Development of Sulfur-Tolerant Palladium-Copper Alloy Membranes for Hydrogen Separation from Coal Gases

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OVERVIEW

- **DOE Award No. DE-FG26-04NT42194**

  Worcester Polytechnic Institute
- **Project Title: Sulfur-Tolerant Palladium-Copper Alloy Membranes for Hydrogen Separation with High Pressure CO2 for Sequestration**
- **Principal Investigator: Yi Hua Ma**
- **Project Duration: 1 October 2004 – 30 September 2008 (One year no cost extension included)**
- **Collaborators:**

  Shell International Exploration and Production Inc.

  Oak Ridge National Laboratory
- **Reporting period: 1 May 2005 – 1 May 2006**

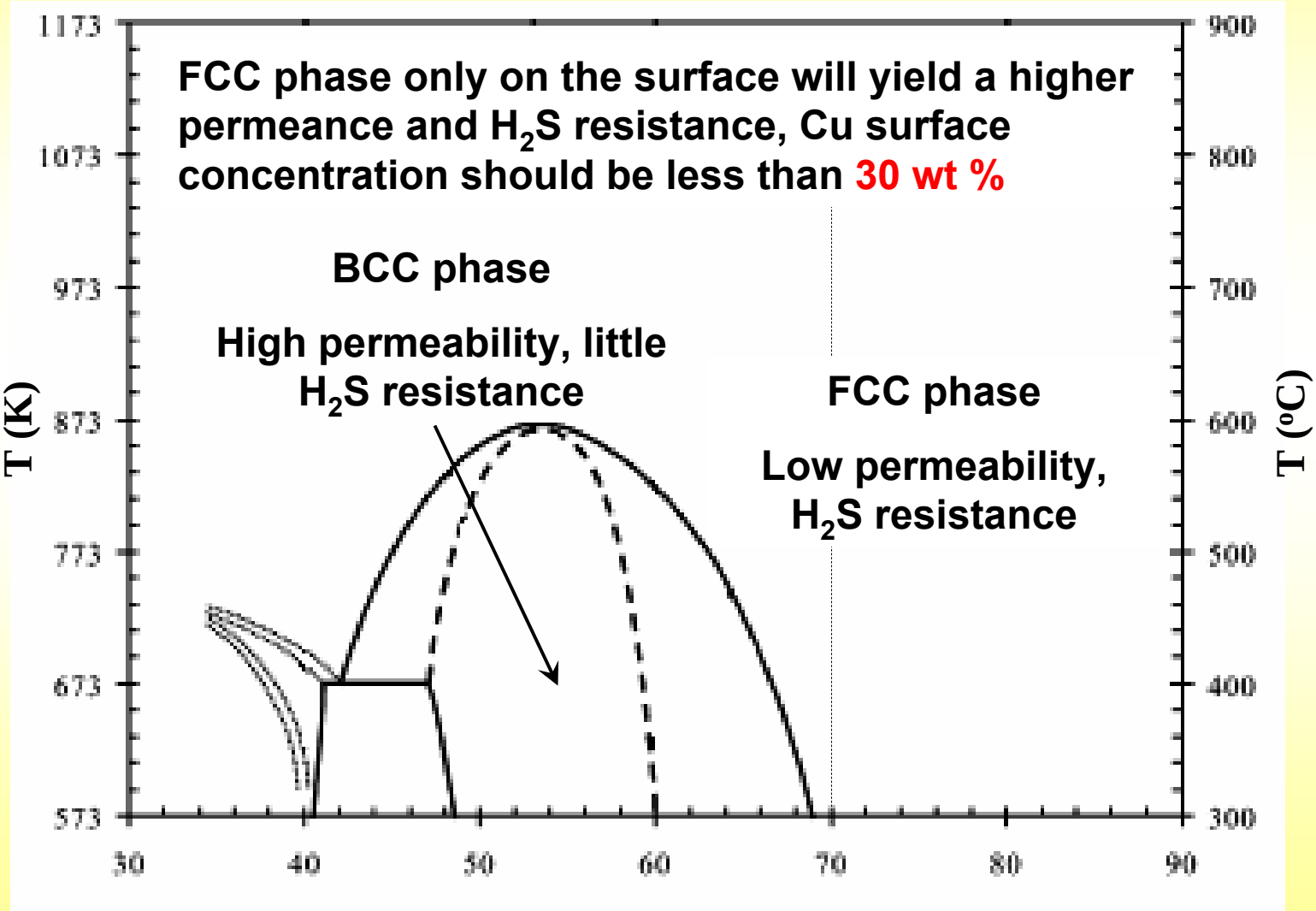
Project Objectives

1. Synthesize sulfur tolerant composite Pd/Cu alloy porous stainless steel membranes by electroless plating based on our patented technology
2. Understand the kinetics of Pd/Cu alloy formation and changes in nanostructure properties of Pd/Cu as a function of temperature and rate of cooling/heating using High Temperature XRD (HTXRD), SEM (with EDX) and TEM
3. Characterize the membrane permeation performance and its relation to changes in nanostructure properties of the alloy
4. Test the membrane in both in ½" and 1" lab scale units using simulated coal gases

Objectives of the Reporting period

- Coupon study to determine the kinetics of the Cu plating bath and the annealing time needed to produce an FCC phase on the surface
- Synthesis of two Pd/Cu alloy membranes with the FCC phase on the surface
- Characterization of the two membranes
- Stability testing at 500 ^{o}C

Pd/Cu phase diagram



Morreale et al., 2004

Electroless plating procedure

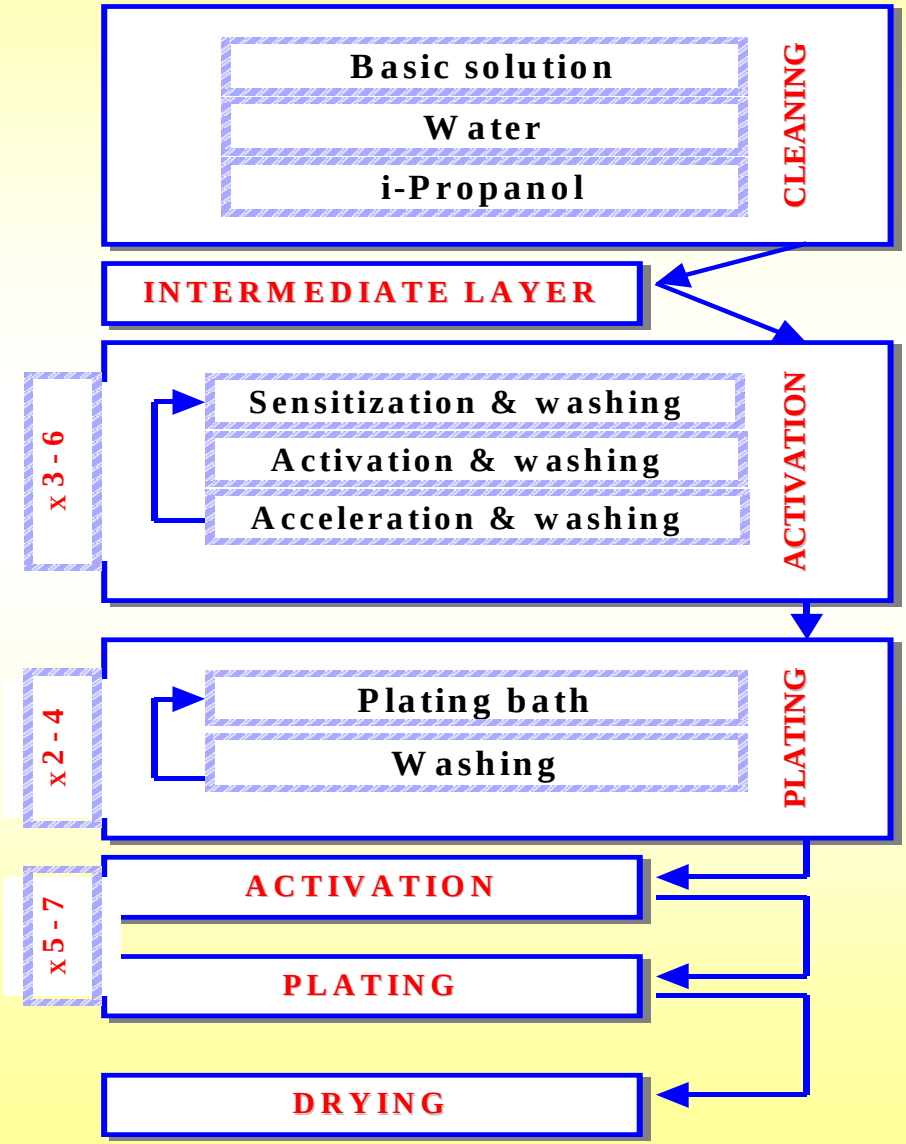
- Sensitize object with acidic $SnCl_2$ solution, activate with acidic $PdCl_2$ solution: object coated with Pd nuclei after several “rounds” of immersion

$$Sn^{4+} + Pd^{2+} \rightarrow Sn^{2+} + Pd^{0}$$

- Immerse in plating solution: Pd nuclei prevent plating on other objects and reduce induction period
- If plating a membrane, He flux is measured
- Procedure repeated until He is impermeable to membrane

Pd deposition procedure by the electroless plating technique

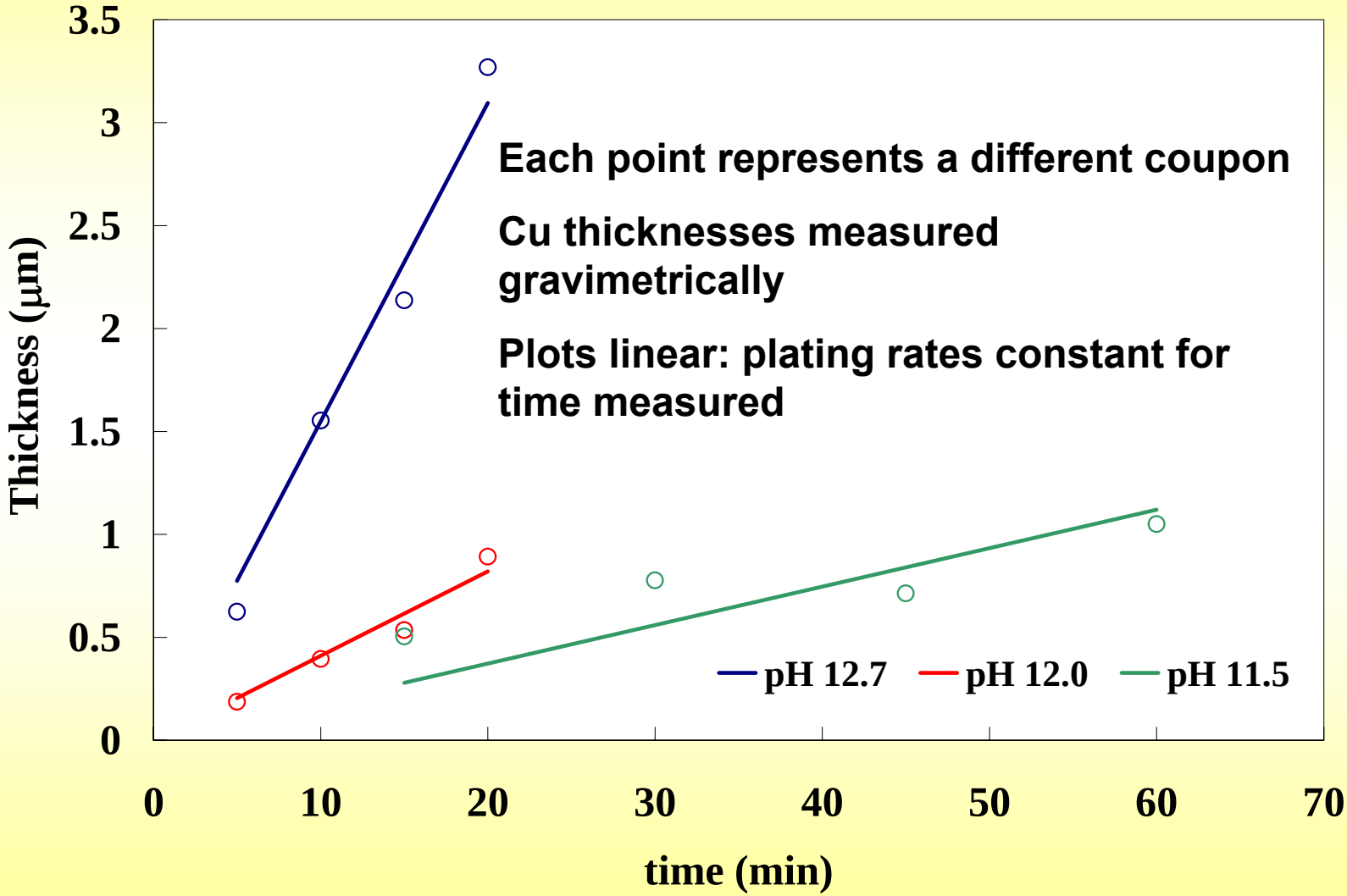
(US Patent 6152987, issue date November 28, 2000



Pd/Cu plating baths

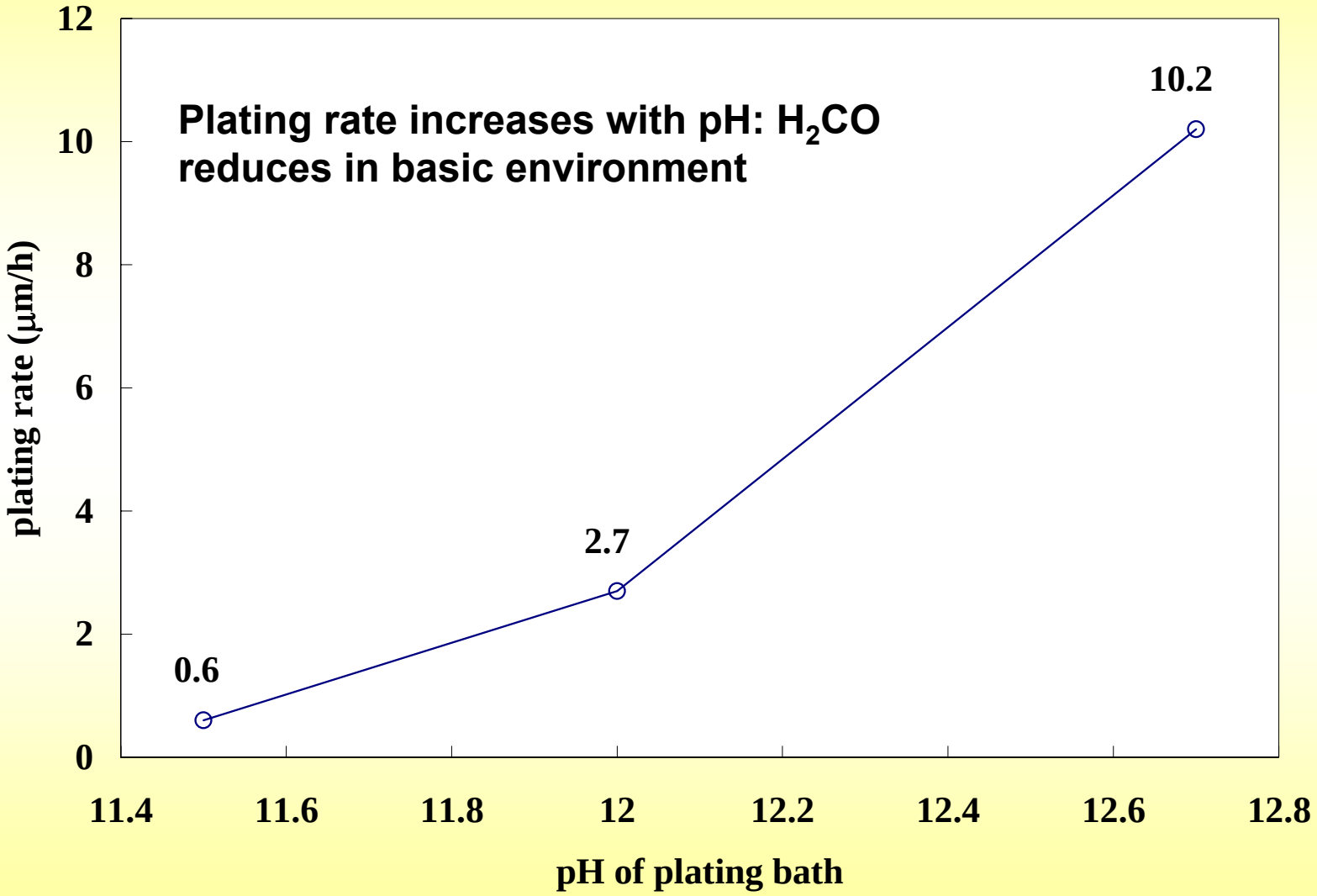
	Pd Bath	Cu Bath	
$Pd(NH_3)_4Cl_2 \cdot H_2O$ (g/l)	4	-	Metal ion source
$CuSO_4 \cdot 5H_2O$ (g/l)	-	25	
$Na_2EDTA \cdot 2H_2O$ (g/l)	40.1	47.5	Complexing agent and stabilizer
NH_4OH (28%) (ml/l)	198	-	
H_2NNH_2 (1 M) (ml/l)	5.6	-	Reducing agent
HCHO (37%) (ml/l)	-	25	
EDA (ppm)	-	112	Grain refiners and stabilizers
$K_4Fe(CN)_6 \cdot 3H_2O$ (ppm)	-	35	
$(C_2H_5)_2NCS_2Na \cdot 3H_2O$ (ppm)	-	5	
pH	10-11	12.7	
Temperature (°C)	60	20-25	

Coupon study: Cu plating kinetics



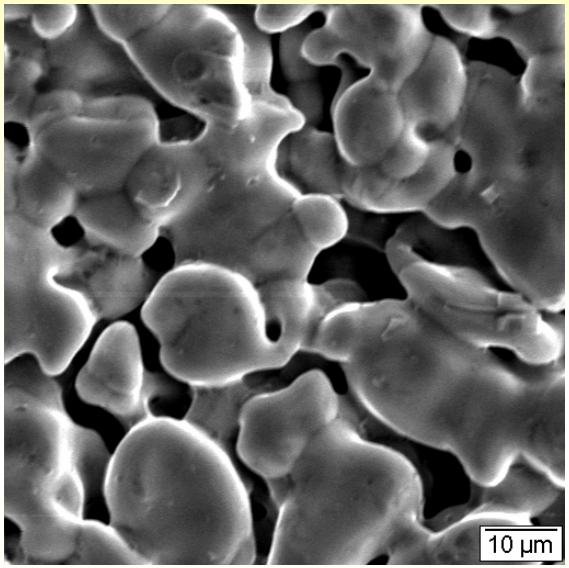
$$Cu^{2+} + 2H_2CO + 4OH^- \rightarrow Cu^0 \downarrow + 2HCOO^- + H_2 \uparrow + 2H_2O$$

Cu plating kinetics, cont.

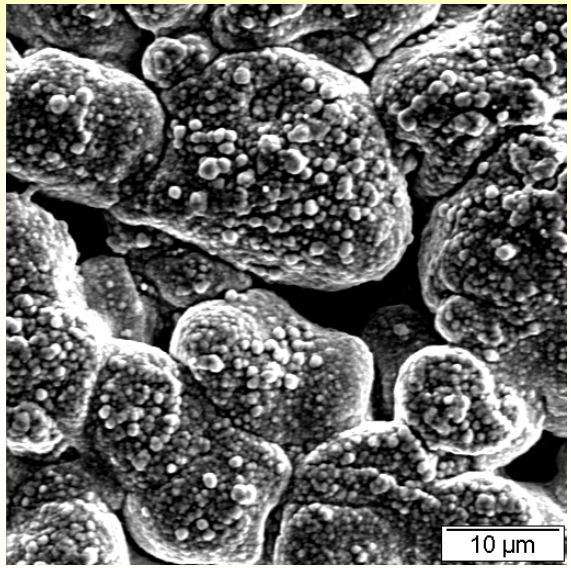


$$Cu^{2+} + 2H_2CO + 4OH^- \rightarrow Cu^0 \downarrow + 2HCOO^- + H_2 \uparrow + 2H_2O$$

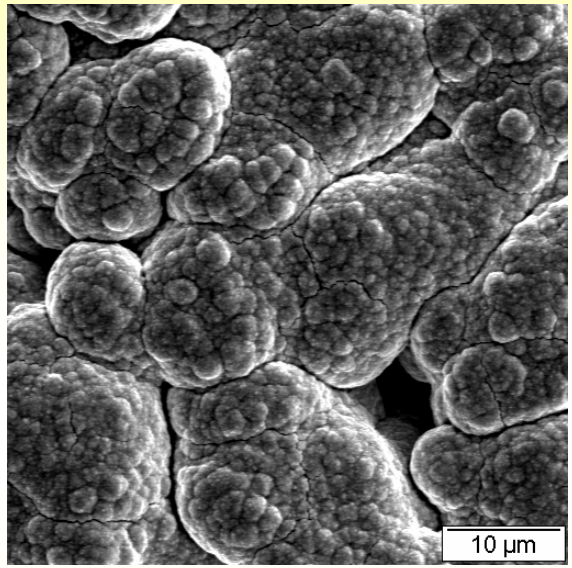
Cu surface morphology
pH = 12.7



Bare PSS



1.1 µm Cu*



2.8 µm Cu*

Cu deposits uniformly, inside and outside of the pores

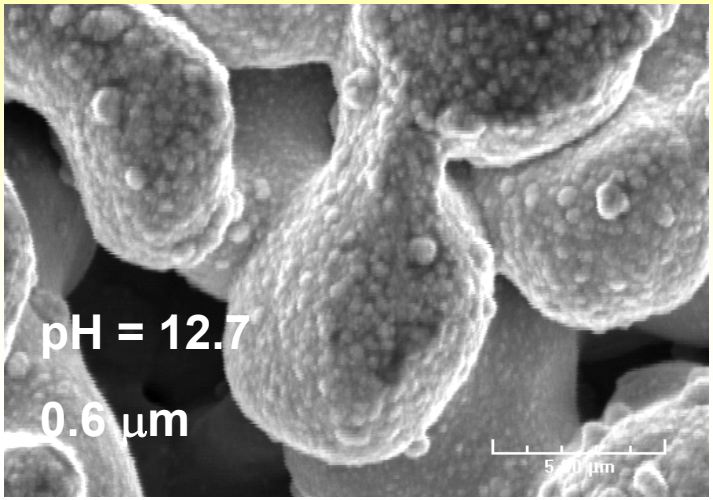
Deposit covers the porous support

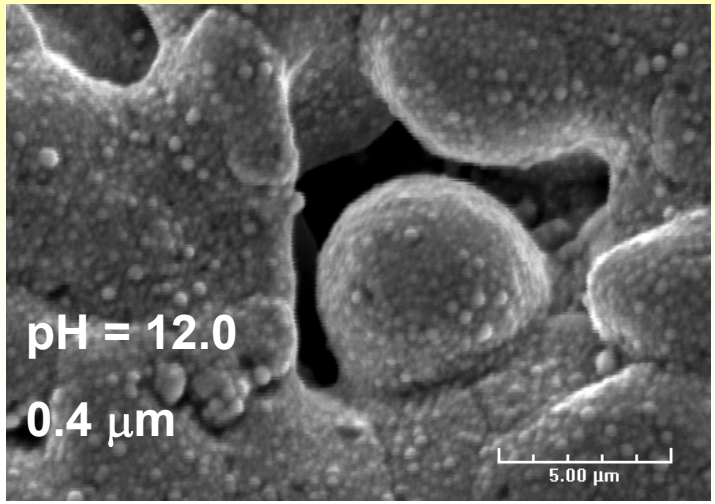
Increasing thickness blocks pores, forming a dense layer similar to Pd

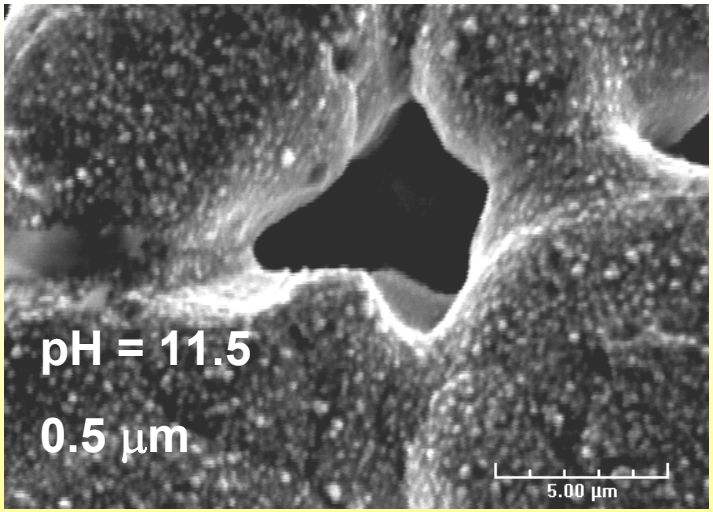
Good, uniform coverage

*Thicknesses determined gravimetrically

Cu morphology, cont.



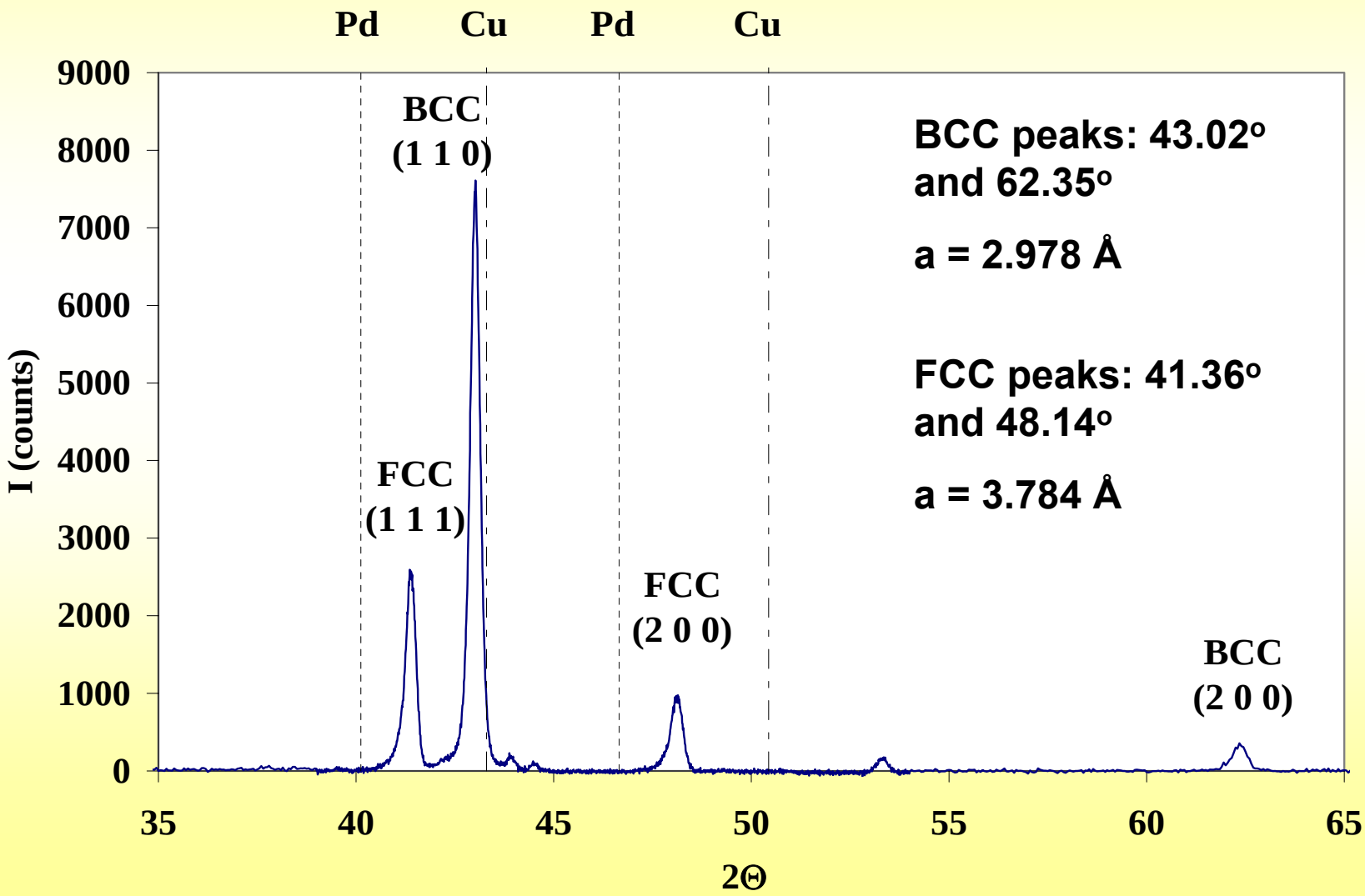




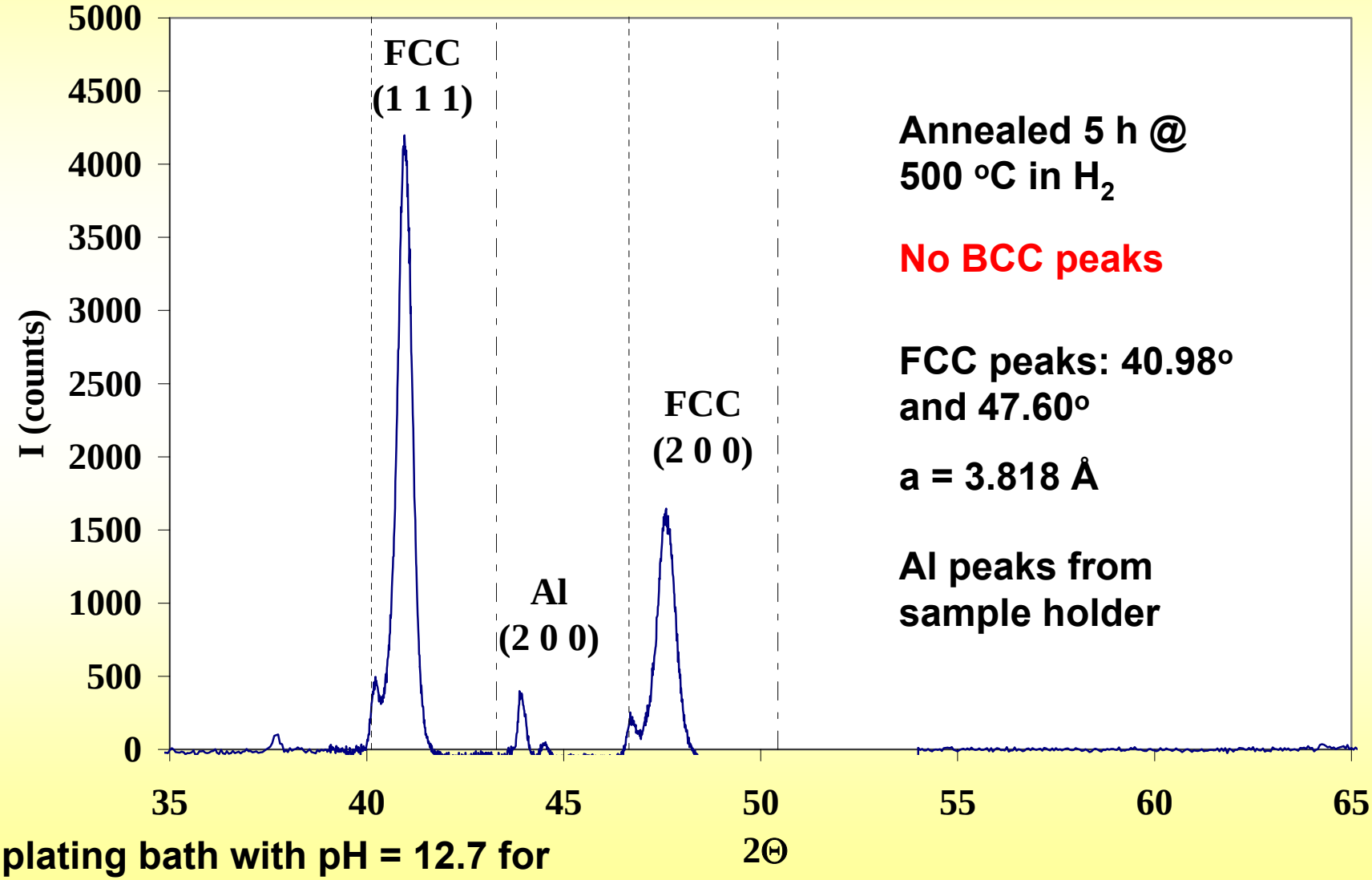
At each pH tested, Cu deposits uniformly inside and outside of the pores

Slower plating rate yields smaller grains

XRD pattern of mixed FCC and BCC phases

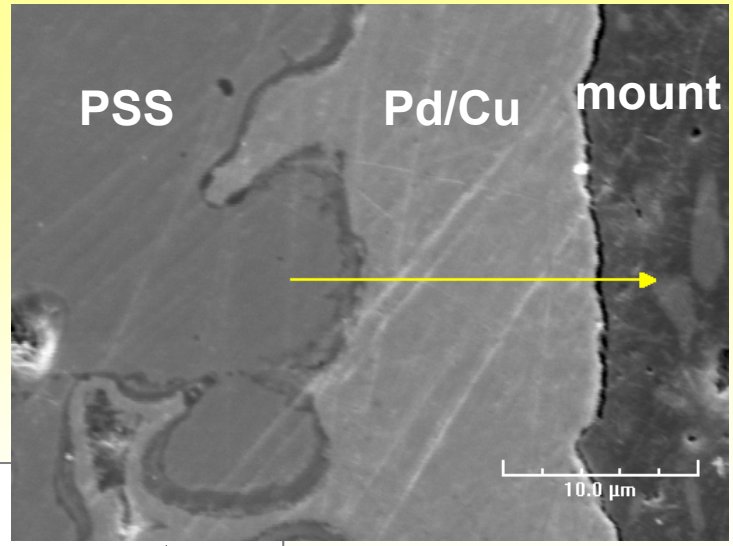


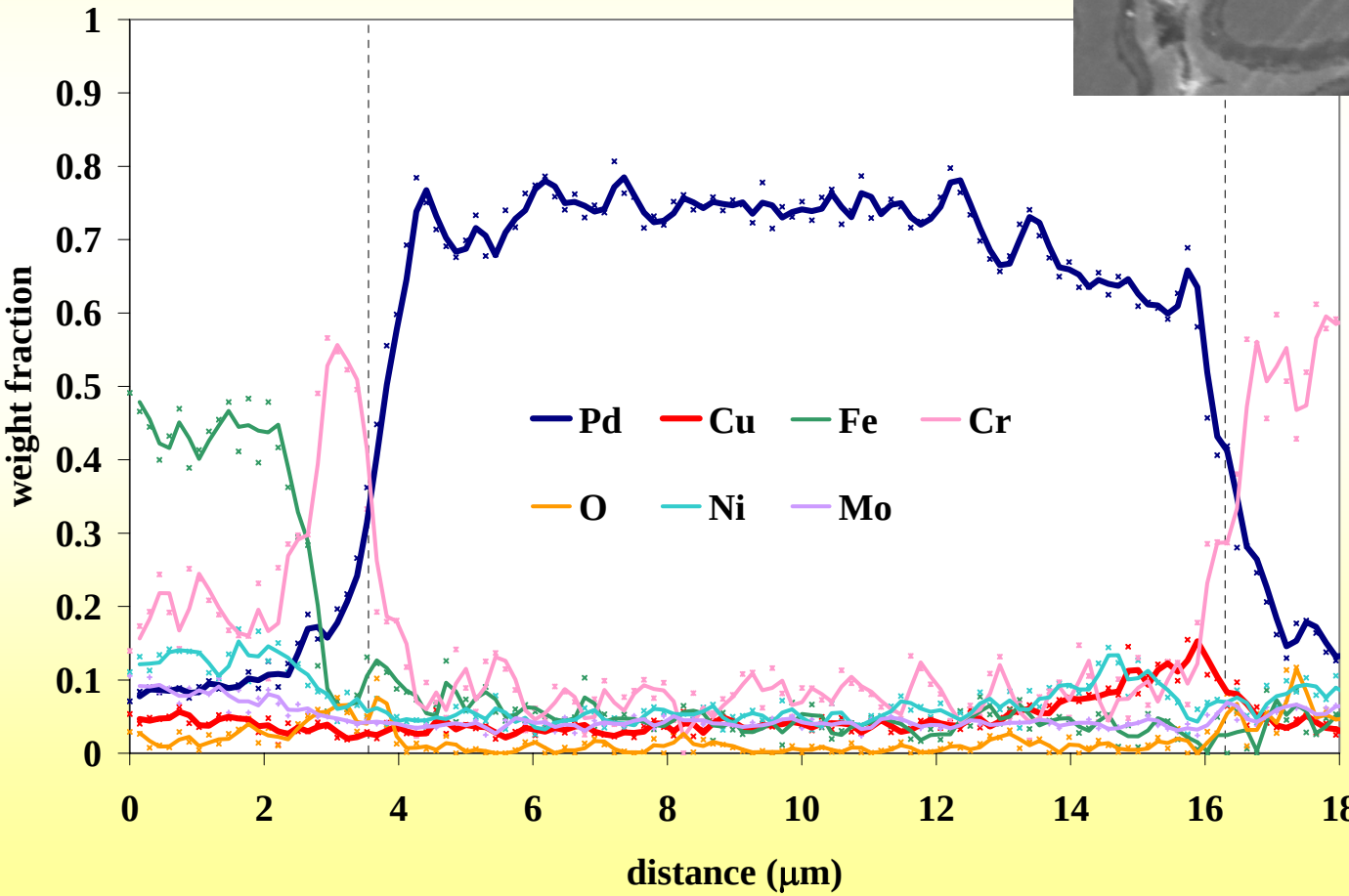
11 wt % Cu, 2.4 µm Cu* on Pd



*Cu plating bath with pH = 12.7 for all experiments in coupon study

11 % wt, 2.4 µm Cu on Pd



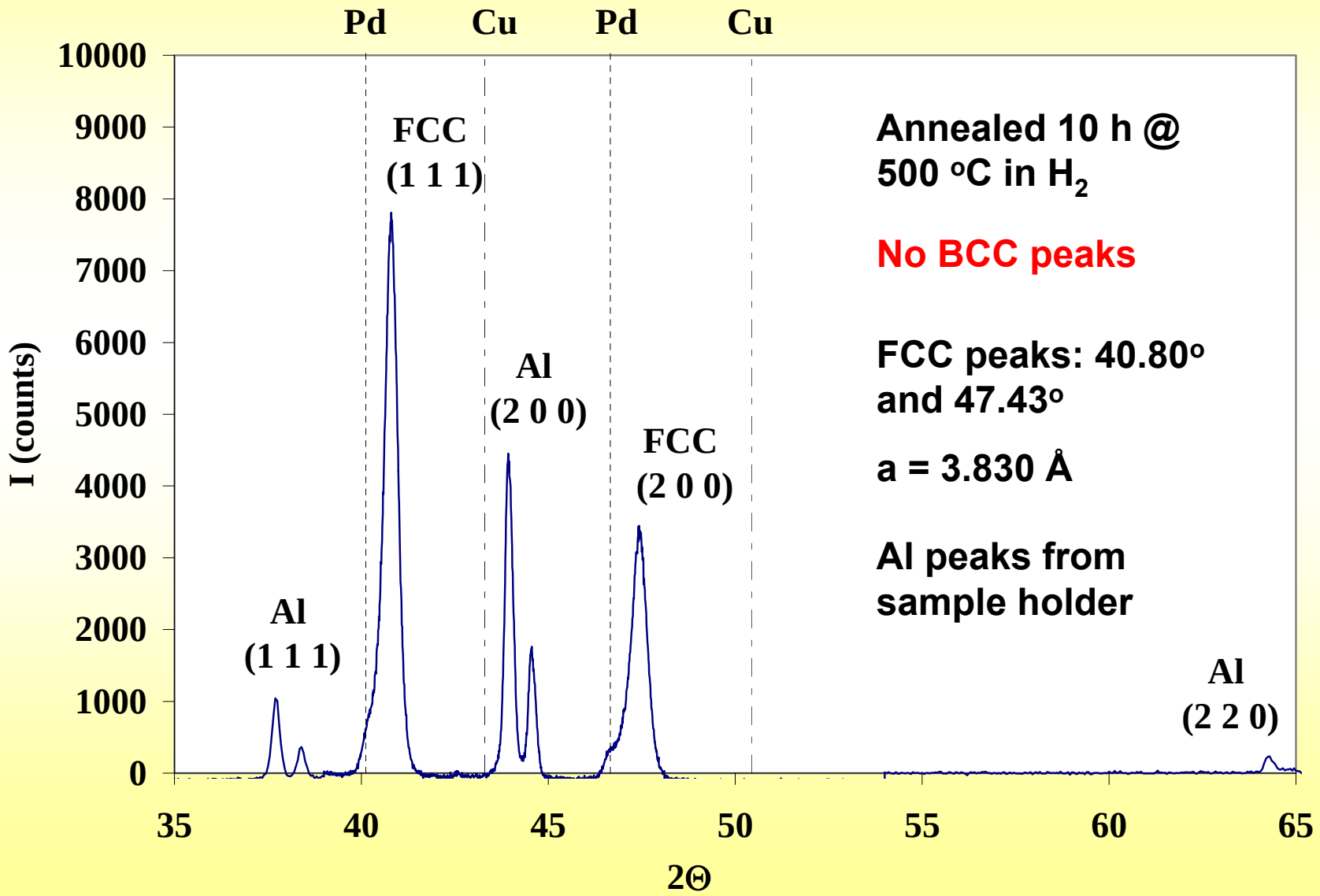


Surface Cu conc.: 15 wt % Cu

without other elements: 20 wt %

Below conc. for BCC phase transition: < 30 %

18 wt % Cu, 4.5 µm Cu on Pd



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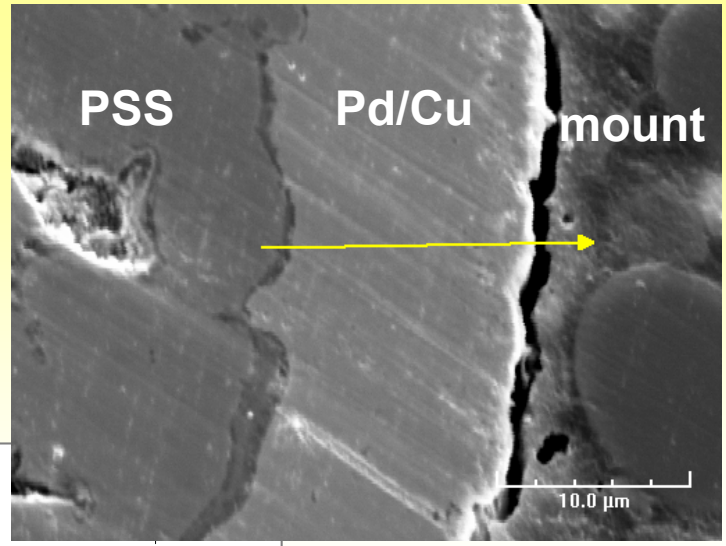
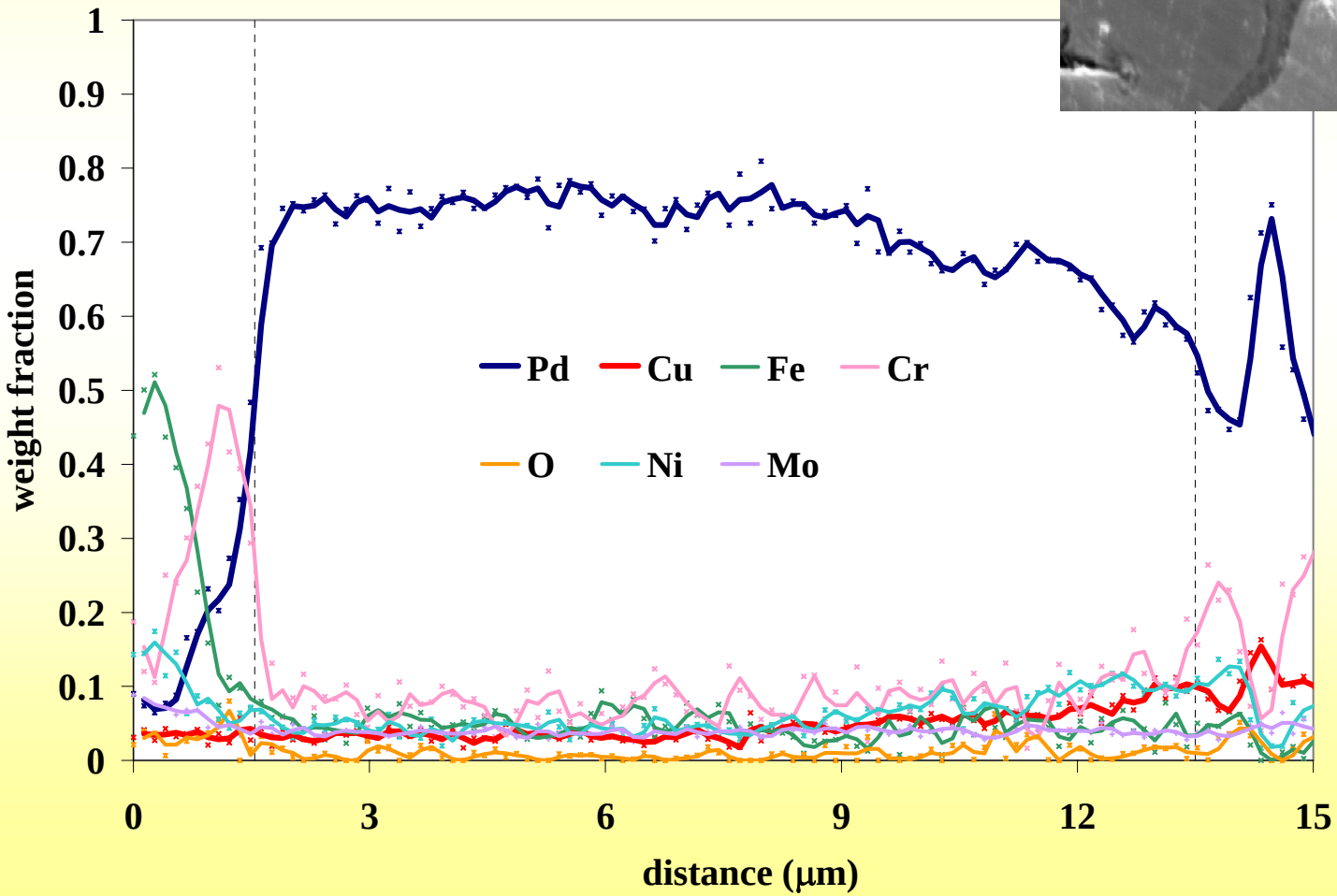




Surface Cu conc.: 10 wt % Cu

without other elements: 15 wt %

Below conc. for BCC phase transition: < 30 %

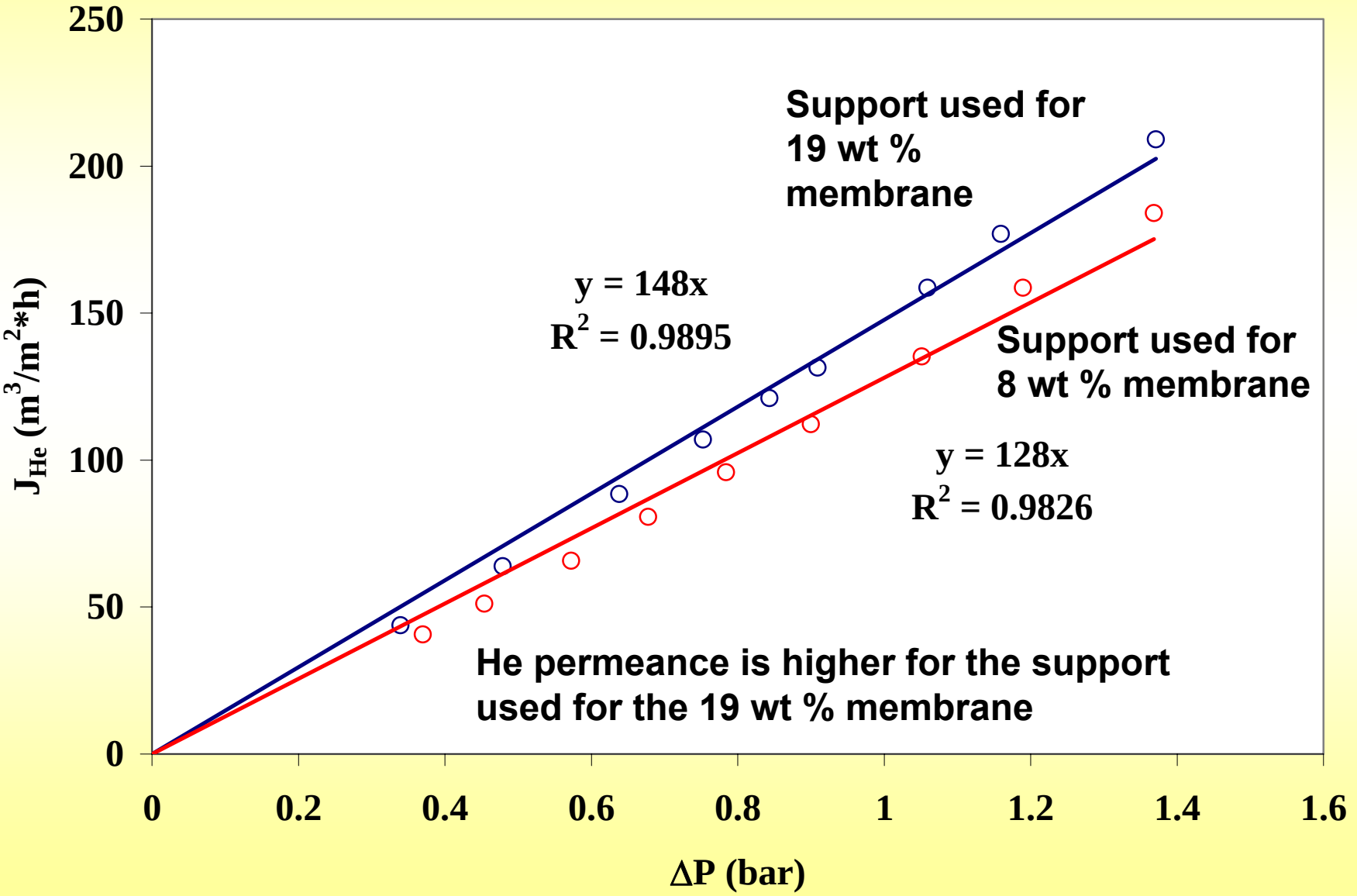
Pd/Cu membrane study: 14 μm thick on porous Inconel supports

Membrane area = 23.8 cm^2

- $J_{He,bare}$ = 159 m^3/m^2*h
- 0.5 μm Ru
- $J_{He,Ru}$ = 148 m^3/m^2*h
- 10.8 μm Pd + 3.4 μm Cu (19 wt % Cu)
- Annealed @ 500 ^oC 10 h in H_2

- $J_{He,bare}$ = 181 m^3/m^2*h
- Oxd @ 700 ^oC for 12 h
- $J_{He,ox}$ = 128 m^3/m^2*h
- 12.5 μm Pd + 1.5 μm Cu (8 wt % Cu)
- Annealed @ 500 ^oC 5 h in H_2

He flux of supports after intermetallic diffusion barrier



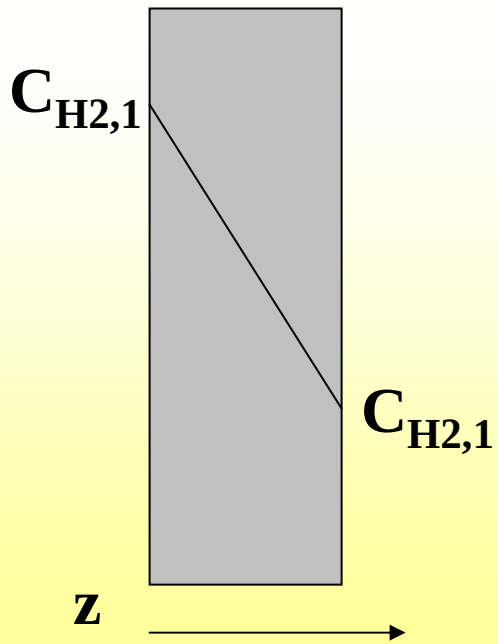
Sieverts' Law: H_2 transport

$$J_{H_2} = \frac{Q}{\Delta z}\left(P_{H_2,1}^{0.5} - P_{H_2,2}^{0.5}\right) \qquad Q = Q_o \exp\left(\frac{E_Q}{RT}\right)$$

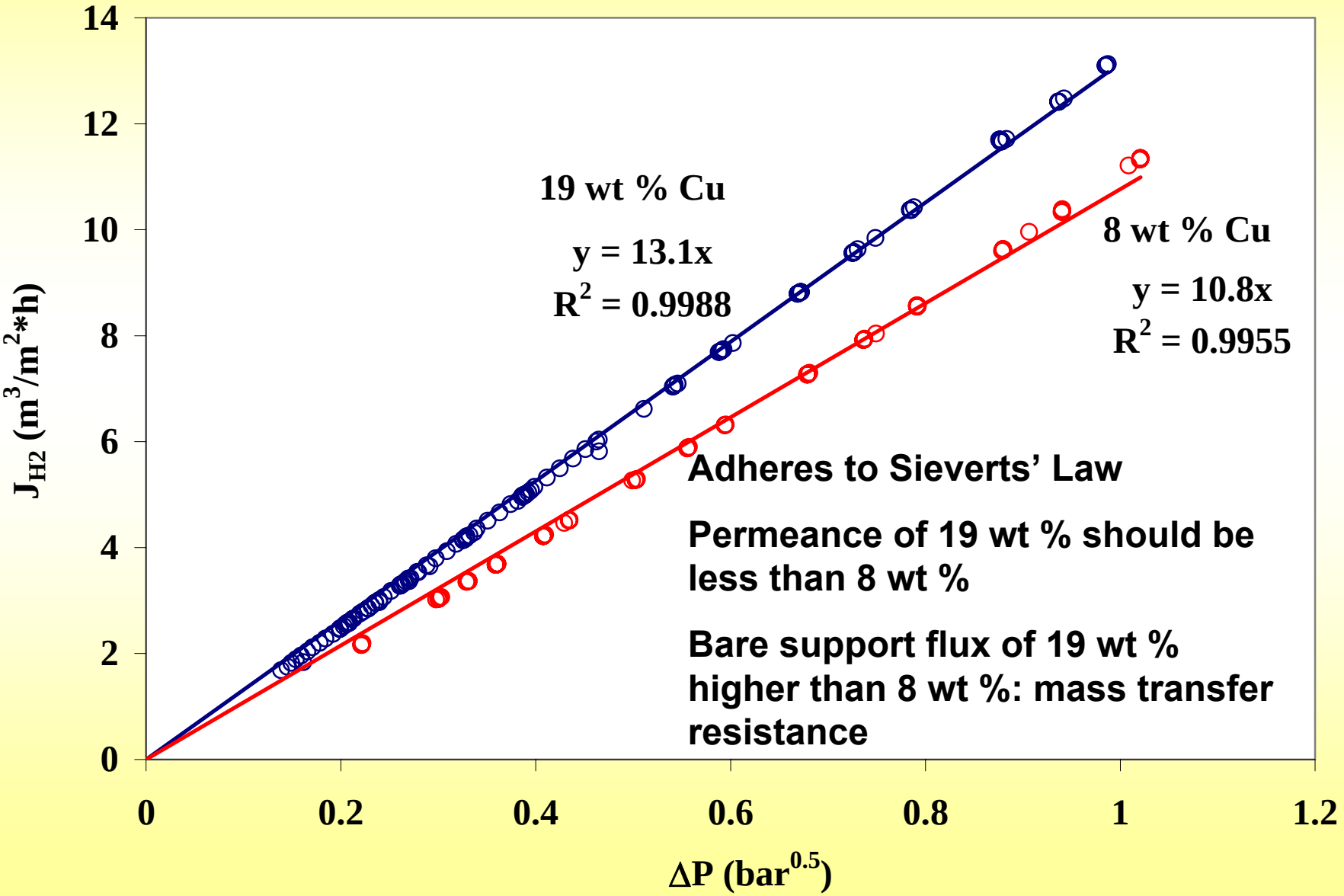
$$F = \frac{Q}{\Delta z}$$

Assumptions:

- **One dimensional diffusion**
- **Diffusion through Pd is rate limiting**
- **Steady state**
- **Small H_2 concentration**



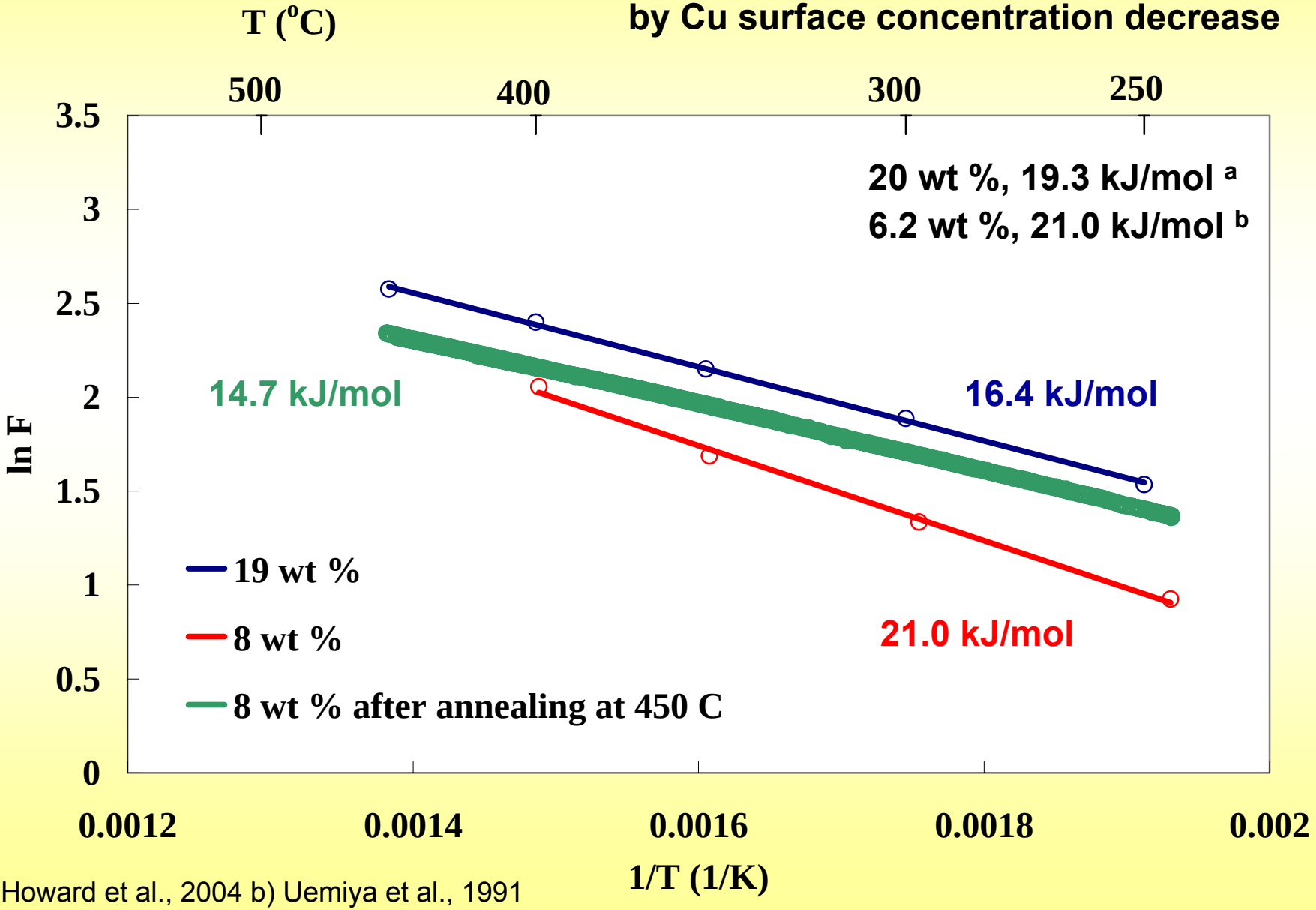
Sieverts' Law at 450 °C



Permeance

Low E_Q similar to pure Pd layer and not homogeneous Pd/Cu layer

Change in E_Q of 8 wt % at 450 °C caused by Cu surface concentration decrease

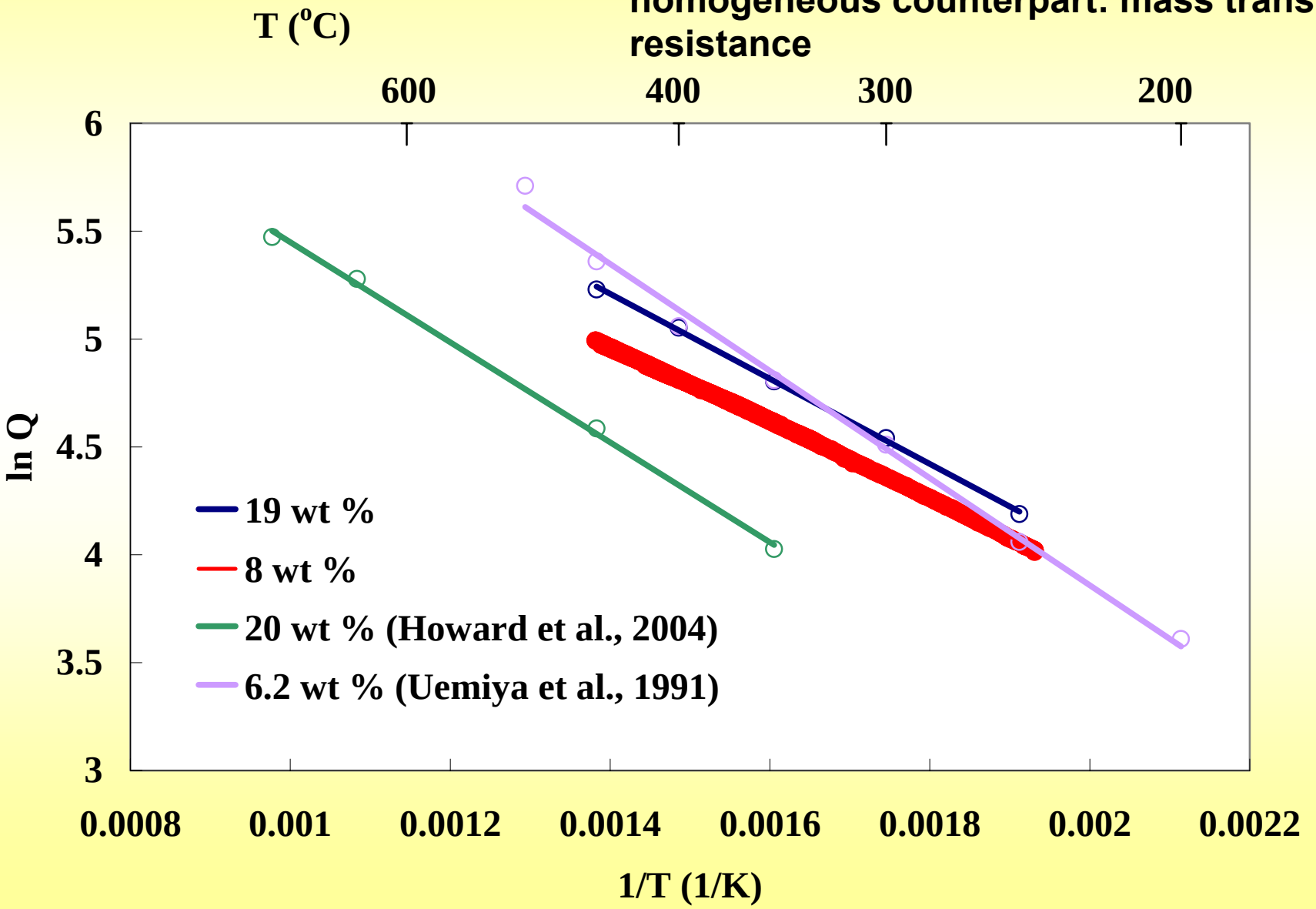


a) Howard et al., 2004 b) Uemiya et al., 1991

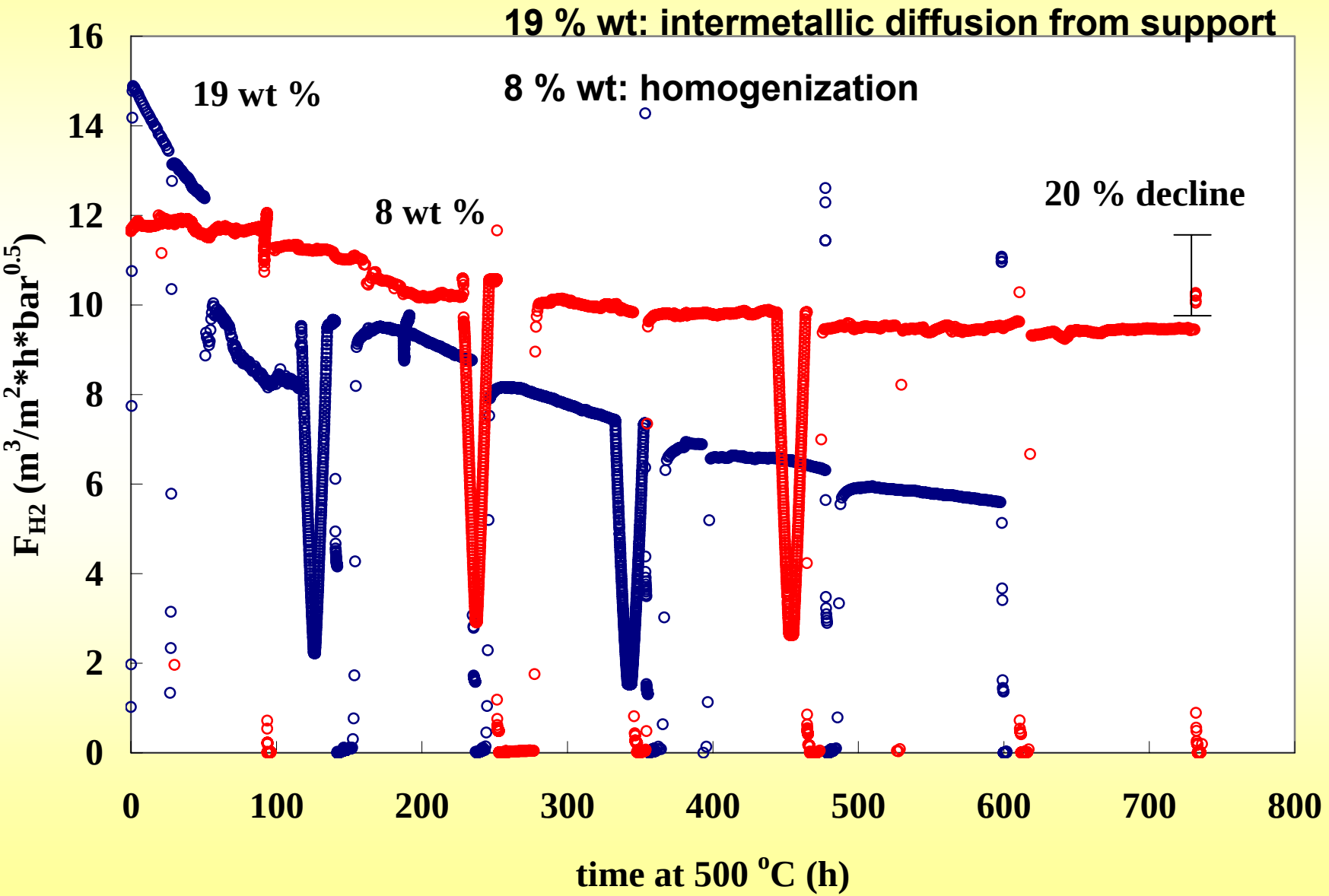
Permeability

Permeability of 19 wt % higher than homogeneous counterpart

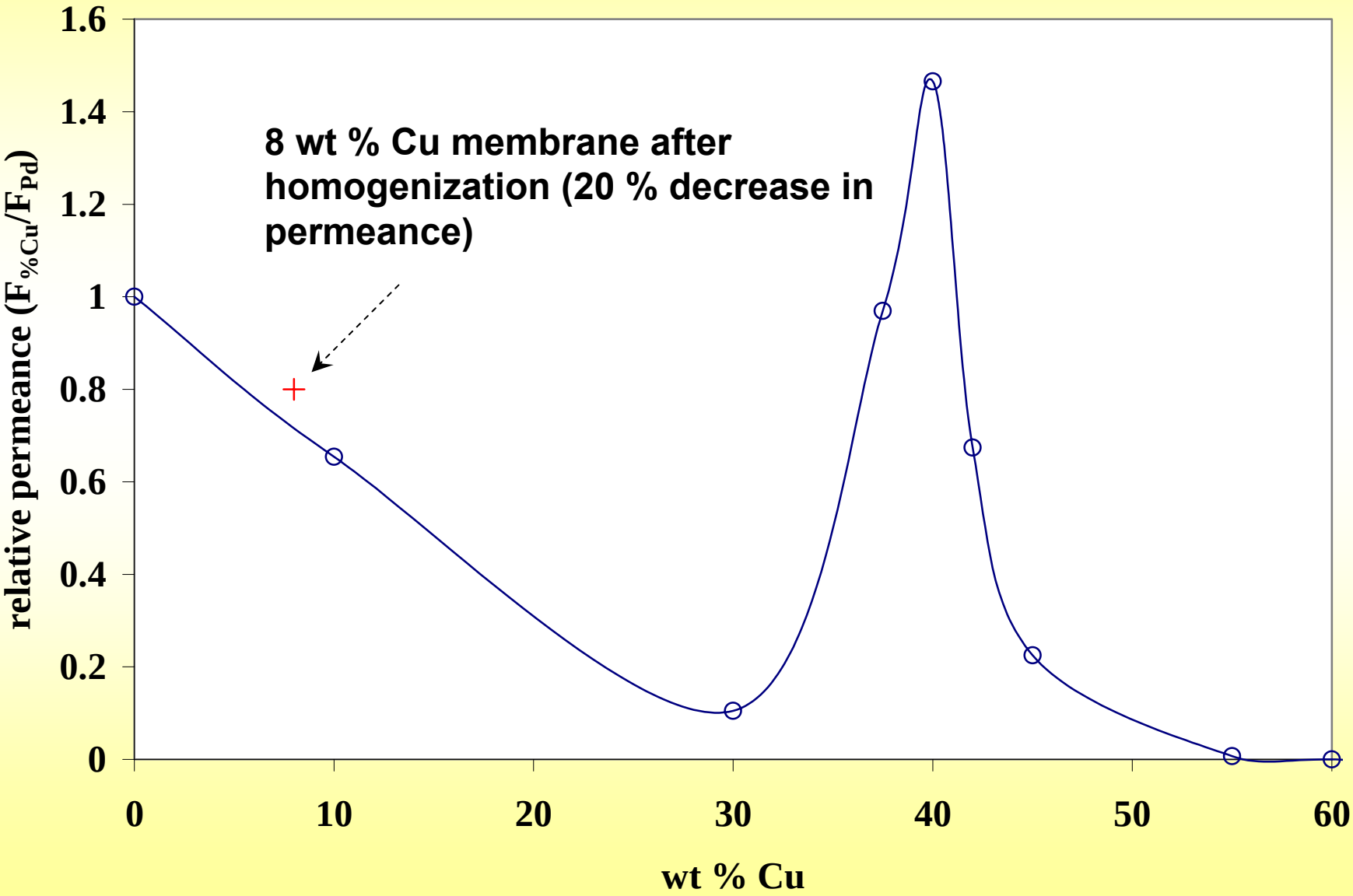
Permeability of 8 wt % lower than homogeneous counterpart: mass transfer resistance



Permeance @ 500 °C

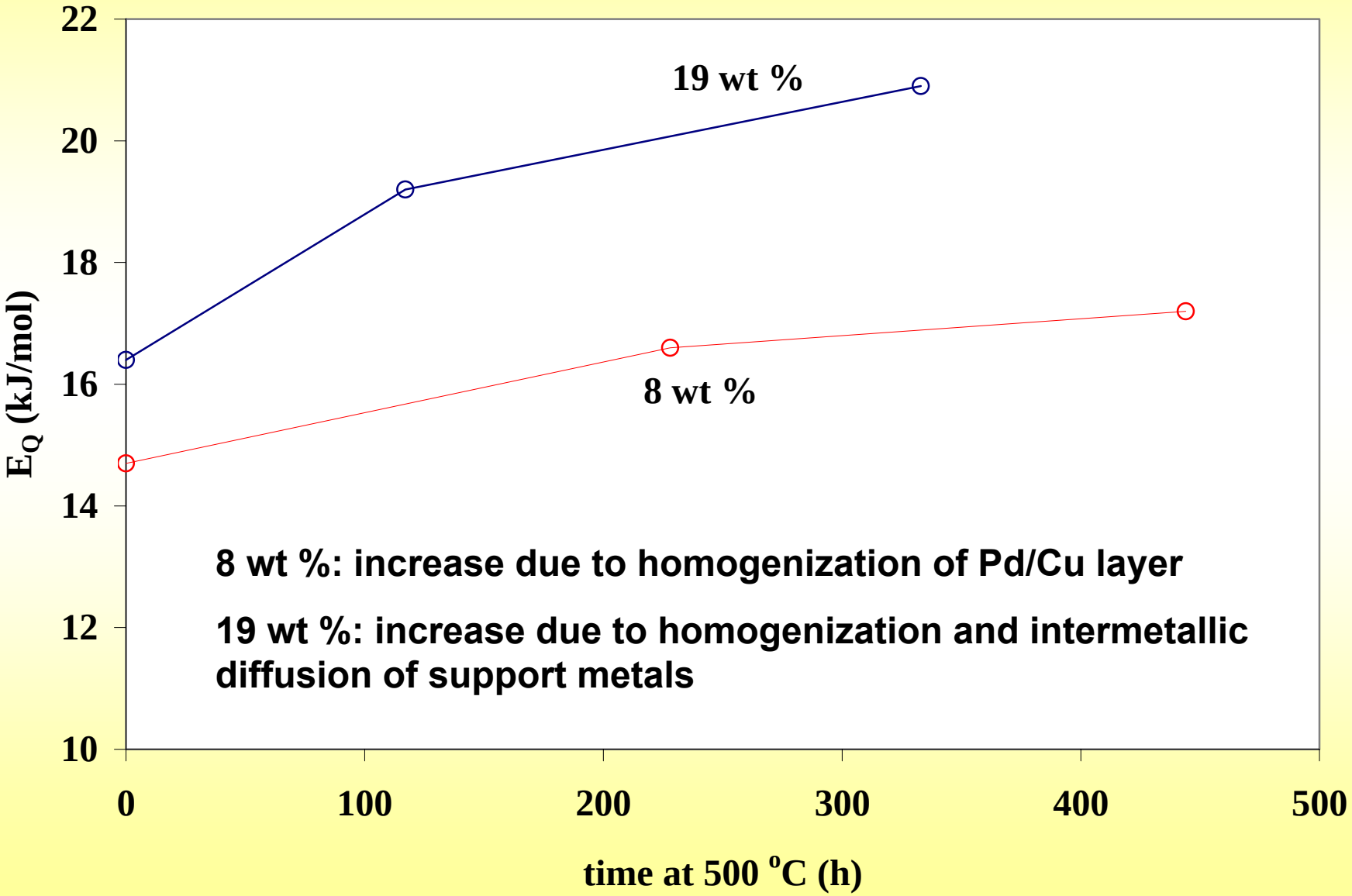


Permeance and % Cu @ 350 °C

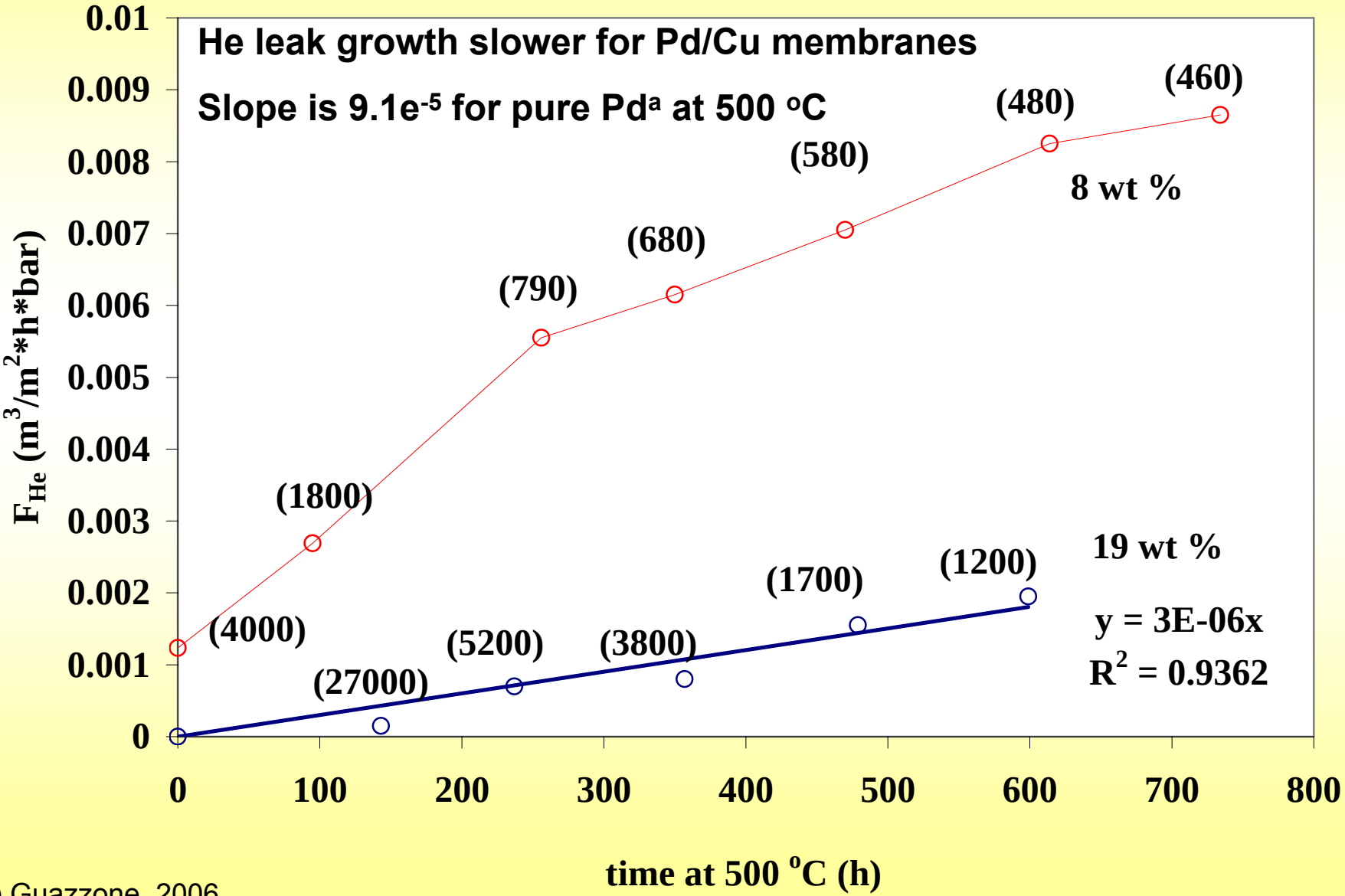


McKinley and Nitro, 1969

Activation energy @ 500 °C



He leak growth

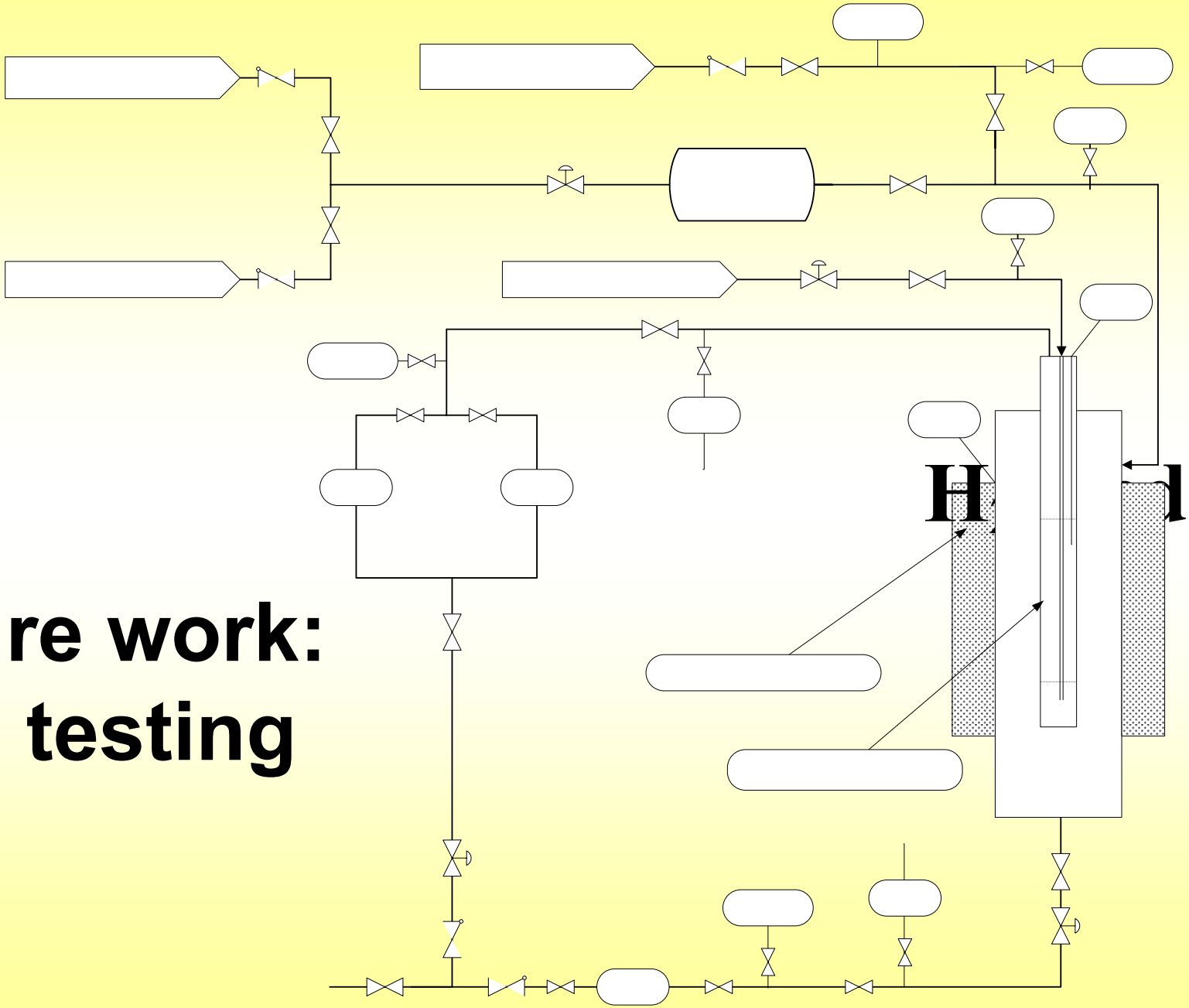


a) Guazzone, 2006

Conclusions

- FCC structure on surface is formed after 5 – 10 hours of annealing at 500 ^{o}C, Pd/Cu membranes easy to fabricate
- Cu gradient changes significantly at 500 ^{o}C
- 0.5 μm Ru is not effective as an intermetallic diffusion barrier
- Supports add mass transfer resistance
- Selectivity of Pd/Cu membranes is high at 500 ^{o}C, 1200 after 600 h for the 19 % wt and leak growth appears to level off for the 8 % wt

Future work: H_2S testing



H_2S test system

Future work, cont.

- Characterization of new thinner Pd/Cu membranes with higher permeances
- Characterization of Pd membranes with thin layer of Au, Ru or Pt on surface
- Testing H_2S resistance of all of these membranes