Composite Pd and Pd/alloy Porous Stainless Steel Membranes for Hydrogen Production, Process Intensification and CO_2 Sequestration

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OUTLINE

- Objectives
- Membrane Synthesis
- Membrane Performance Evaluation
- Effects of Contaminant (H_2S) on Membrane Performance
- Mathematical Modeling for Process Intensification
- Conclusions and Challenges

OBJECTIVES

- Synthesis of composite Pd and Pd/alloy membranes with long term durability
- Membranes with resistant to contaminants (H_2S)
- Long term tests to demonstrate the durability
- Mathematical modeling for process intensification

MEMBRANE SYNTHESIS

- **Formation of Intermetallic diffusion barrier layers**

  In situ controlled oxidation (US Pat. 6,152,987)

  Bi-metal multi-layer (BMML) electroless deposition (US Pat. 7,175,694)

  - **Initiation of the porous structure by EP of Ag first followed by Pd**
  - **Formation of a porous layer by alternating EP of Ag and Pd**
- **Formation of Pd membrane by electroless plating**
- **Formation of Pd/Cu membrane by sequential electroless plating followed by annealing**
- **Formation of Pd/Au membrane by electroless plating of Pd followed by galvanic displacement followed by annealing**

TYPICAL PLATING SOLUTIONS COMPOSITION FOR Pd/Ag-PSS COMPOSITE

- **Pd Plating Solution**

$(Pd(NH_3)_4Cl_2 * H_20$	4.0 g/l
Na_2EDTA	40.1 g/l
NH_4OH (28%)	198 ml/l

Reducing agent (H_2NNH_2)

Adjustable

- **Ag Plating Solution**

$AgNO_3$	0.519 g/l
Na_2EDTA	40.1 g/l
NH_4OH (28%)	198 ml/l

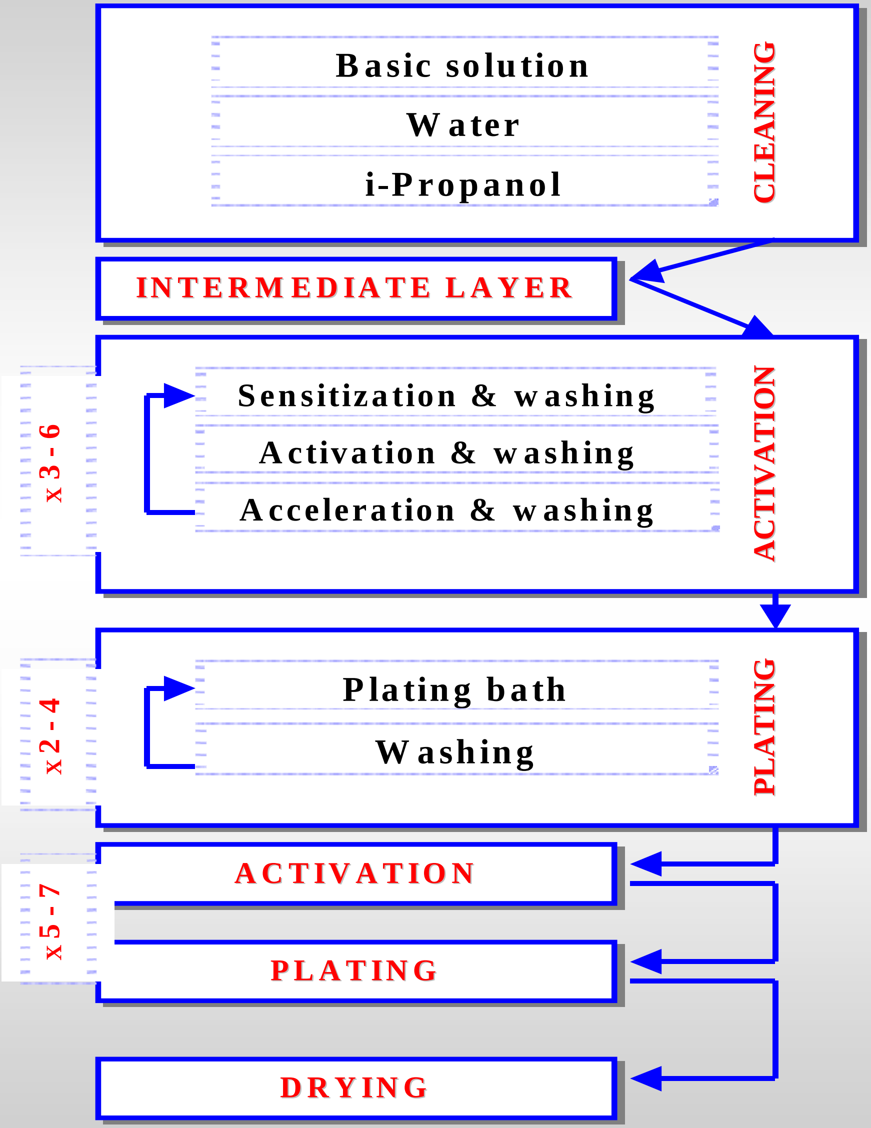
Reducing agent (H_2NNH_2)

Constant

(5.6 ml/l)

Pd deposition procedure by the electroless plating technique

(US Patent 6152987, issue date November 28, 2000



NECESSARY INGREDIENT IN AN ELECTROLESS PLATING SOLUTION

- **Reducing Agent**
  Hydrazine
- **Stabilizing Agent**
  EDTA (Ethylene diamine tetraacetic acid) Salt
- **Plating Agent**
  Palladium Tetramine Chloride
  $[Pd(NH_3)_4Cl_2 \bullet H_2O]$

$$2Pd^{2+} + H_2NNH_2 + 4OH^- = 2Pd^0 + N_2 + 4H_2O$$

ELECTROLESS Pd-PLATING BATH

$Pd(NH_3)Cl_2 \bullet H_2O$, g/l	4.0
NH_4OH (28%),ml/l	198
Na_2EDTA, g/l	40.1
H_2NNH_2 (1 M), ml/l	5.6 – 7.6
pH	~10.4
TEMPERATURE, ^0C	60
$V_{SOLUTION}/S_{PLATING\ AREA}$, cm^3/cm^2	~3.5

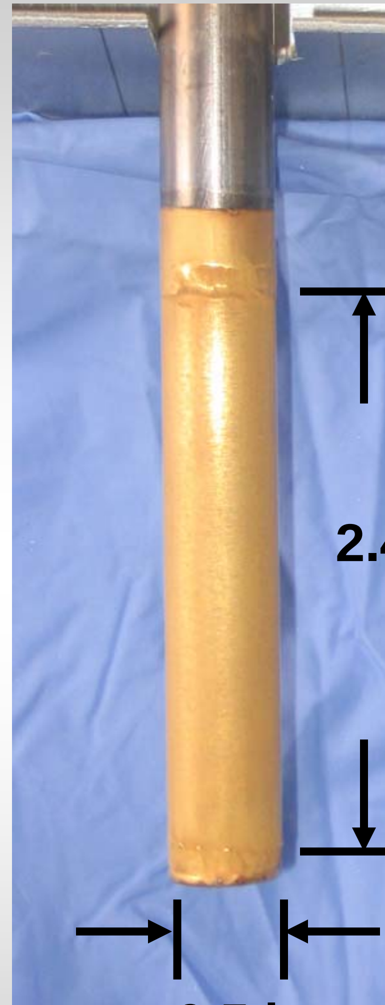
APPEARANCE OF THE MEMBRANES

Thickness:17.5μm

Au content: 2.5~5 wt%

Thickness:16.4μm

Au content: 5~7.5 wt%



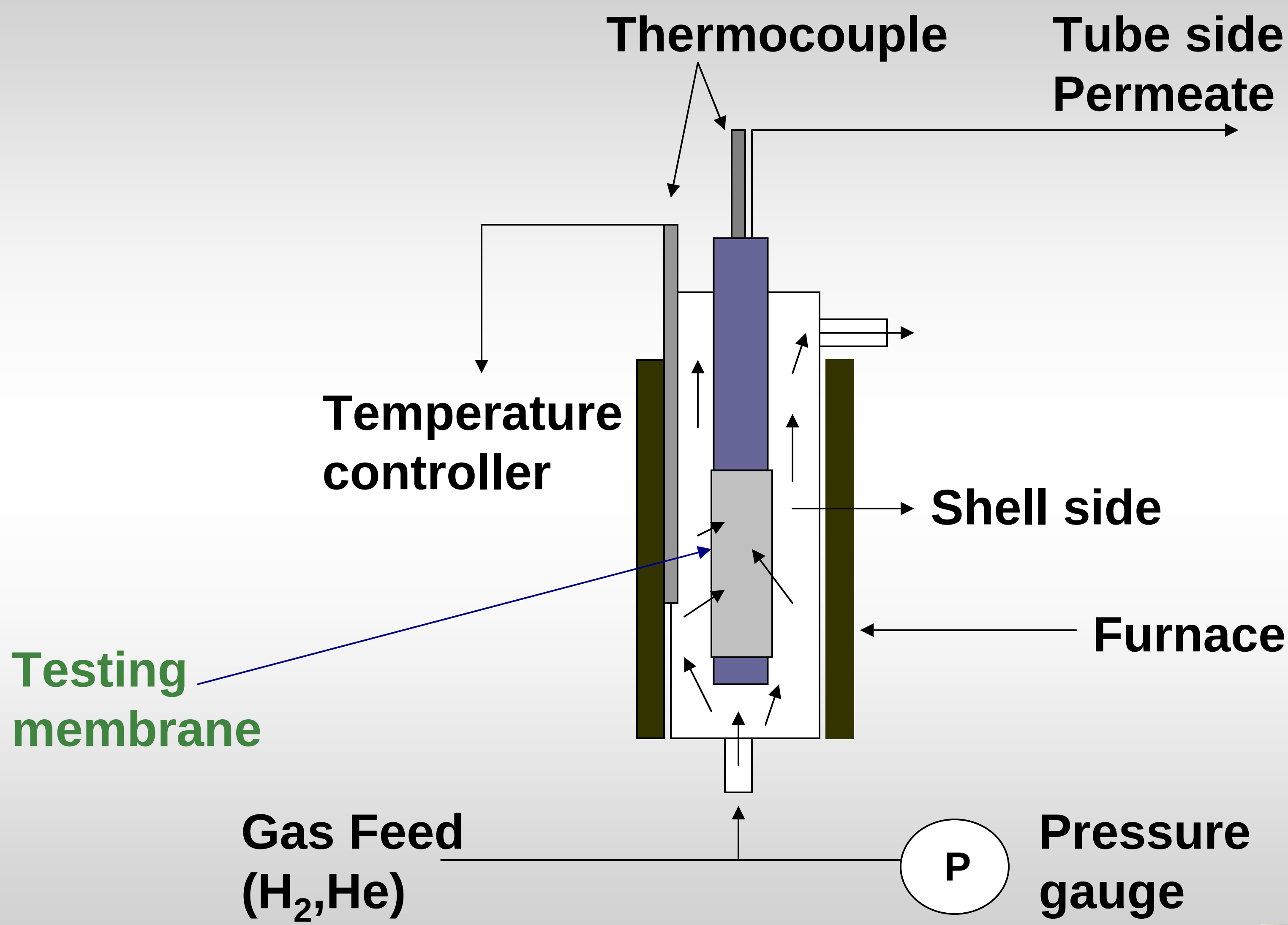
2.4 in

0.5 in

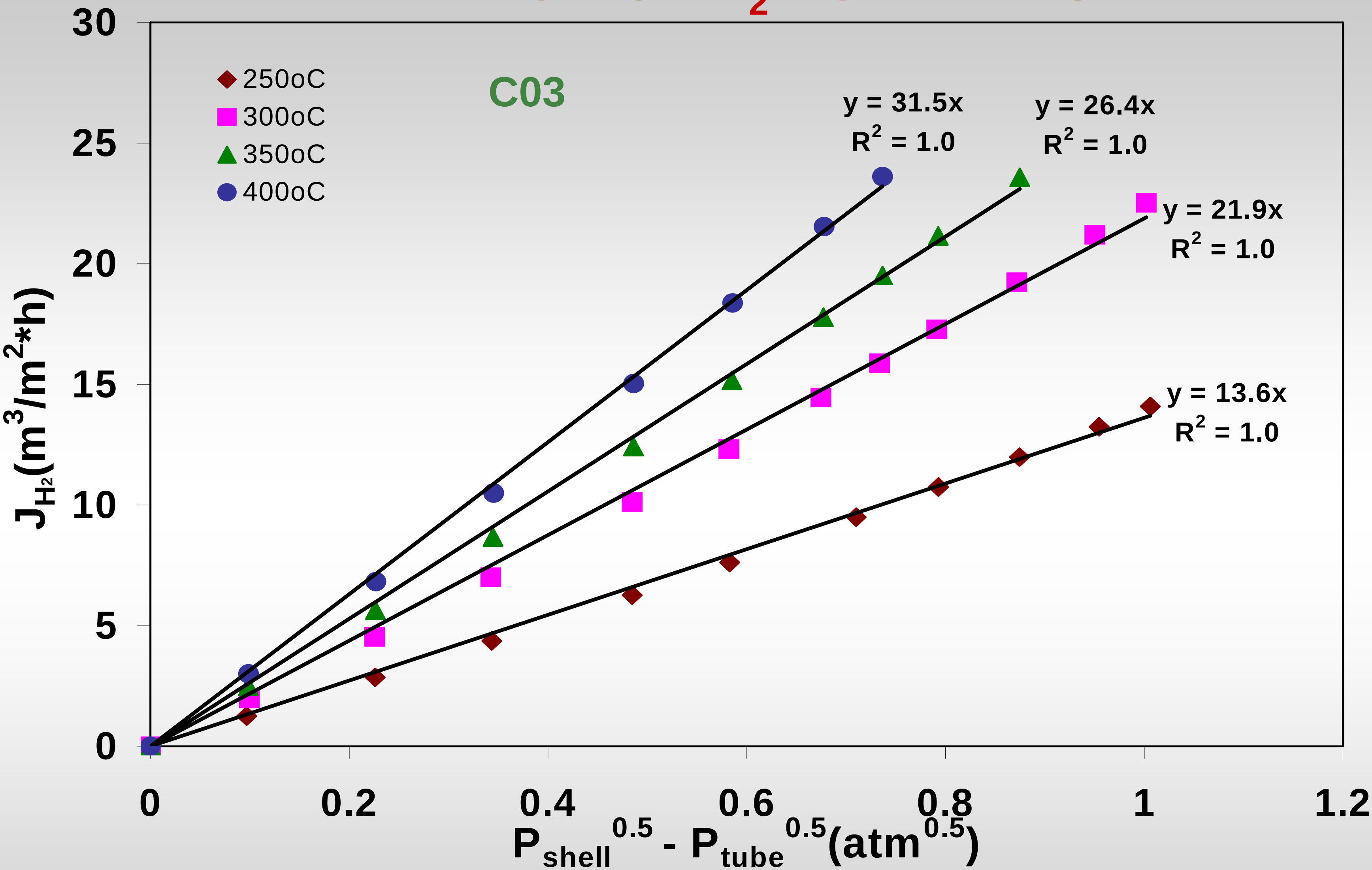
C03

C05

Experimental—Permeating test system

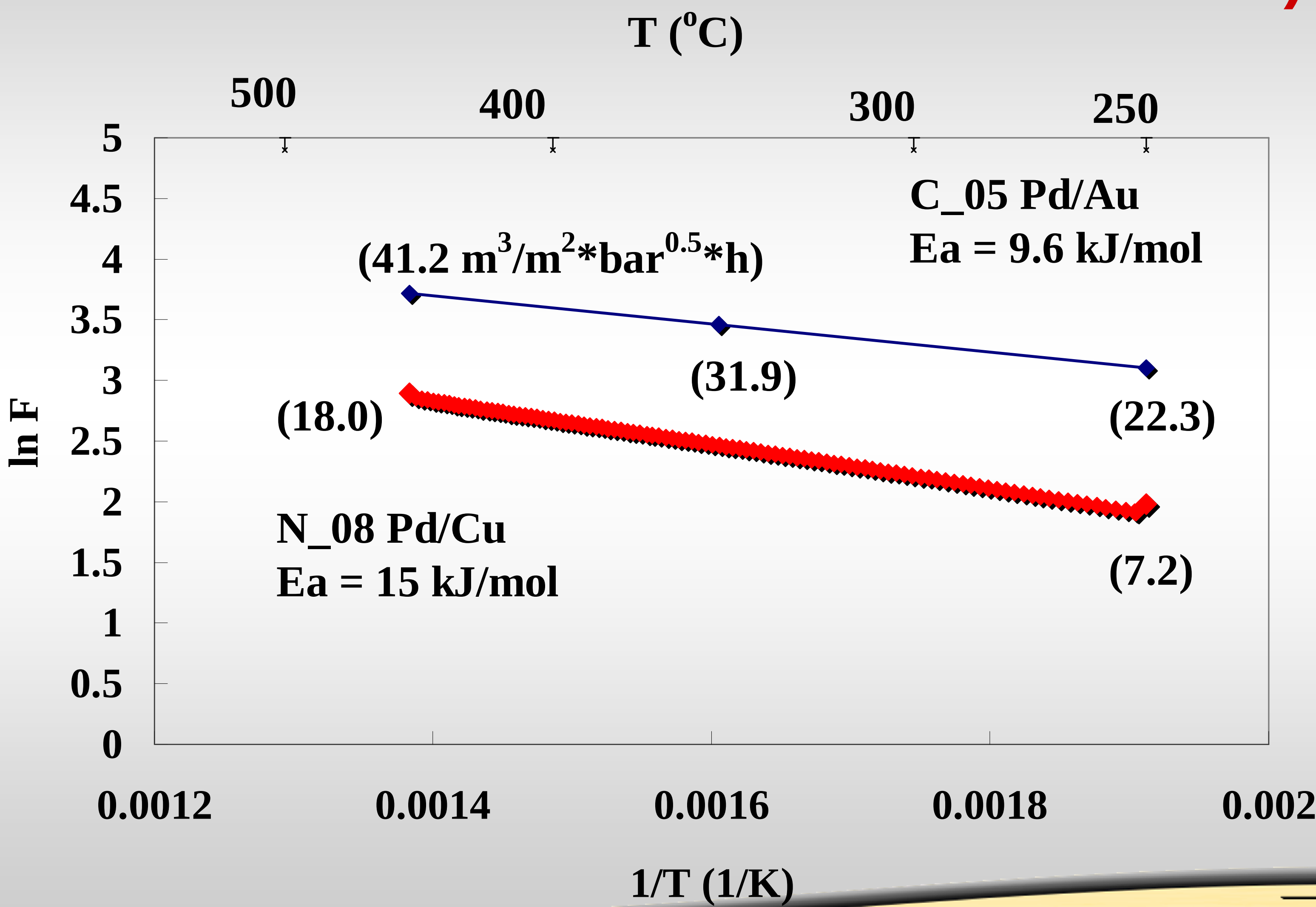


PERMEATION OF H_2 – SIEVERTS' LAW



$$J_{H_2} = F_{H_2}\left(P_{H_2,shell}^{0.5} - P_{H_2,tube}^{0.5}\right)$$

ACTIVATION ENERGY OF PERMEATION (H_2 PERMEANCE VALUES IN PARENTHESES)



WPI

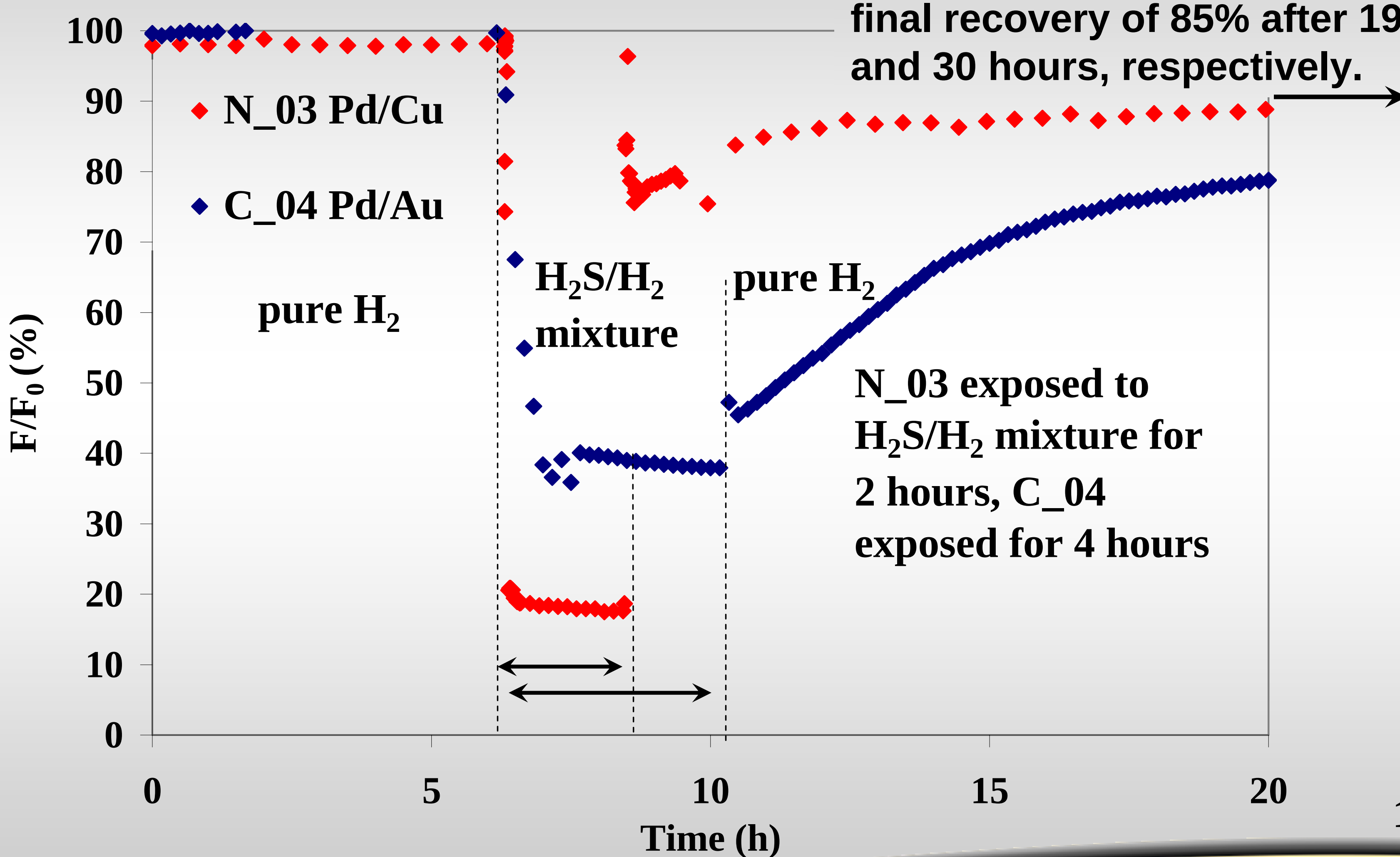
PERFORMANCE SUMMARY OF C03

T (°C)	H_2 flux (m^3/m^2*h)	He flux sccm	H_2/He Selectivity	H_2 permeance ($m^3/m^2*h*atm$)	H_2 (film) permeance ($m^3/m^2*h*atm$)	H_2 (pure Pd) permeance ($m^3/m^2*h*atm$)
250	5.6	0.42	546	13.1	14.3	9.9
300	8.7	0.45	801	20.8	23.1	13.6
350	10.6	0.47	[illegible]	[illegible]	28.9	17.7
400	12.8	0.6[illegible]	[illegible]	[illegible]	34.5	22.1
Ea (kJ/mole)				12.7	12.9	15.6

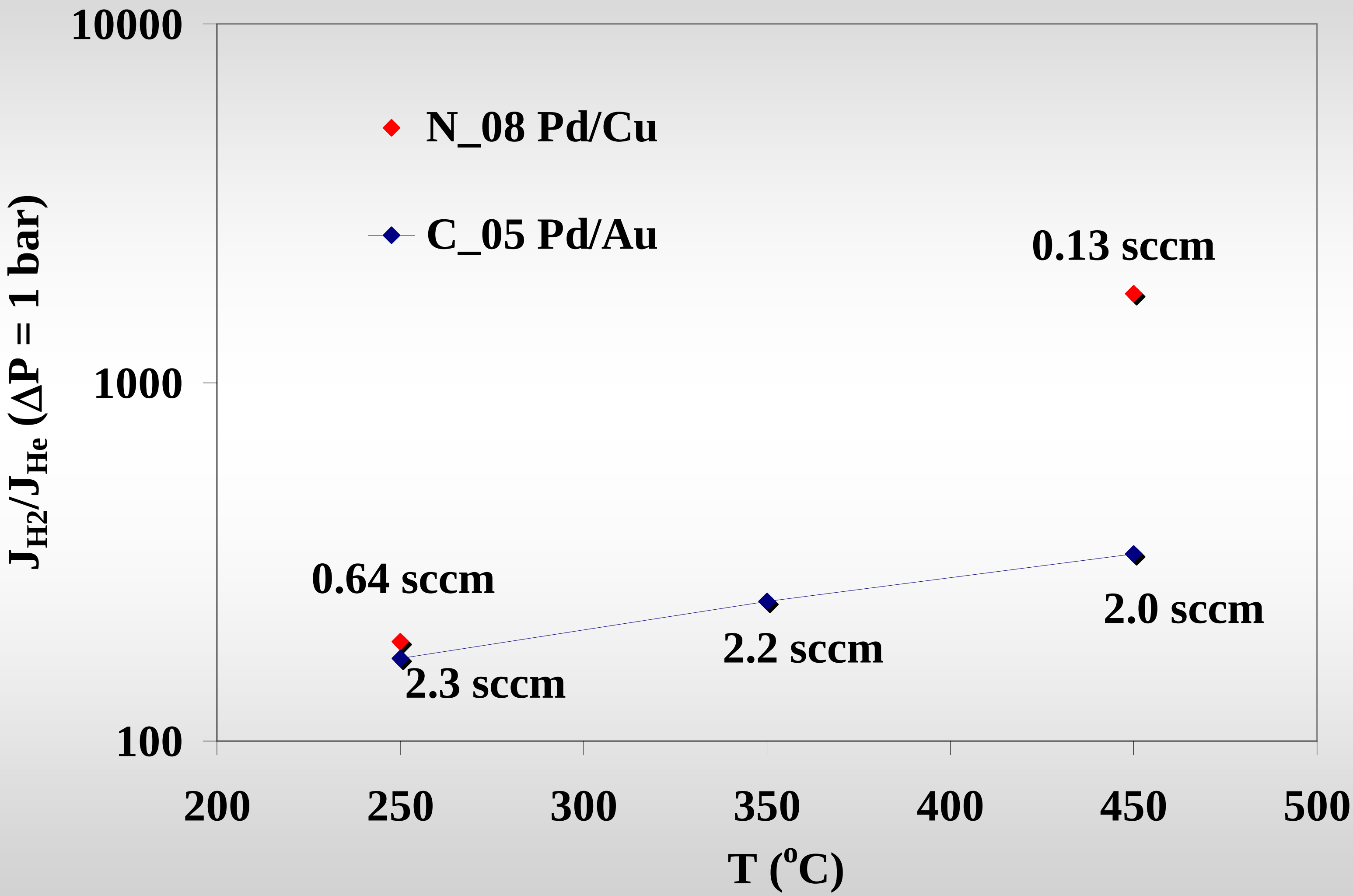
50 % higher H_2 permeance, and lower Ea

POISONING/RECOVERY CYCLE AT 500ºC

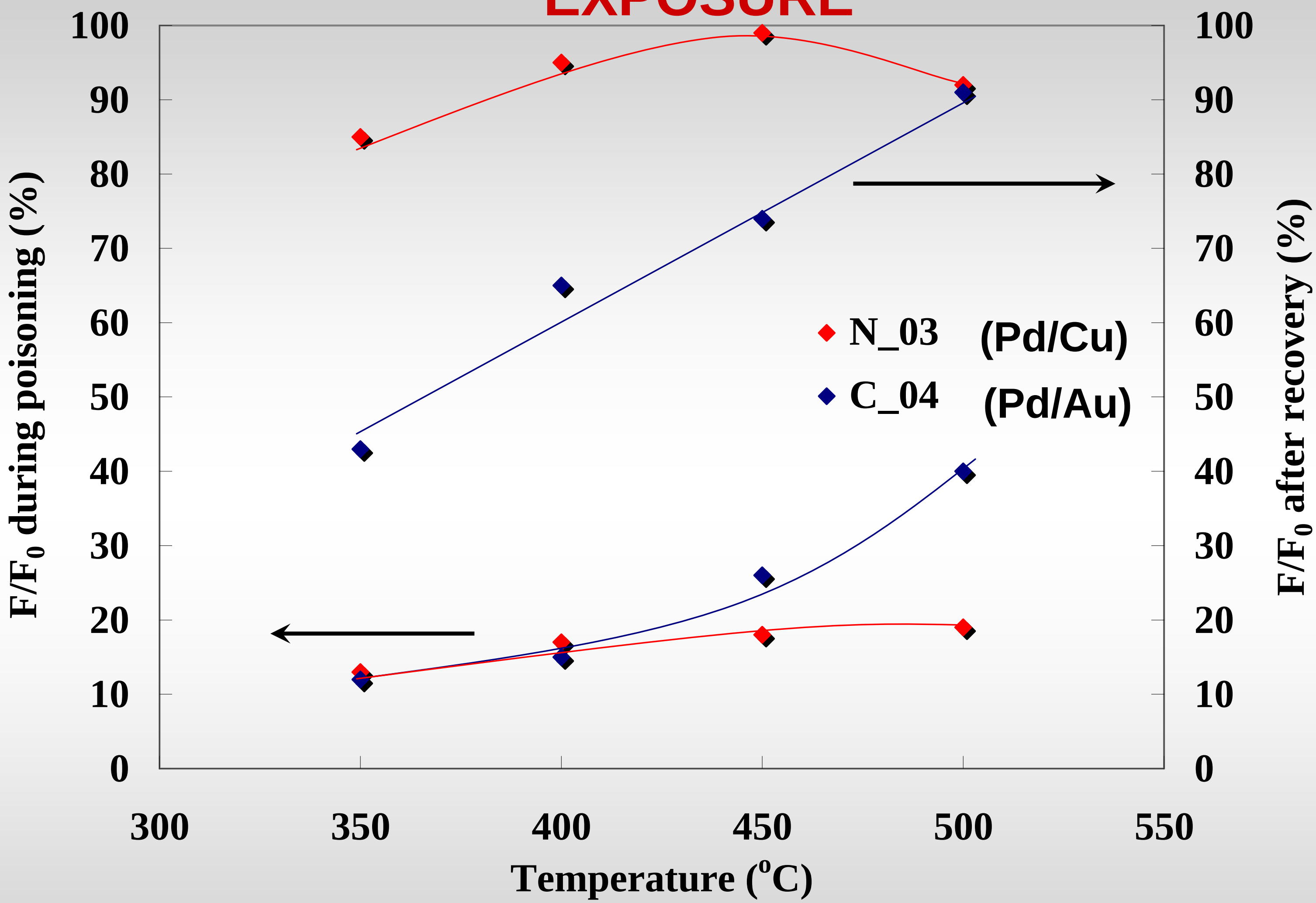
N_03 and C_04 reached a final recovery of 85% after 19 and 30 hours, respectively.



H_2/He IDEAL SELECTIVITY



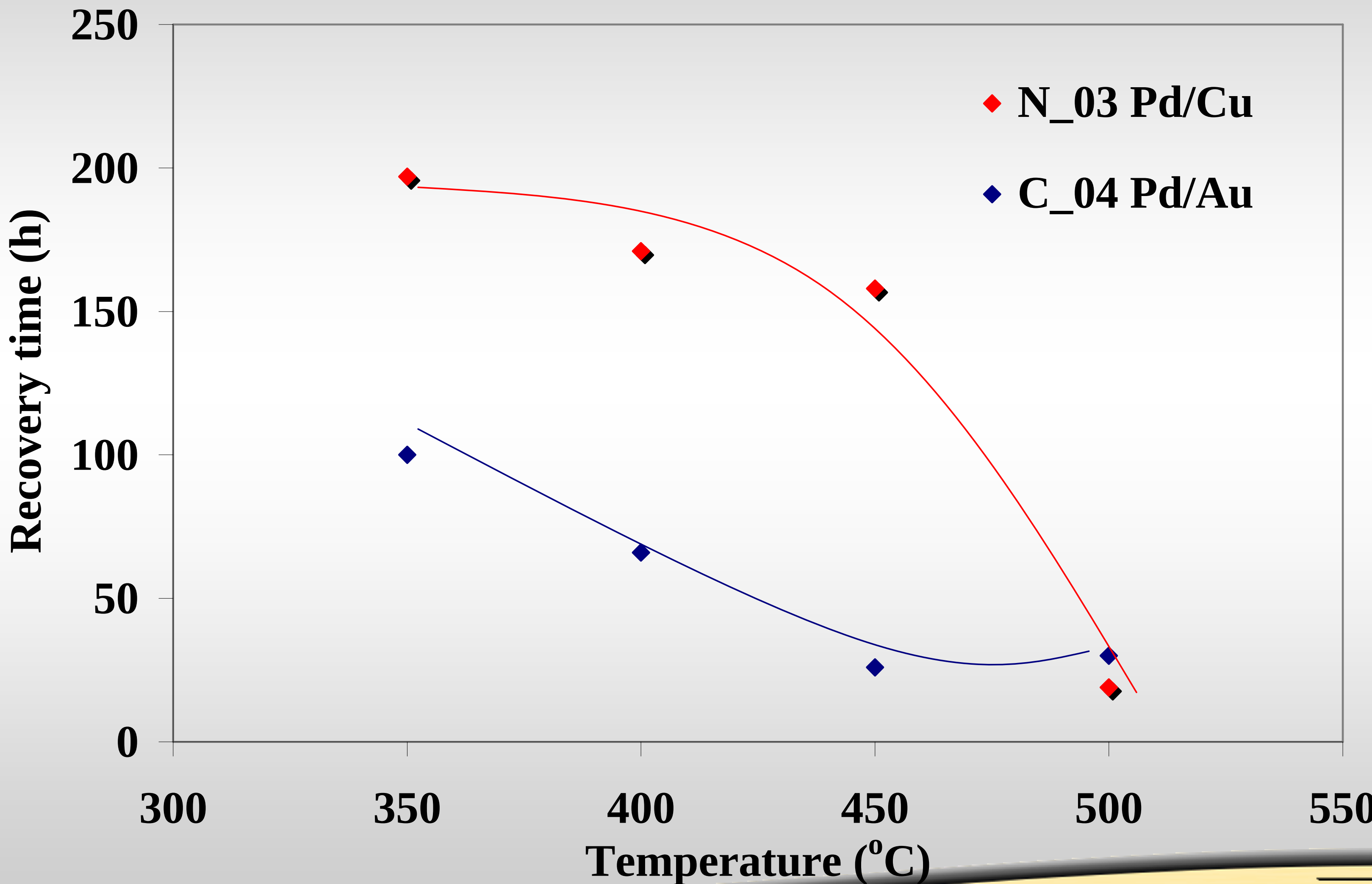
PERMEANCE DECLINE AND RECOVERY AFTER H_2S EXPOSURE



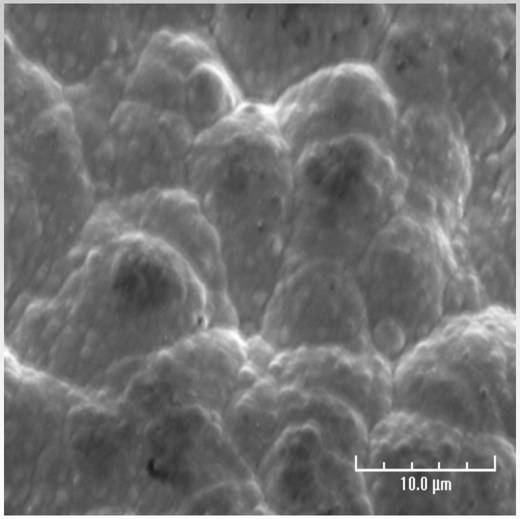
N_03 and C_04 were exposed to the H_2S/H_2 mixture for 2 and 4 hour intervals, respectively, at each temperature.

Recovery time

Recovery time was defined as the time at which the H_2 permeance ceased to increase.



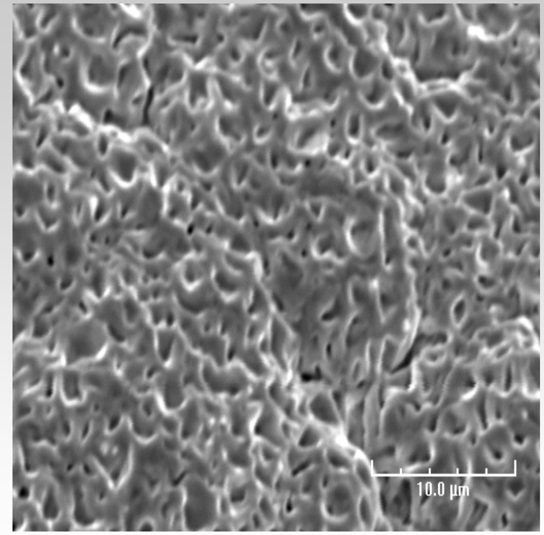
SURFACE MORPHOLOGY OF PURE PD AFTER H_2S POISONING FOR 24 HOURS (3KX)



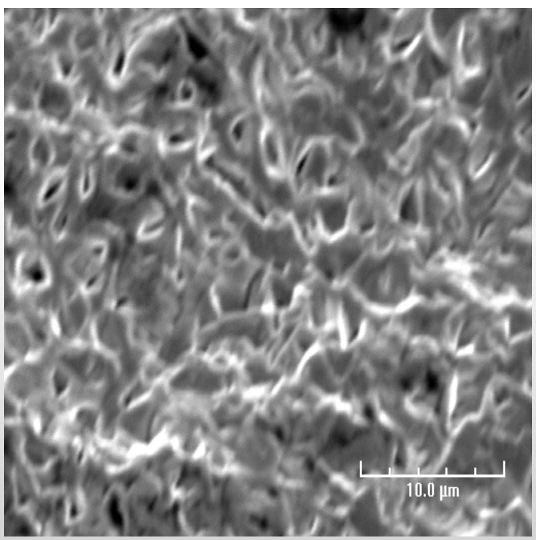
Before poisoning

After poisoning

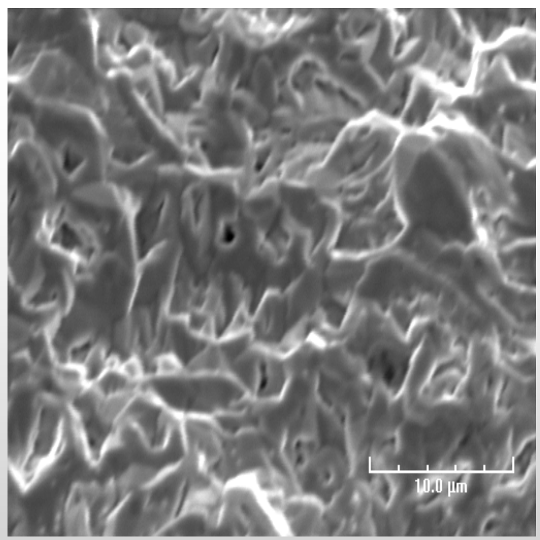
Pure Pd S : 0.31 wt%



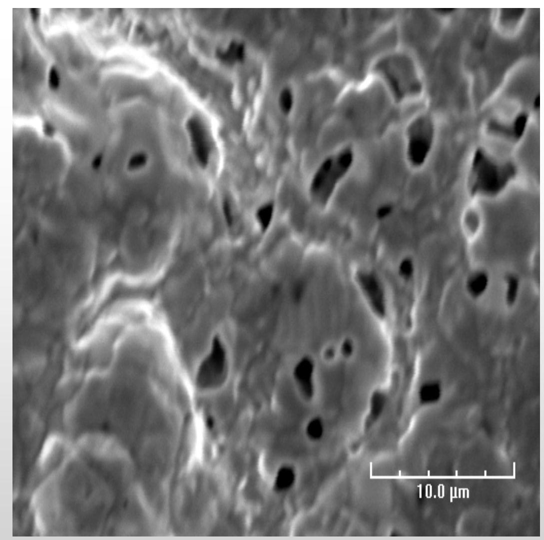
350°C S : 4.09 wt%



400°C S : 4.13 wt%



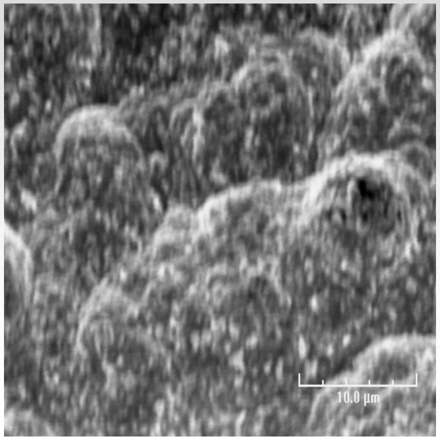
450°C S : 3.69 wt%

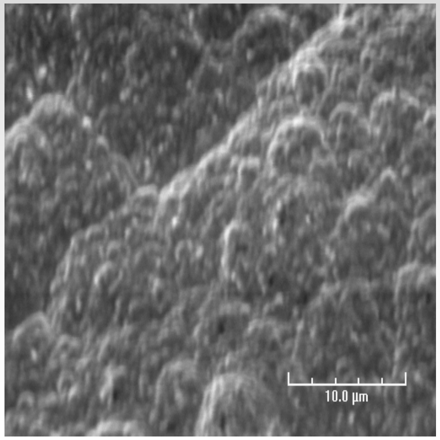


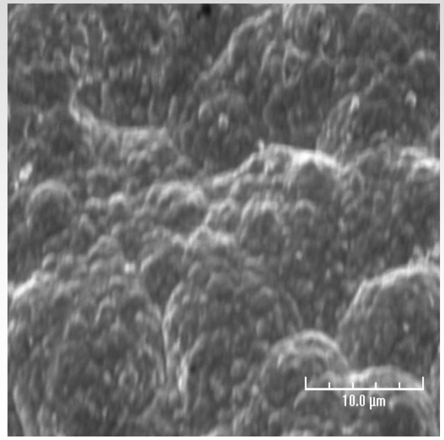
500°C S : 0.01wt%

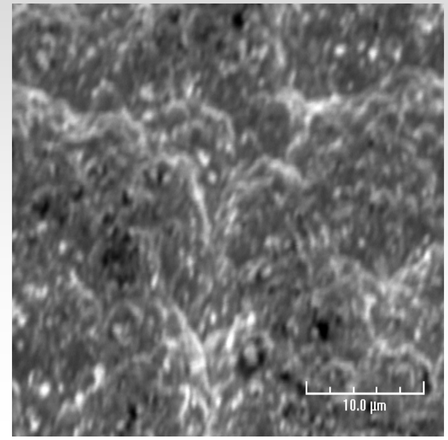
SURFACE MORPHOLOGY OF Pd/Au ALLOYS WITH ~10WT% Au AFTER H_2S POISONING FOR 24 HOURS (B=BEFORE, A=AFTER, MAGNIFICATION: 3KX)

350°C **400°C** **450°C** **500°C**



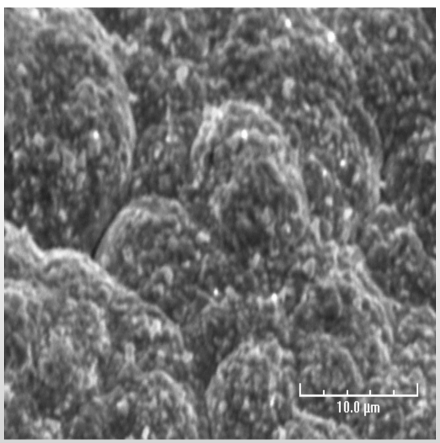


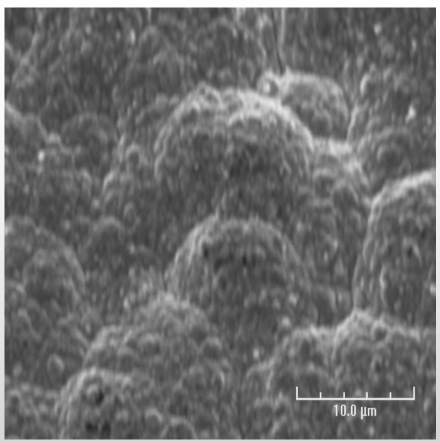


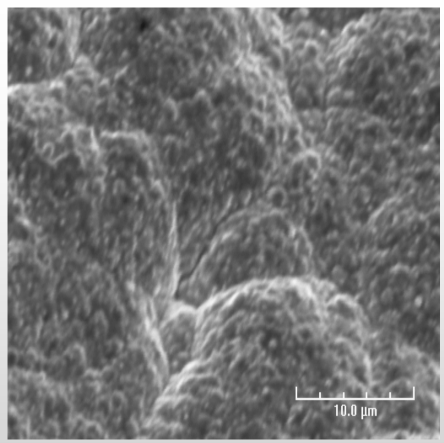


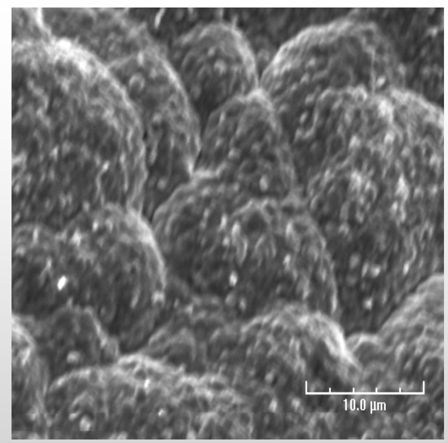
B

S: 0.36 wt% **S: 0.36 wt%** **S: 0.1 wt%** **S: 0.36 wt%**





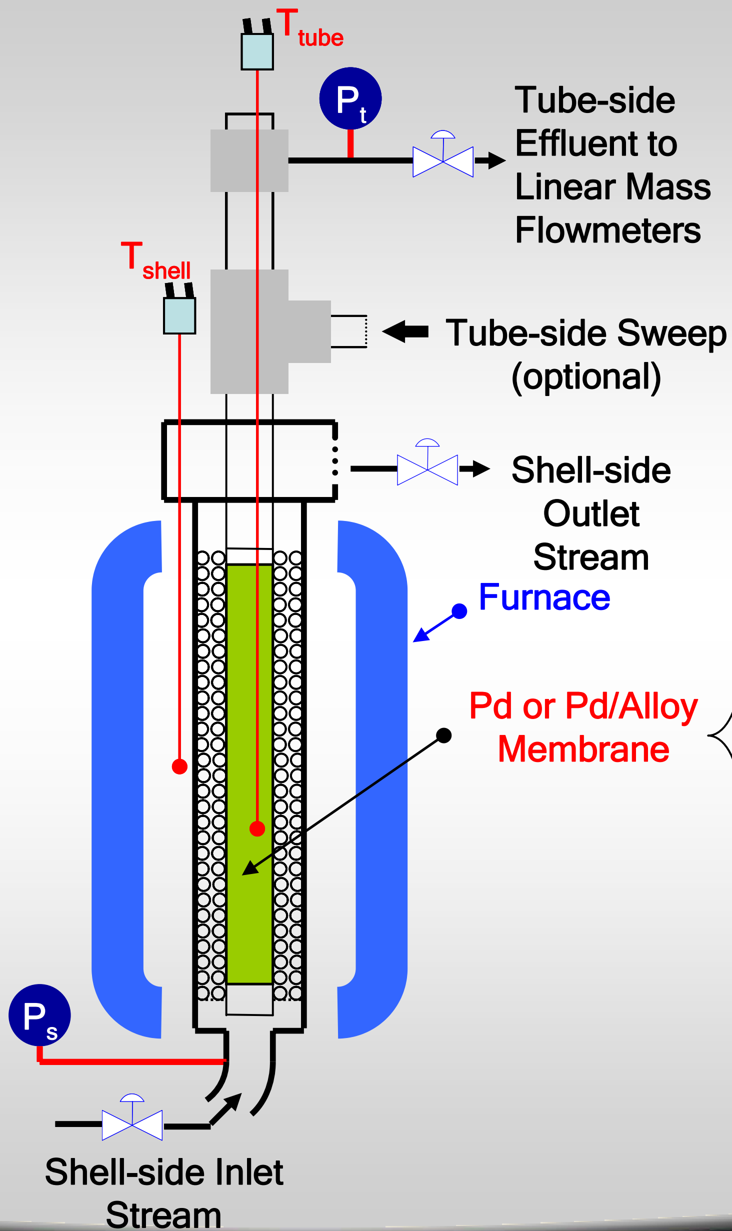




A

S: 0.09 wt% **S: 0.09 wt%** **S: 0.04 wt%** **S: 0.05 wt%**

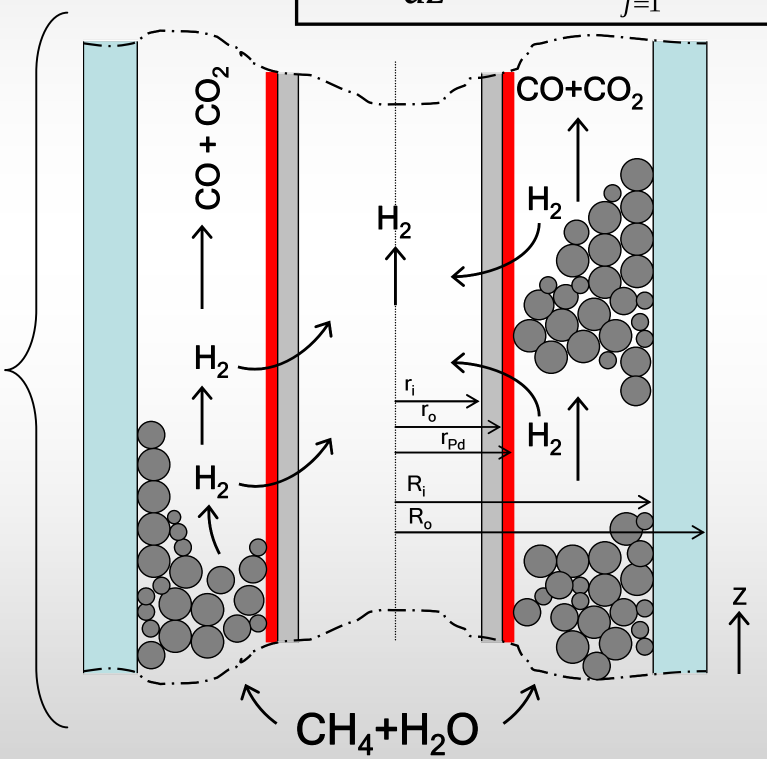
MEMBRANE REACTOR SCHEMATIC



PBR/MR Design Equation:

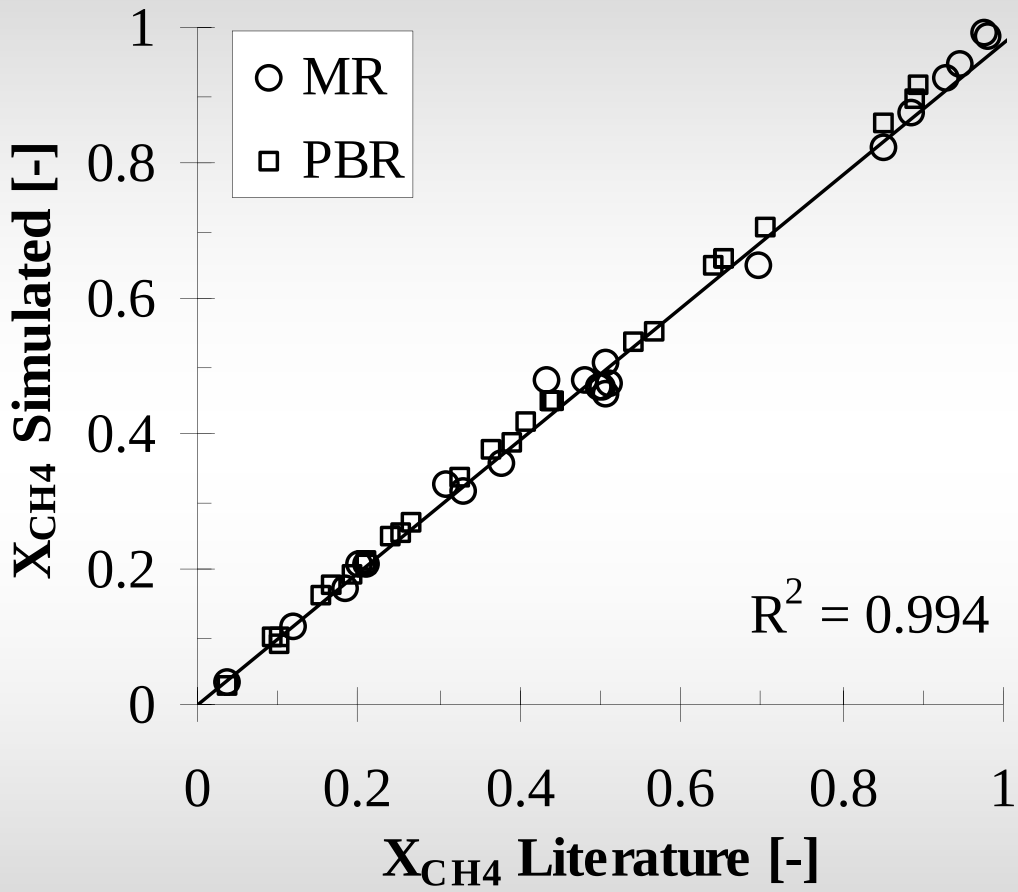
$$\frac{dF_i}{dW} = r_i' - J_i \rightarrow F_{i_0}\frac{dX_i}{dW} = \sum_{j=1}^{n}\eta_j r_{ij} - J_i$$

$$F_{i_0}\frac{dX_i}{dz} = \rho_B A_c \sum_{j=1}^{n}\eta_j r_{ij} - J_i$$

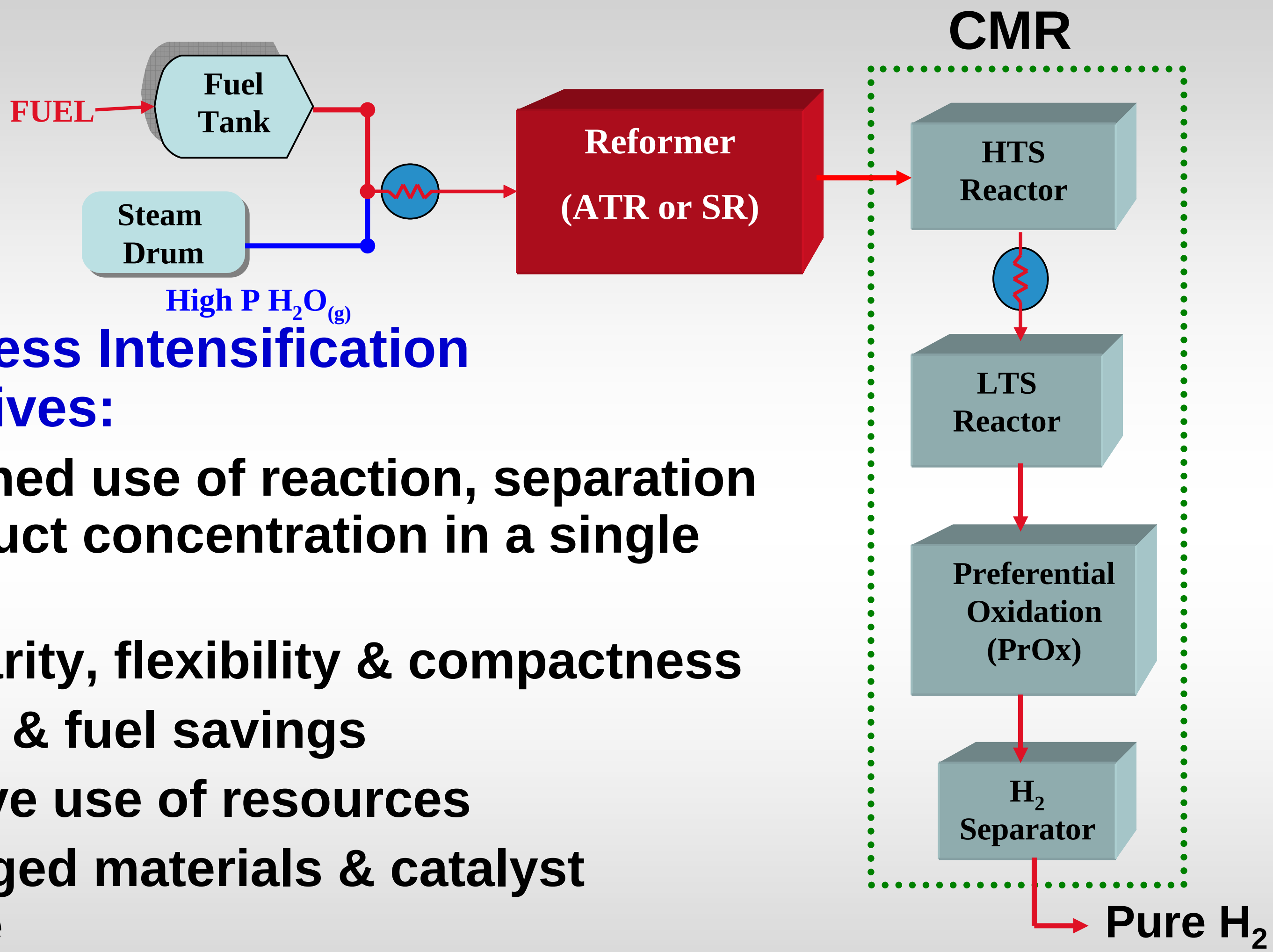


MODEL VALIDATION: LITERATURE BENCHMARKING

- **Xu & Froment, `89**
- **Matzakos *et al.*, `04**
- **Assaf *et al.*, `98**
- **Shu *et al.*, `94**
- **Oertel *et al.*, `87**
- **Hoang *et al.*, `05**
- **Hou & Hughes, `01**
- **Oklany *et al.*, `98**
- **Jorgensen *et al.*, `95**



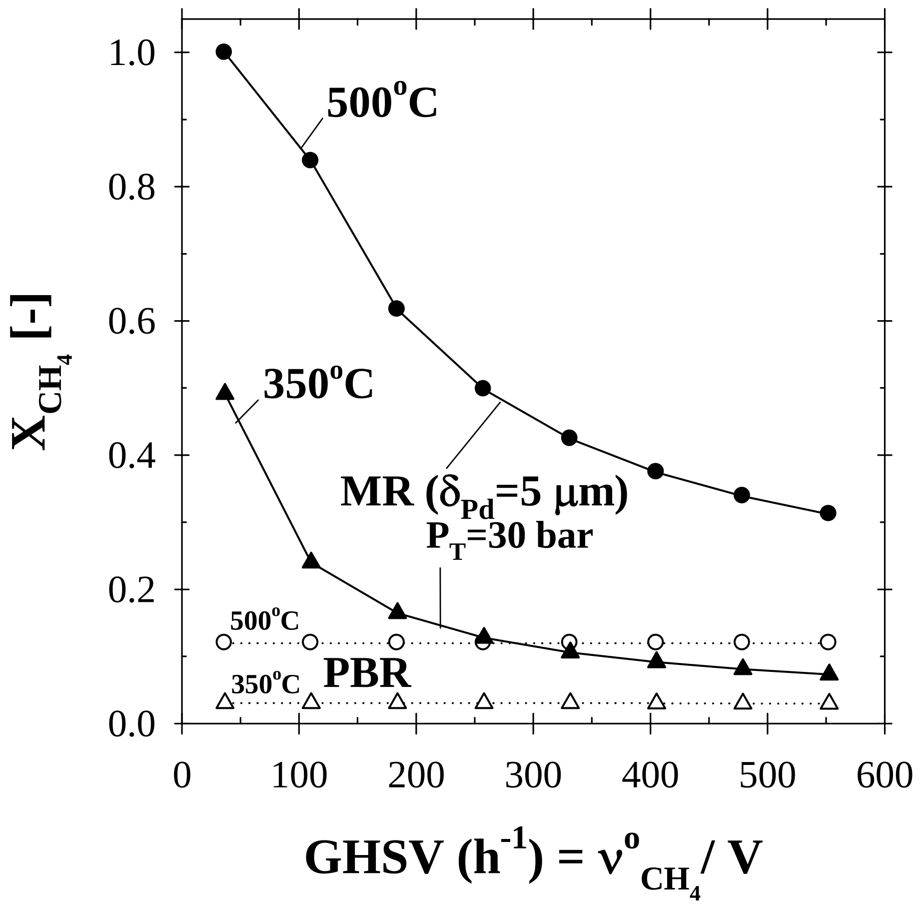
FUEL PROCESSOR FOR H_2 PRODUCTION

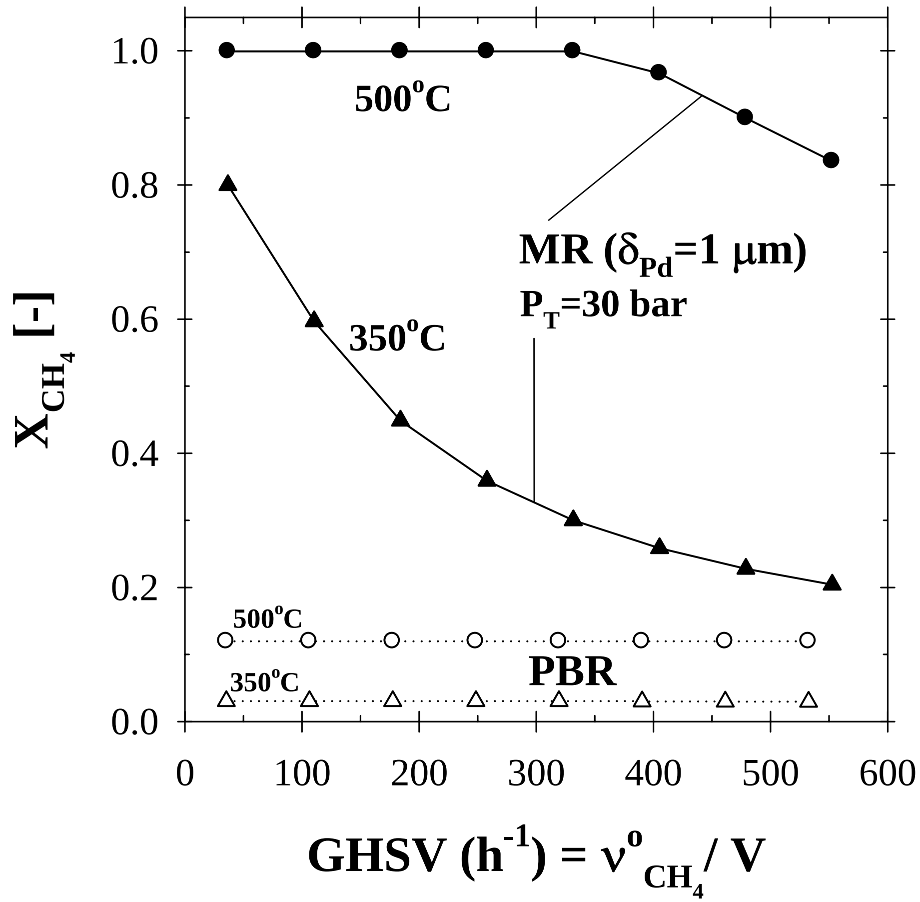


Key Process Intensification Objectives:

- Combined use of reaction, separation & product concentration in a single unit
- Modularity, flexibility & compactness
- Energy & fuel savings
- Effective use of resources
- Prolonged materials & catalyst lifetime
- High pressure CO_2 with good purity for sequestration

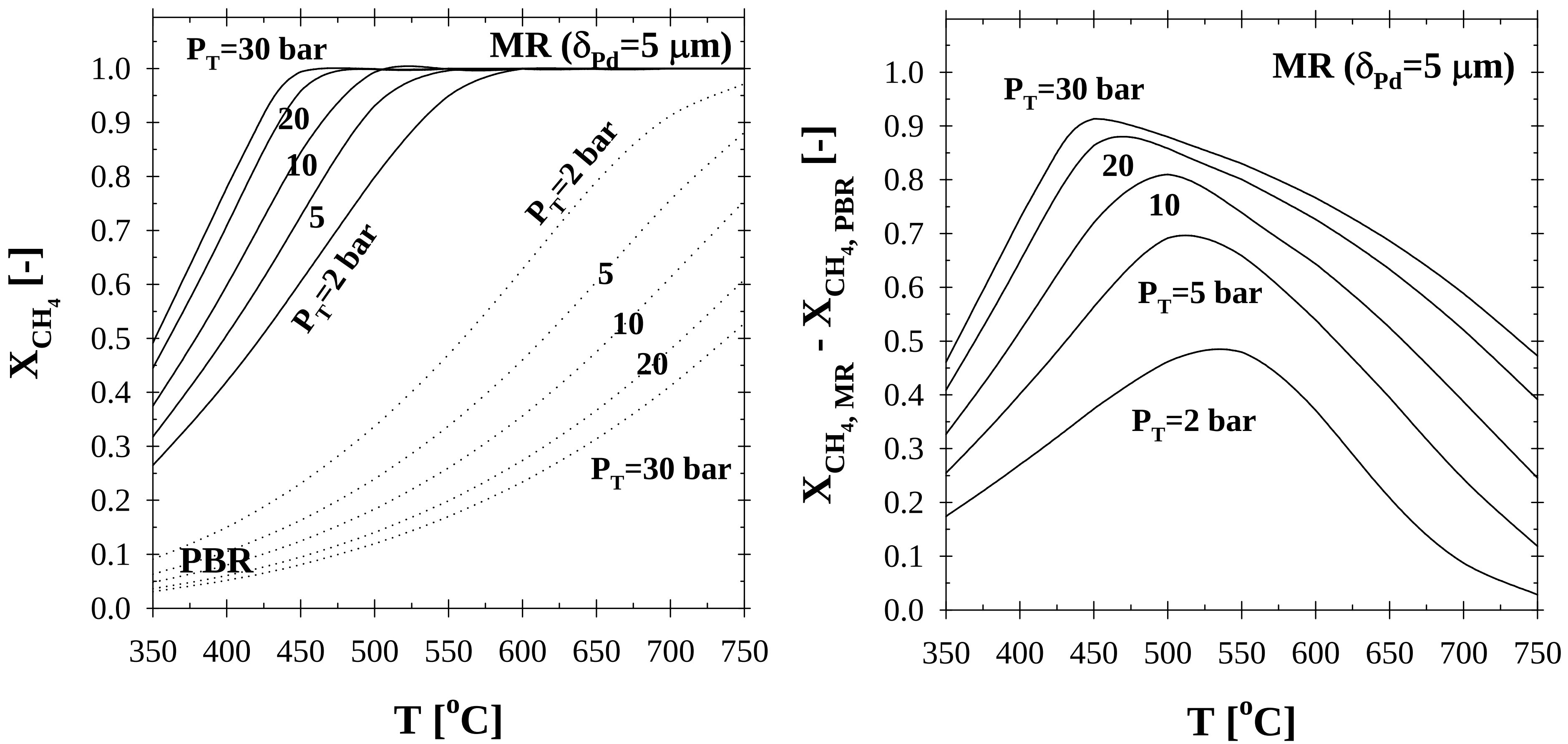
Gas Hourly Space Velocity (GHSV)





Higher X_{CH4} could be maintained even at noticeably high GHSV values.

CONVERSION INDEX



Maximum performance is achieved via the Membrane reactor (MR) at lower temperatures and high pressures.

CONCLUSIONS AND CHALLENGES

Conclusions

- H_2S exposure caused flux decrease for both Pd/Au and Pd/Cu membranes
- Lower reduction in fluxes at higher temperatures
- Flux recovery possible at higher temperatures
- Maximum benefits achieved at low temperature and high pressure from modeling and process intensification computation

Challenges

- Homogenization of Pd-rich alloys at lower temperatures
- Development of other alloys for sulfur resistant membranes
- Development of catalysts with good reforming activity at lower temperatures

ACKNOWLEDGEMENT

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  Project Officer: Dr. Arun Bose, NETL

  Oak Ridge National Laboratory, Oak Ridge, TN

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  Project Officer: Dr. Daniel Driscoll, NETL