Metal Membranes for Hydrogen Separation

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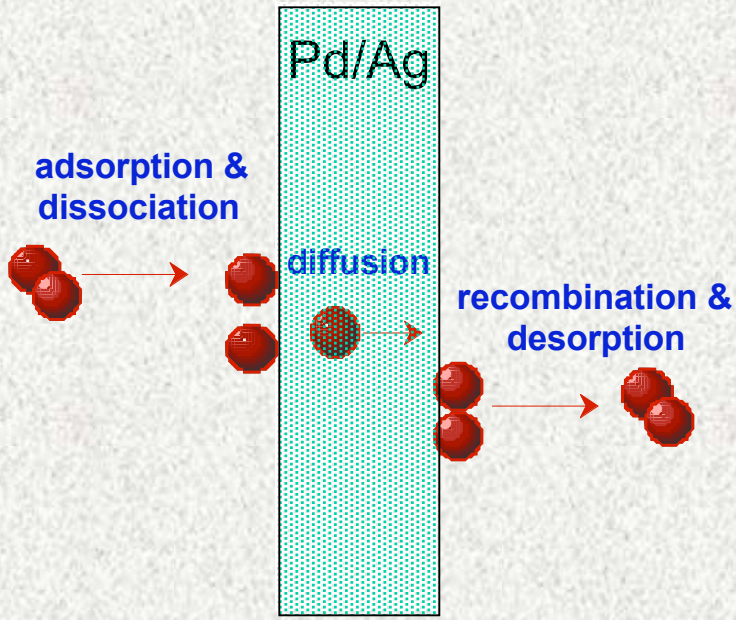
Overview

- Background
  - hydrogen separating membranes
- Iron aluminide porous membrane support
  - metallic interdiffusion barrier
- Fabrication, testing, and analysis of Pd composite membranes
  - Pd and Pd alloy coated V-10Cu, and V-6Ni-5Co
  - hydrogen permeation testing at 350-500°C
  - Auger electron spectroscopy (AES) depth profiles
  - Rutherford backscattering spectroscopy (RBS)

Hydrogen Flux Through a Metal

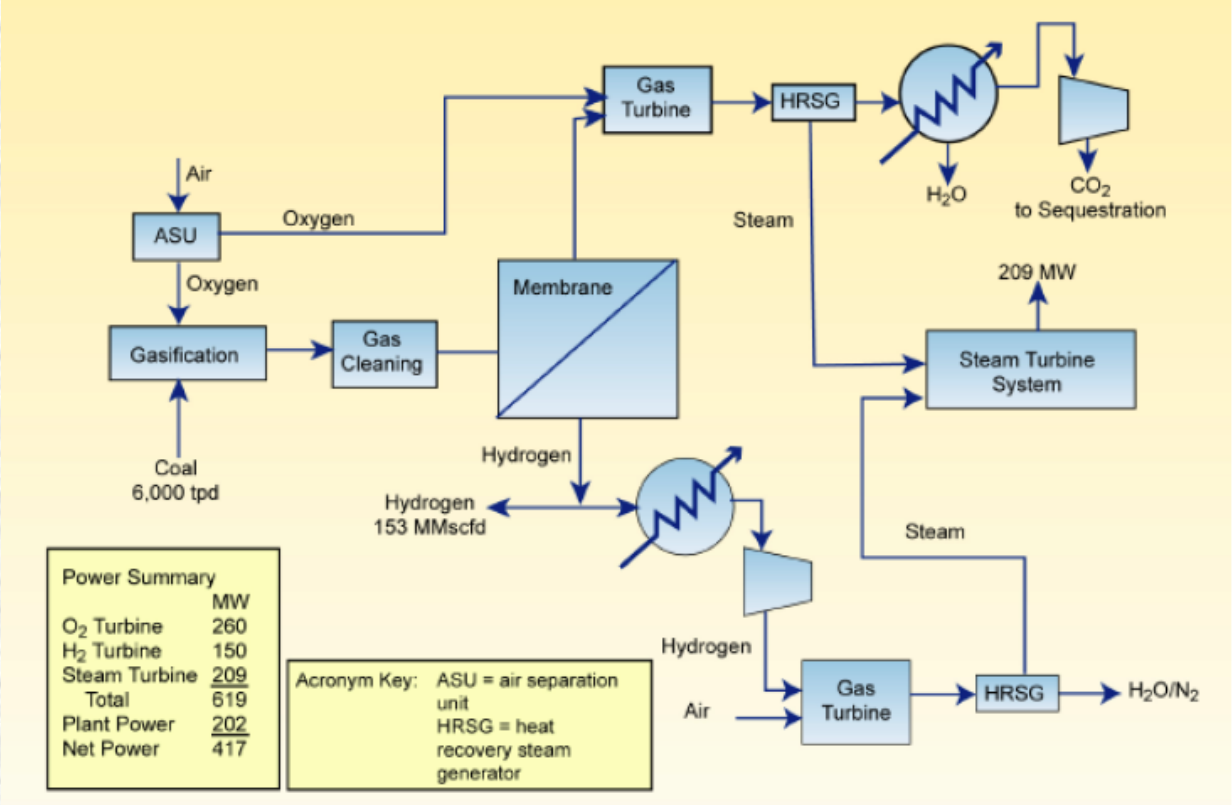


- solution-diffusion mechanism
- flux, J [mol/m^2·s]:

$$J = \frac{P(p_{feed}^{0.5} - p_{perm}^{0.5})}{l}$$

- permeability
  - $P = S \cdot D$ [mol·m/m^2·s·Pa$^{0.5}$]
  - product of solubility and diffusivity

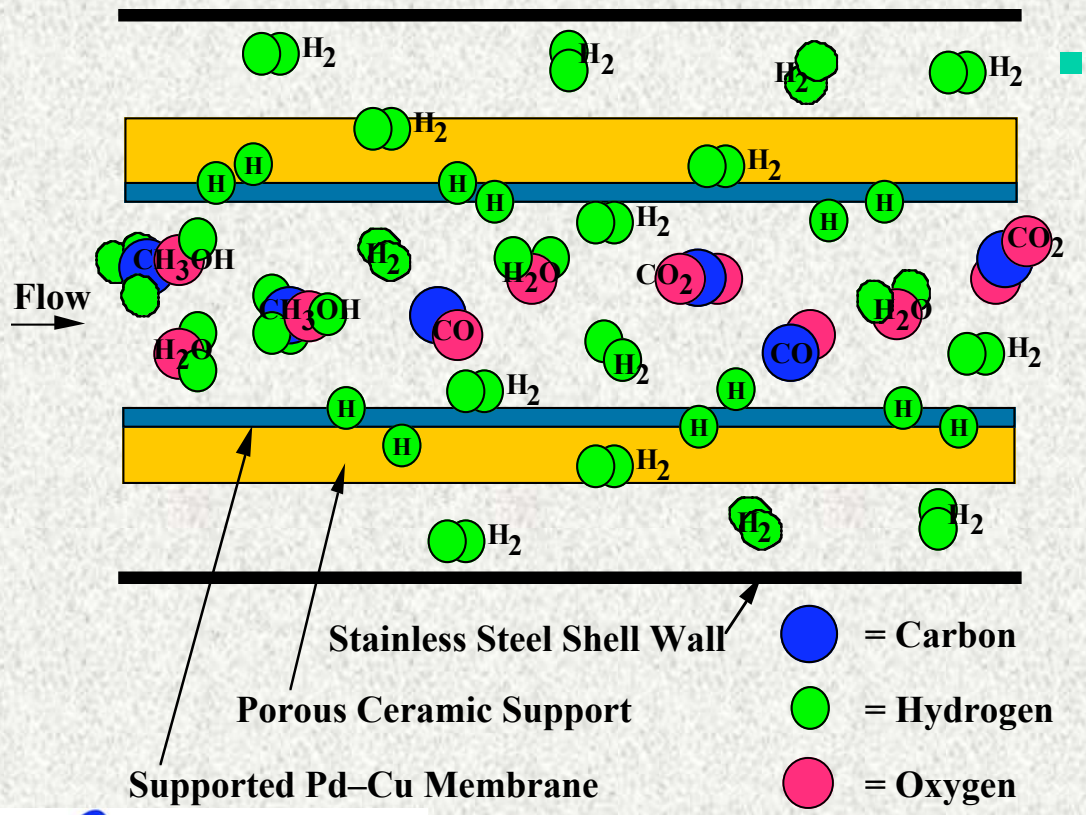
FutureGen: Hydrogen from Coal



Source: Gray, D. and Tomlinson, G. Mitretek Systems. Hydrogen from Coal, Mitretek Technical Paper MTR 2002-31. July 2002.

Fuel Reforming for Hydrogen

Challenge: *apply membrane to small-scale distributed production in one-step shift reactor that is feedstock flexible* – Arlene Anderson, Tech. Devel. Manager, DoE H_2, Fuel Cells & Infrastructure Tech.



- Membrane reactor
  - fuel flexible (liquid, gaseous, coal, biomass)
  - $C_nH_m + nH_2O \leftrightarrow nCO + [(m+2n)/2]H_2$
  - $CO + H_2O \leftrightarrow CO_2 + H_2$
  - pure H_2 plus a high-pressure, CO_2 rich stream in a single unit operation facilitates carbon sequestration

DoE Membrane Performance Targets

Performance Criteria	2007 Target	2010 Target	2015 Target
Flux (scf/h/ft^2) @100 psi ΔP H_2 partial pressure & 50 psia permeate side pressure	100 scf/h/ft^2 ≡ 51 cm^3/cm^2·min ≡ 0.35 mol/m^2·s	200	300
Operating Temp, °C	400-700	300-600	250-500
S tolerance	Yes	Yes	Yes
Cost, \$/ft^2	150	100	<100
WGS Activity	Yes	Yes	Yes
ΔP Operating Capability, system pressure, psi	100	Up to 400	Up to 800 to 1000
CO tolerance	Yes	Yes	Yes
Hydrogen Purity	95%	99.5%	99.99%
Stability/Durability (years)	3	7	>10

- From Office of Fossil Energy *Hydrogen from Coal RD&D Plan*, June 10, 2004 -DRAFT

www.fossil.energy.gov

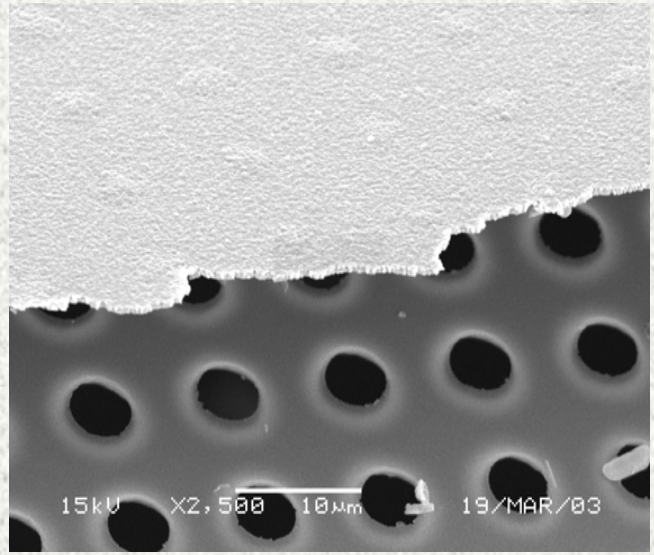
Commercialization Barriers for Pd Membranes

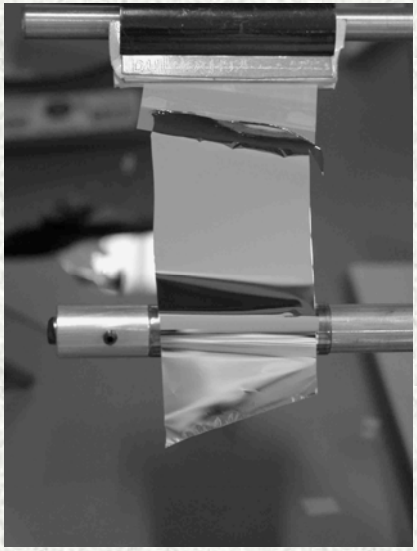
- Cost
  - price of Pd is ~$325/troy ounce (June, 2006)
  - thickness of Pd film must be < 14 μm for $150/ft^2 (based on the price of Pd alone)
- Durability
  - poor resistance to thermal cycling
  - hydrogen embrittlement: $\alpha \rightarrow \beta$ (α') phase transition
  - metallic interdiffusion between Pd and support
- Poisoning by process stream impurities
  - H_2S, carbon monoxide (CO), unsaturated hydrocarbons
- Leak-free sealing (module fabrication)

How do we solve these problems?

- Minimize cost
  - deposit thin films of Pd onto H_2-permeable supports
  - reduce Pd film thickness
- Poisoning
  - reversible vs. irreversible
  - should be able to regenerate in steam or air
- Hydrogen embrittlement
  - alloys reduce distortion upon hydriding/dehydriding
- Durability
  - metallic interdiffusion barrier

State of the Art





- Pd-Ag film supported by a micromachined membrane
  - H.D. Tong et al. *Thin Solid Films* **479** (2005) 89.
- Bundle of 0.8 m long (14 mm diameter) Pd-Ag coated tubes
  - P.P.A.C. Pex et al. *Proc. Int. Conf. Inorg. Membr.* (2004).
- Thin Pd-Ag foil prepared by PVD, supported on porous SS
  - H. Klette et al. *Membrane Technology* **5** (2005) 7.

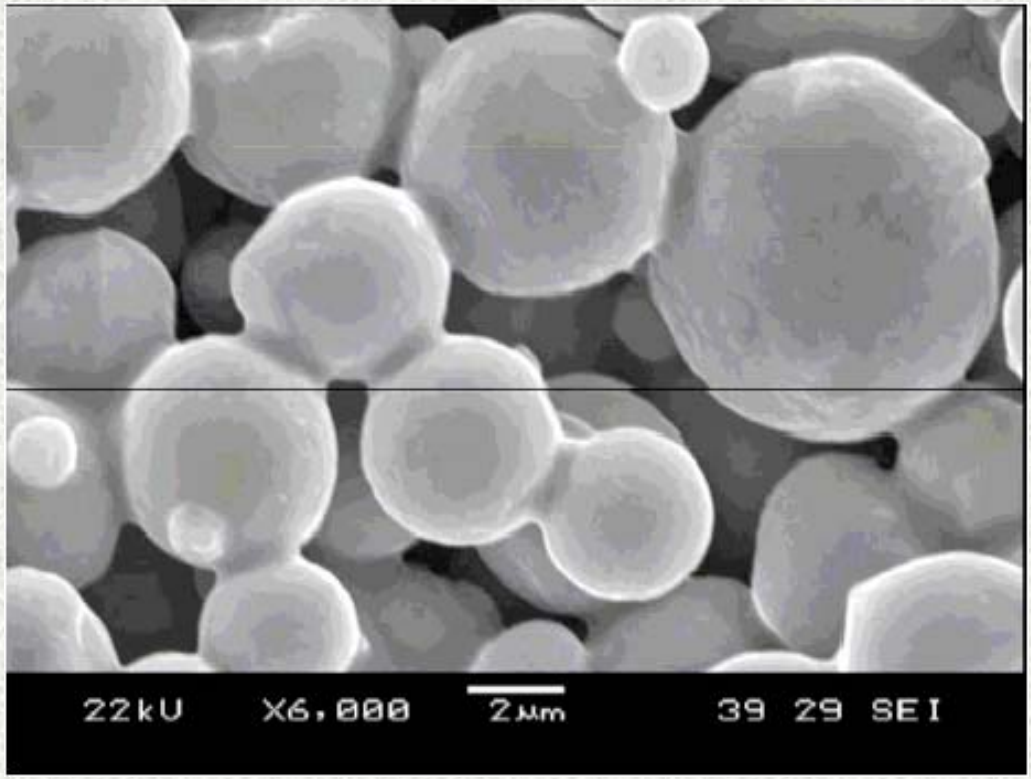
Porous Membrane Support

Powder preparation:
I.E. Anderson, R.L. Terpstra & B. Gleeson
Materials Science & Eng. A, **326**(1) 101 (2002).

- Slurry of uniform superalloy microparticles is applied to a porous substrate and sintered
  - ≤ 3 μm Fe-16Al-2Cr microparticles
- A thin oxide layer forms on all exposed surfaces
  - aluminum diffuses to the surface
- Forms a barrier to metallic interdiffusion
  - Al_2O_3 interlayer between a thin Pd alloy film and the particles in the porous support

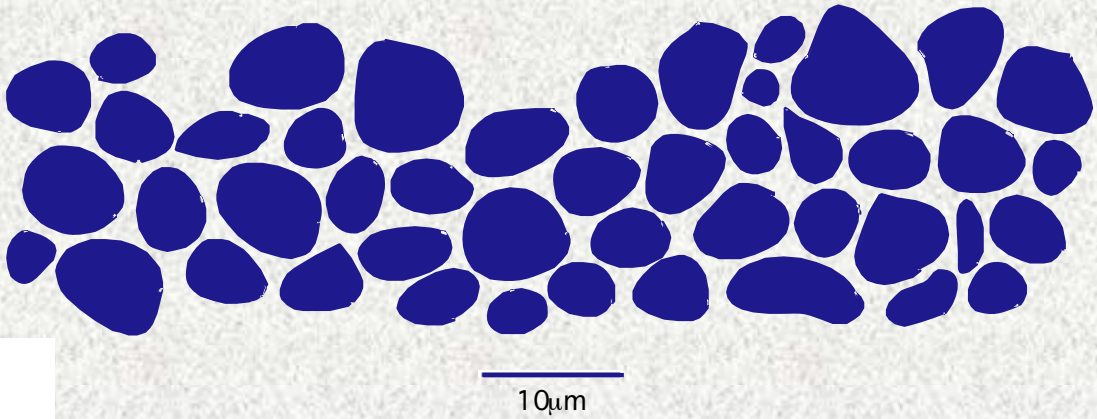
SEM Micrograph of Sintered Powder

- Fe-16Al-2Cr (wt.%) powder
- 3-5 μm particles
- Sintered at 1050°C for 4 h
  - I.E. Anderson et al.



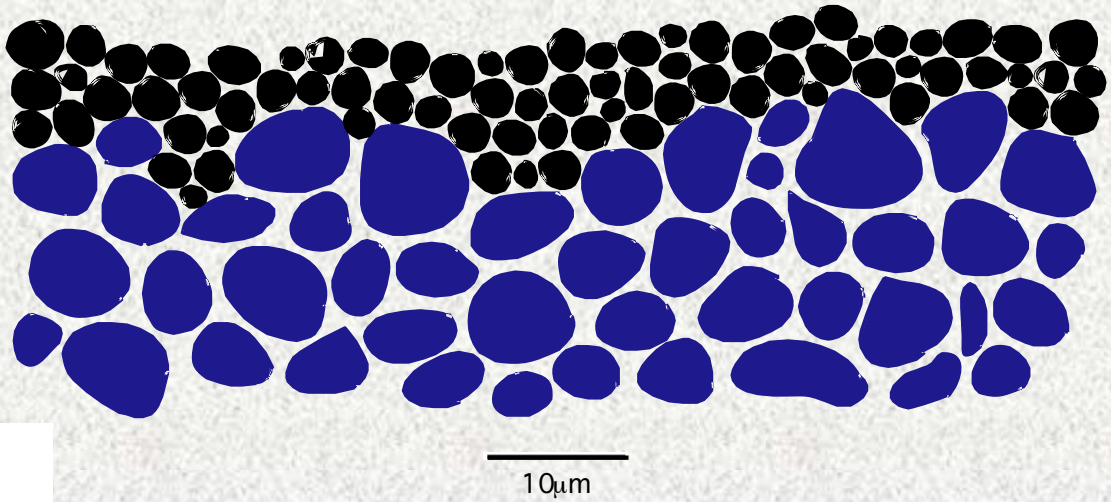
Membrane Fabrication

- Commercially available porous metal support
  - for example, porous stainless steel with a 0.1 μm particle cut-off



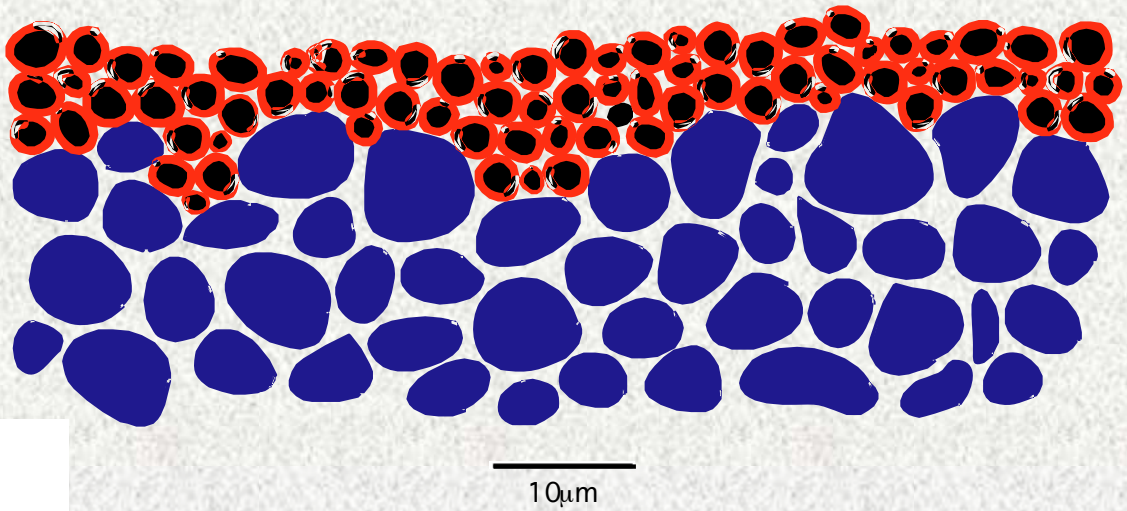
Membrane Fabrication

- Commercially available porous metal support
  - for example, porous stainless steel with a 0.1 μm particle cut-off
- Fe-16Al-2Cr microsphere slurry applied, dried, sintered



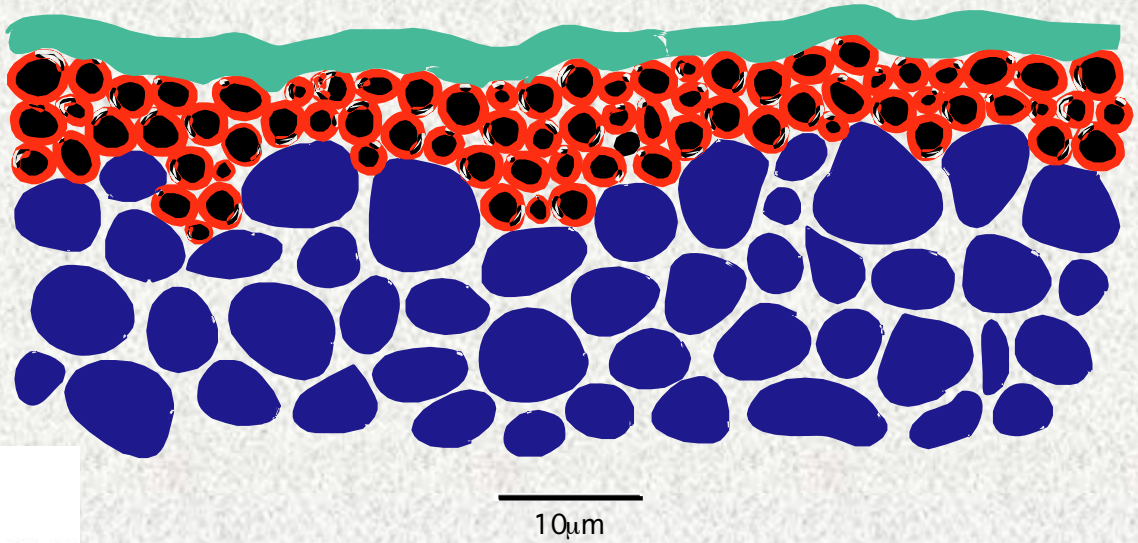
Membrane Fabrication

- Commercially available porous metal support
  - for example, porous stainless steel with a 0.1 μm particle cut-off
- Superalloy microsphere slurry applied, dried, sintered
- Treat to form thin alumina layer

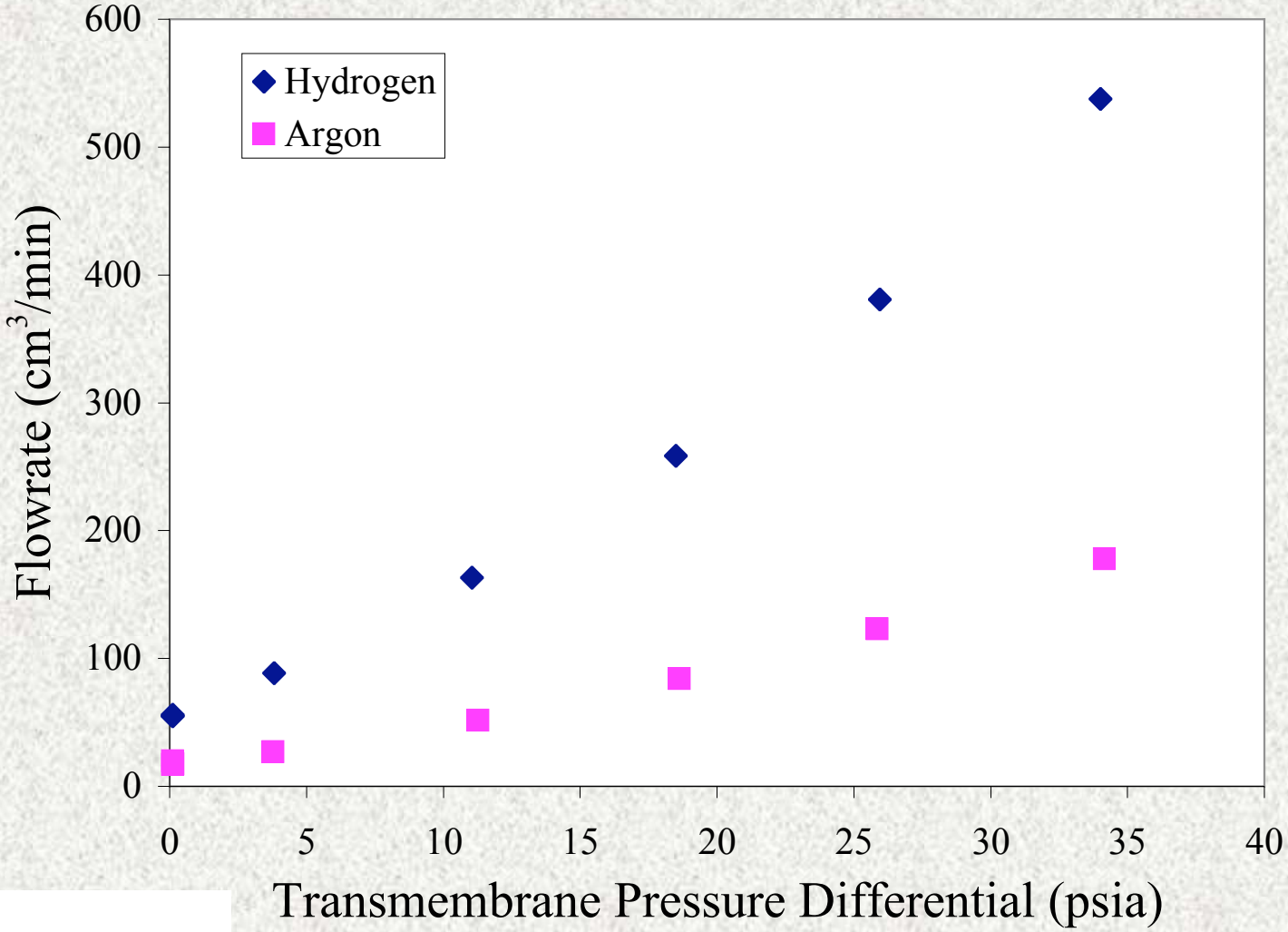


Membrane Fabrication

- Commercially available porous metal support
  - for example, porous stainless steel with a 0.1 μm particle cut-off
- Superalloy microsphere slurry applied, dried, sintered
- Treat to form thin alumina layer
- Deposit thin hydrogen selective layer
  - PVD, CVD, electroless plating



H_2 and Ar Flowrates through Fe-16Al-2Cr (3-μm Particle) Membrane at 350ºC and ΔP = 0-35 psia



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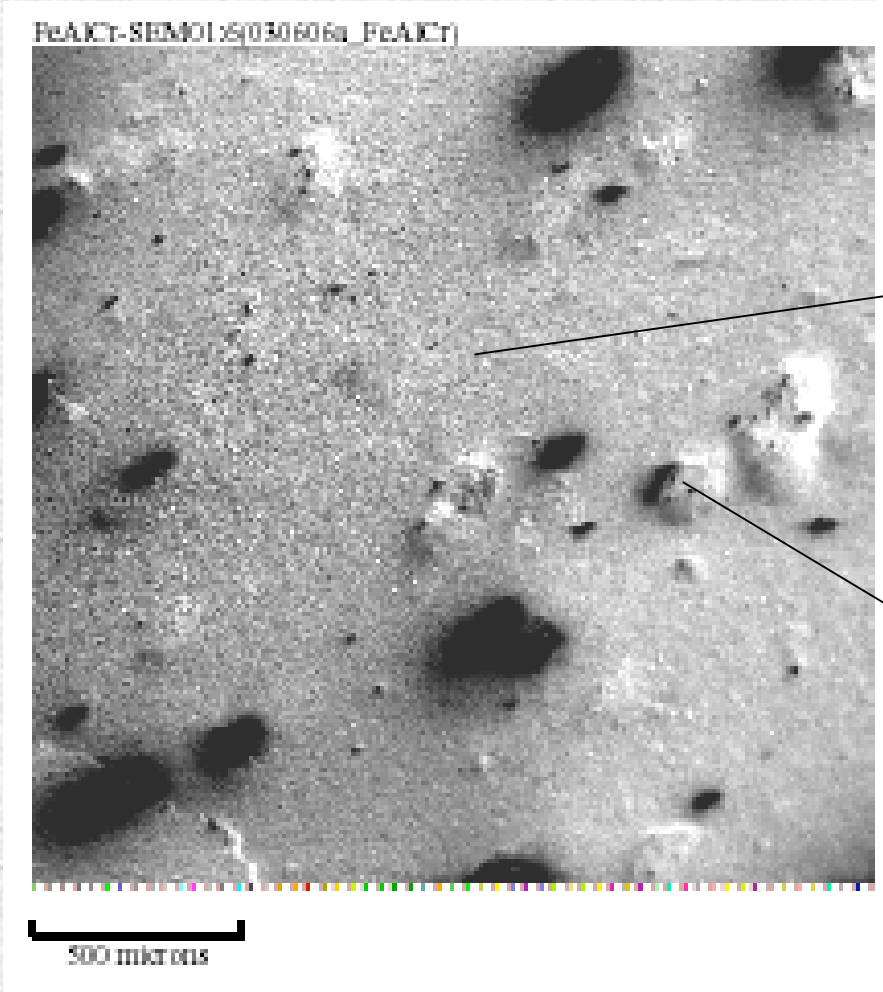
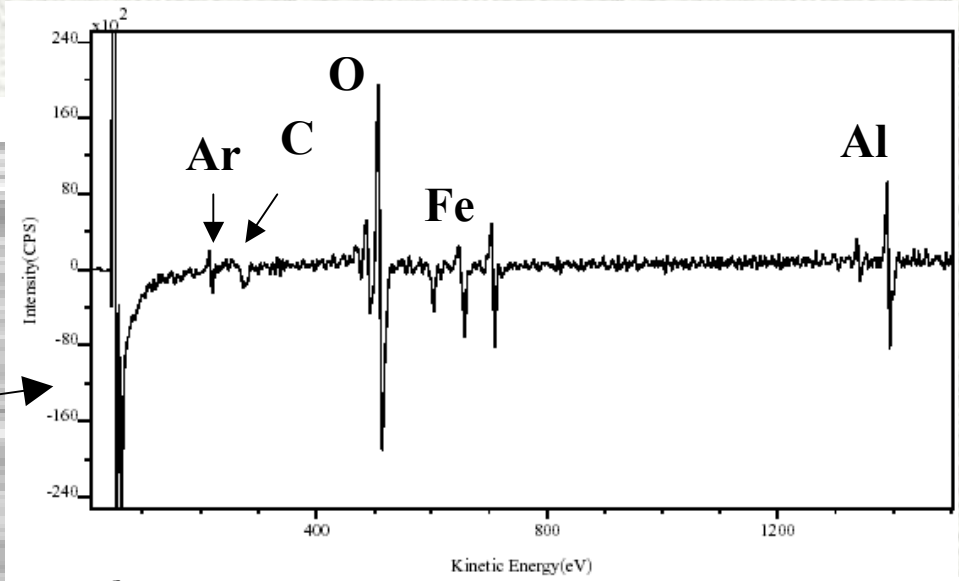
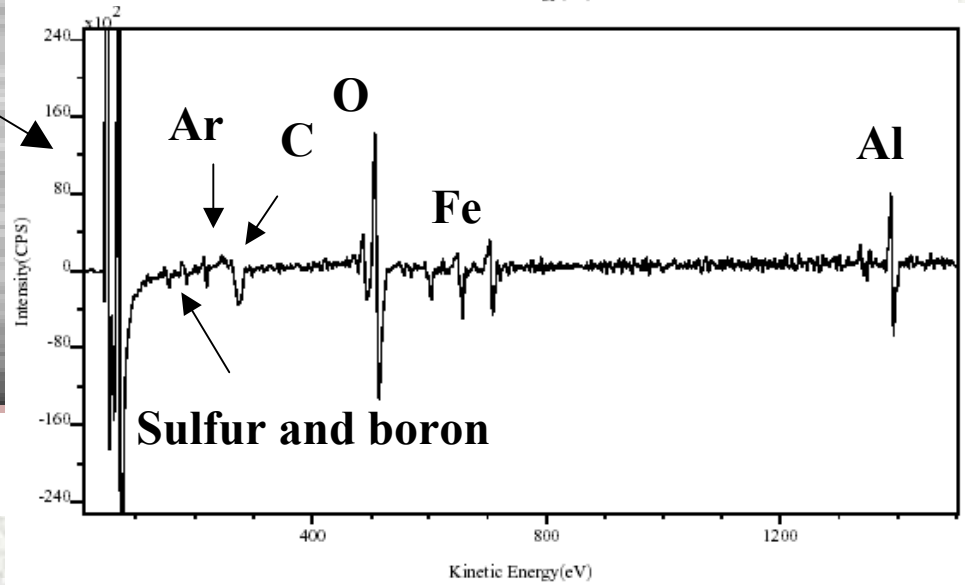
Membrane Analysis Tools

- Scanning electron microscopy (SEM)
- Auger electron spectroscopy (AES)
  - surface chemical composition (1st few monolayers)
- X-ray photoelectron spectroscopy (XPS)
  - surface chemical composition plus some info on chemical state
- Rutherford backscattering spectrometry (RBS)
  - *non-destructive*, helium ion backscattering
- Atomic force microscopy (AFM)
  - used to image surface structure, provides information on roughness
- Profilometry (optical or laser)
  - similar to AFM but for samples with larger surface structure

Auger Analysis

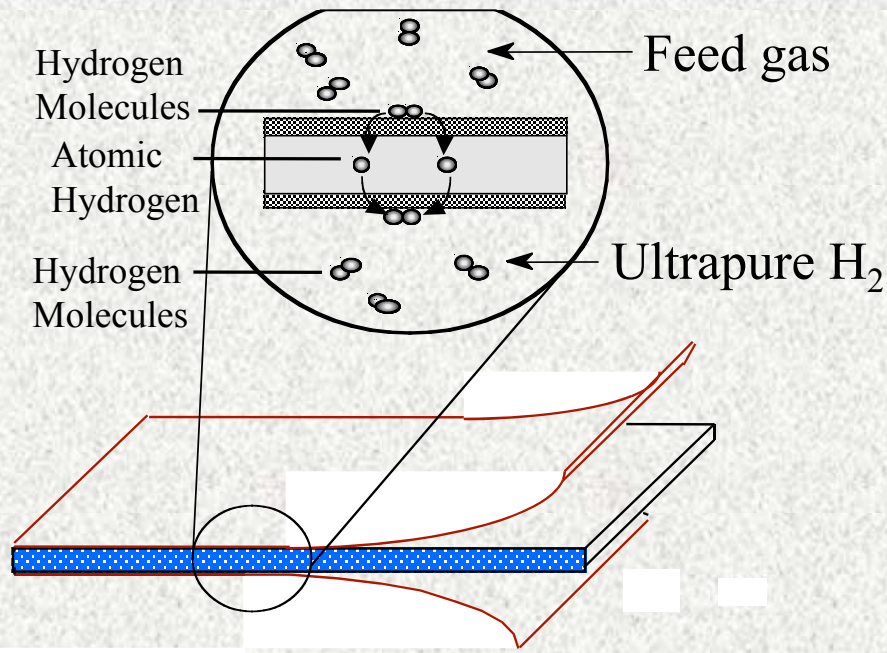






A Composite Membrane Configuration

- many bcc metals have high H_2 permeabilities
  - surfaces readily poisoned (V, Nb, Ta, Ti)
  - must coat with Pd on both sides of metal foil or tube
- ion-milling followed by *in-situ* sputter deposition of Pd or Pd-alloy
- *alloys* of vanadium reduce hydrogen embrittlement

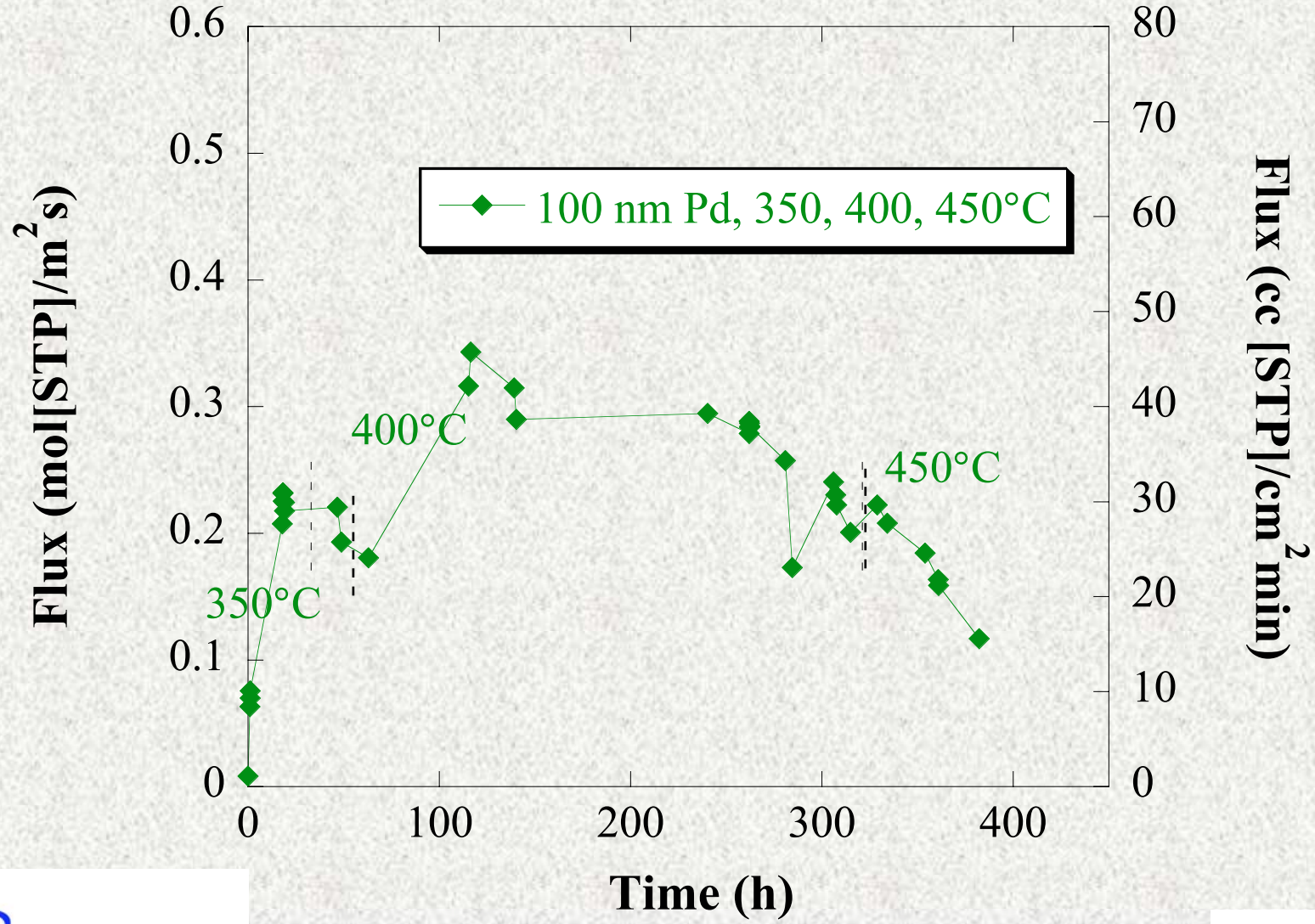


Membrane Testing

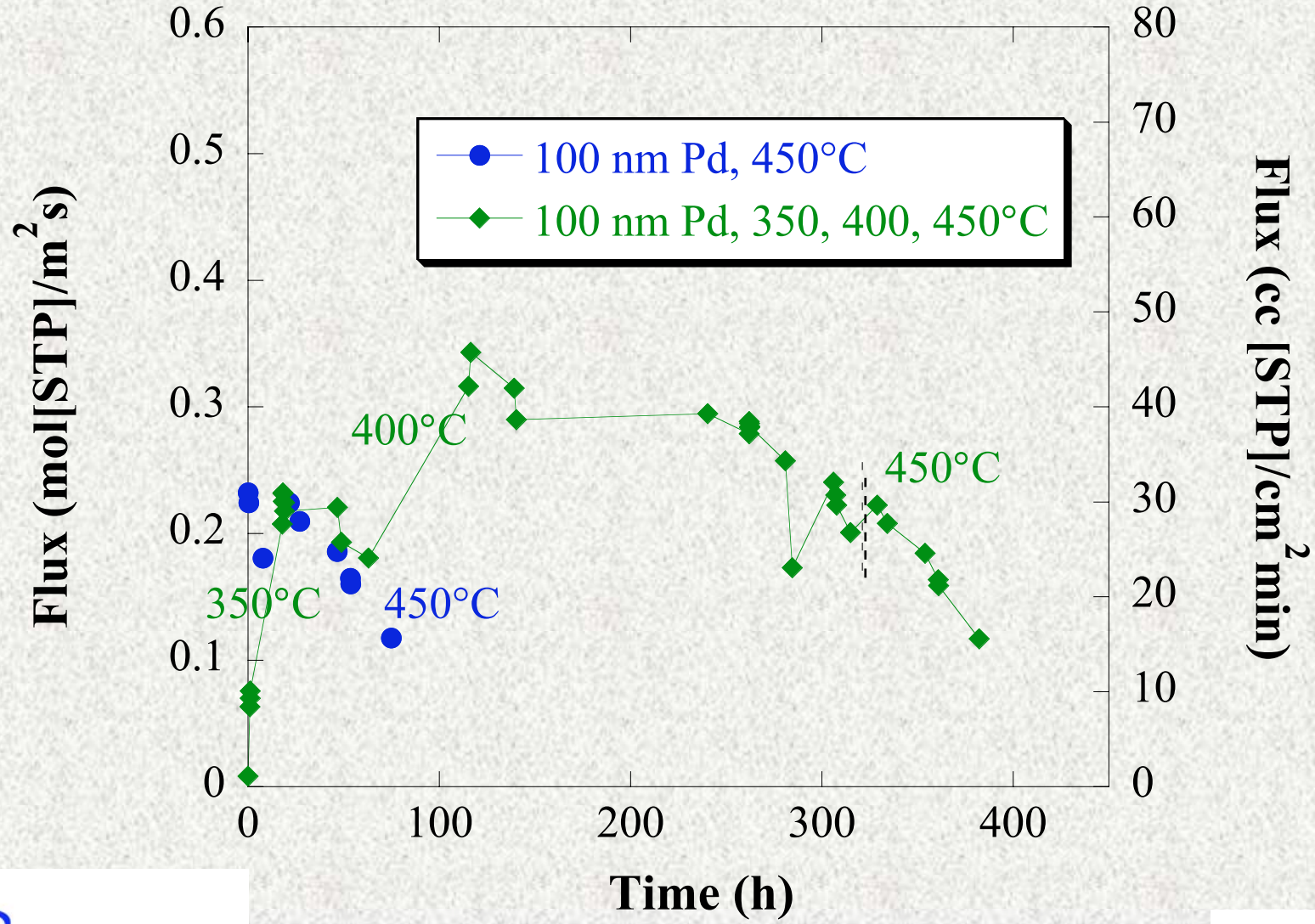
- Coated foil cut into 1.9 cm diameter discs
- disc sealed into testing module between two VCR gaskets
  - upstream side purged with argon during heating
  - downstream side evacuated continuously

0.37-mm thick V-6Ni-5Co (at%) membrane (coated with 100 nm Pd per side) after testing at 450°C for 170 h.

H_2 flux through 75-μm thick $Pd/V_{0.90}Cu_{0.10}/Pd$ membranes (100 nm Pd per side) at 350-450ºC and ΔP=1 atm



H_2 flux through 75-μm thick $Pd/V_{0.90}Cu_{0.10}/Pd$ membranes (100 nm Pd per side) at 350-450ºC and ΔP=1 atm



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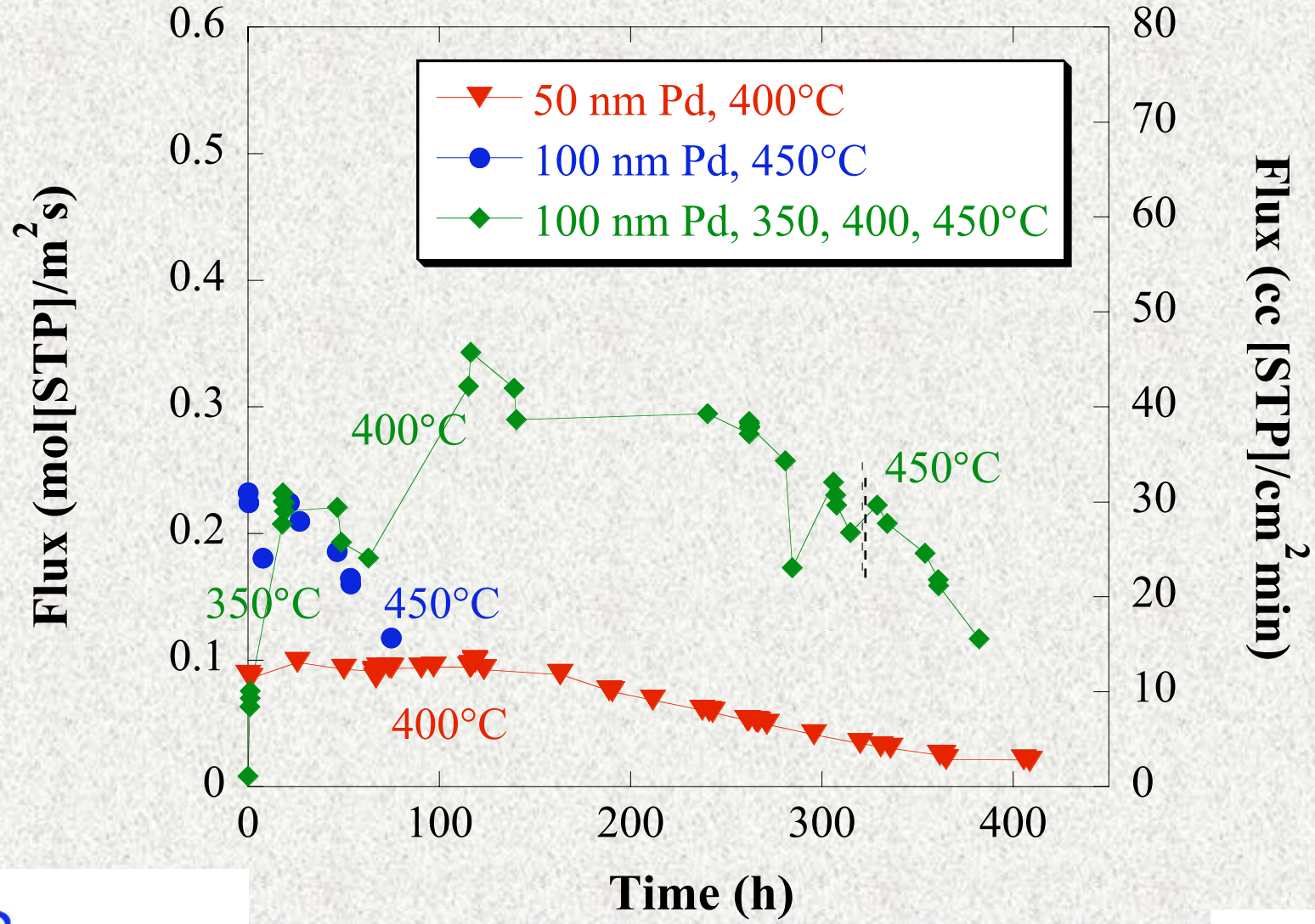
H_2 flux through 75-μm thick $Pd/V_{0.90}Cu_{0.10}/Pd$ membranes (50 or 100 nm Pd per side) at 350-450ºC and ΔP=1 atm



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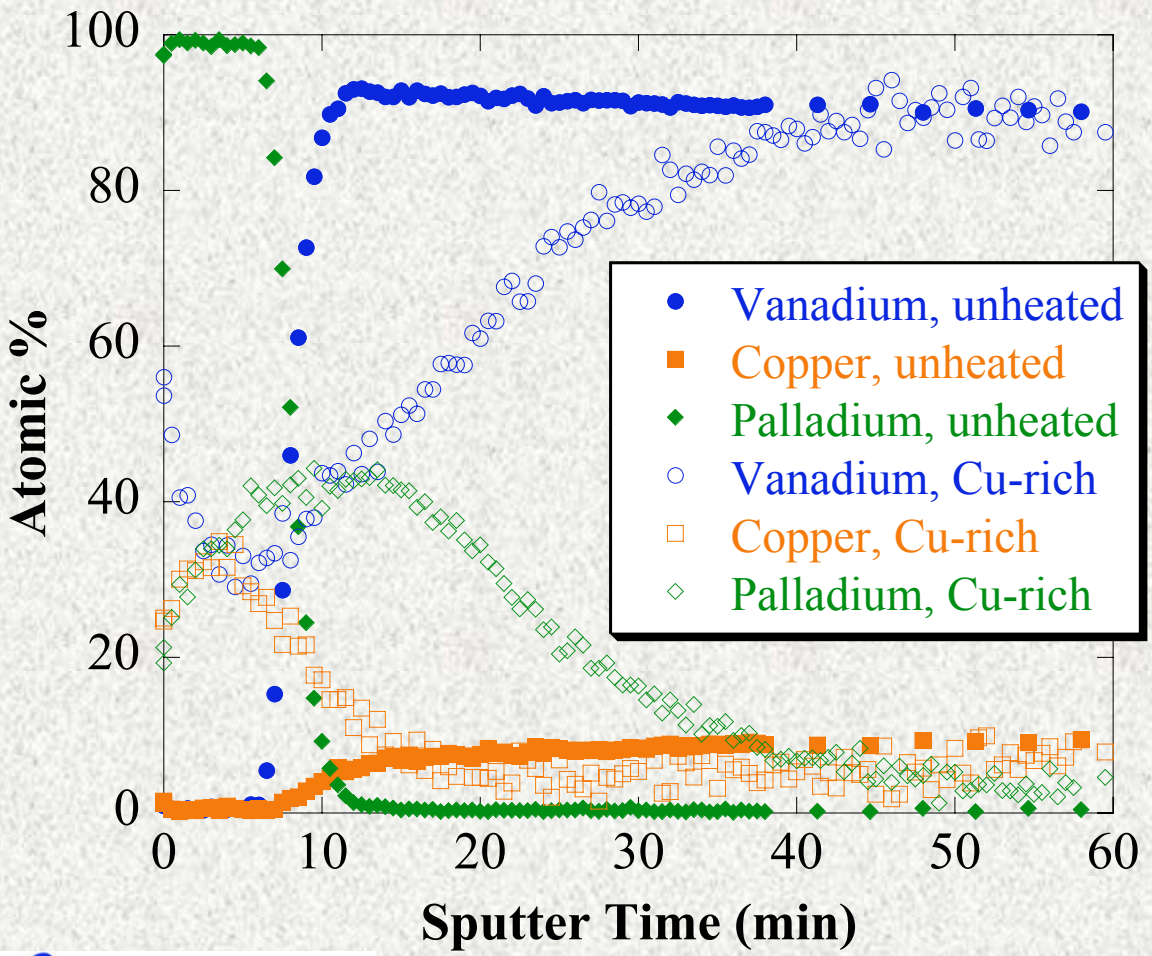
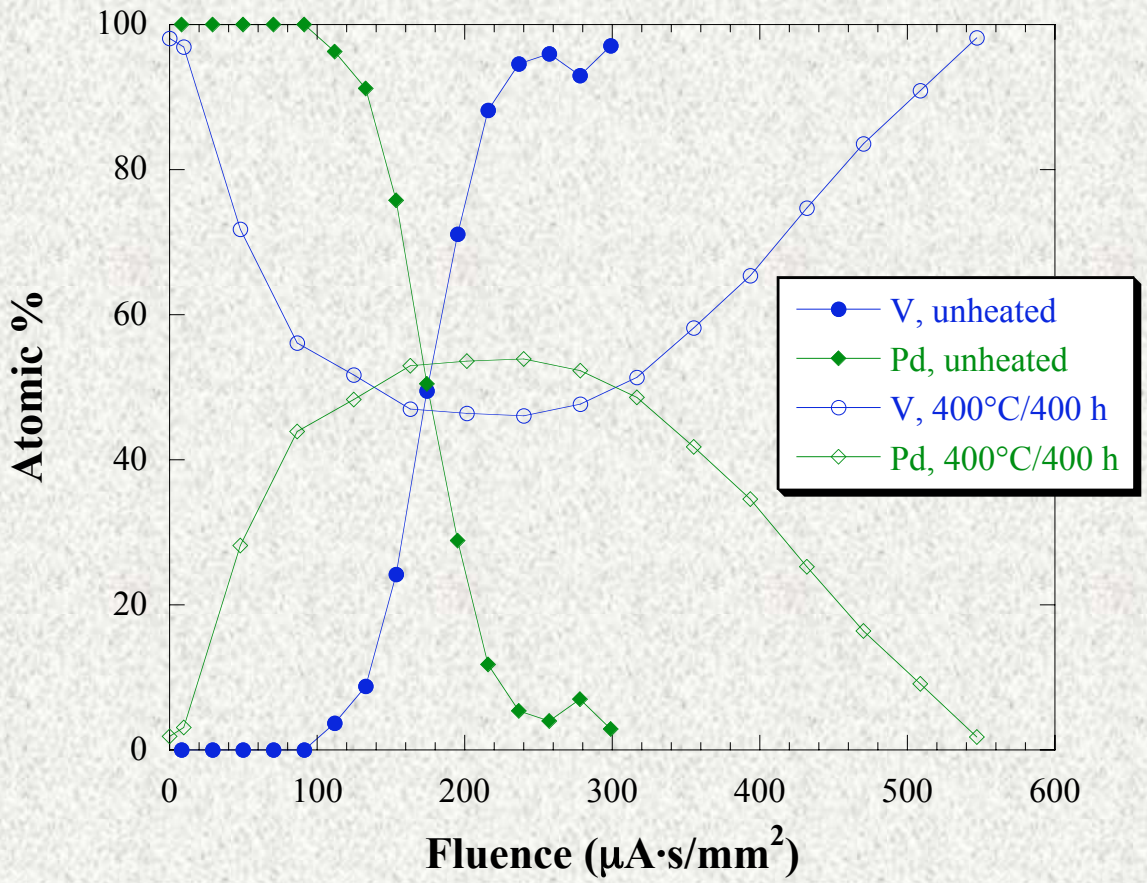
AES Depth Profiles of $V_{0.90}Cu_{0.10}$ Membrane



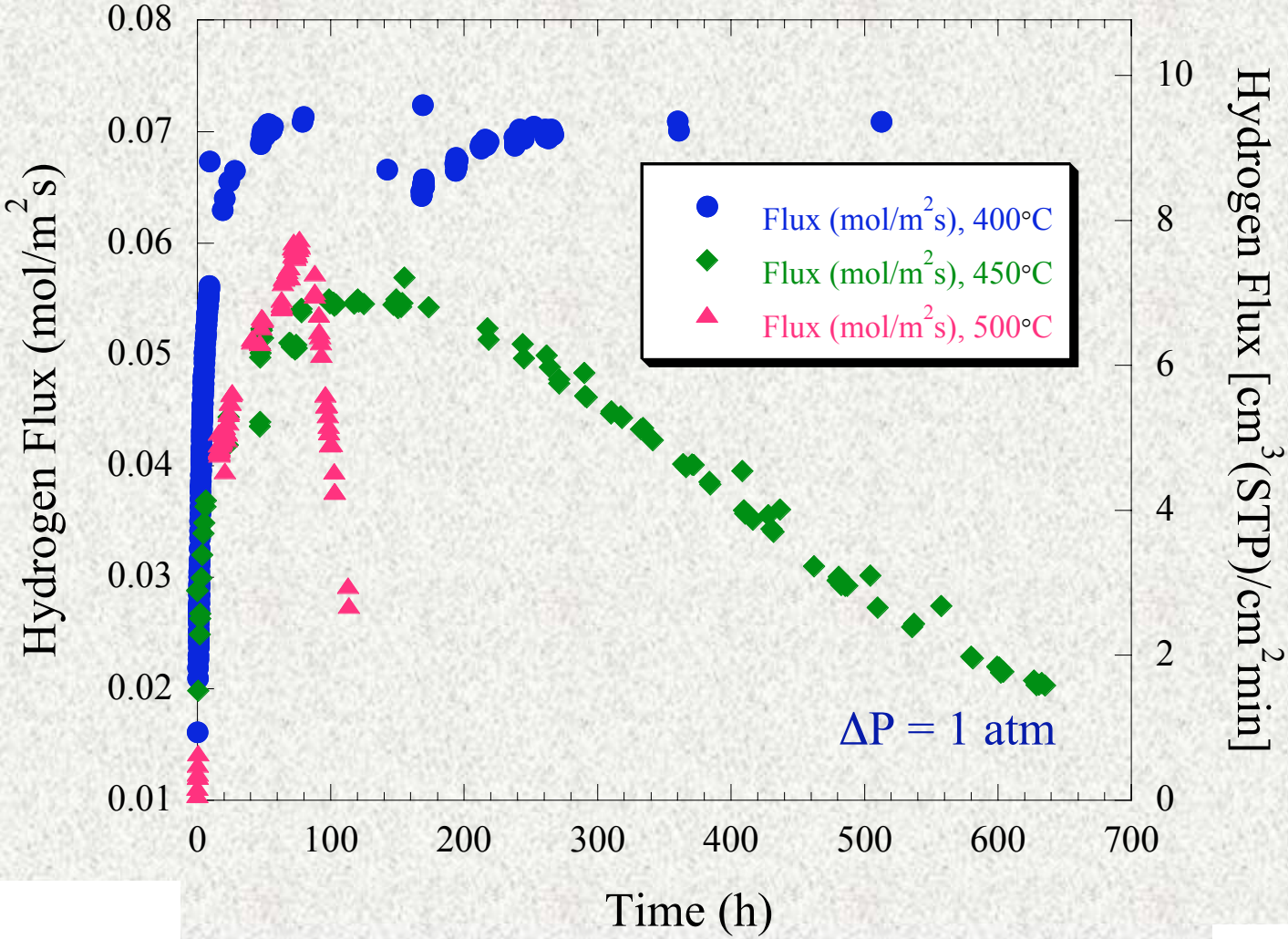
- V–Cu foil ion-milled and coated with 100 nm of Pd
- Comparison of tested and untested membranes
- Tested at 450ºC for 75 hours under hydrogen

AES Depth Profiles of Pd/V Membrane



- 40 μm thick V foil ion-milled and coated with 50 nm of Pd
- Comparison of tested and untested membranes
- Tested at 400ºC for 400 hours under hydrogen

H_2 flux at 400, 450, or 500ºC through 0.37-mm thick V–6Ni-5Co (at.%) membranes (100 nm Pd per side)



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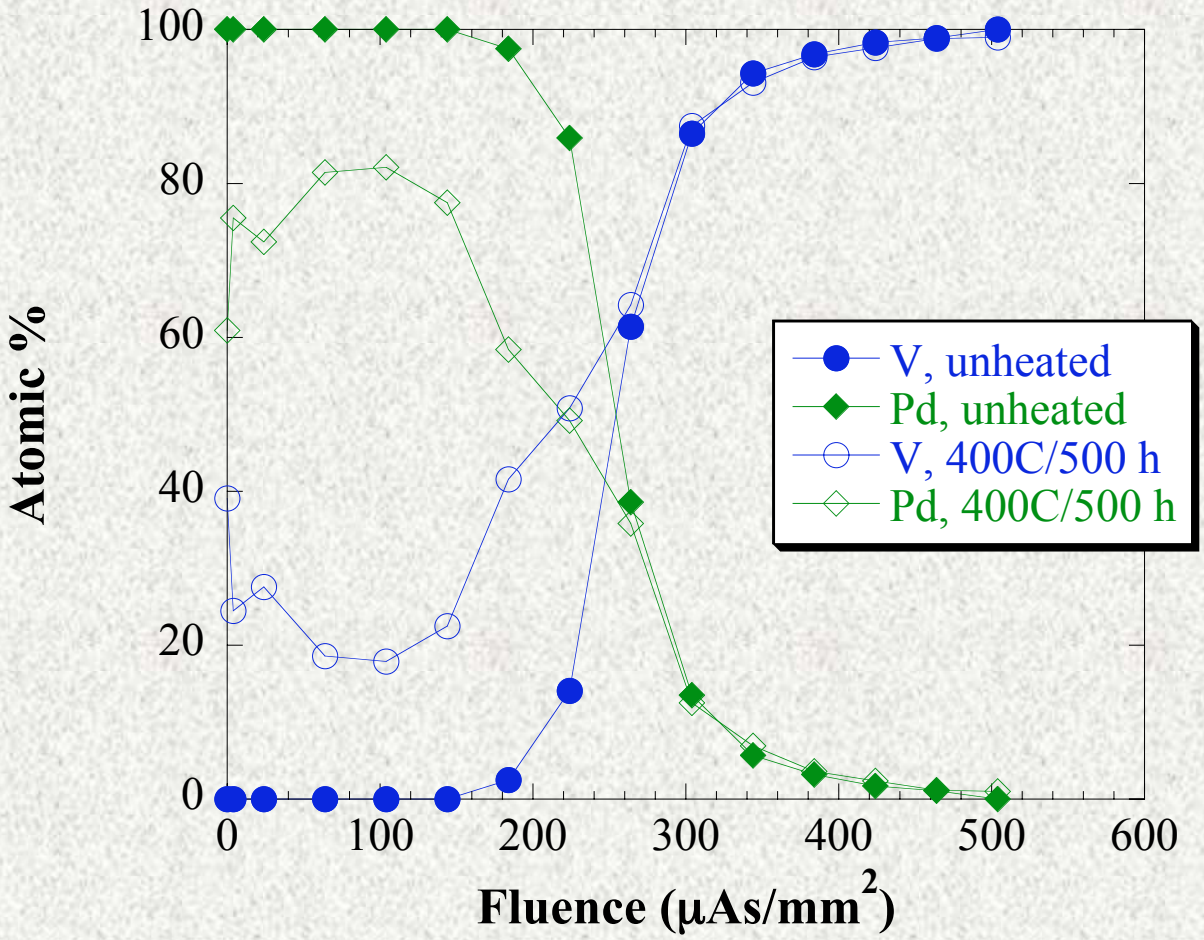
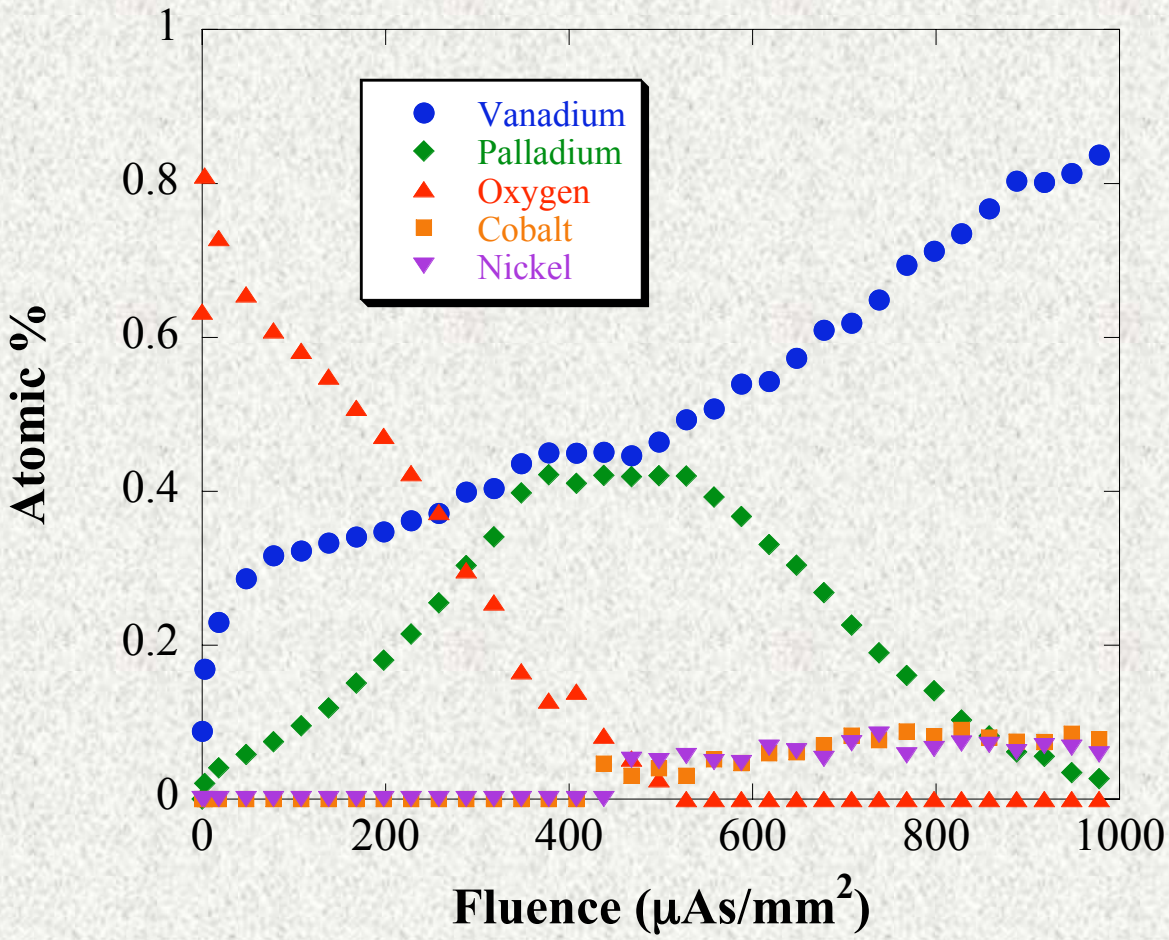
AES Depth Profiles of Pd/V-6Ni-5Co Membranes



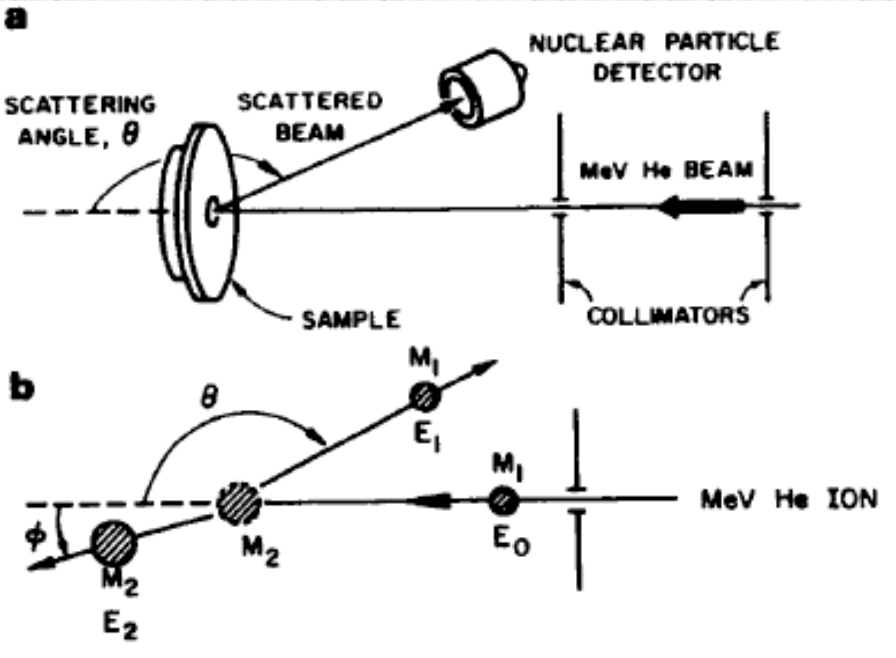
- 0.37-mm thick V-6Ni-5Co foil ion-milled and coated with 100 nm of Pd
- Comparison of tested and untested membranes
- Tested at 400ºC for 500 hours under hydrogen
- Hydrogen flux through membrane was constant

AES Depth Profiles of Pd/V-6Ni-5Co Membrane



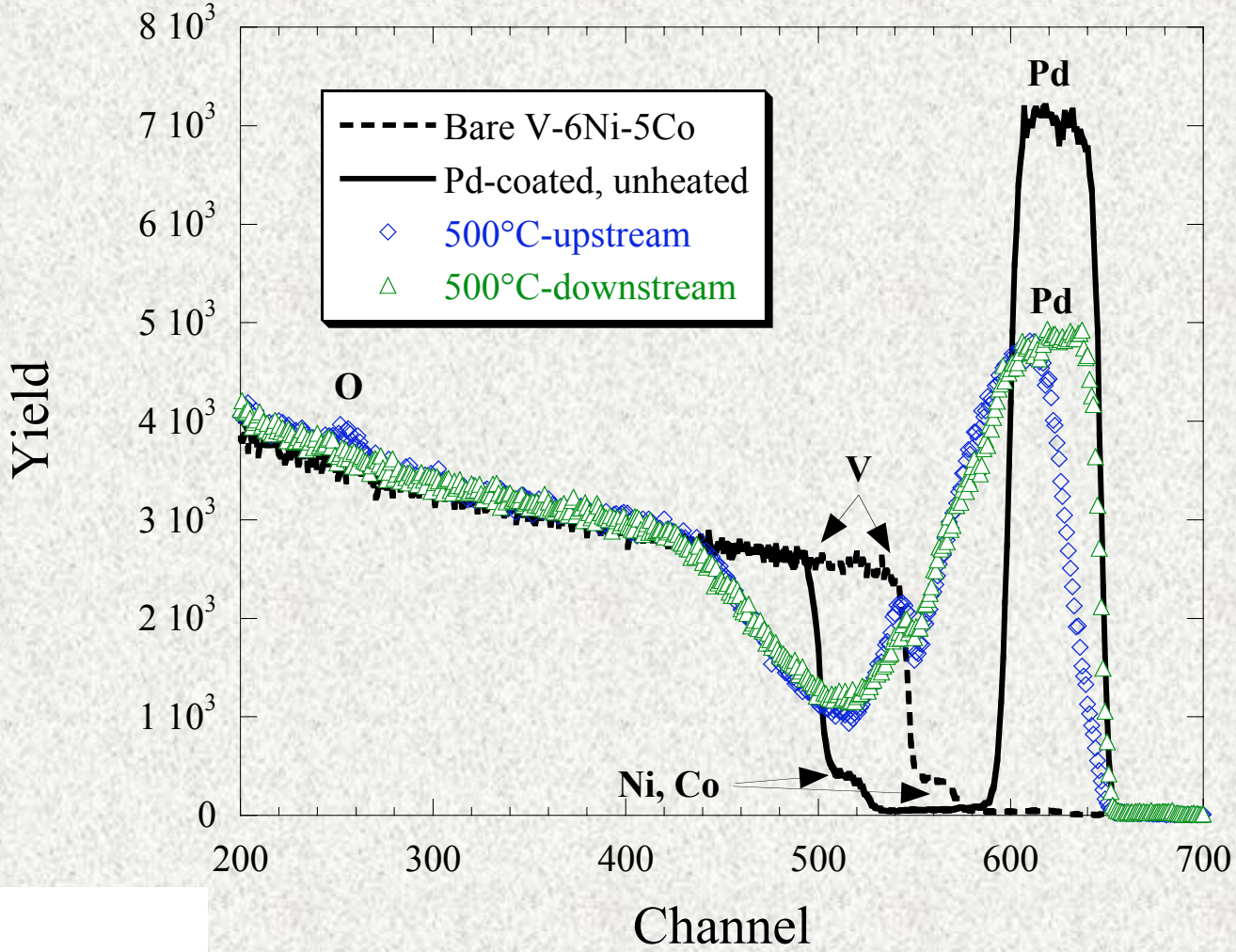
- 0.37-mm thick V-6Ni-5Co foil ion-milled and coated with 100 nm of Pd
- Tested at 500ºC for 114 hours under hydrogen
- Hydrogen flux through membrane decreased by 55%
- Substantial oxygen content

Rutherford Backscattering Spectrometry (RBS)



- backscattering of He^{++}
- non-destructive
- useful for measuring thickness of thin films, metallic interdiffusion
- semi-quantitative elemental composition
- Feldman and Mayer, Fundamentals of Surface and Thin Film Analysis (1986).

RBS spectra of V-6Ni-5Co membranes



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Comparison to DoE Targets

Performance Criteria	2007 Target	This work
Flux (scf/h/ft^2) @100 psi ΔP H_2 partial pressure & 50 psia permeate side pressure	100 scf/h/ft^2 ≡ 51 cm^3/cm^2·min ≡ 0.35 mol/m^2·s	100 cm^3/cm^2·min or 0.75 mol/m^2·s at ΔP = 58 psia
Operating Temp, °C	400-700	200-400
S tolerance	Yes	Pd–Cu coating
Cost, \$/ft^2	150	~\$1/ft^2 Pd
WGS Activity	Yes	?
ΔP Operating Capability, system pressure, psi	100	~60 psia
CO tolerance	Yes	?
Hydrogen Purity	95%	>99%
Stability/Durability (years)	3	500 h @ 400°C

Conclusions

- A porous membrane support was prepared from Fe-16Al-2Cr particles and the gas flux was measured
- H_2 flux through Pd/V-10Cu/Pd declined gradually at 400ºC
  - AES depth profiles showed substantial interdiffusion between Pd and V, as well as Cu segregation
- H_2 flux through V-6Ni-5Co membranes was stable at higher temperatures
  - hydrogen flux constant at 400°C for 500 h and 1 week at 450°C
  - AES depth profiles and RBS showed decreased metallic interdiffusion compared to other alloy systems
  - substantial oxidation observed
  - embrittlement still needs to be reduced

Future Work

- deposit a defect-free palladium film onto the porous iron aluminide membrane
- investigate other V-6Ni-5Co based alloys with palladium alloy surface coatings
  - test hydrogen flux stability and impurity resistance of membrane materials/coatings
  - durability tests: thermal cycling in hydrogen
- membrane reactor for hydrogen generation

Acknowledgements

- Ronny Snow – PVD coating
- Dr. Hain Oona – data collection and logging
- Dr. Duncan Hammon – alloy development and foil rolling
- Dr. Joseph Wermer & Blake Nolen – assistance with data collection
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- Vince Hesch & Felix Garcia – laser cutting
- John Moya, Stan Bennett, Stephen Cole, Jerry Schobert, & Richard Basinger – experimental setup
- Fino Armijo & Eluterio Garcia – machining
- Dr. Marilyn Hawley – AFM
- Dr. Robert Day – profilometry
- Dr. Craig Tewell – AES

Acknowledgements

- Pd/iron-aluminide composite membrane development and testing/analysis of V-10Cu membranes were funded by US DOE Office of Fossil Energy, Advanced Research-Materials Program
- V-6Ni-5Co: collaboration with Dr. Robert E. Buxbaum of REB Research and Consulting, National Energy Technology Laboratory, and Ames Laboratory: contract DE-FC26-05NT42400

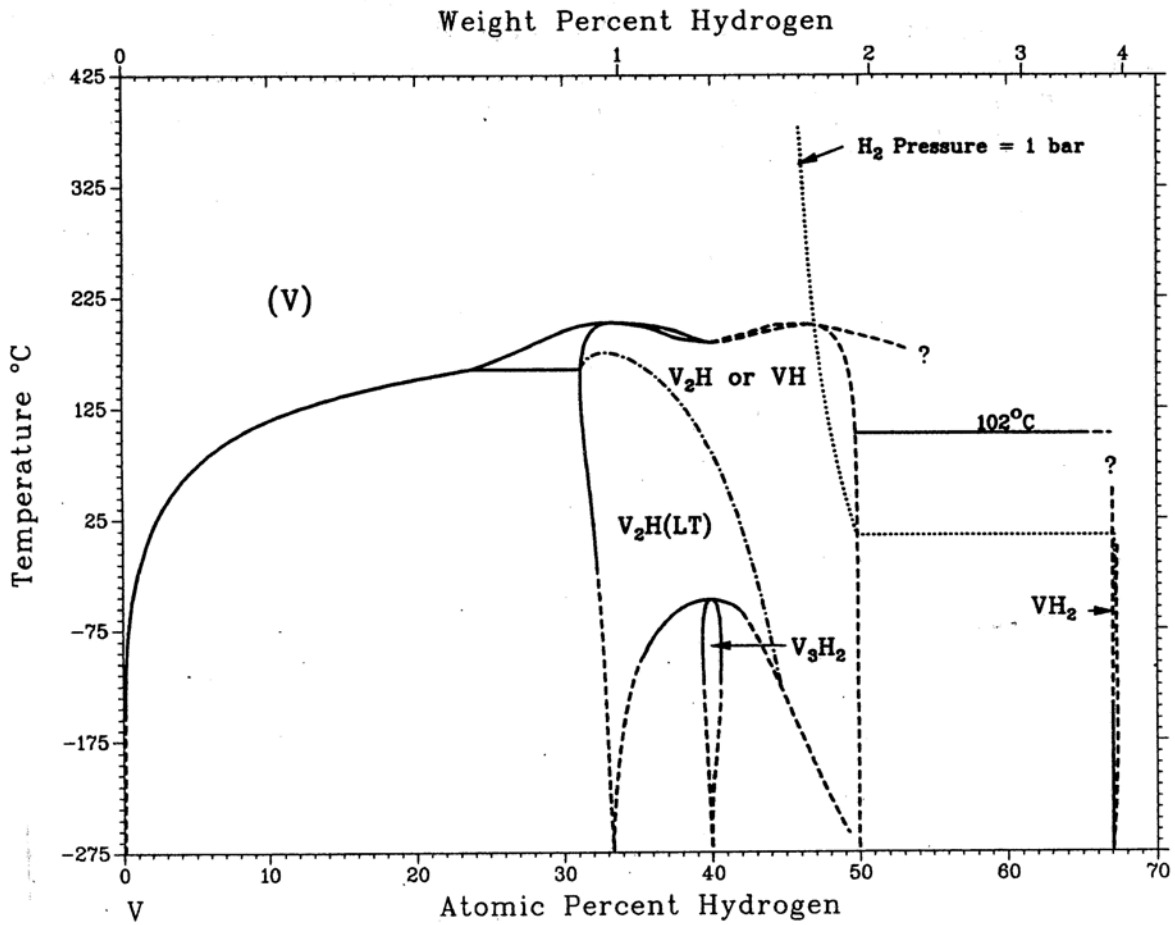
Back-up Slides

Pd/V-alloy/Pd Membrane

- *e*-beam welded into the shape of a tube
  - 75-μm thick foil
  - brazed to standard SS VCR fittings
- Palladium coating is very thin
  - 1000 Å on both sides

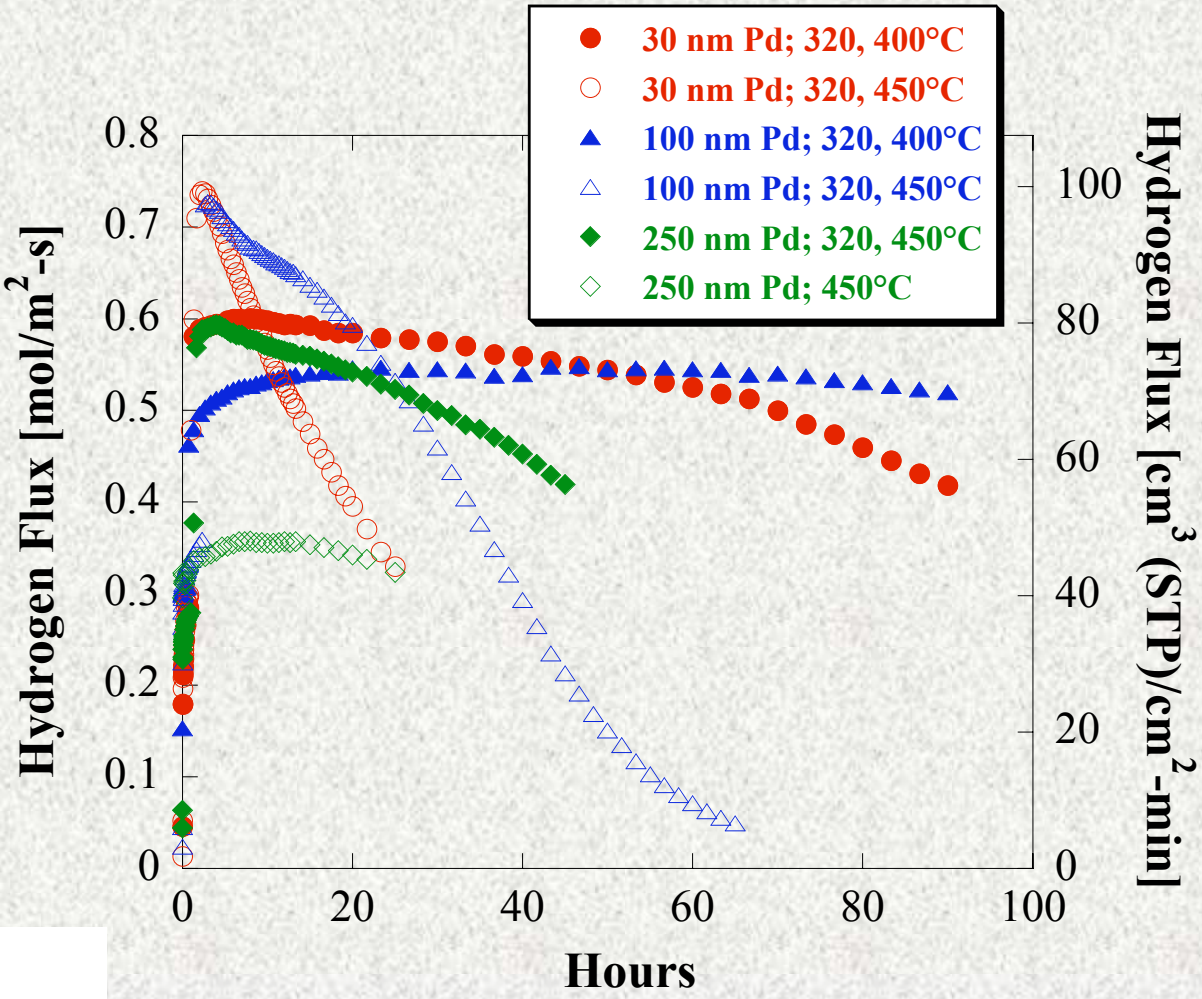
V-H Phase Diagram

From: Phase Diagrams of Binary Vanadium Alloys, J.F. Smith, Editor (1989)



J.F. Smith and D.T. Peterson, 1989.

Influence of Pd coating thickness on H_2 flux stability of 40-µm thick $V_{0.95}Ti_{0.05}$



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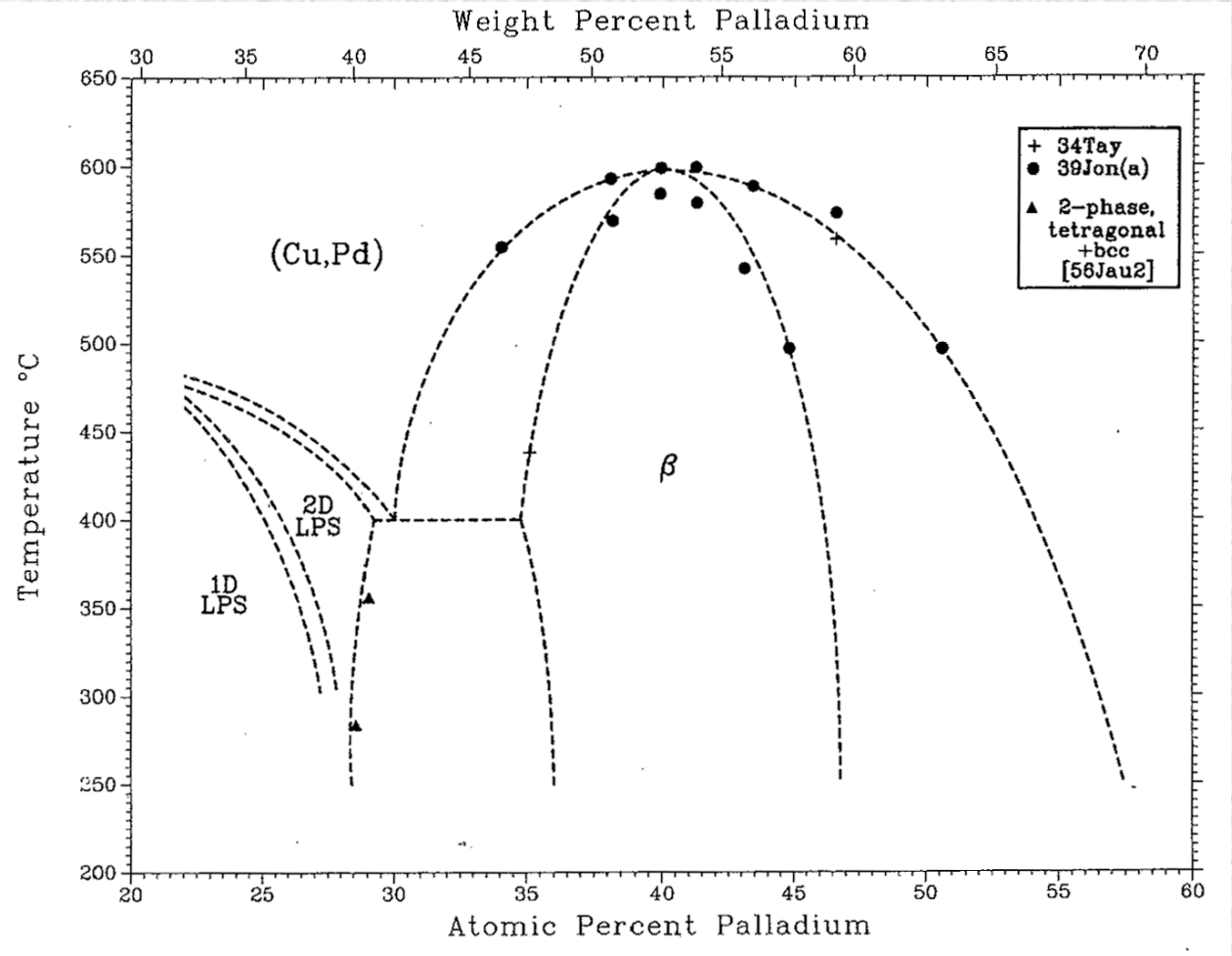
Advantages of Palladium Alloys

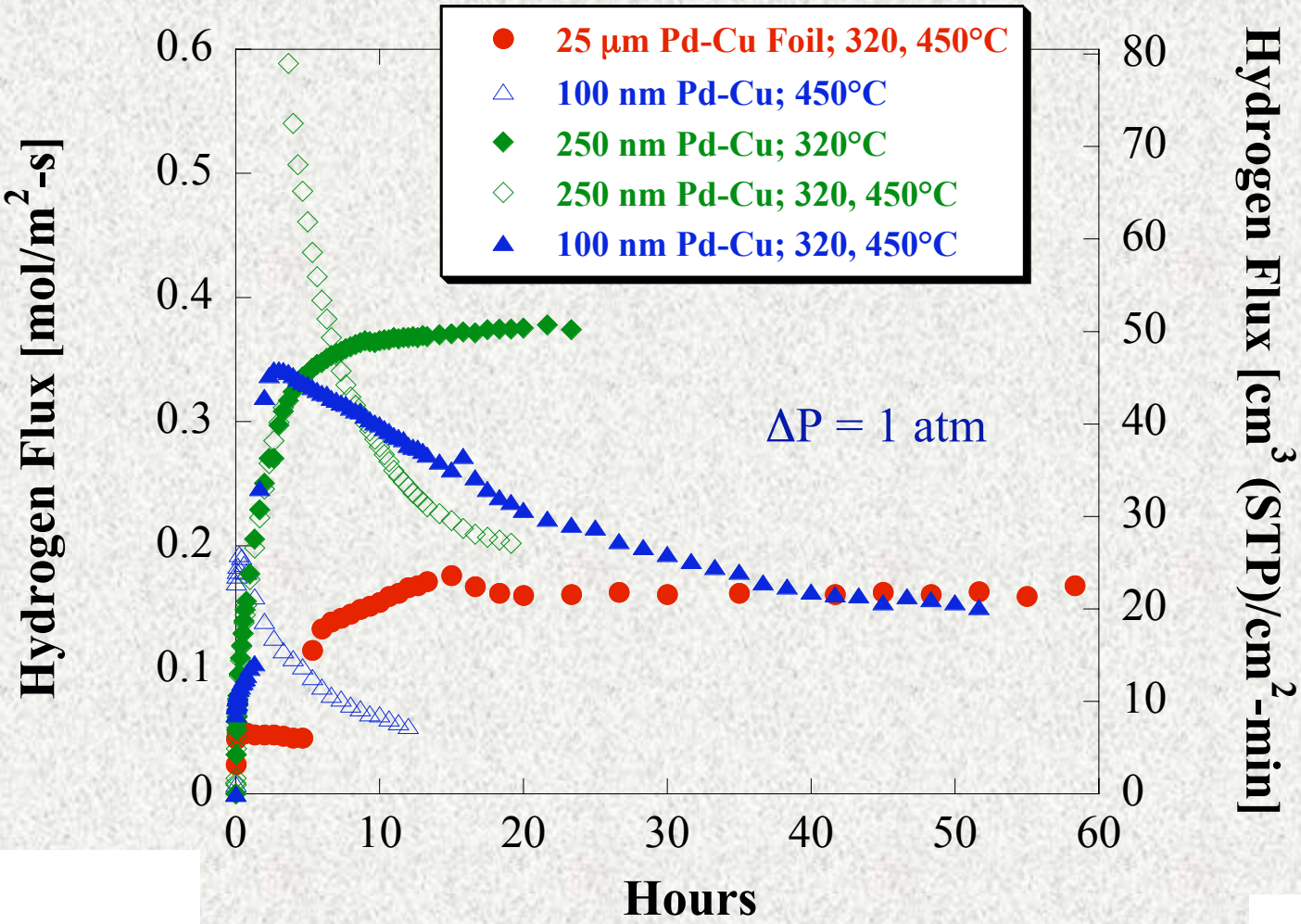
- Increased hydrogen permeability and durability
- $Pd_{0.77}Ag_{0.23}$
  - tubes (>25 μm thick) commonly used to purify hydrogen for semiconductor industry and hydrogen isotope recovery
  - grain coarsening during operation at higher temperatures (>500°C)
- $Pd_{0.47}Cu_{0.53}$
  - less subject to hydrogen embrittlement
  - sulfur resistance
  - D.L. McKinley, U.S. Patent 3,439,474 (1969)
  - D.J. Edlund. A Membrane Reactor for H_2S Decomposition. Advanced Coal-Fired Power Systems '96 Review Meeting, Jul 16-18; Morgantown, West Virginia, USA (1996).

Pd-Cu Phase Diagram

From: Phase Diagrams of Binary Copper Alloys, P.R. Subramanian et al. (1994)

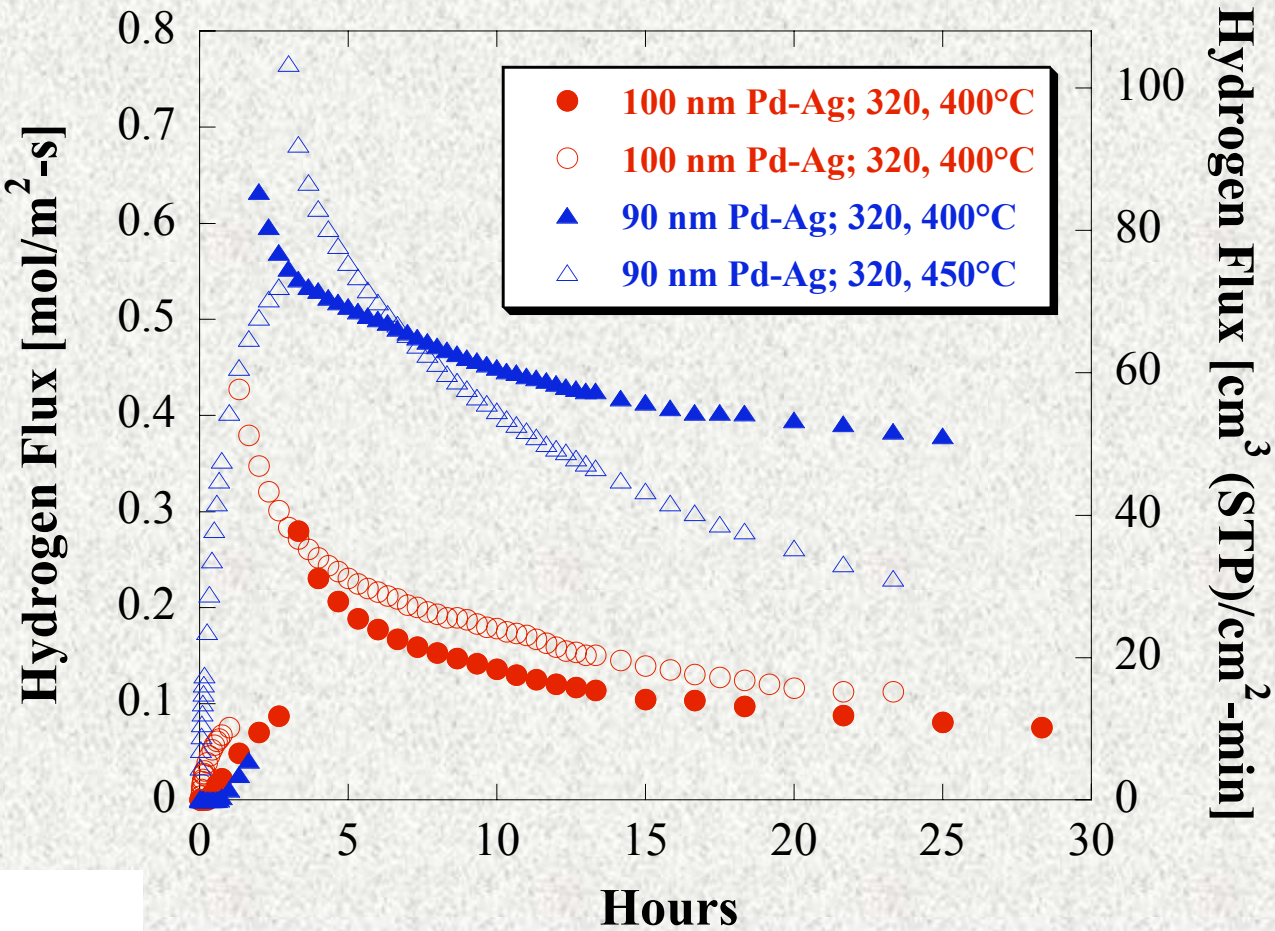


Influence of $Pd_{0.47}Cu_{0.53}$ thickness on H_2 flux stability of 40-µm thick $V_{0.95}Ti_{0.05}$



Influence of $Pd_{0.5}Ag_{0.5}$ thickness on H_2 flux stability of 40-μm thick $V_{0.95}Ti_{0.05}$

$\Delta P = 1$ atm



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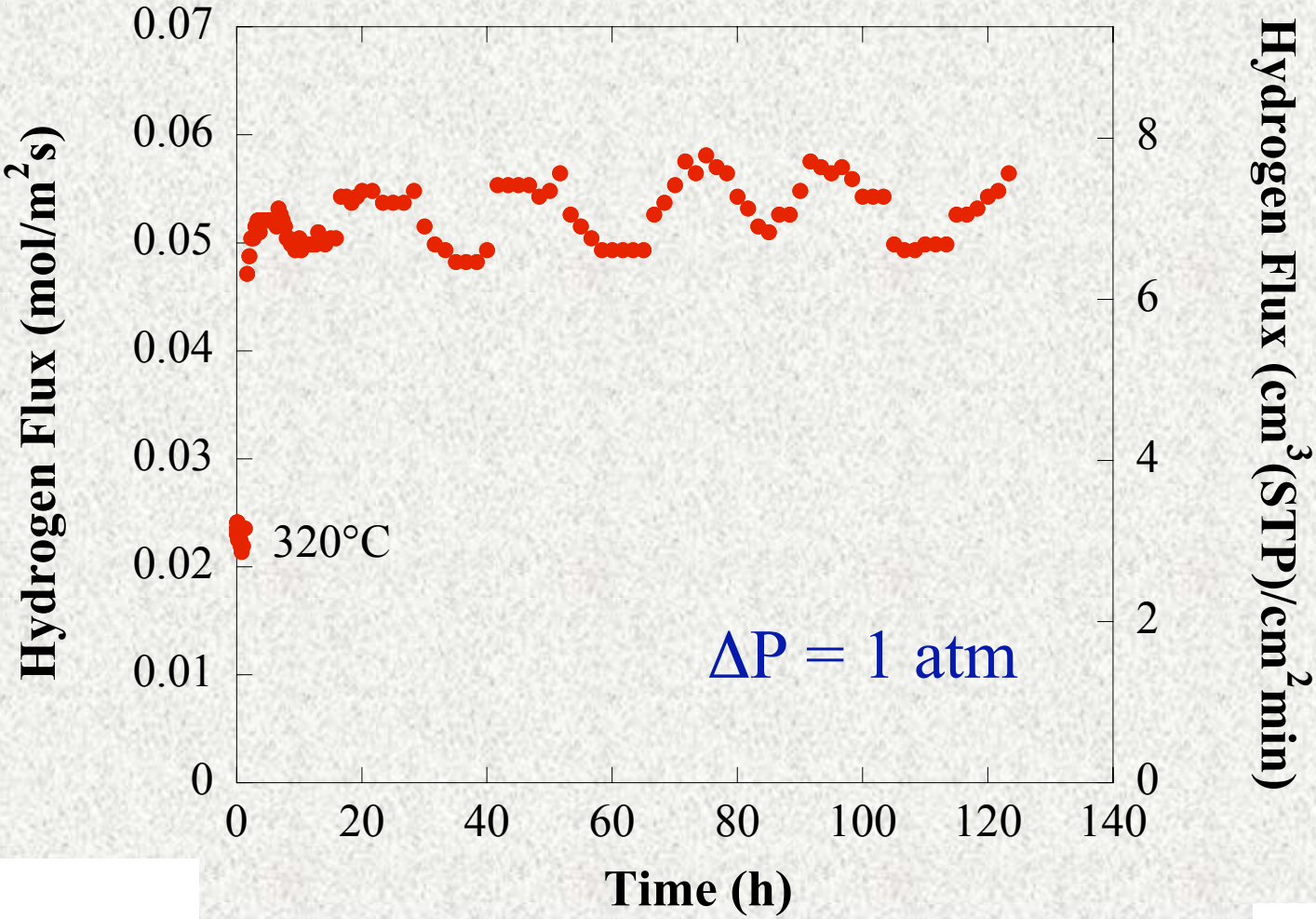
Hydrogen flux vs. time through 40 μm thick Ta at 400°C (coated with 100 nm Pd per side)



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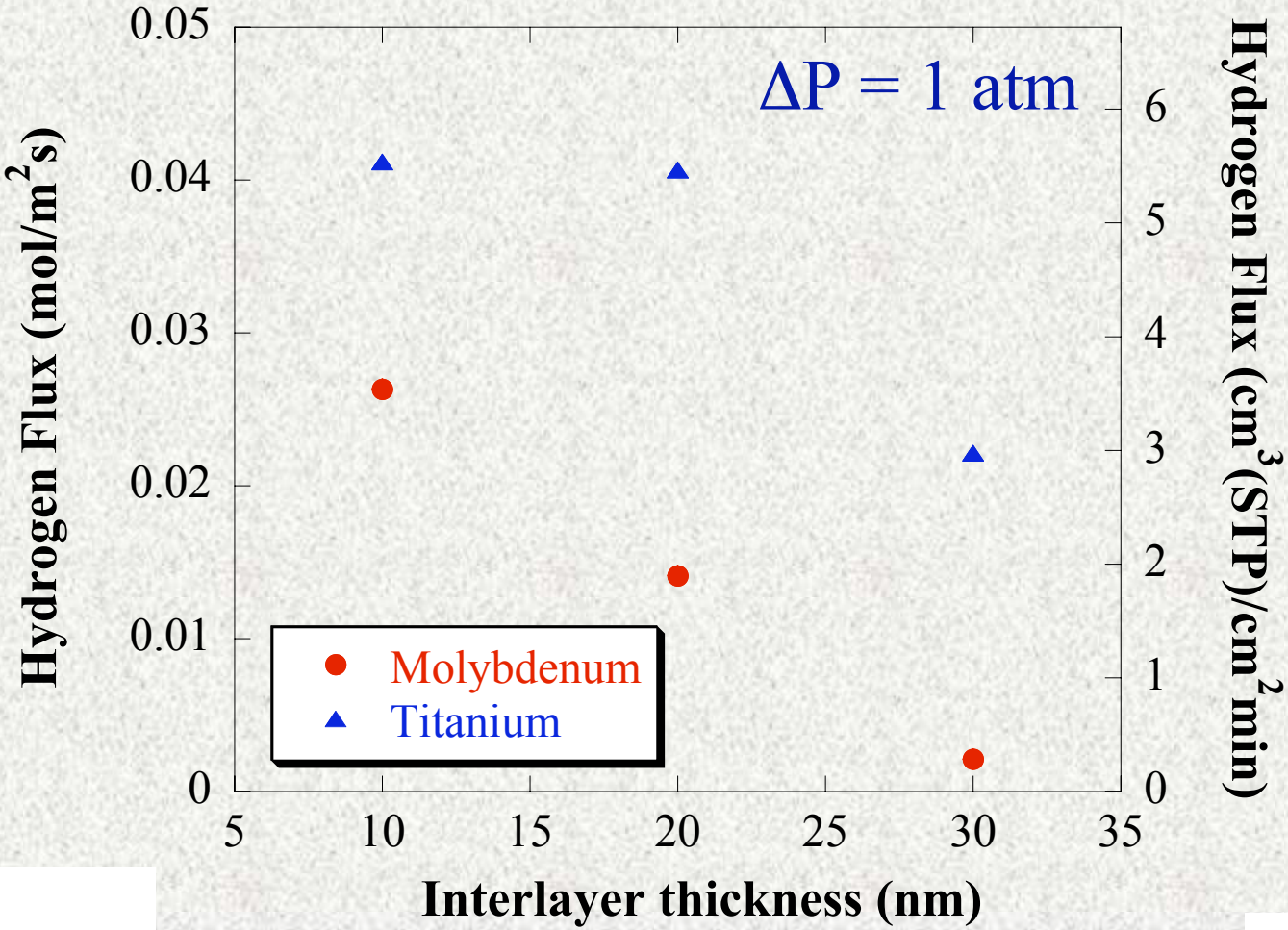
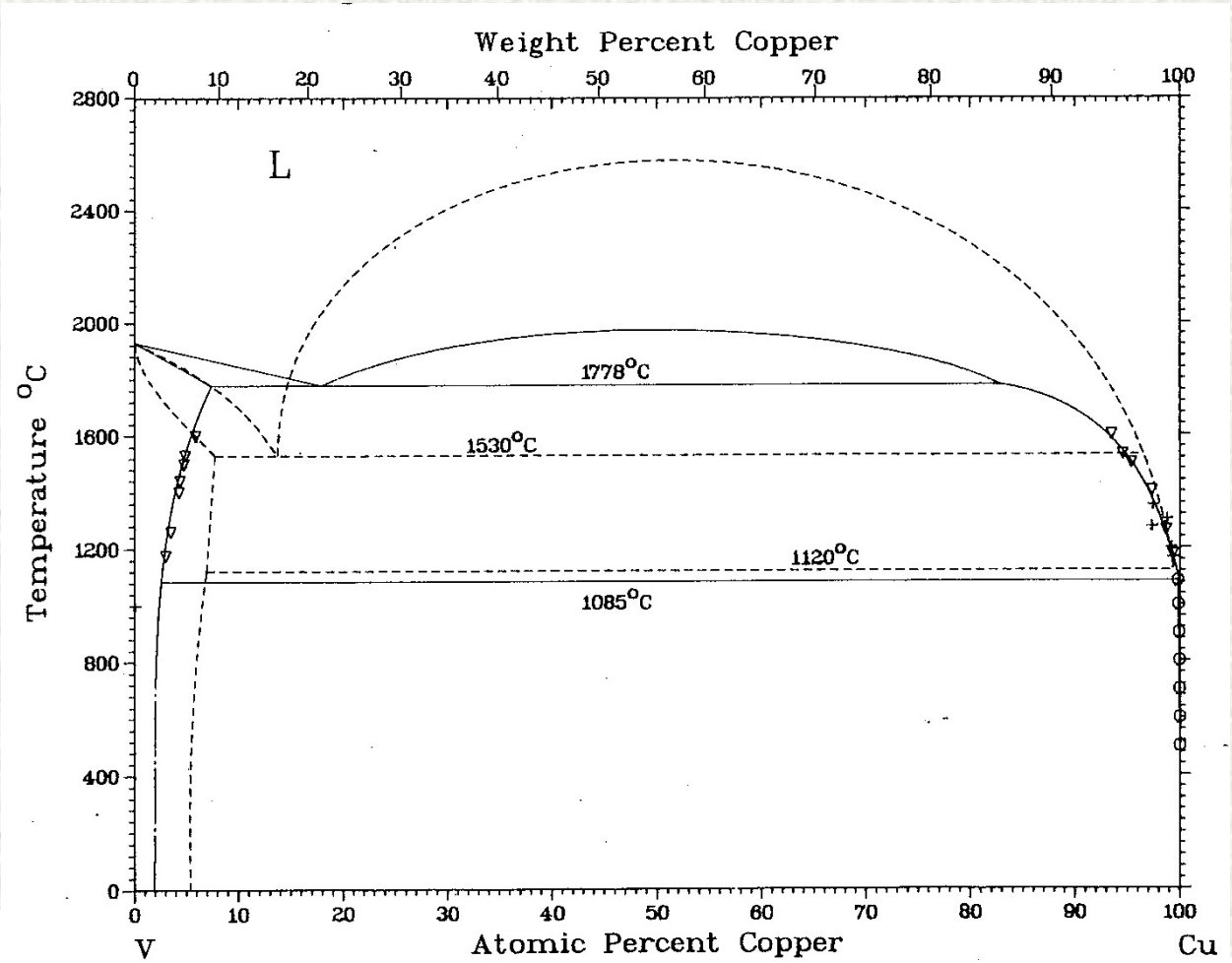
H_2 flux through 50 μm thick Ta at 400°C vs. interlayer thickness (coated with 200 nm Pd)



V-Cu Phase Diagram

From: Phase Diagrams of Binary Vanadium Alloys, J.F. Smith, Editor (1989)



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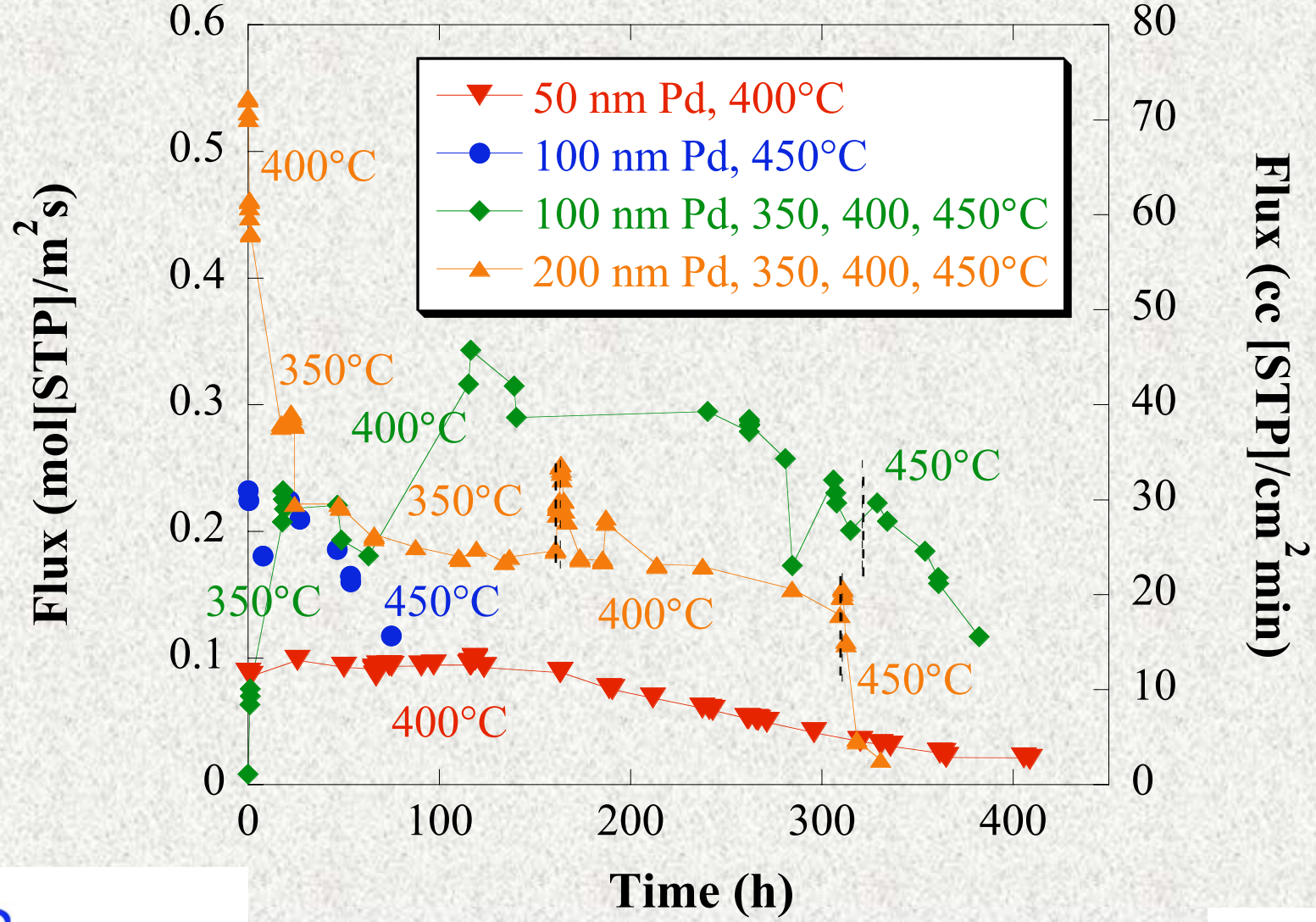
H_2 flux through 75-μm thick $Pd/V_{0.90}Cu_{0.10}/Pd$ membranes (50, 100, or 200 nm Pd per side) at 350-450ºC and ΔP=1 atm



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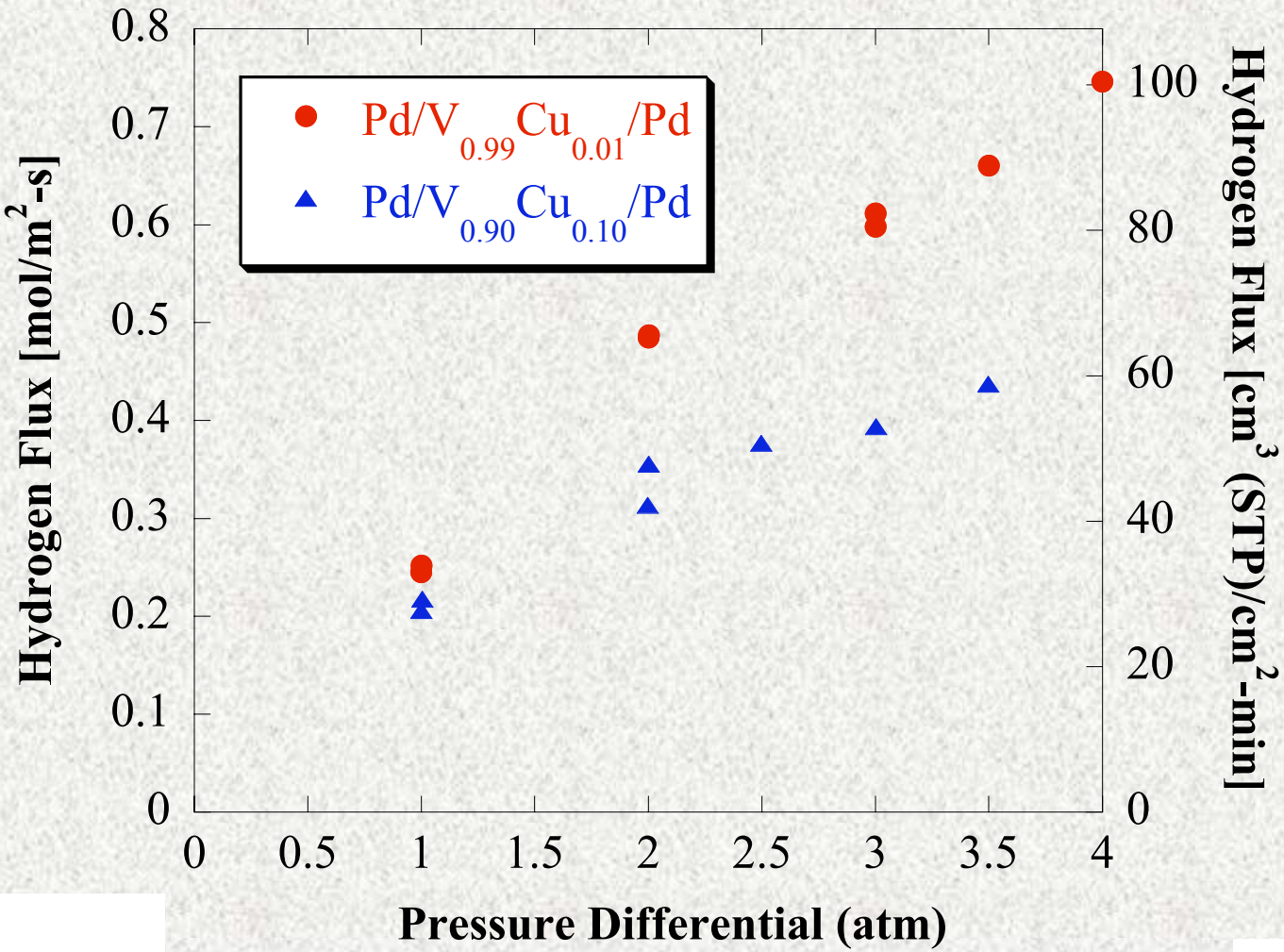
H_2 flux through 75 μm Pd/V–Cu/Pd membranes at 350ºC (100 nm Pd per side)



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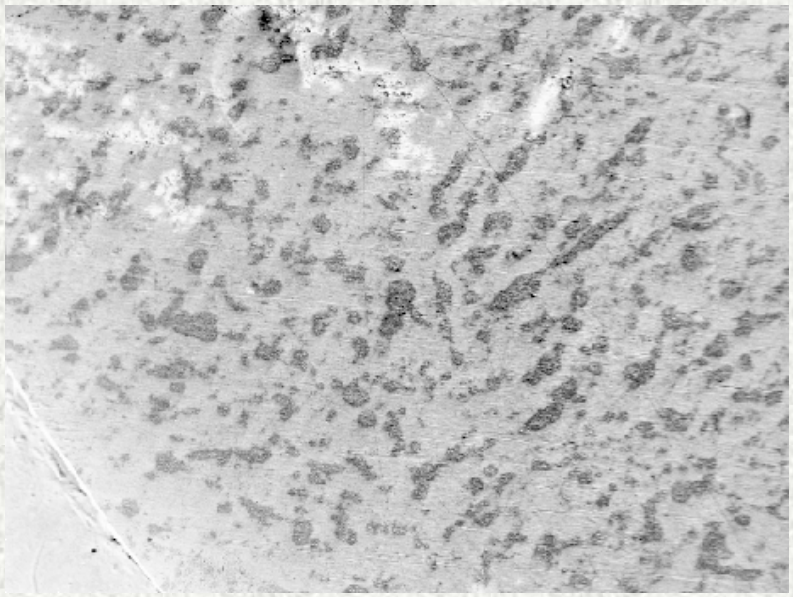
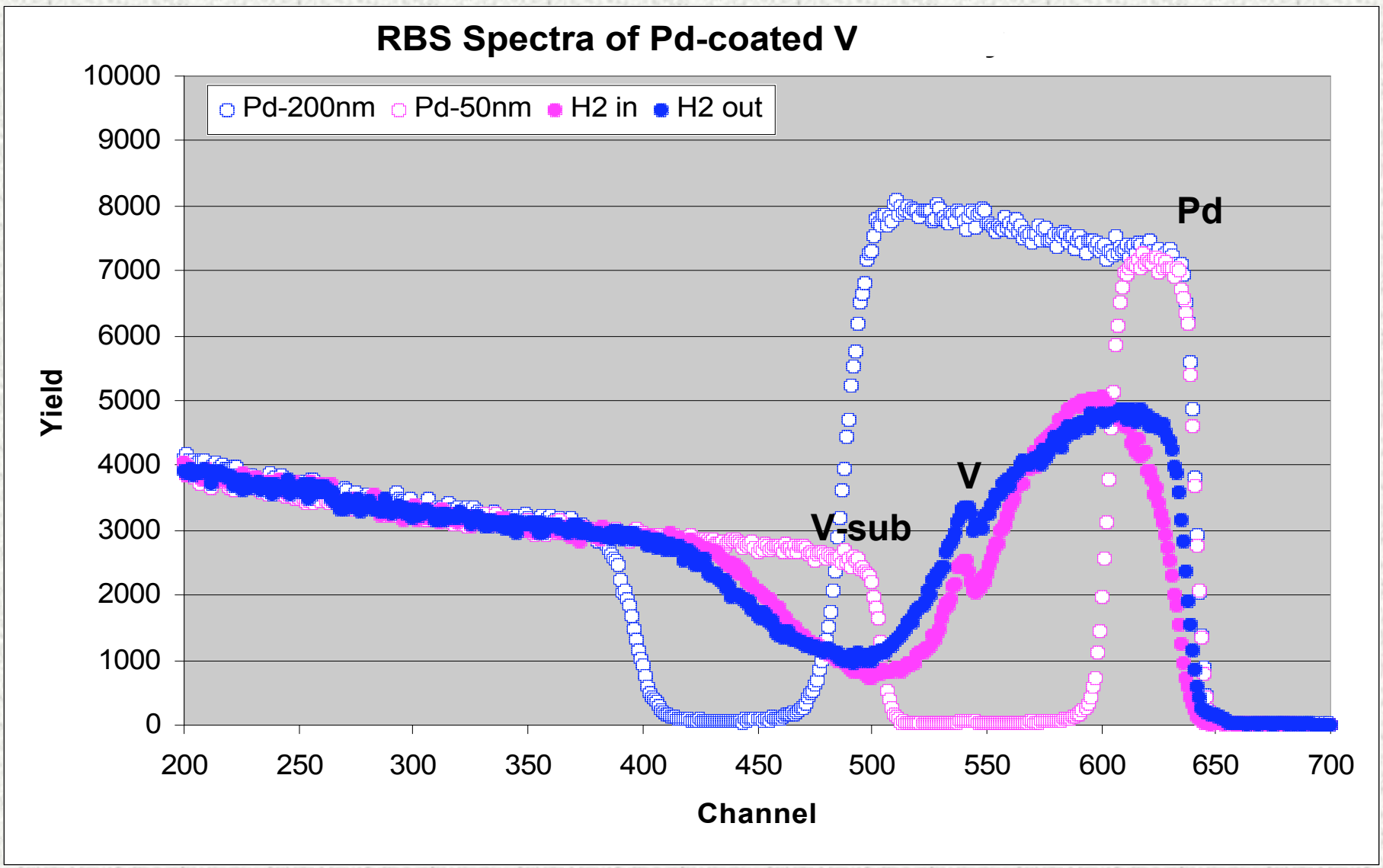
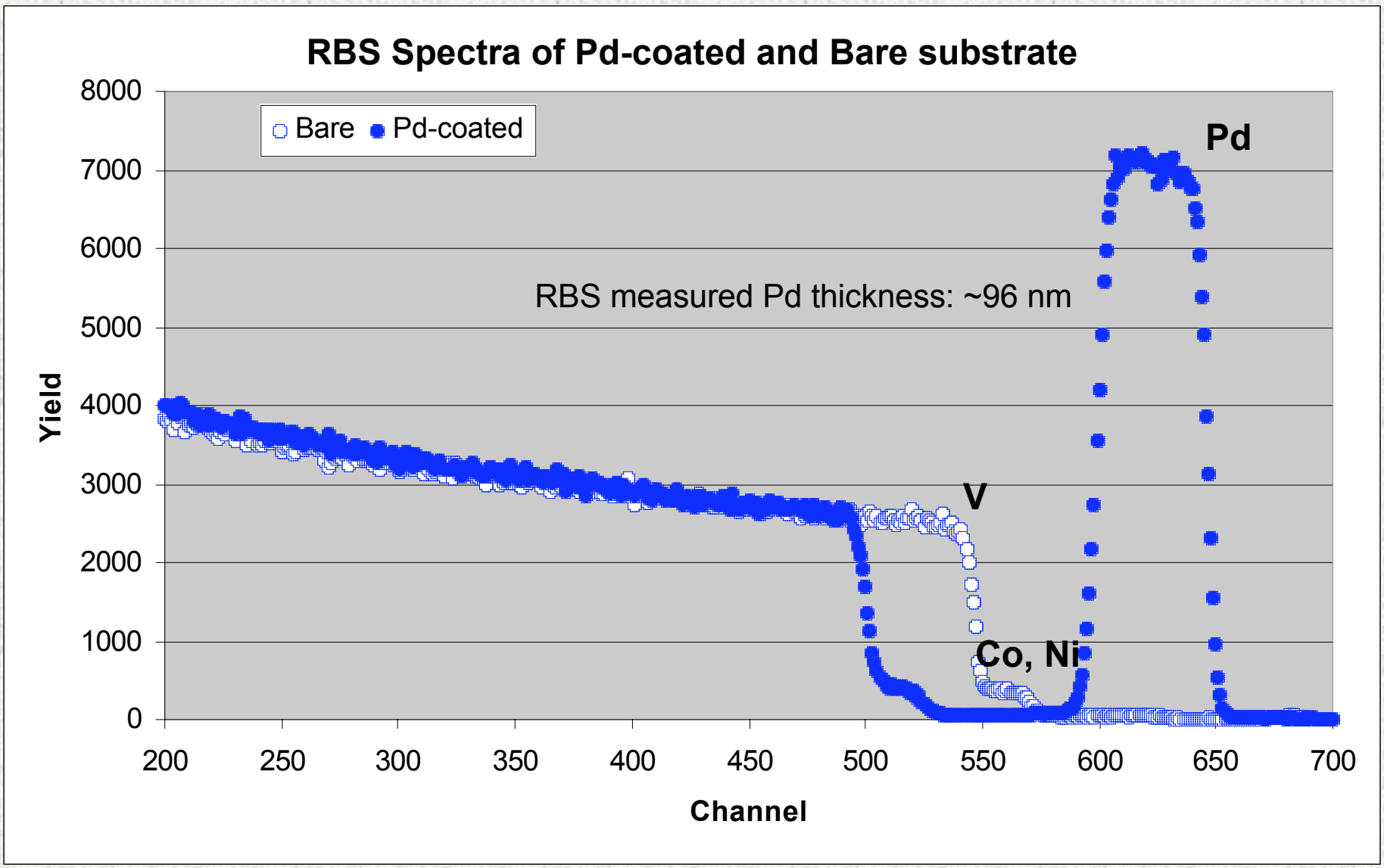
SEM Image of $V_{0.90}Cu_{0.10}$ Membrane



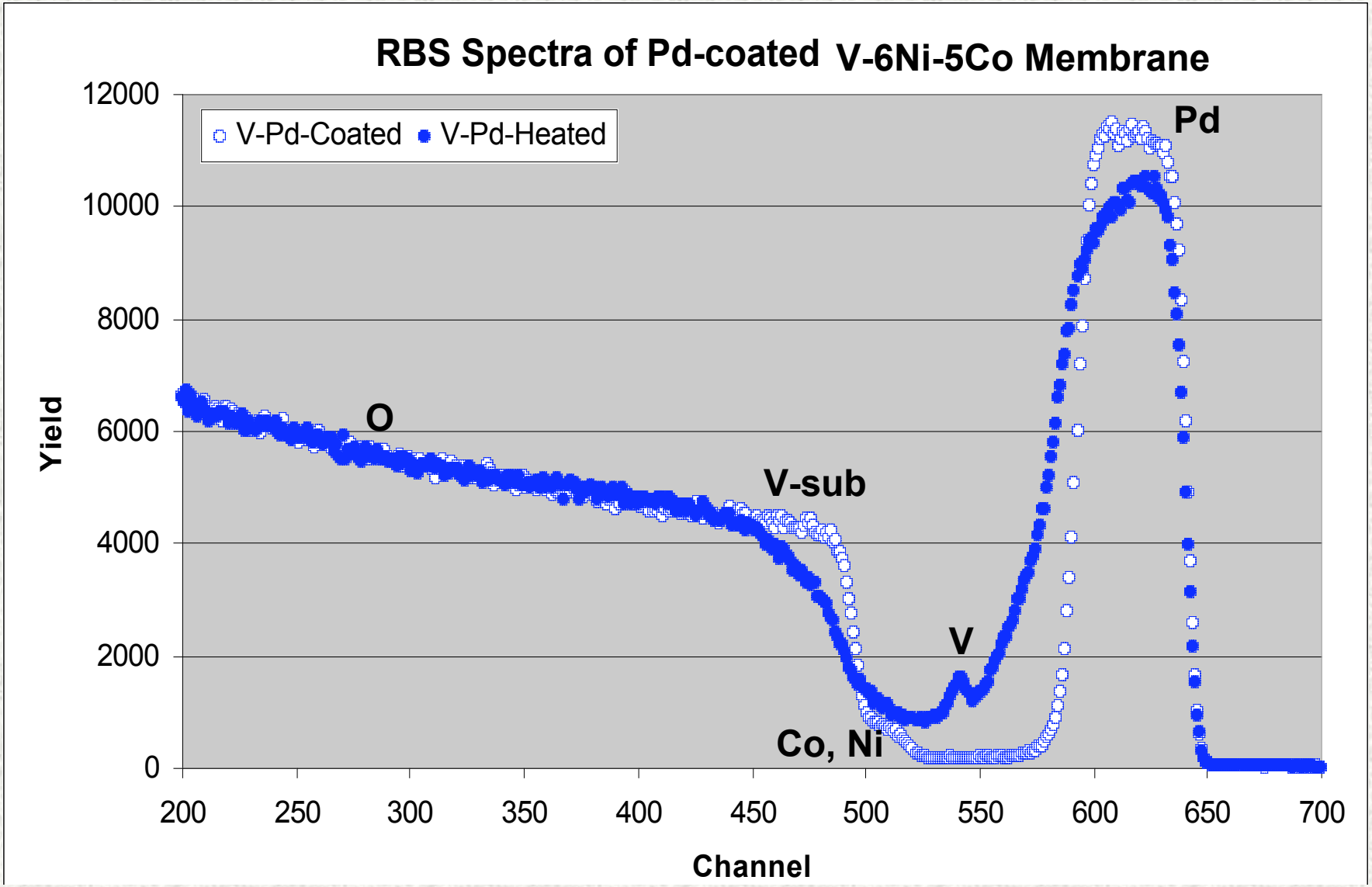
- coated with 100 nm Pd
- tested at 450ºC for 75 h
- upstream side, 48.7X
- AES analysis indicated that the dark regions are Cu-rich



- Membrane with 50 nm Pd coating tested under H_2 at 400°C for 400 h



- V-6Ni-5Co membrane with 100 nm Pd coating



- Tested in hydrogen for 500 hrs at 400°C

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