6440	4.7703
8	2186	764	2.00	0.7169	5.3569
9	2364	764	2.25	0.7869	5.8238
10	2541	764	2.50	0.8539	6.3445
11	2719	764	2.75	0.9190	6.8592
12	2897	764	3.00	0.9820	7.2184

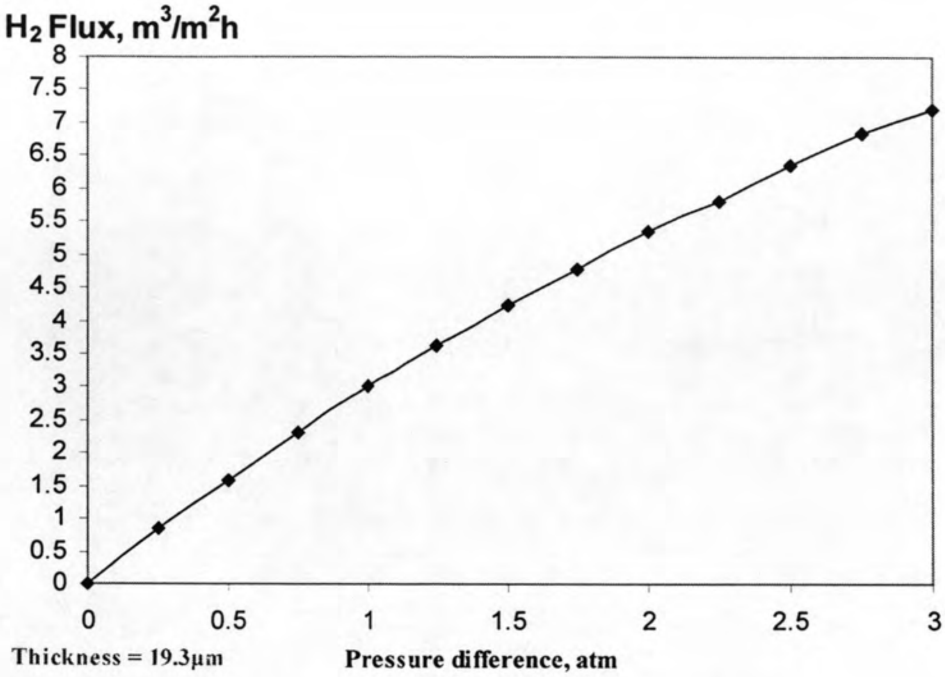


Figure A6 Hydrogen permeation flux of palladium membrane on porous stainless steel support as a function of pressure difference.

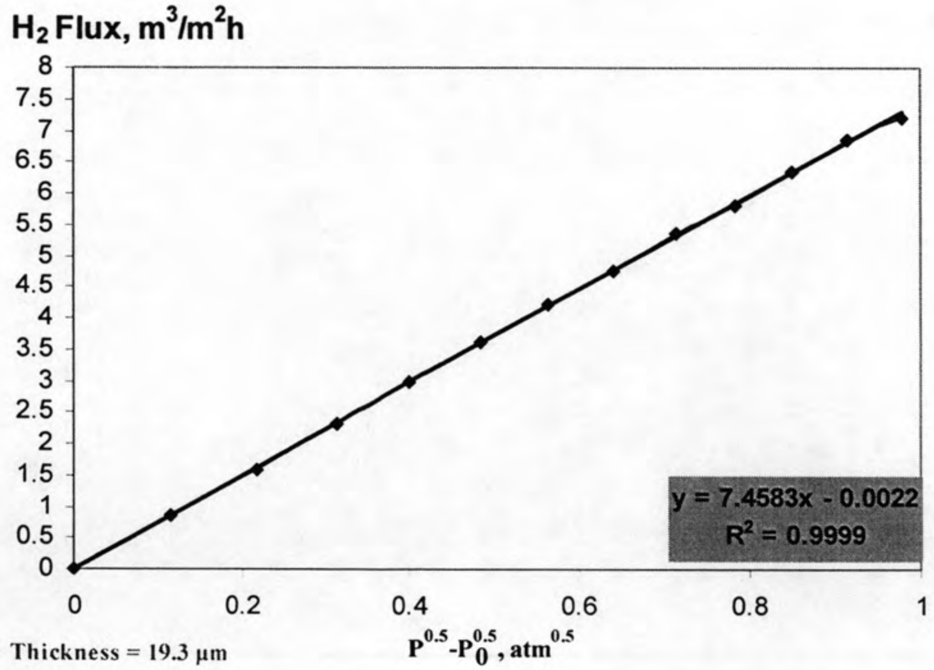


Figure A7 Hydrogen permeation flux of palladium membrane on porous stainless steel support as a function of the square roots of the pressure difference.

Temperature: 450ºC

#	P_s	P_o	ΔP	$P_s^{0.5} - P_o^{0.5}$	**Flux (m^3/m^2h)**
0	764	764	0	0	0
1	942	764	0.25	0.1144	0.9714
2	1119	764	0.50	0.2179	1.8237
3	1297	764	0.75	0.3140	2.6641
4	1475	764	1.00	0.4037	3.4416
5	1653	764	1.25	0.4882	4.1718
6	1830	764	1.50	0.5677	4.8062
7	2008	764	1.75	0.6440	5.4646
8	2186	764	2.00	0.7169	6.1350
9	2364	764	2.25	0.7869	6.6976
10	2541	764	2.50	0.8539	7.2782
11	2719	764	2.75	0.9190	7.9007
12	2897	764	3.00	0.9820	8.3915

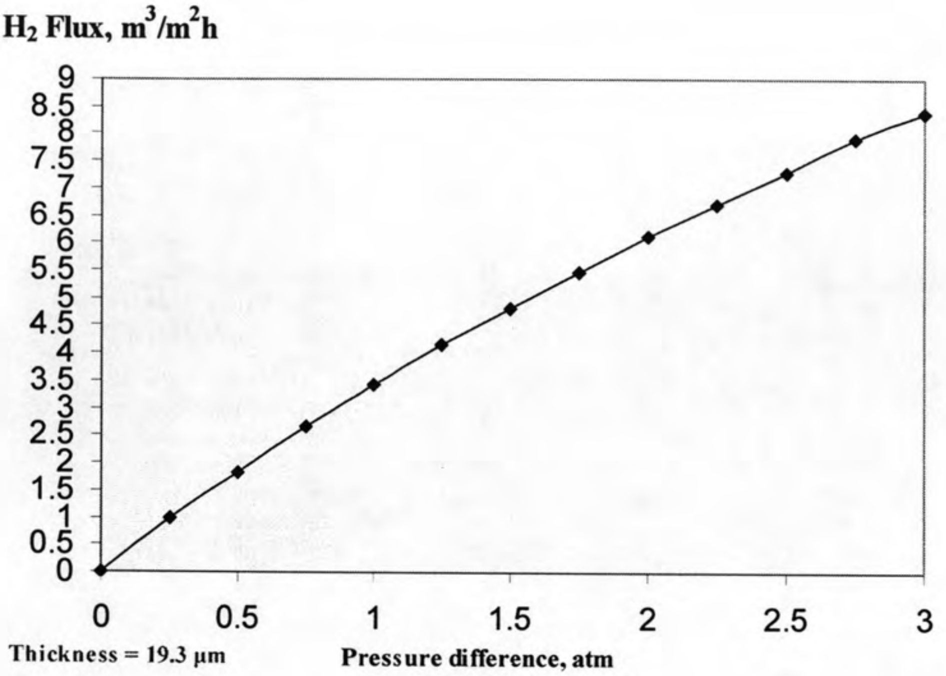


Figure A8 Hydrogen permeation flux of palladium membrane on porous stainless steel support as a function of pressure difference.

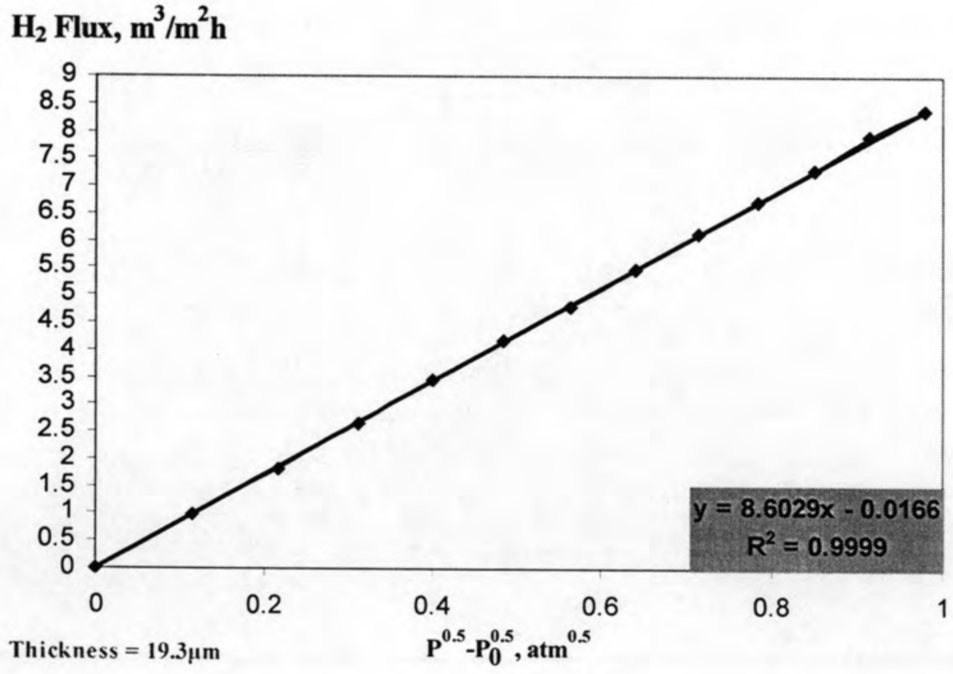


Figure A9 Hydrogen permeation flux of palladium membrane on porous stainless steel support as a function of the square roots of the pressure difference.

Determination of Activation energy of hydrogen diffusing through palladium membrane

Temperature		Permeance (F),	$\frac{1000}{T}$	Ln F
Celsius, ^{O}C	Kelvin, K	$m^3/m^2h\ atm^{0.5}$		
350	643	5.8812	1.5552	1.7718
400	693	7.4583	1.4430	2.0093
450	743	8.6029	1.3458	2.1521

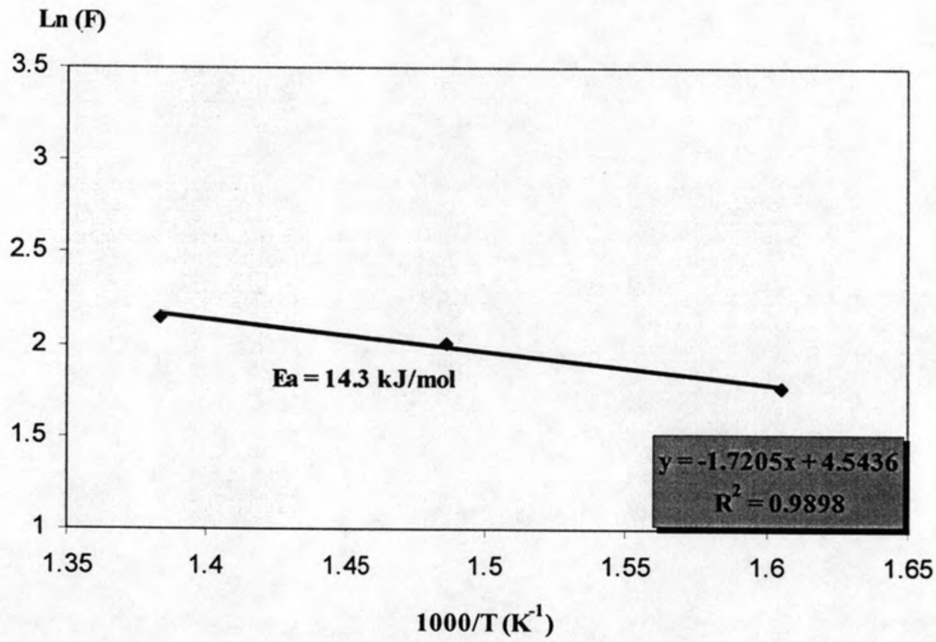


Figure A10 Arrhenius relation between the hydrogen permeance and invert operation temperature.

Tube 02

Date : 09/07/03

Sample # : Membrane-02 (Wat73801-03)

Sample background :

Porous stainless steel 0.1 μm

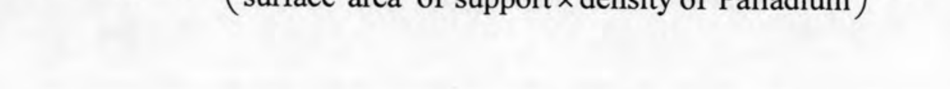
Coated surface area 38.8811 cm^2

Active surface area 20.0387 cm^2

Dense testing

	Weight (g)	ΔWt (g)	Pd Thickness (μm)	He flux (m^3/m^2h)
Before Pd plating	130.47	-	-	173.77
After Pd plating#1	130.66	0.21	4.49	52.05
After Pd plating#2	130.89	0.23	4.92	0.0257
After Pd plating#3	130.07	0.18	3.85	0.0005
After Pd plating#4	130.28	0.20	4.28	Dense
Palladium thickness total (μm)			17.5	

Active surface area of support, 6.7 cm



Coated surface area of support, 13 cm

$$\text{Pd thickness } (\mu\text{ m}) = \left(\frac{\text{plated support weight - original support weight}}{\text{surface area of support} \times \text{density of Palladium}}\right) \times 10^4$$

$$\text{Flux } (\text{m}^3/\text{m}^2\text{h}) = \left(\frac{\text{Flow rate of He on Tube side (ml/min)}}{\text{surface area of support } (\text{cm}^2)}\right) \times 0.6$$

Where Density of palladium = 12.02 g/ml

Coated surface area = $\pi \cdot d \cdot l$ = 3.14x0.9525x13 = 38.8811 cm^2

Active surface area = $\pi \cdot d \cdot l$ = 3.14x0.9525x6.7 = 20.0387 cm^2

Type of Gas: Helium

Temperature: Room temperature

#	ΔP	P_s	P_o	Flow rate (ml/min)								Flux
				1	2	3	4	5	Avg	SD	RSD	(m^3/m^{2}h)
0	0	764	764	0	0	0	0	0	0	0	-	0
1	0.25	942	764	0	0	0	0	0	0	0	-	0
2	0.50	1119	764	0	0	0	0	0	0	0	-	0
3	0.75	1297	764	0	0	0	0	0	0	0	-	0
4	1.00	1475	764	0	0	0	0	0	0	0	-	0
5	1.25	1653	764	0	0	0	0	0	0	0	-	0
6	1.50	1830	764	0	0	0	0	0	0	0	-	0
7	1.75	2008	764	0	0	0	0	0	0	0	-	0
8	2.00	2186	764	0	0	0	0	0	0	0	-	0
9	2.25	2364	764	0	0	0	0	0	0	0	-	0
10	2.50	2541	764	0	0	0	0	0	0	0	-	0
11	2.75	2719	764	0	0	0	0	0	0	0	-	0
12	3.00	2897	764	0	0	0	0	0	0	0	-	0
13	1.00	1475	764	0	0	0	0	0	0	0	-	0

Type of Gas:.........................Hydrogen gas............................

Temperature:............................350°C................................

#	ΔP	P_s	P_o	Flow rate (ml/min)								Flux
				1	2	3	4	5	Avg	SD	RSD	(m^3/m^2h)
0	0	773	773	0	0	0	0	0	0	-	-	0.0000
1	0.25	966	773	22	22	22	22	22	22	-	-	0.6584
2	0.50	1160	773	47	47	47	47	47	47	-	-	1.4066
3	0.75	1353	773	71	71	71	71	71	71	-	-	2.1248
4	1.00	1546	773	93	93	93	93	93	93	-	-	2.7832
5	1.25	1739	773	114	114	114	114	114	114	-	-	3.4117
6	1.50	1933	773	135	135	135	135	135	135	-	-	4.0401
7	1.75	2126	773	153	153	153	153	153	153	-	-	4.5788
8	2.00	2319	773	172	172	172	172	172	172	-	-	5.1474
9	2.25	2512	773	190	190	190	190	190	190	-	-	5.6861
10	2.50	2706	773	208	208	208	208	208	208	-	-	6.2248
11	2.75	2899	773	224	224	224	224	224	224	-	-	6.7335
12	3.00	3092	773	241	241	241	241	241	241	-	-	7.2124
13	1.00	1546	773	93	93	93	93	93	93	-	-	2.7832

Type of Gas: Hydrogen gas

Temperature: 400ºC

#	ΔP	P_s	P_o	Flow rate (ml/min)								Flux
				1	2	3	4	5	Avg	SD	RSD	(m^3/m^2h)
0	0	773	773	0	0	0	0	0	0	-	-	0.0000
1	0.25	966	773	28	28	28	28	28	28	-	-	0.8380
2	0.50	1160	773	59	59	59	59	59	59	-	-	1.7657
3	0.75	1353	773	88	88	88	88	88	88	-	-	2.6336
4	1.00	1546	773	114	114	114	114	114	114	-	-	3.4117
5	1.25	1739	773	140	140	140	140	140	140	-	-	4.1898
6	1.50	1933	773	164	164	164	164	164	164	-	-	4.9080
7	1.75	2126	773	187	187	187	187	187	187	-	-	5.5963
8	2.00	2319	773	208	208	208	208	208	208	-	-	6.2248
9	2.25	2512	773	230	230	230	230	230	230	-	-	6.8832
10	2.50	2706	773	251	251	251	251	251	251	-	-	7.5116
11	2.75	2899	773	271	271	271	271	271	271	-	-	8.1102
12	3.00	3092	773	290	290	290	290	290	290	-	-	8.6788
13	1.00	1546	773	114	114	114	114	114	114	-	-	3.4117

Type of Gas: Hydrogen gas

Temperature: 450°C

#	ΔP	P_s	P_o	Flow rate (ml/min)								Flux
				1	2	3	4	5	Avg	SD	RSD	(m^3/m^2h)
0	0	773	773	0	0	0	0	0	0	-	-	0.0000
1	0.25	966	773	37	37	37	37	37	37	-	-	1.1073
2	0.50	1160	773	76	76	76	76	76	76	-	-	2.2744
3	0.75	1353	773	112	112	112	112	112	112	-	-	3.3518
4	1.00	1546	773	146	146	146	146	146	146	-	-	4.3693
5	1.25	1739	773	178	178	178	178	178	178	-	-	5.3270
6	1.50	1933	773	208	208	208	208	208	208	-	-	6.2248
7	1.75	2126	773	237	237	237	237	237	237	-	-	7.0927
8	2.00	2319	773	265	265	265	265	265	265	-	-	7.9306
9	2.25	2512	773	292	292	292	292	292	292	-	-	8.7386
10	2.50	2706	773	318	318	318	318	318	318	-	-	9.5167
11	2.75	2899	773	342	342	342	342	342	342	-	-	10.2350
12	3.00	3092	773	366	366	366	366	366	366	-	-	10.9532
13	1.00	1546	773	145	145	145	145	145	145	-	-	4.3394

Selectivity test

From the above data, the selectivity ($\alpha_{H_2/He}$) of prepared palladium membrane was the ratio of H_2 flux (J_{H_2}) and He flux (J_{He}) at 350°C, 400 °C, and 450 °C at different pressure (ΔP) 1 atm.

Temperature (°C)	J_{H_2}	J_{He}	$\alpha_{H_2/He}$
350	2.3481	0.00003	78,270
400	2.9969	0.00004	74,923
450	3.4416	0.00004	8,604

Long term stability test

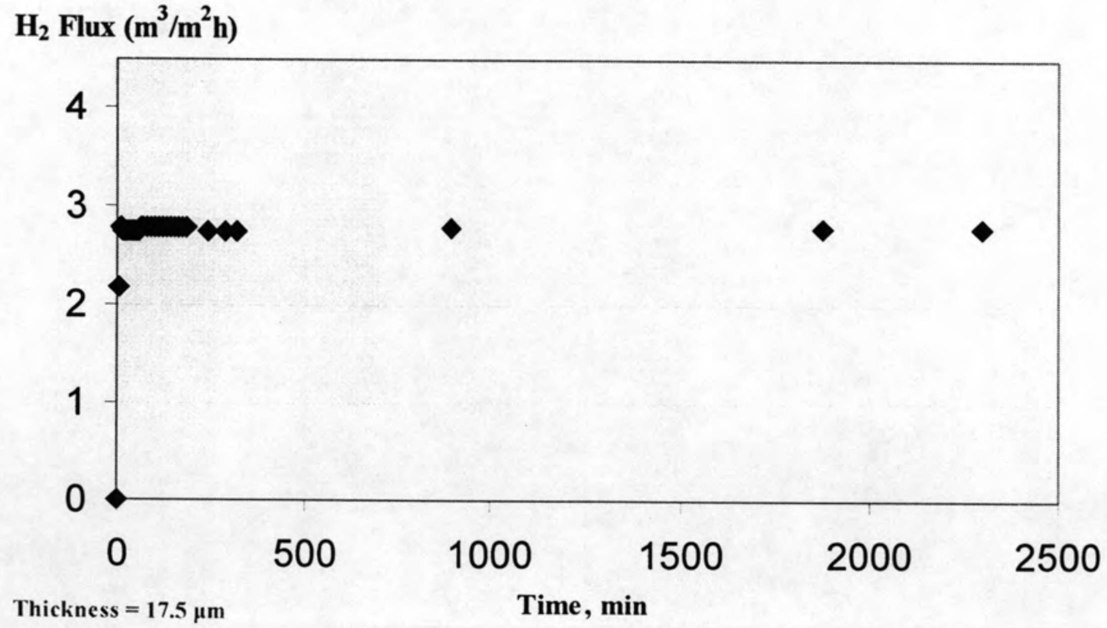


Figure A11 Hydrogen permeation flux as a function of time at 350°C, pressure 1 atm.

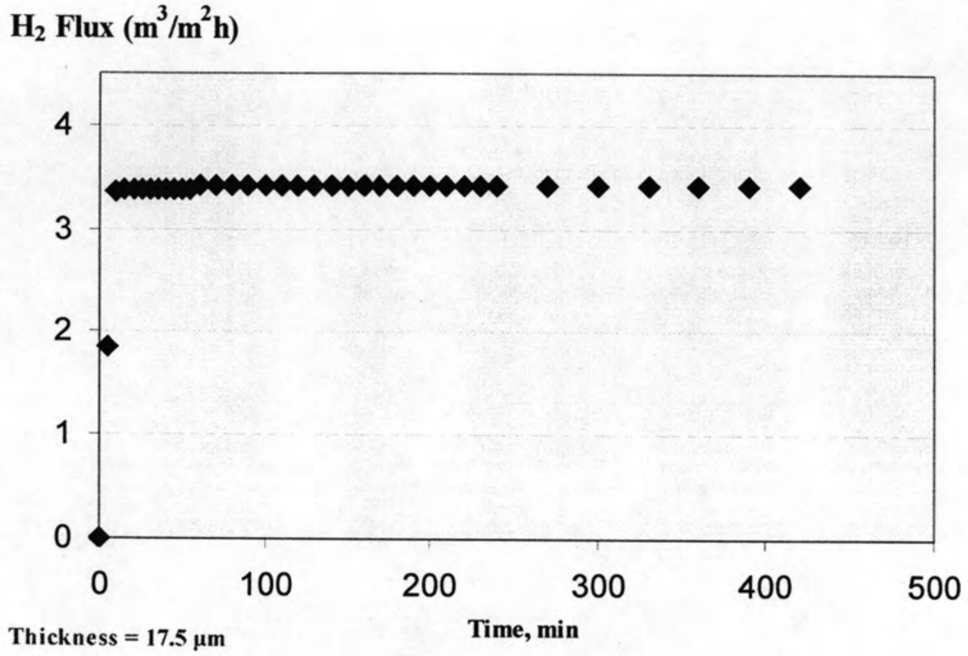


Figure A12 Hydrogen permeation flux as a function of time at 400°C, pressure 1 atm.

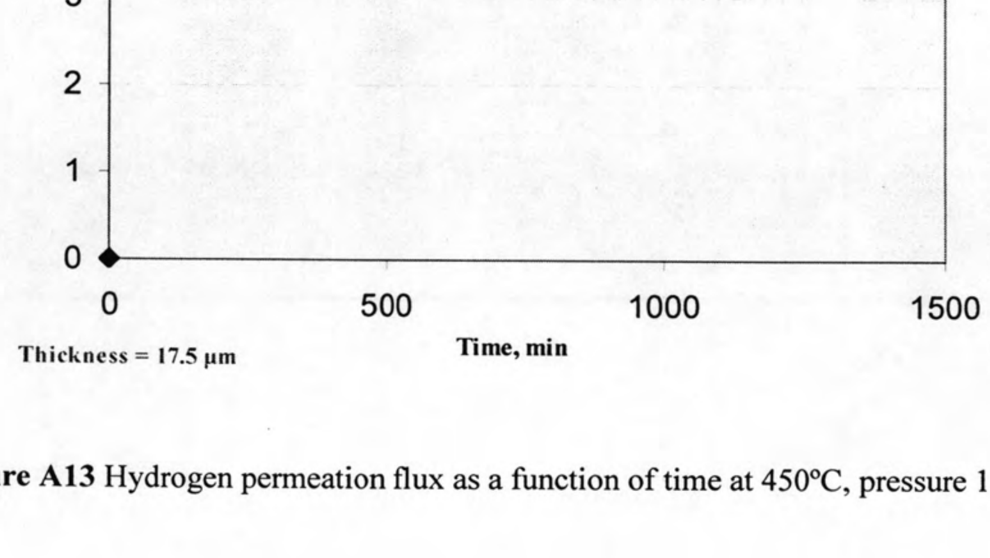


Figure A13 Hydrogen permeation flux as a function of time at 450°C, pressure 1 atm.

Permeance test

#	P_s	P_o	ΔP	$P_s^{0.5} - P_o^{0.5}$	Flux (m^3/m^2h)
0	764	764	0	0	0.0000
1	942	764	0.25	0.1189	0.6584
2	1119	764	0.50	0.2269	1.4066
3	1297	764	0.75	0.3257	2.1248
4	1475	764	1.00	0.4177	2.7832
5	1653	764	1.25	0.5041	3.4117
6	1830	764	1.50	0.5863	4.0401
7	2008	764	1.75	0.6640	4.5788
8	2186	764	2.00	0.7383	5.1474
9	2364	764	2.25	0.8095	5.6861
10	2541	764	2.50	0.8784	6.2248
11	2719	764	2.75	0.9446	6.7335
12	2897	764	3.00	1.0085	7.2124
13	1475	764	1.00	0.4177	2.7832

Temperature: 350°C

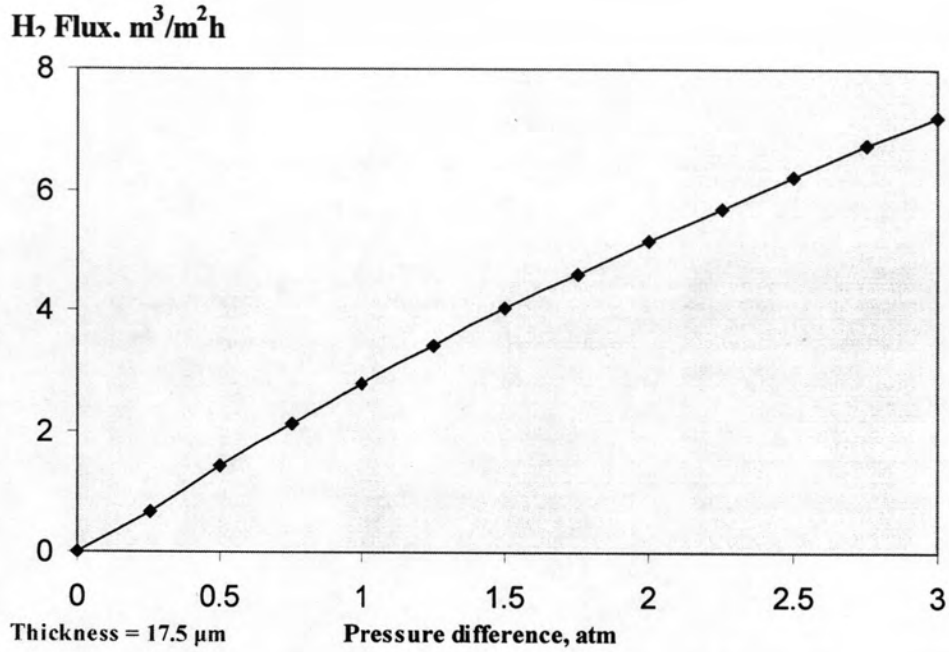


Figure A14 Hydrogen permeation flux of palladium membrane on porous stainless steel support as a function of pressure difference.

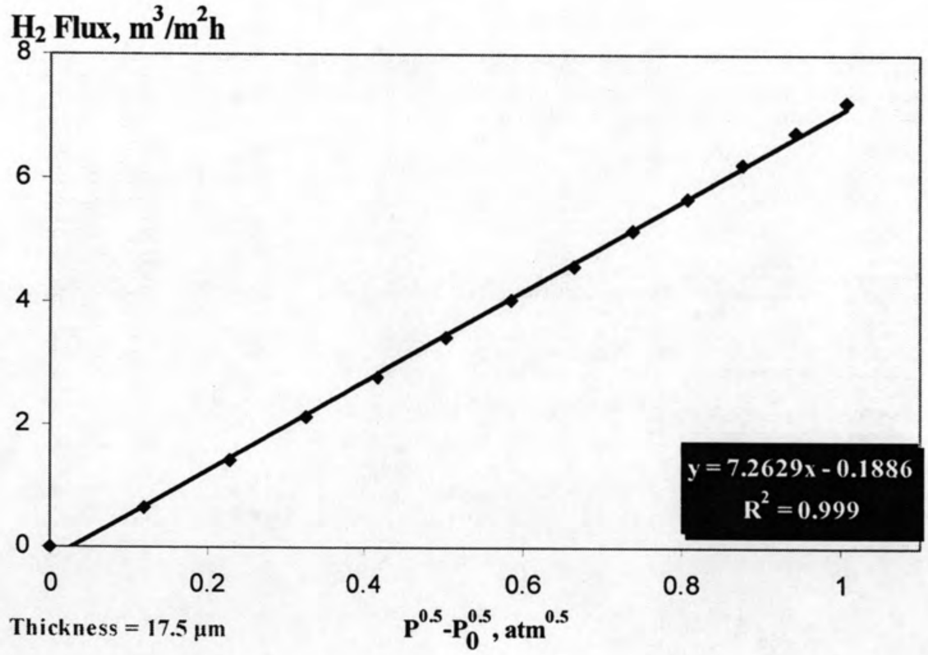


Figure A15 Hydrogen permeation flux of palladium membrane on porous stainless steel support as a function of square root of the pressure difference.

Temperature: 400°C

#	P_s	P_o	ΔP	$P_s^{0.5} - P_o^{0.5}$	Flux (m^3/m^2h)
0	764	764	0	0	0.0000
1	942	764	0.25	0.1189	0.8380
2	1119	764	0.50	0.2269	1.7657
3	1297	764	0.75	0.3257	2.6336
4	1475	764	1.00	0.4177	3.4117
5	1653	764	1.25	0.5041	4.1898
6	1830	764	1.50	0.5863	4.9080
7	2008	764	1.75	0.6640	5.5963
8	2186	764	2.00	0.7383	6.2248
9	2364	764	2.25	0.8095	6.8832
10	2541	764	2.50	0.8784	7.5116
11	2719	764	2.75	0.9446	8.1102
12	2897	764	3.00	1.0085	8.6788
13	1475	764	1.00	0.4177	3.4117

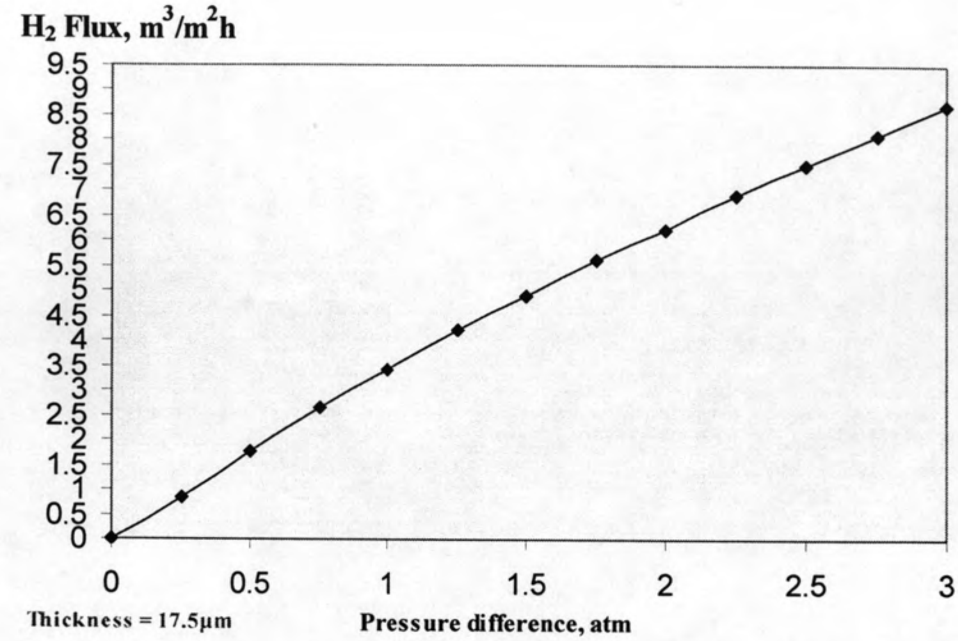


Figure A16 Hydrogen permeation flux of palladium membrane on porous stainless steel support as a function of pressure difference.

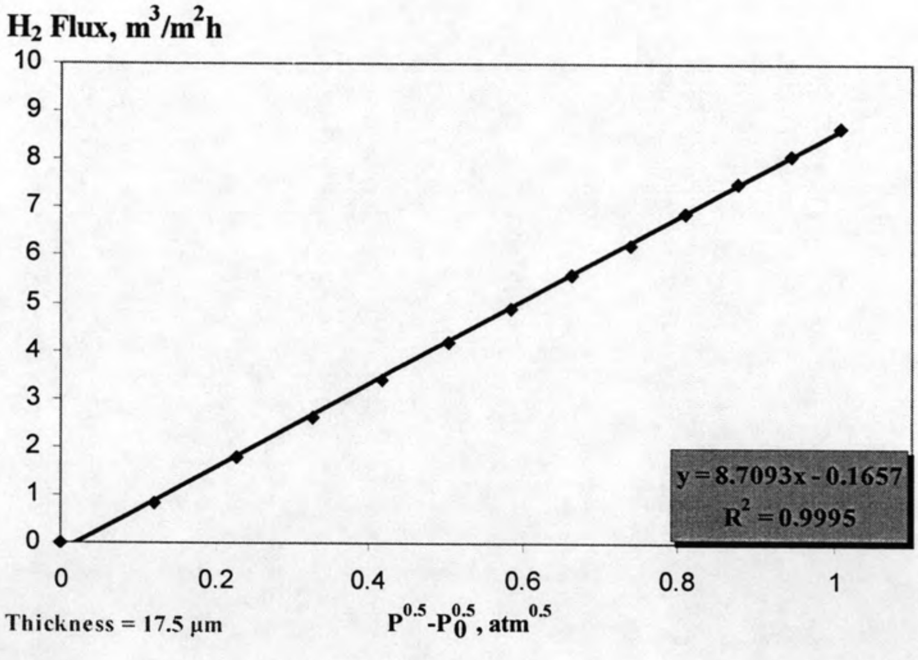


Figure A17 Hydrogen permeation flux of palladium membrane on porous stainless steel support as a function of square root of the pressure difference.

Temperature: 450°C

#	P_s	P_o	ΔP	$P_s^{0.5} - P_o^{0.5}$	Flux (m^3/m^2h)
0	764	764	0	0	0.0000
1	942	764	0.25	0.1189	1.1073
2	1119	764	0.50	0.2269	2.2744
3	1297	764	0.75	0.3257	3.3518
4	1475	764	1.00	0.4177	4.3693
5	1653	764	1.25	0.5041	5.3270
6	1830	764	1.50	0.5863	6.2248
7	2008	764	1.75	0.6640	7.0927
8	2186	764	2.00	0.7383	7.9306
9	2364	764	2.25	0.8095	8.7386
10	2541	764	2.50	0.8784	9.5167
11	2719	764	2.75	0.9446	10.2350
12	2897	764	3.00	1.0085	10.9532
13	1475	764	1.00	0.4177	4.3394

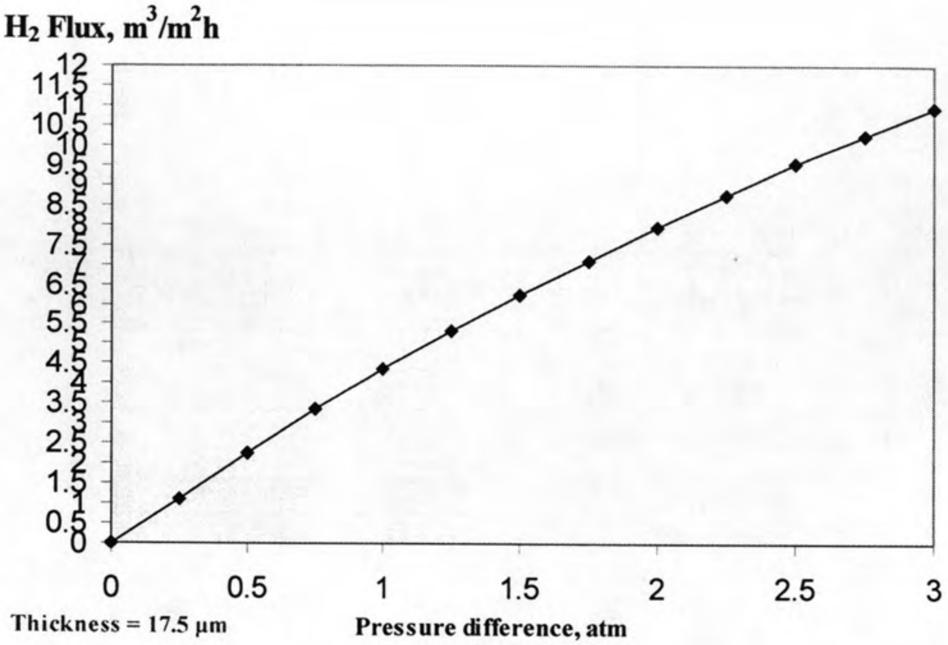


Figure A18 Hydrogen permeation flux of palladium membrane on porous stainless steel support as a function of pressure difference.

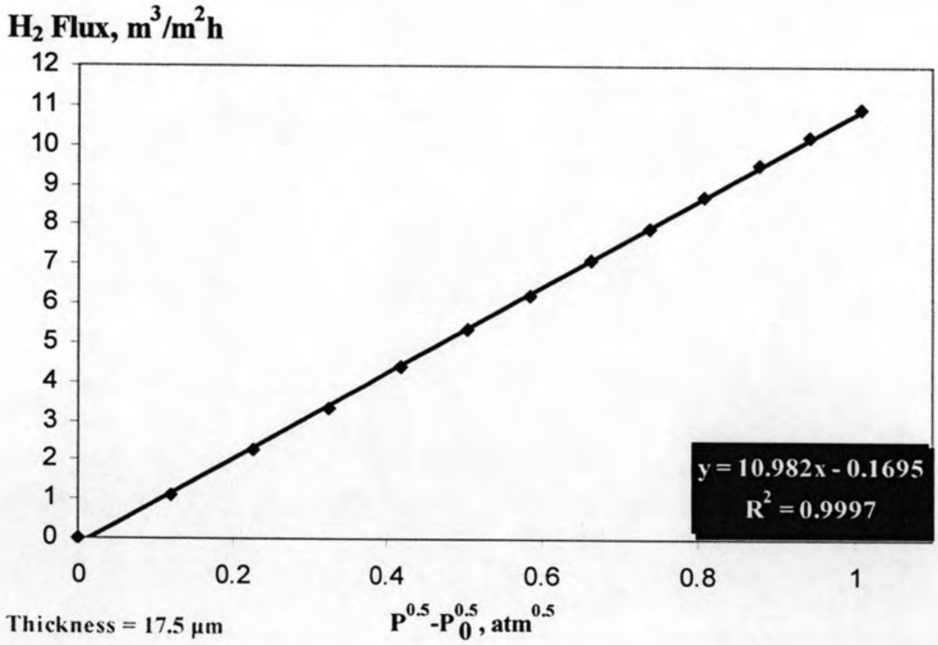


Figure A19 Hydrogen permeation flux of palladium membrane on porous stainless steel support as a function of square root of the pressure difference.

Determination of Activation energy of hydrogen diffusion through Palladium membrane

Temperature		Permeance (F),	$\frac{1000}{T}$	Ln F
Celsius, ^{O}C	Kelvin, K	$m^3/m^2h\ atm^{0.5}$		
350	643	7.2629	1.5552	1.7718
400	693	8.7093	1.4430	2.0093
450	743	10.9820	1.3458	2.1521

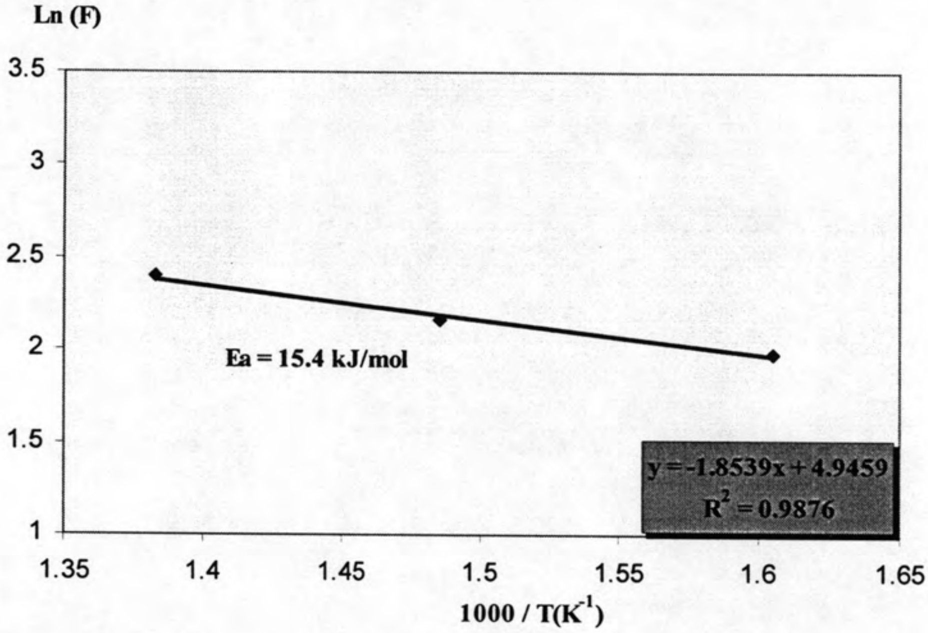


Figure A20 Arrhenius relation between the hydrogen permeance and invert operation temperature.

Tube 3

Date: 04/08/06

Sample #: Tube 3

Sample background:

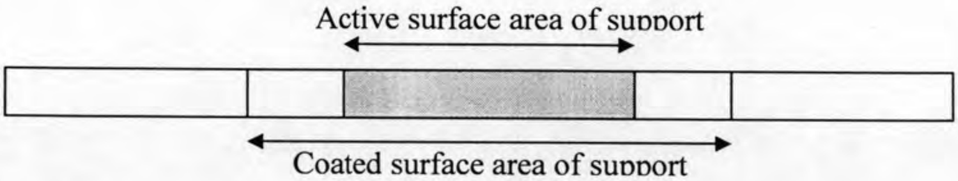
Porous stainless steel 0.1 μm

Coated surface area 25.4222 cm^2

Active surface area 20.0489 cm^2

Dense test

	Weight (g)	ΔWt (g)	Thickness(μm)	He flux (m^3/m^2h)
Before Cr plating#1	144.42	-	-	>14.96
After Cr plating#1	144.46	0.04	1.98	>14.96
After Pd plating#1	144.63	0.17	7.54	>14.96
After Pd plating#2	144.79	0.16	12.78	0.0359
After Pd plating#3	144.94	0.15	17.69	0.0003
After Pd plating#4	145.14	0.20	24.25	0.0001
After Pd plating#5	145.45	0.31	34.37	dense
thickness total (μm)			34.37	
Chromium thickness total (μm)			1.98	
Palladium thickness total (μm)			32.39	



$$\text{Pd thickness}\ (\mu\text{m}) = \left(\frac{\text{plated support weight - original support weight}}{\text{Coated surface area of support} \times \text{density of Palladium}}\right) \times 10^4$$

$$\text{Cr thickness}\ (\mu\text{m}) = \left(\frac{\text{plated support weight - original support weight}}{\text{Coated surface area of support} \times \text{density of Chromium}}\right) \times 10^4$$

$$\text{Flux}\ (\text{m}^3/\text{m}^2\text{h}) = \left(\frac{\text{Flow rate of He on Tube side (ml/min)}}{\text{Active surface area of support (cm}^2\text{)}}\right) \times 0.6$$

Where

Density of palladium = 12.02 g/ml

Density of chromium = 7.14 g/ml

Hydrogen flux test

Type of Gas: Helium

Temperature: Room temperature

#	ΔP	P_s	P_o	Flow rate (ml/min)								Flux
				1	2	3	4	5	Avg	SD	RSD	(m^3/m^2h)
0	0	764	764	0	0	0	0	0	0	0	-	0
1	0.25	942	764	0	0	0	0	0	0	0	-	0
2	0.50	1119	764	0	0	0	0	0	0	0	-	0
3	0.75	1297	764	0	0	0	0	0	0	0	-	0
4	1.00	1475	764	0	0	0	0	0	0	0	-	0
5	1.25	1653	764	0	0	0	0	0	0	0	-	0
6	1.50	1830	764	0	0	0	0	0	0	0	-	0
7	1.75	2008	764	0	0	0	0	0	0	0	-	0
8	2.00	2186	764	0	0	0	0	0	0	0	-	0
9	2.25	2364	764	0	0	0	0	0	0	0	-	0
10	2.50	2541	764	0	0	0	0	0	0	0	-	0
11	2.75	2719	764	0	0	0	0	0	0	0	-	0
12	3.00	2897	764	0	0	0	0	0	0	0	-	0
13	1.00	1475	764	0	0	0	0	0	0	0	-	0

Type of Gas: Hydrogen gas

Temperature: 350°C

#	ΔP	P_s	P_o	Flow rate (ml/min)								Flux
				1	2	3	4	5	Avg	SD	RSD	(m^3/m^2h)
0	0	764	764	0	0	0	0	0	0	0	-	0
1	0.25	942	764	15	15	15	15	15	15	0.1	0.4	0.4489
2	0.50	1119	764	34	34	34	34	34	34	0.1	0.3	1.0175
3	0.75	1297	764	53	53	53	53	53	53	0.1	0.2	1.5861
4	1.00	1475	764	70	70	70	70	70	70	0.1	0.2	2.0949
5	1.25	1653	764	86	86	86	86	86	86	0.0	0.1	2.5737
6	1.50	1830	764	102	102	102	102	102	102	0.1	0.1	3.0525
7	1.75	2008	764	116	116	116	116	116	116	0.0	0.0	3.4715
8	2.00	2186	764	130	130	130	130	130	130	0.1	0.1	3.8905
9	2.25	2364	764	144	144	144	144	144	144	0.0	0.0	4.3095
10	2.50	2541	764	156	156	156	156	156	156	0.0	0.0	4.6686
11	2.75	2719	764	169	169	169	169	169	169	0.0	0.0	5.0576
12	3.00	2897	764	181	181	181	181	181	181	0.1	0.0	5.4168
13	1.00	1475	764	70	70	70	70	70	70	0.1	0.2	2.0949

Type of Gas: Hydrogen gas

Temperature: 400°C

#	ΔP	P_s	P_o	Flow rate (ml/min)								Flux
				1	2	3	4	5	Avg	SD	RSD	(m^3/m^2h)
0	0	764	764	0	0	0	0	0	0	0	-	0
1	0.25	942	764	20	20	20	20	20	20	0.0	0.0	0.5985
2	0.50	1119	764	46	46	46	46	46	46	0.1	0.3	1.3766
3	0.75	1297	764	70	70	70	70	70	70	0.1	0.2	2.0949
4	1.00	1475	764	93	93	93	93	93	93	0.1	0.2	2.7832
5	1.25	1653	764	114	114	114	114	114	114	0.0	0.0	3.4117
6	1.50	1830	764	134	134	134	134	134	134	0.1	0.1	4.0102
7	1.75	2008	764	154	154	154	154	154	154	0.1	0.1	4.6087
8	2.00	2186	764	173	173	173	173	173	173	0.1	0.1	5.1773
9	2.25	2364	764	191	191	191	191	191	191	0.4	0.2	5.6861
10	2.50	2541	764	208	208	208	208	208	208	0.1	0.0	6.2248
11	2.75	2719	764	224	224	224	224	224	224	0.2	0.1	6.7036
12	3.00	2897	764	240	240	240	240	240	240	0.1	0.0	7.1824
13	1.00	1475	764	93	93	93	93	93	93	0.1	0.2	2.7832

Type of Gas: Hydrogen gas

Temperature: 450ºC

#	ΔP	P_s	P_o	Flow rate (ml/min)								Flux
				1	2	3	4	5	Avg	SD	RSD	(m^3/m^2h)
0	0	764	764	0	0	0	0	0	0	0	-	0
1	0.25	942	764	24	24	24	24	24	24	0.1	0.3	0.7258
2	0.50	1119	764	55	55	55	55	55	55	0.1	0.1	1.6671
3	0.75	1297	764	85	85	85	85	85	85	0.3	0.4	2.5424
4	1.00	1475	764	112	112	112	112	112	112	0.1	0.1	3.3592
5	1.25	1653	764	138	138	138	138	138	138	0.1	0.1	4.1292
6	1.50	1830	764	162	162	162	162	162	162	0.7	0.7	4.8544
7	1.75	2008	764	185	185	185	185	185	185	0.1	0.1	5.5494
8	2.00	2186	764	207	207	207	207	207	207	0.1	0.1	6.2151
9	2.25	2364	764	229	229	229	229	229	229	0.1	0.1	6.8542
10	2.50	2541	764	249	249	249	249	249	249	0.0	0.0	7.4659
11	2.75	2719	764	269	269	269	269	269	269	0.0	0.0	8.0610
12	3.00	2897	764	288	288	288	288	288	288	0.3	0.3	8.6361
13	1.00	1475	764	112	112	112	112	112	112	0.1	0.1	3.3592

Type of Gas: Hydrogen gas

Temperature: 500°C

#	ΔP	P_s	P_o	Flow rate (ml/min)								Flux
				1	2	3	4	5	Avg	SD	RSD	(m^3/m^2h)
0	0	764	764	0	0	0	0	0	0	0	-	0
1	0.25	942	764	21	21	21	21	21	21	0.1	0.2	0.6266
2	0.50	1119	764	58	58	58	58	58	58	0.1	0.1	1.7528
3	0.75	1297	764	93	93	93	93	93	93	0.1	0.1	2.8000
4	1.00	1475	764	126	126	126	126	126	126	0.0	0.0	3.7772
5	1.25	1653	764	157	157	157	157	157	157	0.7	0.5	4.6985
6	1.50	1830	764	186	186	186	186	186	186	0.1	0.0	5.5661
7	1.75	2008	764	213	213	213	213	213	213	0.1	0.0	6.3975
8	2.00	2186	764	240	240	240	240	240	240	0.0	0.0	7.1939
9	2.25	2364	764	266	266	266	266	266	266	0.1	0.0	7.9586
10	2.50	2541	764	290	290	290	290	290	290	0.0	0.0	8.6903
11	2.75	2719	764	314	314	314	314	314	314	0.0	0.0	9.4024
12	3.00	2897	764	337	337	337	337	337	337	0.1	0.0	10.0903
13	1.00	1475	764	126	126	126	126	126	126	0.0	0.0	3.7772

Selectivity test

From the above data, the selectivity ($\alpha_{H_2/He}$) of prepared palladium membrane was the ratio of H2 flux (J_{H_2}) and He flux (J_{He}) at 350°C, 400 °C, and 450 °C at different pressure (ΔP) 1 atm.

Temperature (°C)	J_{H_2}	J_{He}	$\alpha_{H_2/He}$
350	2.0949	0.00000	Can not define
400	2.7832	0.00000	Can not define
450	3.3592	0.00000	Can not define
500	3.7772	0.0000	Can not define

Permeance test

Temperature:..............................350°C..................................

#	P_s	P_o	ΔP	$P_s^{0.5} - P_o^{0.5}$	Flux (m^3/m^{2}h)
0	764	764	0	0	0
1	942	764	0.25	0.1135	0.4489
2	1119	764	0.50	0.2163	1.0175
3	1297	764	0.75	0.3119	1.5861
4	1475	764	1.00	0.4011	2.0949
5	1653	764	1.25	0.4852	2.5737
6	1830	764	1.50	0.5644	3.0525
7	2008	764	1.75	0.6403	3.4715
8	2186	764	2.00	0.7130	3.8905
9	2364	764	2.25	0.7828	4.3095
10	2541	764	2.50	0.8496	4.6686
11	2719	764	2.75	0.9146	5.0576
12	2897	764	3.00	0.9774	5.4168

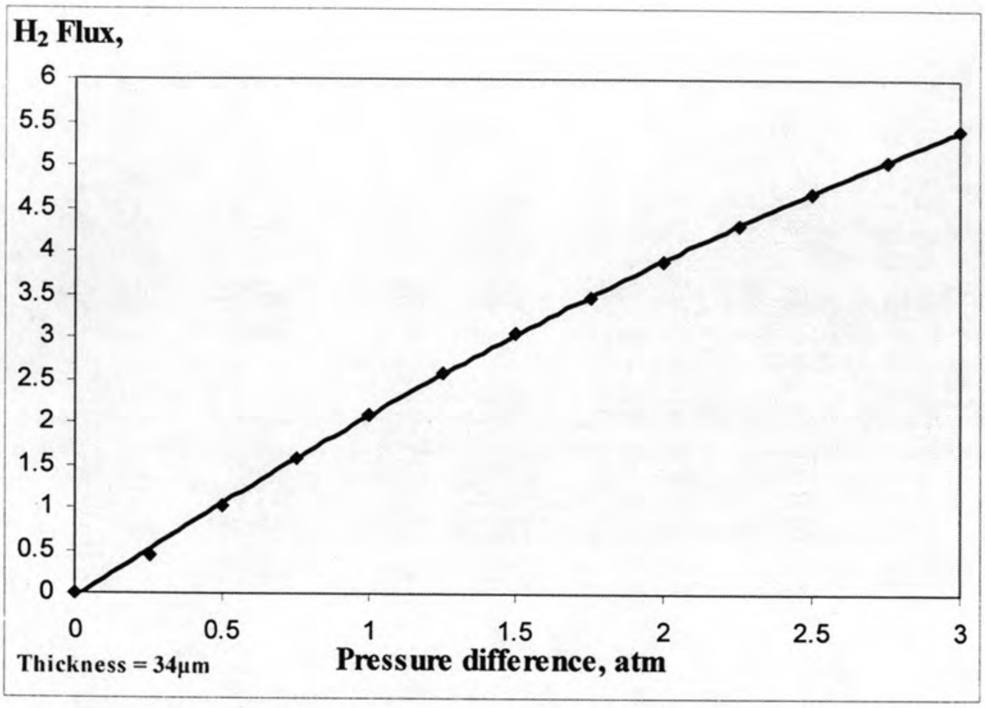


Figure A21 Hydrogen permeation flux of palladium membrane on porous stainless steel support as a function of pressure difference.

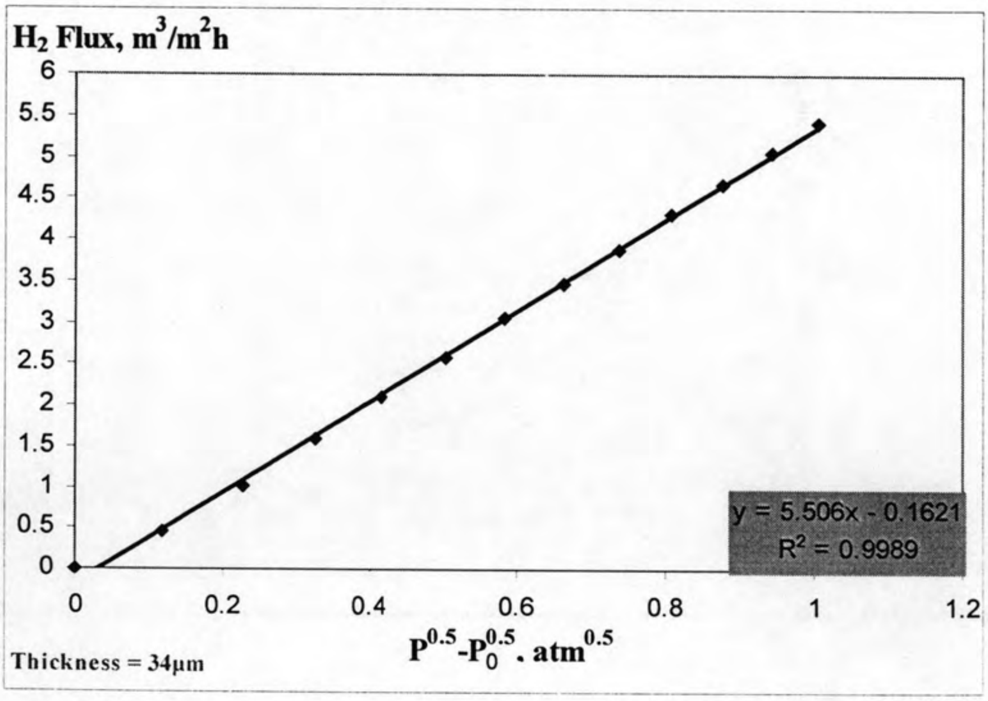


Figure A22 Hydrogen permeation flux of palladium membrane on porous stainless steel support as a function of the square roots of the pressure difference.

Temperature: 400 ºC

#	P_s	P_o	ΔP	$P_s^{0.5} - P_o^{0.5}$	Flux (m^3/m^2h)
0	764	764	0	0	0
1	942	764	0.25	0.1135	0.5985
2	1119	764	0.50	0.2163	1.3766
3	1297	764	0.75	0.3119	2.0949
4	1475	764	1.00	0.4011	2.7832
5	1653	764	1.25	0.4852	3.4117
6	1830	764	1.50	0.5644	4.0102
7	2008	764	1.75	0.6403	4.6087
8	2186	764	2.00	0.7130	5.1773
9	2364	764	2.25	0.7828	5.6861
10	2541	764	2.50	0.8496	6.2248
11	2719	764	2.75	0.9146	6.7036
12	2897	764	3.00	0.9774	7.1824

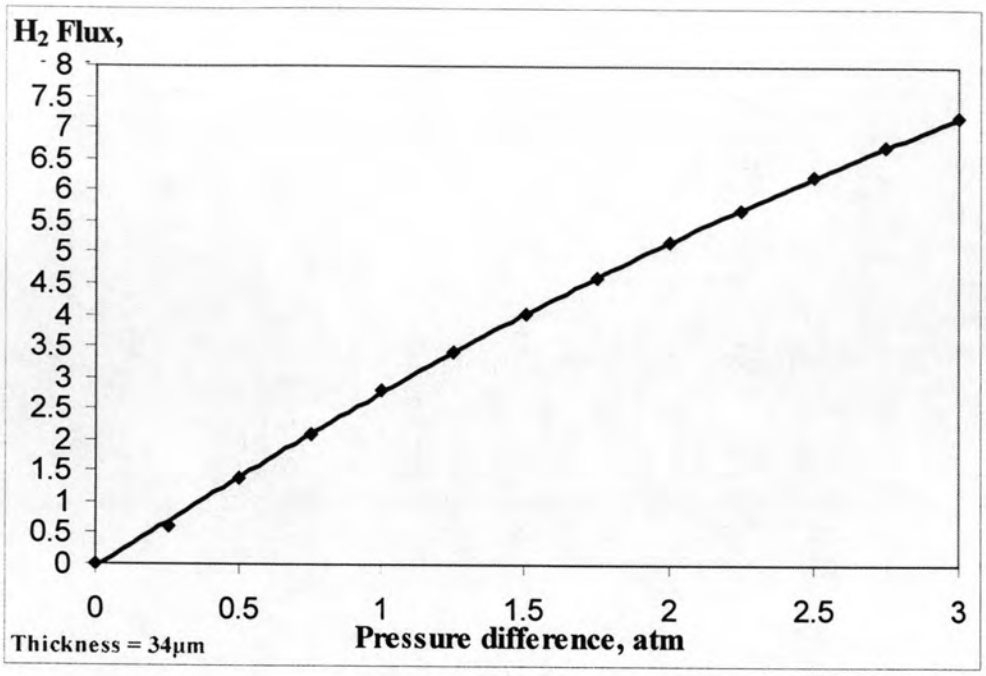


Figure A23 Hydrogen permeation flux of palladium membrane on porous stainless steel support as a function of pressure difference.

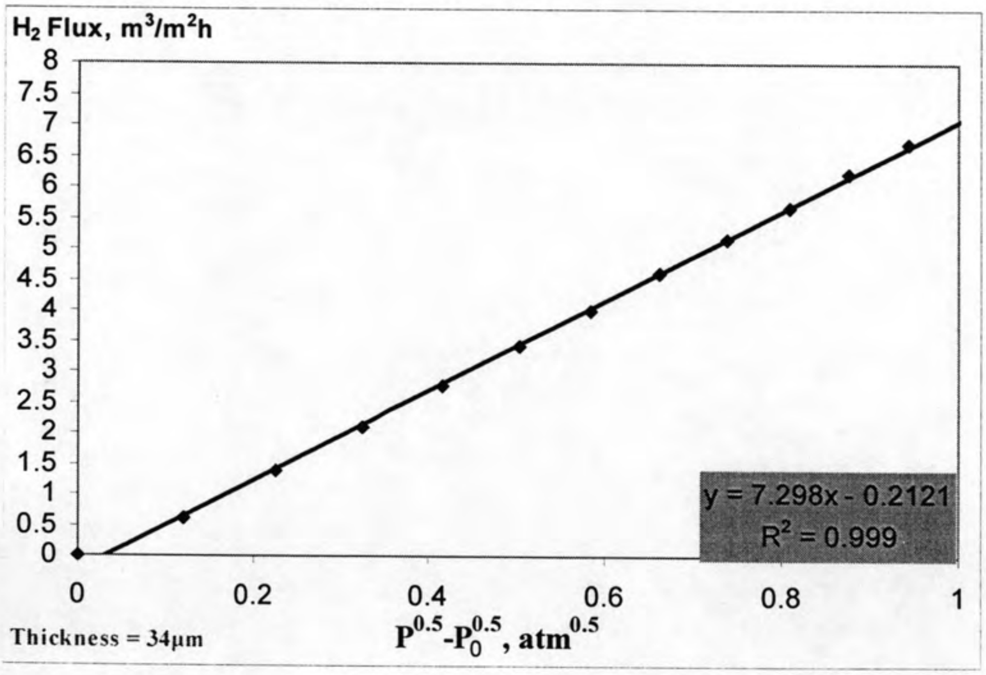


Figure A24 Hydrogen permeation flux of palladium membrane on porous stainless steel support as a function of the square roots of the pressure difference.

Temperature: 450°C

#	P_s	P_o	ΔP	$P_s^{0.5} - P_o^{0.5}$	Flux (m^3/m^2h)
0	764	764	0	0	0
1	942	764	0.25	0.1135	0.7258
2	1119	764	0.50	0.2163	1.6671
3	1297	764	0.75	0.3119	2.5424
4	1475	764	1.00	0.4011	3.3592
5	1653	764	1.25	0.4852	4.1292
6	1830	764	1.50	0.5644	4.8544
7	2008	764	1.75	0.6403	5.5494
8	2186	764	2.00	0.7130	6.2151
9	2364	764	2.25	0.7828	6.8542
10	2541	764	2.50	0.8496	7.4659
11	2719	764	2.75	0.9146	8.0610
12	2897	764	3.00	0.9774	8.6361

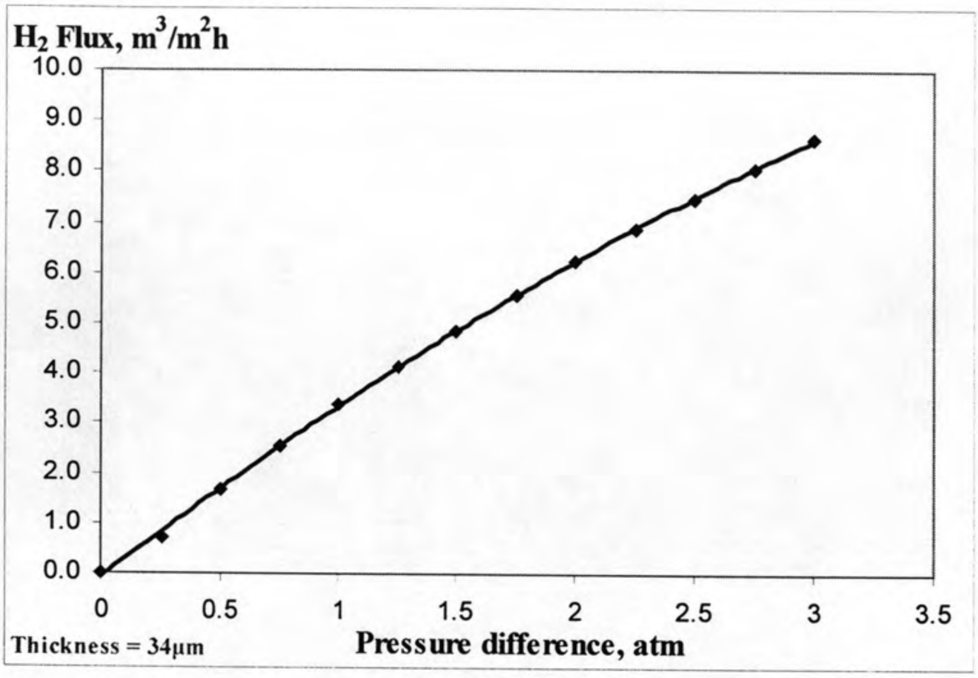


Figure A25 Hydrogen permeation flux of palladium membrane on porous stainless steel support as a function of pressure difference.

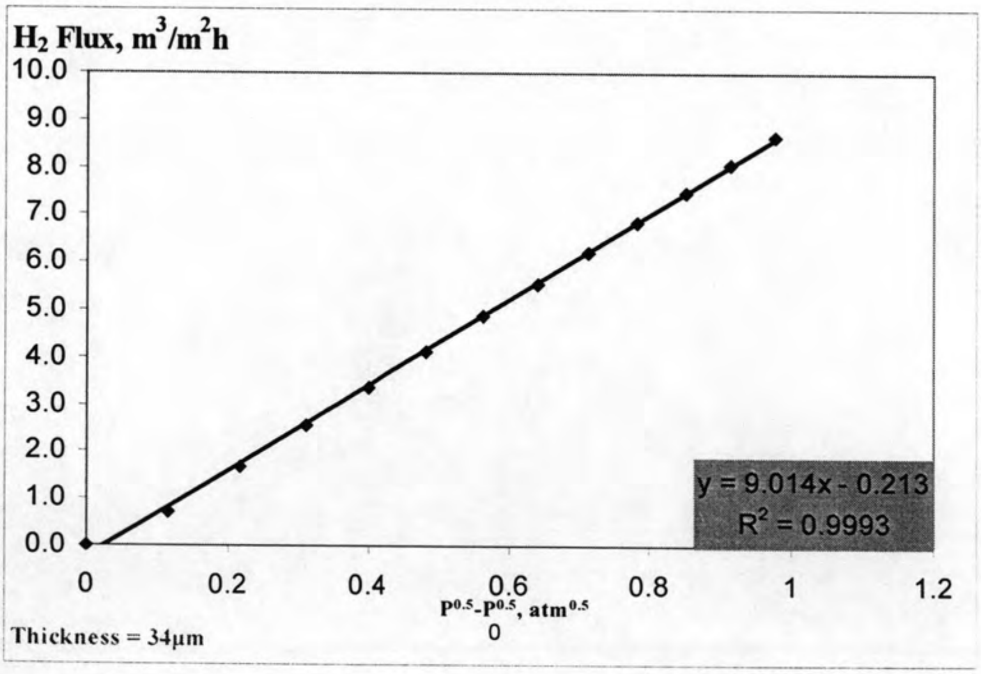


Figure A26 Hydrogen permeation flux of palladium membrane on porous stainless steel support as a function of the square roots of the pressure difference.

Temperature: ....500ºC..

#	P_s	P_o	ΔP	$P_s^{0.5} - P_o^{0.5}$	Flux (m^3/m^2h)
0	764	764	0	0	0
1	942	764	0.25	0.1135	0.6266
2	1119	764	0.50	0.2163	1.7528
3	1297	764	0.75	0.3119	2.8000
4	1475	764	1.00	0.4011	3.7772
5	1653	764	1.25	0.4852	4.6985
6	1830	764	1.50	0.5644	5.5661
7	2008	764	1.75	0.6403	6.3975
8	2186	764	2.00	0.7130	7.1939
9	2364	764	2.25	0.7828	7.9586
10	2541	764	2.50	0.8496	8.6903
11	2719	764	2.75	0.9146	9.4024
12	2897	764	3.00	0.9774	10.0903

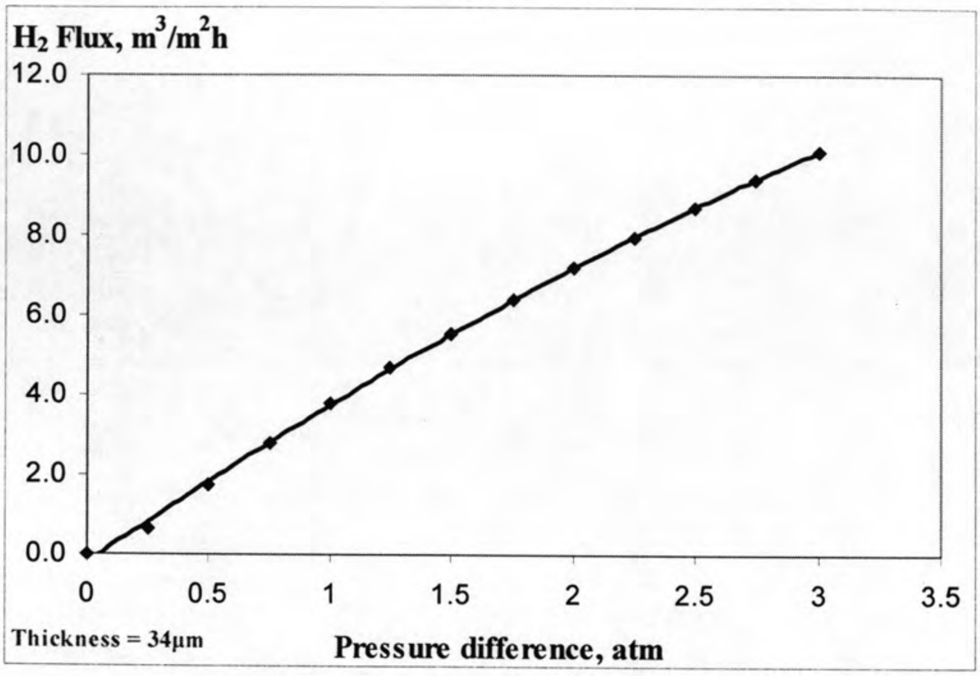


Figure A27 Hydrogen permeation flux of palladium membrane on porous stainless steel support as a function of pressure difference.

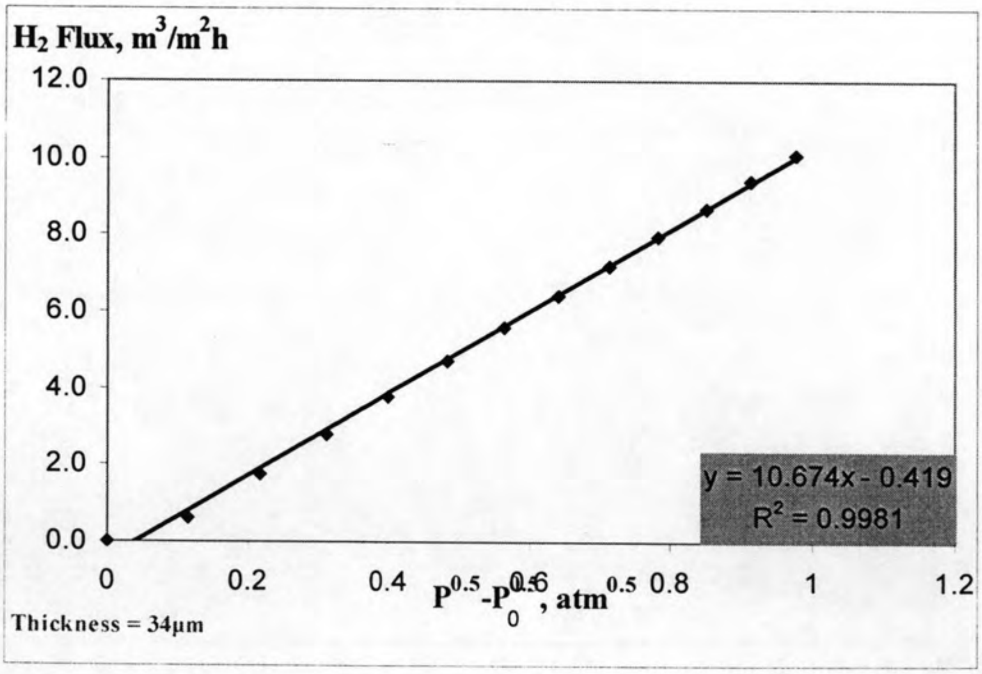


Figure A28 Hydrogen permeation flux of palladium membrane on porous stainless steel support as a function of the square roots of the pressure difference.

Determination of Activation energy of hydrogen diffusing through palladium membrane

Temperature		Permeance (F),	$\frac{1000}{T}$	Ln F
Celsius,°C	Kelvin, K	$m^3/m^2h\ atm^{0.5}$		
350	623.16	5.6125	1.6	1.7250
400	673.16	7.4372	1.5	2.0065
450	723.16	9.014	1.4	2.1988
500	773.16	10.9550	1.3	2.3938

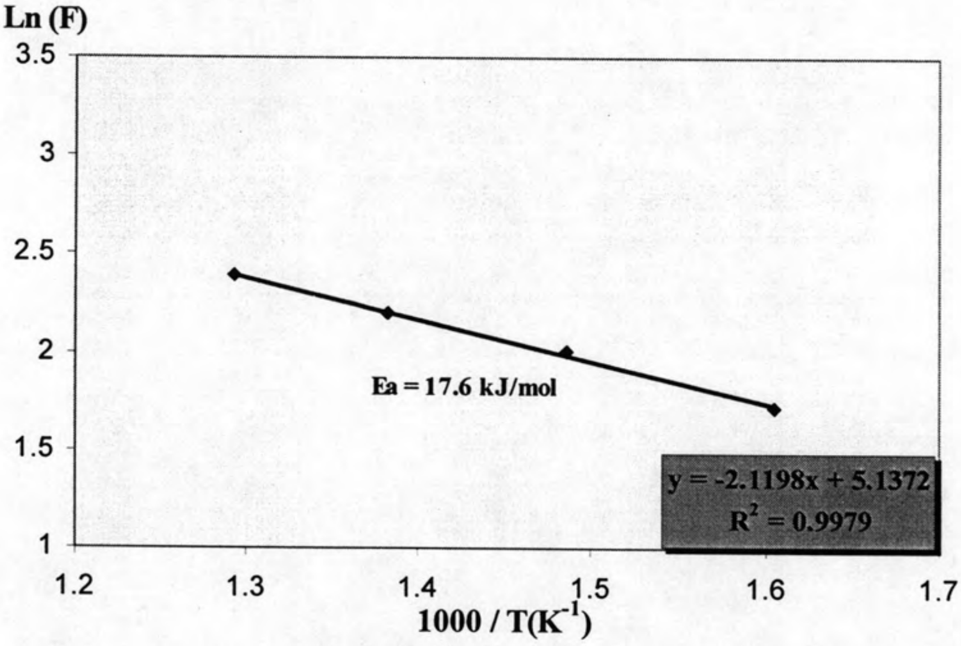


Figure A29 Arrhenius relation between the hydrogen permeance and invert operation temperature.

APPENDIX B

APPENDIX B

EQUILIBRIUM CURVE

The conversion curve is computed by using the thermodynamic data like Gibb's free energy and enthalpy. The relation ship is shown as following.

Determination of K_p

From

	$CH_{4(g)}$ +	$CO_{2(g)}$ ⇌	$2H_{2(g)}$ +	$2CO_{(g)}$	Total
Start:	n	n	0	0	$2n$
Change	$-\infty n$	$-\infty n$	$2\infty n$	$2\infty n$	$2\infty n$
Equilibrium	$n-\infty n$	$n-\infty n$	$2\infty n$	$2\infty n$	$2n(1+\infty)$

Since the mole of methane and Carbon dioxide was equimolar,

Thus $$n_{CH_4} = n_{CO_2} = n$$

Mole fraction: $y_i = \dfrac{n_i}{n_{total}}$

where

$$y_{CH_4} = \frac{n_{CH_4}}{n_{total}} = \frac{n-\infty n}{2n(1+\infty)} = \frac{(1-\infty)}{2(1+\infty)} \qquad y_{CO_2} = \frac{n_{CO_2}}{n_{total}} = \frac{n-\infty n}{2n(1+\infty)} = \frac{(1-\infty)}{2(1+\infty)}$$

$$y_{CO} = \frac{n_{CO}}{n_{total}} = \frac{2\infty n}{2n(1+\infty)} = \frac{\infty}{(1+\infty)} \qquad y_{H_2} = \frac{n_{H_2}}{n_{total}} = \frac{2\infty n}{2n(1+\infty)} = \frac{\infty}{(1+\infty)}$$

Partial pressure: $p_i = y_i P_t$

$$p_{CH_4} = \frac{(1-\infty)p_t}{2(1+\infty)} \qquad p_{CO_2} = \frac{(1-\infty)p_t}{2(1+\infty)}$$

$$p_{CO} = \frac{\infty p_t}{(1+\infty)} \qquad p_{H_2} = \frac{\infty p_t}{(1+\infty)}$$

$$P_t = p_{CH_4} + p_{CO_2} + p_{CO} + p_{H_2} = \left(\frac{(1-\infty)p}{2(1+\infty)}\right) + \left(\frac{(1-\infty)p}{2(1+\infty)}\right) + \left(\frac{\infty p}{(1+\infty)}\right) + \left(\frac{\infty p}{(1+\infty)}\right) = p$$

Then

$$K_p = \frac{p_{co}^2 \cdot p_{H_2}^2}{p_{CH_4} \cdot p_{CO_2}} = \frac{\left(\frac{\infty p}{1+\infty}\right)^2 \cdot \left(\frac{\infty p}{1+\infty)}\right)^2}{\left(\frac{(1-\infty)p}{2(1+\infty)}\right) \cdot \left(\frac{(1-\infty)p}{2(1+\infty)}\right)} = \frac{4(\infty p)^4 \cdot (1+\infty)^2}{(1+\infty)^2 \cdot (1-\infty)^2 p^2} = \frac{4(\infty p)^4}{(1-\infty)^2 p^2} = 4\left(\frac{\infty^2}{1-\infty}\right)^2 p^2$$

Therefore

$$K_p = \frac{4\infty^4 p^2}{(1+\infty)^2 (1-\infty)^2}$$

To determine the ∞ the Gibbs free energy was calculated from below equation.

$$\ell n K_c = \frac{-\Delta G^0_{Rxms}}{RT}$$

Or

$$K_p = e^{\frac{-\Delta G^0_{Rxms}}{RT}}$$

Where

$$\Delta G^0_{Rxms} = 2\Delta G^0_{CO} + 2\Delta G^0_{H_2} - \Delta G^0_{CH_4} - \Delta G^0_{CO_2}$$

From Perry's handbook

Temp(°C)	Temp(K)	ΔG, kcal/mol				ΔG_{rxms}, kcal/mol	ΔG_{rxms}, kJ/mol	K	ALPHA = X_{CH4}	X_{CH4}, %
		CO	H_2	CO_2	CH_4					
25	298	-40.497	-9.305	-109.275	-31.148	40.819	170.787	1.1554E-30	0.0000E+00	0.00
27	300	-40.585	-9.363	-109.370	-31.230	40.704	170.306	2.2187E-30	0.0000E+00	0.00
127	400	-45.416	-12.592	-114.623	-35.819	34.426	144.038	1.5482E-19	0.0000E+00	0.00
227	500	-50.428	-15.996	-120.131	-40.656	27.939	116.897	6.1297E-13	6.1100E-04	0.06
327	600	-55.584	-19.540	-125.856	-45.717	21.325	89.224	1.7065E-08	8.1000E-03	0.81
427	700	-60.864	-23.201	-131.769	-50.987	14.626	61.195	2.7127E-05	5.0000E-02	5.00
527	800	-66.251	-26.964	-137.849	-56.453	7.872	32.936	7.0696E-03	2.0000E-01	20.00
627	900	-71.732	-30.816	-144.079	-62.107	1.090	4.561	5.4363E-01	5.2000E-01	52.00
727	1000	-77.298	-34.750	-150.445	-67.939	-5.712	-23.899	1.7717E+01	8.2300E-01	82.30
827	1100	-82.942	-38.756	-156.937	-73.941	-12.518	-52.375	3.0703E+02	9.4700E-01	94.70
927	1200	-88.658	-42.830	-163.544	-80.106	-19.326	-80.860	3.3103E+03	9.8300E-01	98.30
1027	1300	-94.440	-46.966	-170.260	-86.428	-26.124	-109.303	2.4660E+04	9.9400E-01	99.40
1127	1400	-100.284	-51.160	-177.078	-92.901	-32.909	-137.691	1.3725E+05	9.9700E-01	99.70
1227	1500	-106.187	-55.408	-183.992	-99.518	-39.680	-166.021	6.0475E+05	1.0000E+00	100.00
1327	1600	-112.144	-59.708	-190.997	-106.273	-46.434	-194.280	2.2020E+06	1.0000E+00	100.00
1427	1700	-118.154	-64.056	-198.090	-113.162	-53.168	-222.455	6.8463E+06	1.0000E+00	100.00
1527	1800	-124.213	-68.451	-205.265	-120.179	-59.884	-250.555	1.8671E+07	1.0000E+00	100.00
1627	1900	-130.320	-72.890	-212.521	-127.318	-66.581	-278.575	4.5586E+07	1.0000E+00	100.00
1727	2000	-136.473	-77.370	-219.854	-134.574	-73.258	-306.511	1.0129E+08	1.0000E+00	100.00

Therefore

$$\Delta G^0_{Rxms} = 2(-40.497) + 2(-9.305) - (-31.148) - (-109.275) = 40.819 kcal/mol$$

Thus

$$K_p = e^{\frac{-\Delta G^0_{Rxms}}{RT}}$$

Then

$$K_p = \frac{4\infty^4 p^2}{(1+\infty)^2(1-\infty)^2} = e^{\frac{-\Delta G^0_{Rxms}}{RT}}$$

Where $P_{Total} = P = 1$ atm

As shown in the above table

Thus

$$K_p = 1.554x10^{-30} = \frac{4\infty^4 p^2}{(1+\infty)^2(1-\infty)^2}$$

$$\infty = 0$$

From

$$\textit{The percentage of Methane conversion}(\%\chi_{CH_4}) = \frac{n_{CH_4(in)} - n_{CH_4(out)}}{n_{CH_4(in)}} x100$$

$$= \frac{n-(n-n\infty)}{n} x100 = \infty x100$$

Therefore the plot between methane conversion percent and temperature was exhibited as below:

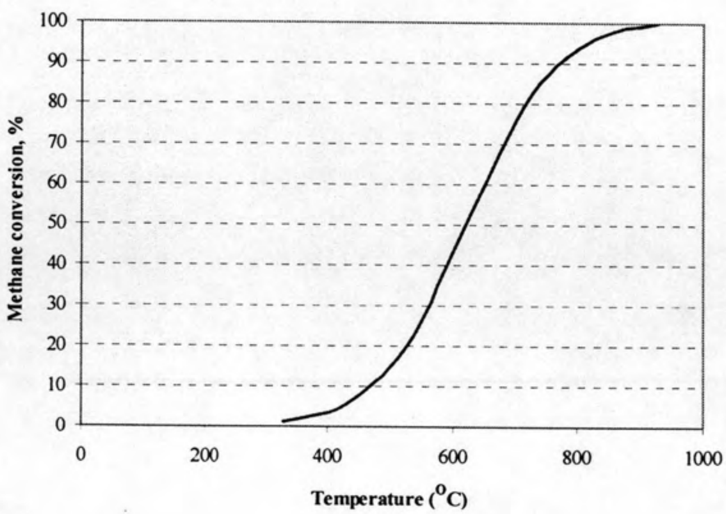


Figure B1 The theoretical conversion of methane in dry reforming reaction.

APPENDIX C

Table D1 List of meting point and Tamman temperature of metal and metal oxide.

Materials	Melting Point (°C)	Tamman Temperature (°C)
Palladium, Pd	1,555 (1,828 K)	641 (914 K)
Iron, Fe	1,538 (1,811 K)	632.5 (905.5 K)
Nickel, Ni	1,455 (1,728 K)	591 (864 K)
Chromium,Cr	1,907 (2,180 K)	817 (1,090 K)
Tungsten,W	3,422 (3,695 K)	1,574.5 (1,847.5 K)
Copper, Cu	1,085 (1,358 K)	406 (679 K)
Silver, Ag	962 (1,235 K)	344.5(617.5 K)
Cobalt, Co	1,495 (1,768 K)	611 (884 K)
Stainless steel	1,375-1,400 (1,648-1,673 K)	550-560 (823-833 K)
Tin Oxide, SnO_2	1,127 (1,400 K)	427 (700 K)
Copper Oxide, CuO	1,235-1,326 (1,508-1,599K)	481-526.5 (754-799.5 K)
Silica, SiO_2	1,710 (1,983 K)	718.5 (991.5 K)
Alumina, Al_2O_3	2,054 (2,327 K)	890.5 (1163.5 K)
Nickel Oxide, NiO_2	600 (873 K)	163.5 (436.5 K)
Iron oxide, Fe_2O_3	1,565(1,838 K)	646 (919 K)
Zirconium Oxide, ZrO_2	2,715 (2,988 K)	1,221 (1,494 K)
Tungsten Oxide, WO_3	1,473 (1,746 K)	600 (873 K)
Chromium Oxide, Cr_2O_3	2,435 (2,708 K)	1,081 (1,354 K)

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In 2004 Sutheerawat Samingprai, Supawan Tantayanon, and Yi Hua Ma,"Preparation of Dense Palladium Membrane Supported on Porous Stainless Steel and Preliminary Investigation of Its Application on Methane Conversion via Dry Reforming", *30th Congress on Science and Technology of Thailand, Oct 19-21, 2004, Bangkok.*

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