NCA&TSU

Reforming of Liquid Hydrocarbons in a Novel Hydrogen-selective Membrane-based Fuel Processor

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Meet NCATSU

David Richmond, Franklin McCain, Ezell Blair, Jr. (Jibreel Khazan) and Joseph McNeil (from left): These four A&T freshmen envisioned and carried out the lunch counter sit-in of February 1, 1960 in downtown Greensboro. Their courageous act against social injustice inspired similar protests across the nation and is remembered as a defining moment in the struggle for civil rights.

Dr. Ron McNair Engineering Building

Presentation Outline

- Background
- Objectives
- H_2-selective Membrane Fabrication
  - H_2-Permselectivity Study
  - Membrane-Reactor Separator
- Conclusions
- Current and Future Work
- Acknowledgments

Background

- The availability and the affordability of high purity hydrogen is a major issue in industrial applications (Chemical Feed Stocks, Fuel for Fuel Cells)
- Conventional processes involve the use of reactors and separation units to produce this type of fuel.
- These processes are usually complex, energy intensive, and costly.
- Many of the industrially important reforming or dehydrogenation reactions for production of hydrogen are thermodynamically equilibrium limited that limit the productivity.

Need for High Purity Hydrogen

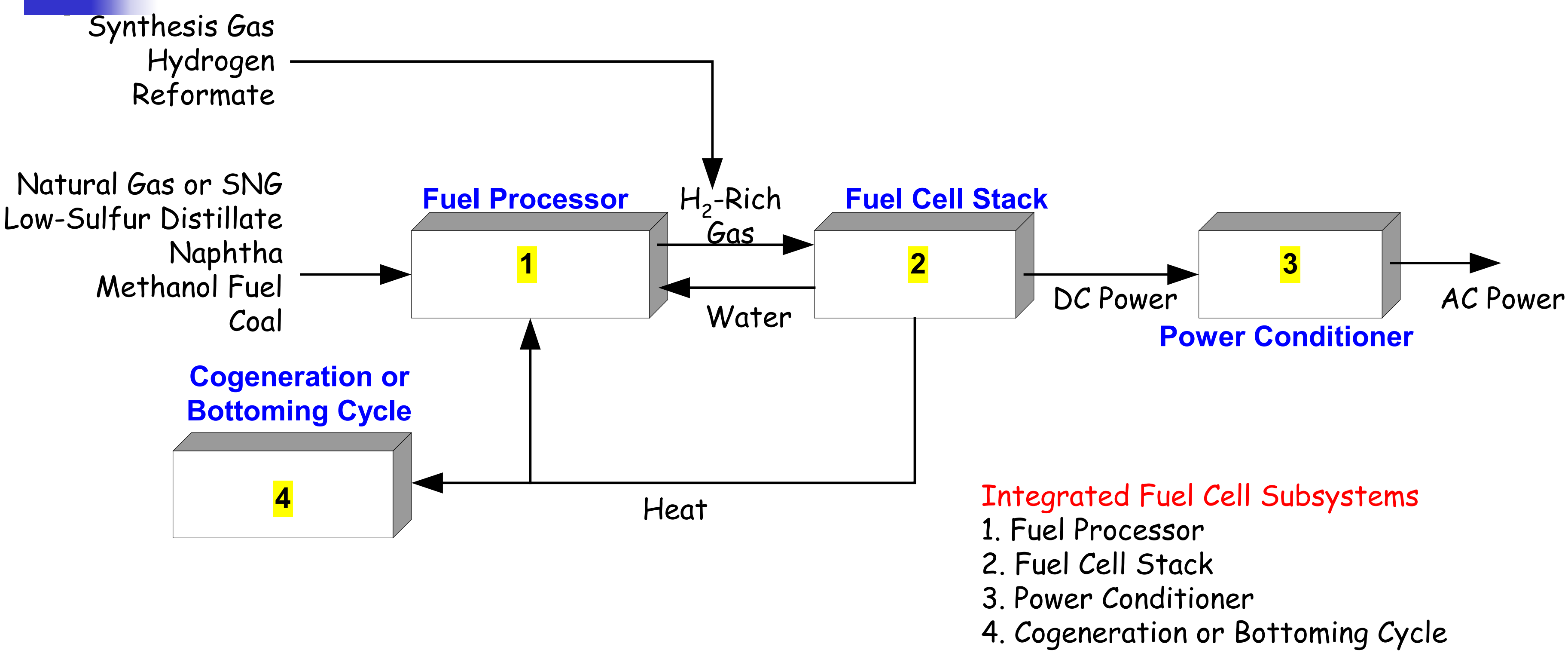


Fig: Fuel Cell System: Key Components

Proton Exchange Membrane Fuel Cell (PEMFC) is a major contender for Vehicular Market.

Major Issues:

- Availability and affordability of high purity hydrogen as fuel.
- Presence of CO (>10 ppm) and S as H_2S and COS greatly deteriorate the performance of PEMFC electrodes.
- Pt-based catalysts are used in PEMFC electrodes which are expensive and susceptible to CO- and S-poisoning.

Hydrocarbon Fuel Reforming

Steam Reforming of Methane:

$$CH_4 + H_2O \rightleftarrows CO + 3H_2$$
$$CO + H_2O \rightleftarrows CO_2 + H_2$$

Steam Reforming of Generic Hydrocarbons:

$$C_nH_m + nH_2O \rightleftarrows nCO + \left(\frac{m}{2} + n\right) H_2$$
$$CO + H_2O \rightleftarrows CO_2 + H_2$$

Endothermic Reaction
Temp: 760 to 980 °C

Typical Steam Reformed Natural Gas Products

Mole %	Reformer Effluent	Shifted Reformate
H_2	46.3	52.9
CO	7.1	0.5
CO_2	6.4	13.1
CH_4	2.4	2.4
N_2	0.8	0.8
H_2O	37.0	30.4
Total	100.0	100.0

Hydrocarbon Fuel Reforming

Liquid Fuel Processing: Partial Oxidation of Hydrocarbons

$$C_5H_{12} + \frac{5}{2}O_2 \rightleftarrows 5CO + 6H_2$$

Exothermic Reaction
Temp: 1300 to 1500 °C

In a PEMFC system, CO must pass through selective catalytic oxidizer, even after being shifted in a shift reactor:

$$CO + \frac{1}{2}O_2 \rightarrow CO_2$$
$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$

Typical Steam Reformed Natural Gas Products

Mole % (dry basis)	Reformer Effluent
H_2	48.0
CO	46.1
CO_2	4.3
CH_4	0.4
N_2	0.3
H_2S	0.9
Total	100.0

Hydrocarbon Fuel Reforming

Major Technological Challenges:

- In the light of the PEMFC sensitivity to CO (as poison), CO_2 (as diluent) and CH_4 (as diluent), fuel processing represents a significant portion of the fuel cell system.
  - Innovation is needed in fuel reforming

- Pt-based catalysts are highly active, but are susceptible to fuel impurities. High costs of Pt-catalyst is a major concern.
  - Development of low cost electro-catlysts to reduce Pt-loading is necessary.

Fuel Reforming

Conventional Process:
Reactor(s) and Separation Units – Complex process, energy and cost intensive

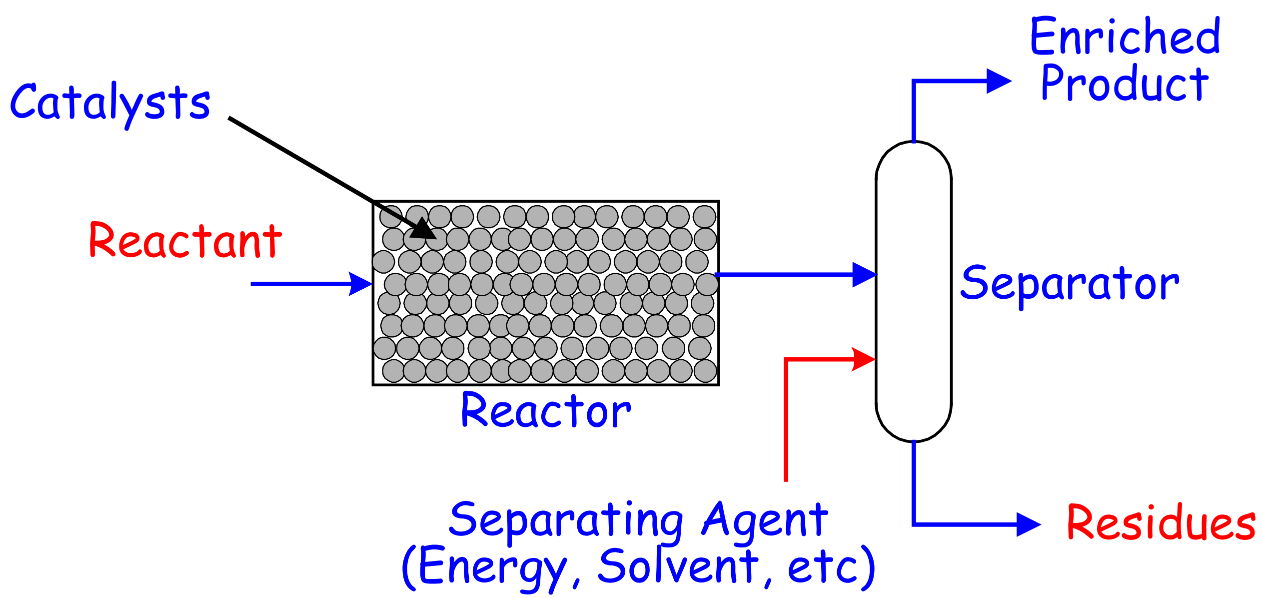


Fig: Schematic of Conventional Fuel Processing Operations

Fuel Reforming: Membrane Reactor-Separator

Our Approach: Membrane Reactor-Separator in a single process operation.

Advantages: High conversion, high product purity, reduced complexity and cost

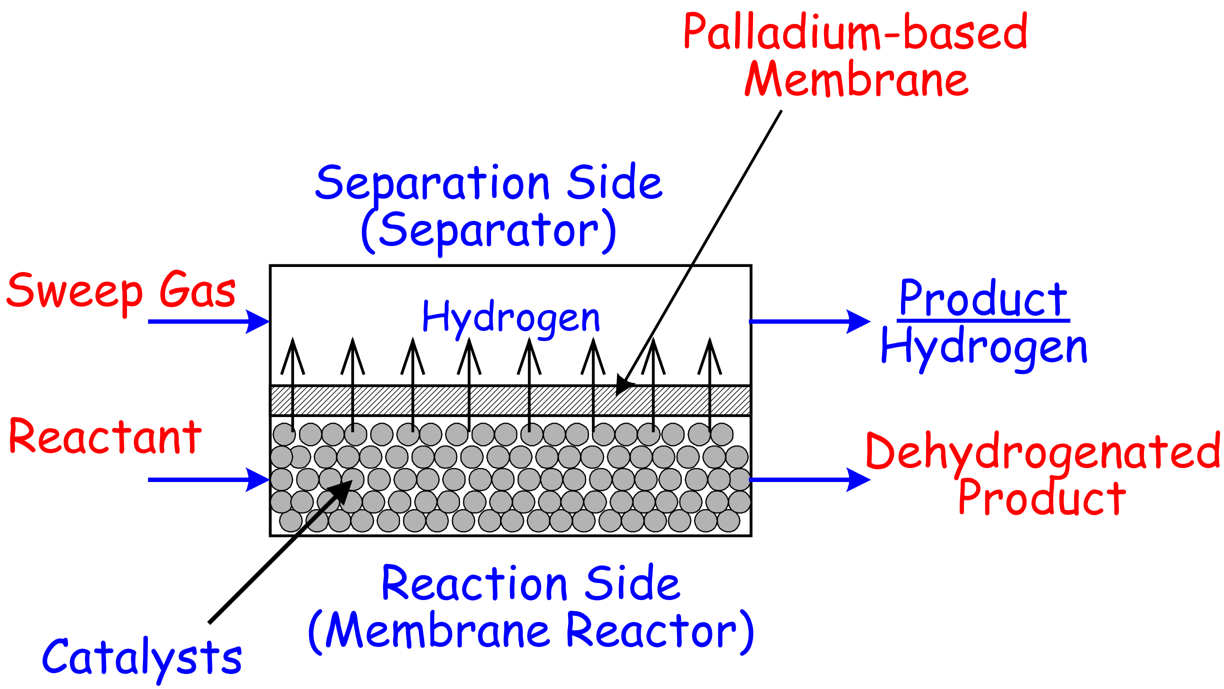


Fig: Membrane-Reactor-Separator as Fuel Processor

OBJECTIVES

The primary objectives of this work are:

- Develop a Pd- and Pd-Ag alloy microporous stainless steel H_2-selective membranes suitable for high temperature gas separations and membrane reactors by electroless plating.
- Couple the conventional electroless plating process with an osmotic pressure field to improve plating of metal substrates.
- Design a membrane reactor to study the steam reforming of methanol by equilibrium shifts and permeation characteristics.
- Develop a suitable membrane-reactor model for the methanol reforming reaction and develop computer code to simulate the reactor performance.
- Validate membrane reactor model with experimental data.

ELECTROLESS PLATING

Electroless plating is a three step process:

- Pretreatment of the substrate,
- Sensitization and activation of the substrate surface,
- Electroless plating.

Sensitization Solution

Component	Concentration
$SnCl_2$	1 g/l
HCl	0.2 N

Activation Solution

Component	Concentration
$PdCl_2$	0.09 g/l
HCl	0.2 N

Electroless Plating Solution

Component / Variables	Concentration
Palladium chloride	5.4 g/l
Ammonium hydroxide	290 ml/l
Hydrazine (1 molar solution)	10 ml/l
EDTA	40 g/l
pH	11
Temperature	45 °C

ELECTROLESS PLATING

This process is explained by a combination of cathodic deposition of metal and anodic oxidation of reductant at the immersion potential.

Anodic Reaction: $N_2H_4 + 4OH^{-1} \rightarrow N_2 + 4H_2O + 4e^-$

Cathodic Reaction: $2Pd[NH_3]_4^{2+} + 4e^- \rightarrow Pd^o + 8NH_3$

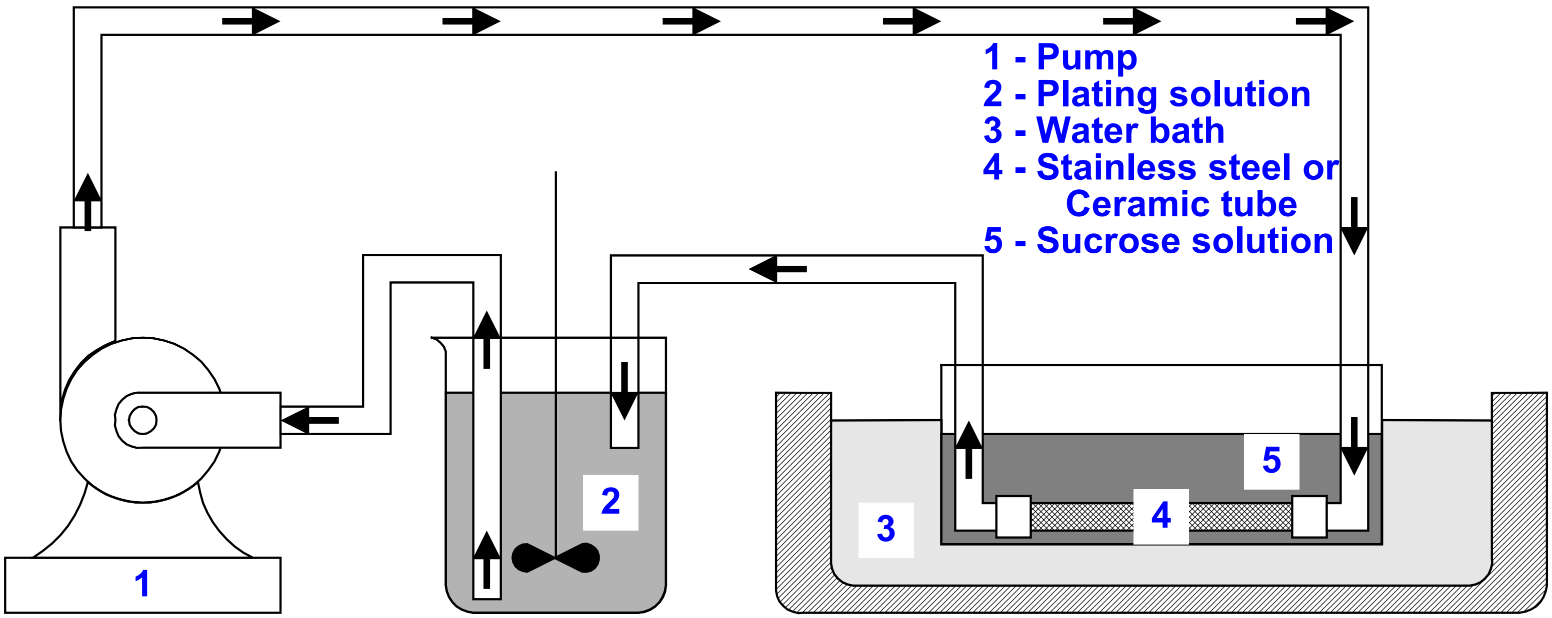
Autocatalytic Reaction:

$$2Pd[NH_3]_4^{2+} + N_2H_4 + 4OH^{-1} \rightarrow 2Pd^o + N_2 + 4H_2O + 8NH_3$$

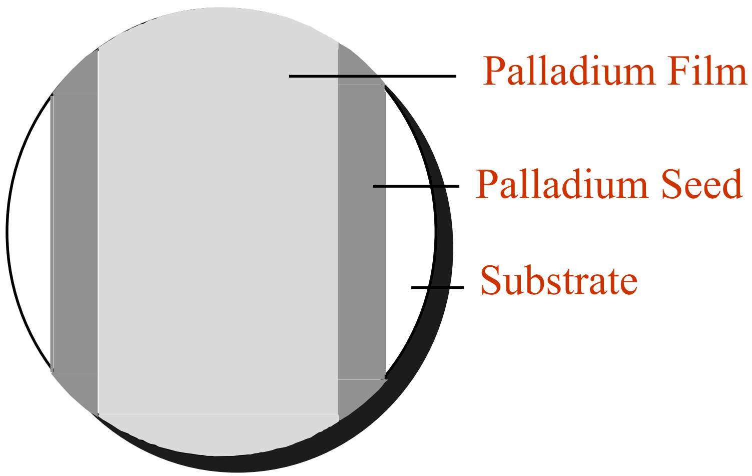
The substrates used are microporous (nominal pore size of 0.15 μm). The two types of substrates used for this work are ceramic alumina and stainless steel.

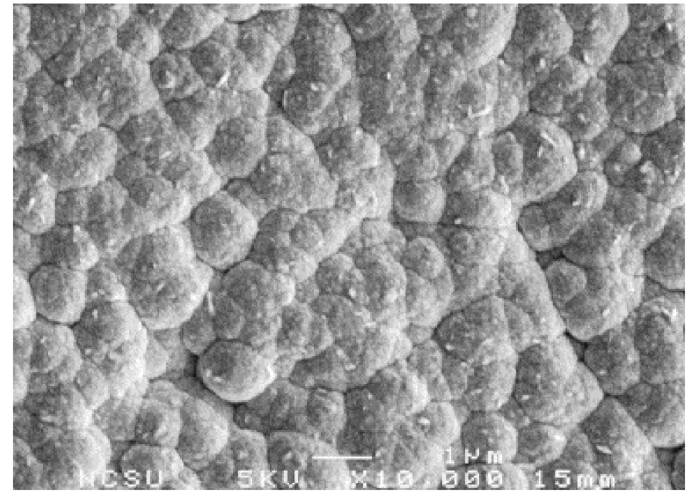
In order to improve the plating process for metal and metal-alloy substrates, the conventional plating method was coupled with an osmotic pressure field. This new technique allows for uniform and deep coating of Pd on the substrate surface.

Electroless Plating Under Osmotic Pressure Field

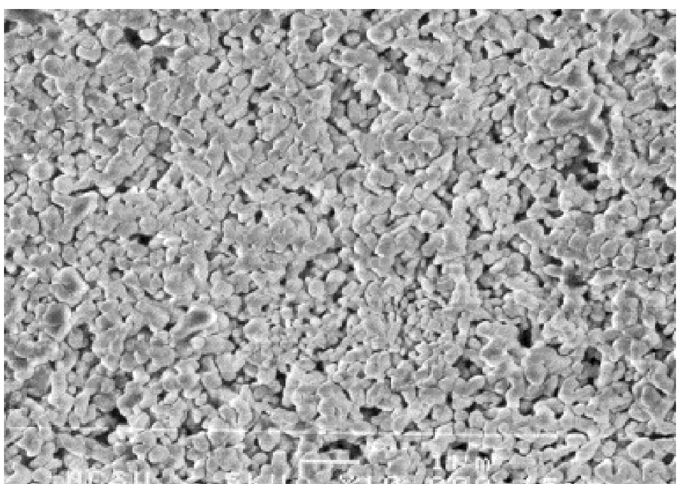


Electroless Plating: SEM Micrographs

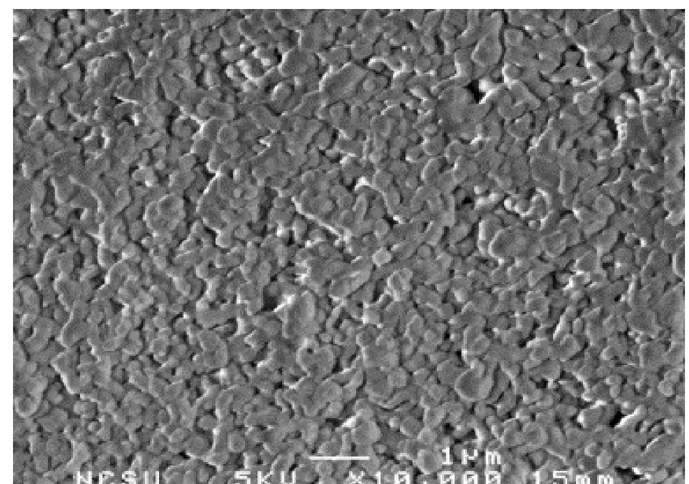




Palladium Film

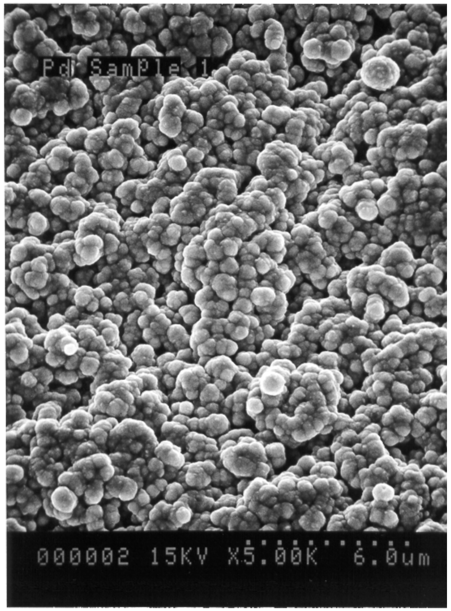


Ceramic Substrate

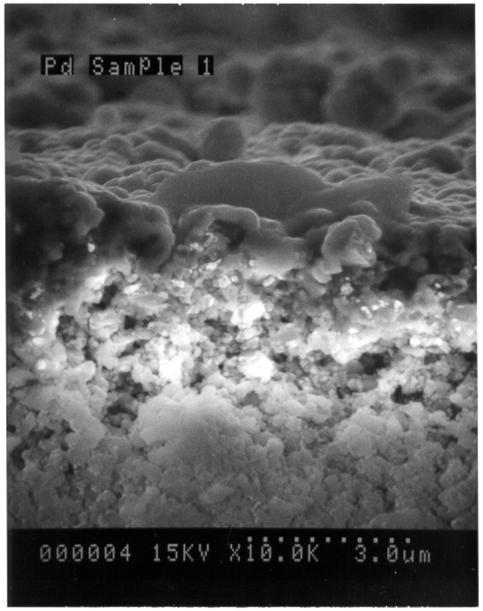


Palladium Seed

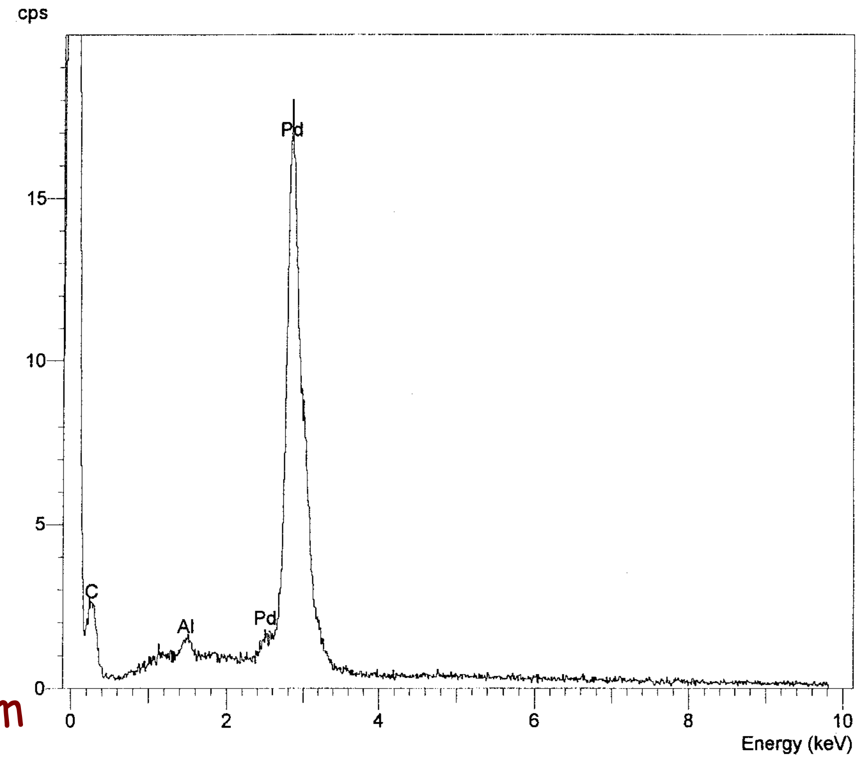
SEM & EDX of Pd-film on Ceramic Substrate



Pd-film on ceramic substrate



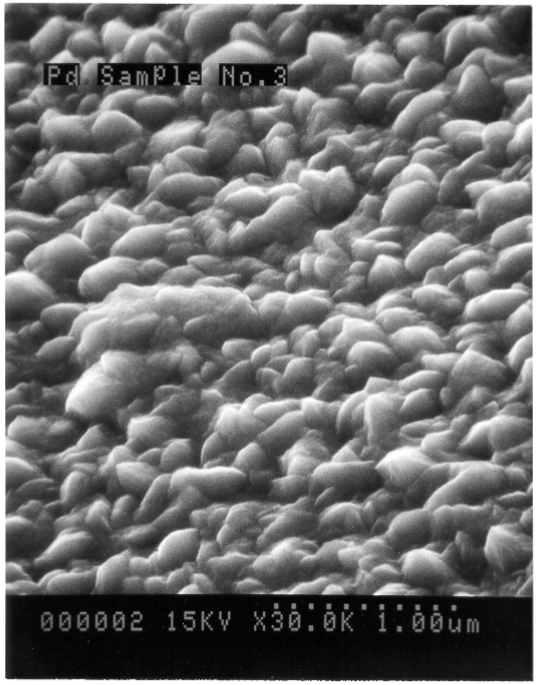
Penetration of Pd-film through pores



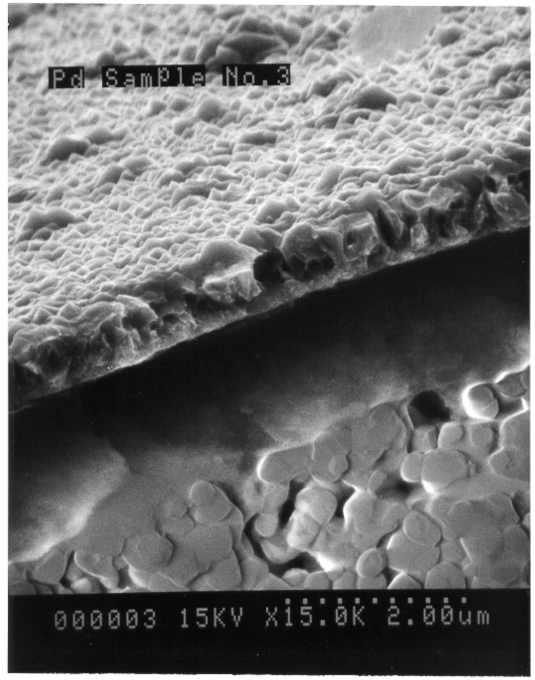
EDX analysis of electrodeposited Pd-film of ceramic substrate (0.2 μm pores)

Membrane prepared without osmotic pressure field

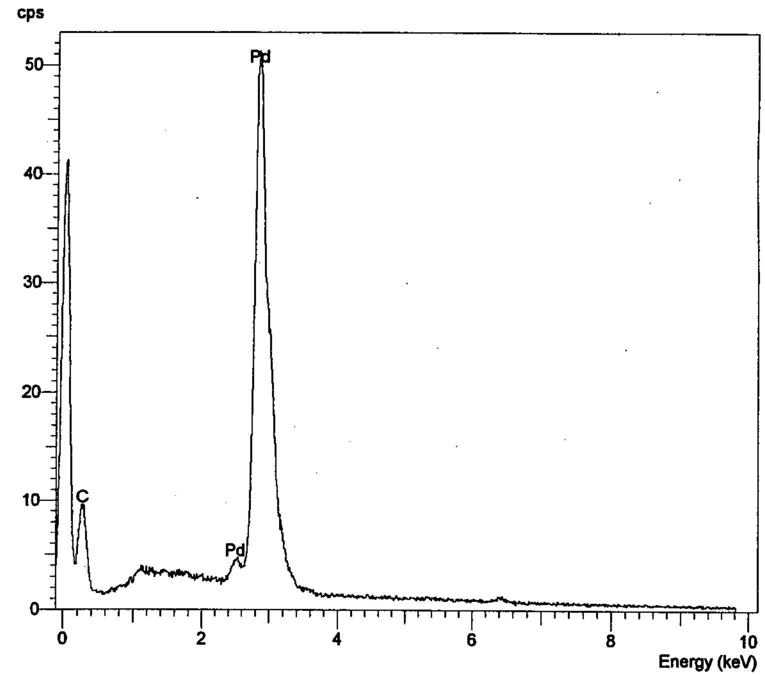
SEM & EDX of Pd-film on Ceramic Substrate



Pd-film on ceramic substrate



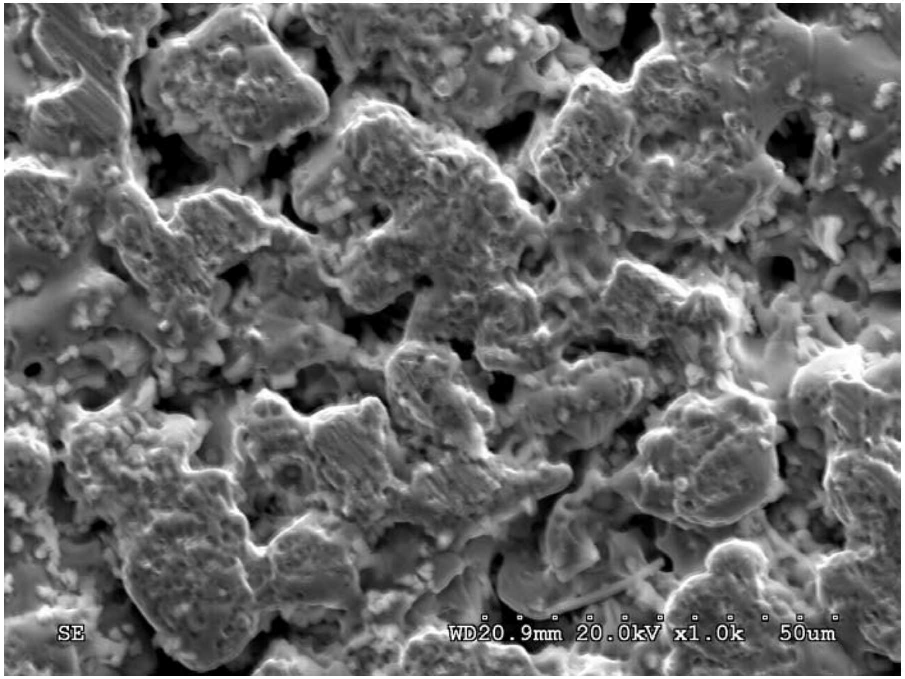
Penetration of Pd-film through pores



EDX analysis of electrodeposited Pd-film of ceramic substrate (0.2 μm pores)

Membrane prepared without osmotic pressure field

SEM of Stainless Substrate and Pd-Film

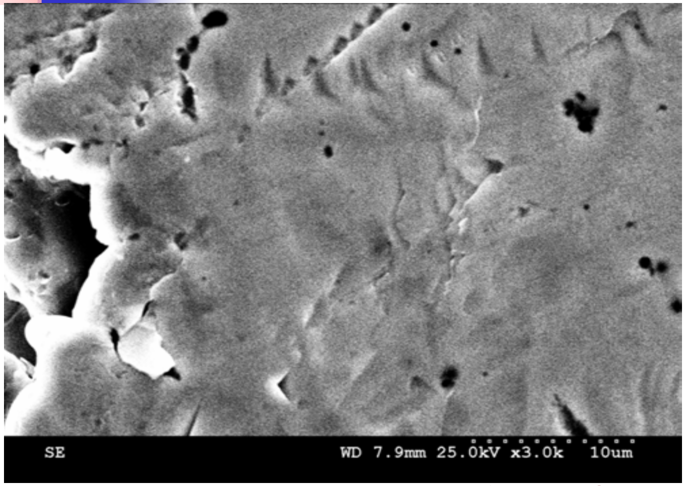


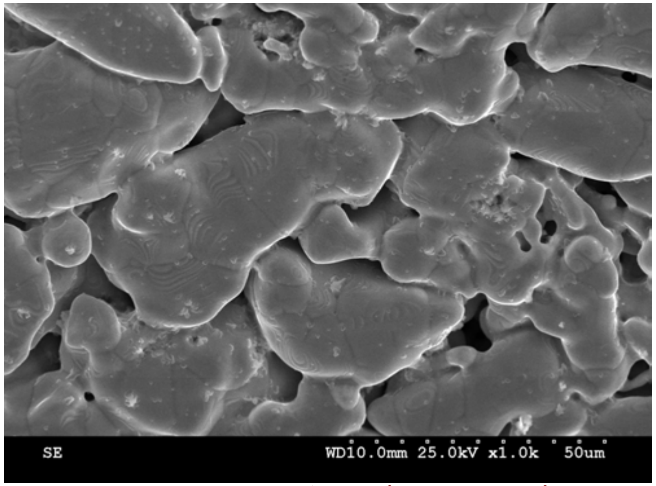
SEM of stainless steel tube substrate (0.2 micro) at 1000 magnifications.

SEM of Pd-film on stainless steel tube at 2000 magnifications.

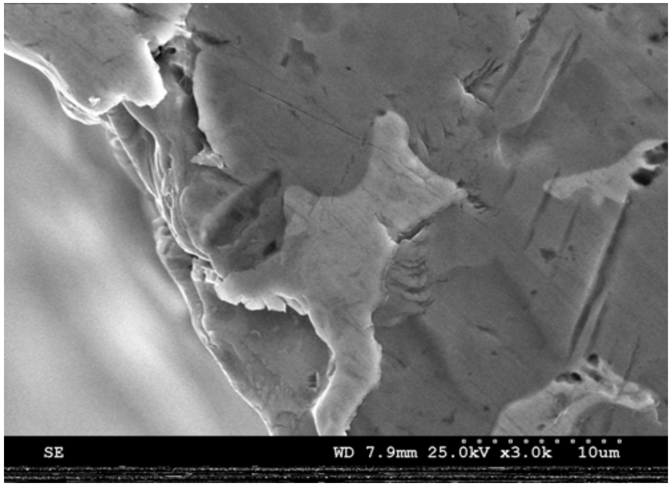
Membrane prepared without osmotic pressure field

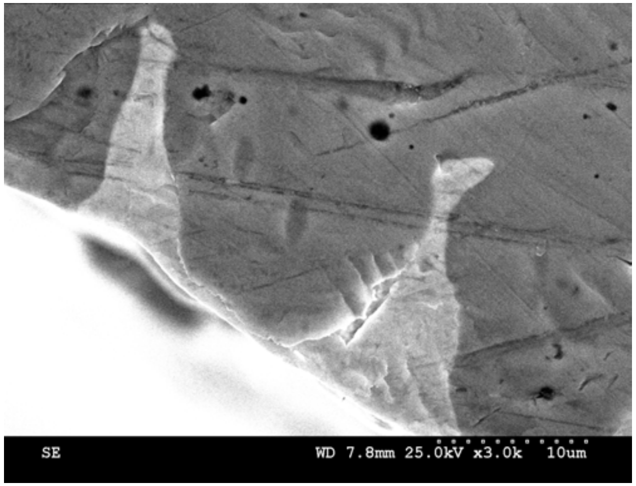
SEM of Stainless Substrate and Pd-Film





Cross section and surface of an uncoated porous SS tube (0.2 μm)

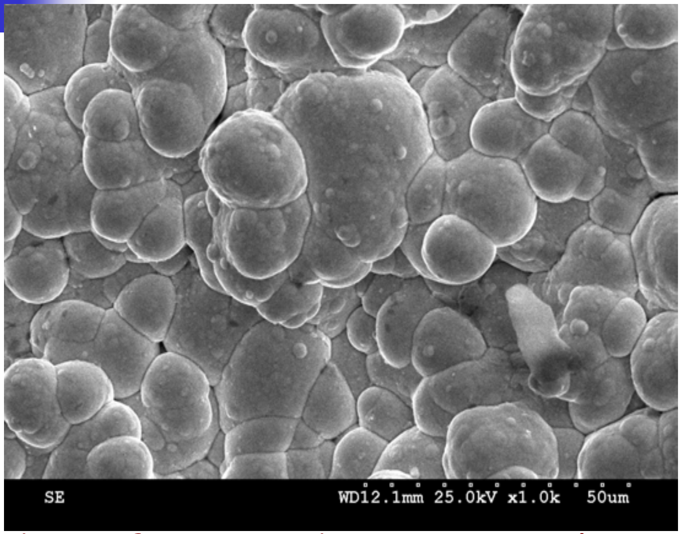


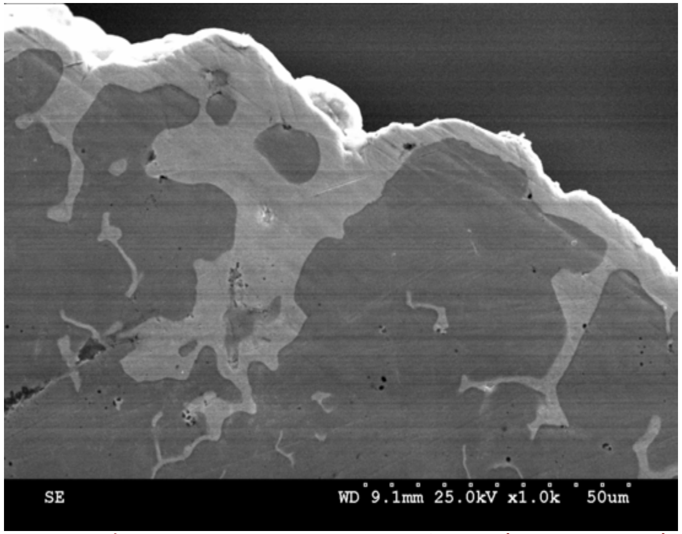


Cross section (inside view) of a Pd-coated porous SS tube at two different angles

Membrane prepared without osmotic pressure field

SEM of Stainless Substrate and Pd-Film

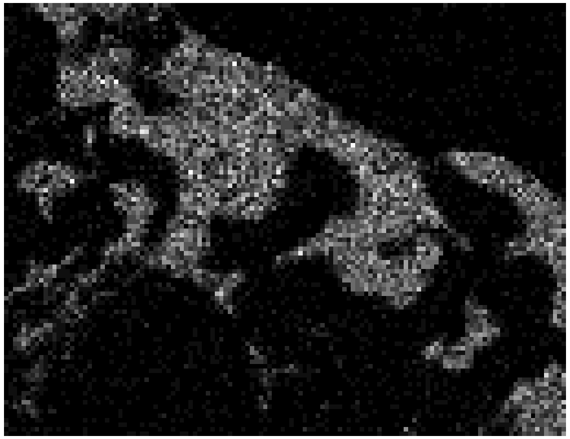




Pd-surface and x-sectional view of a coated porous SS tube (0.2 μm)

Cross section

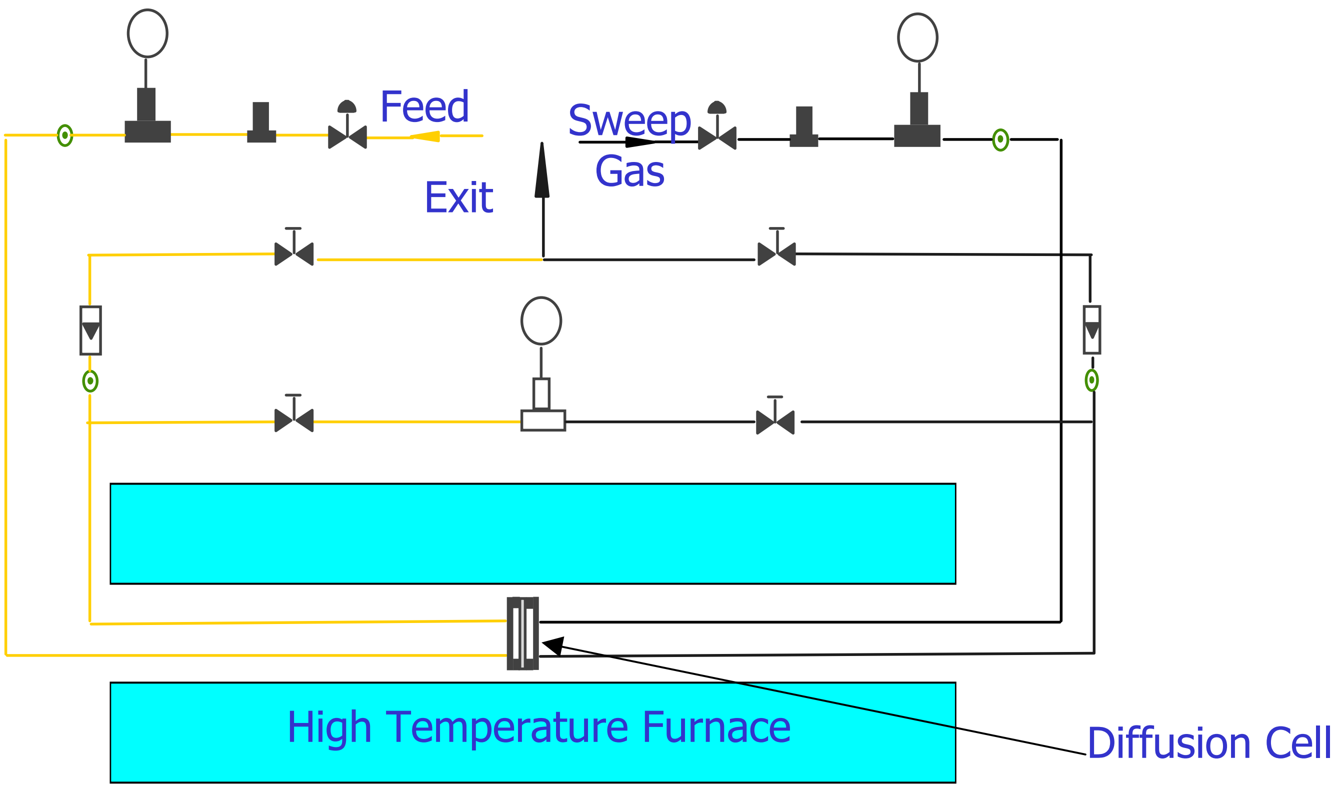
Stainless steel (gray color)



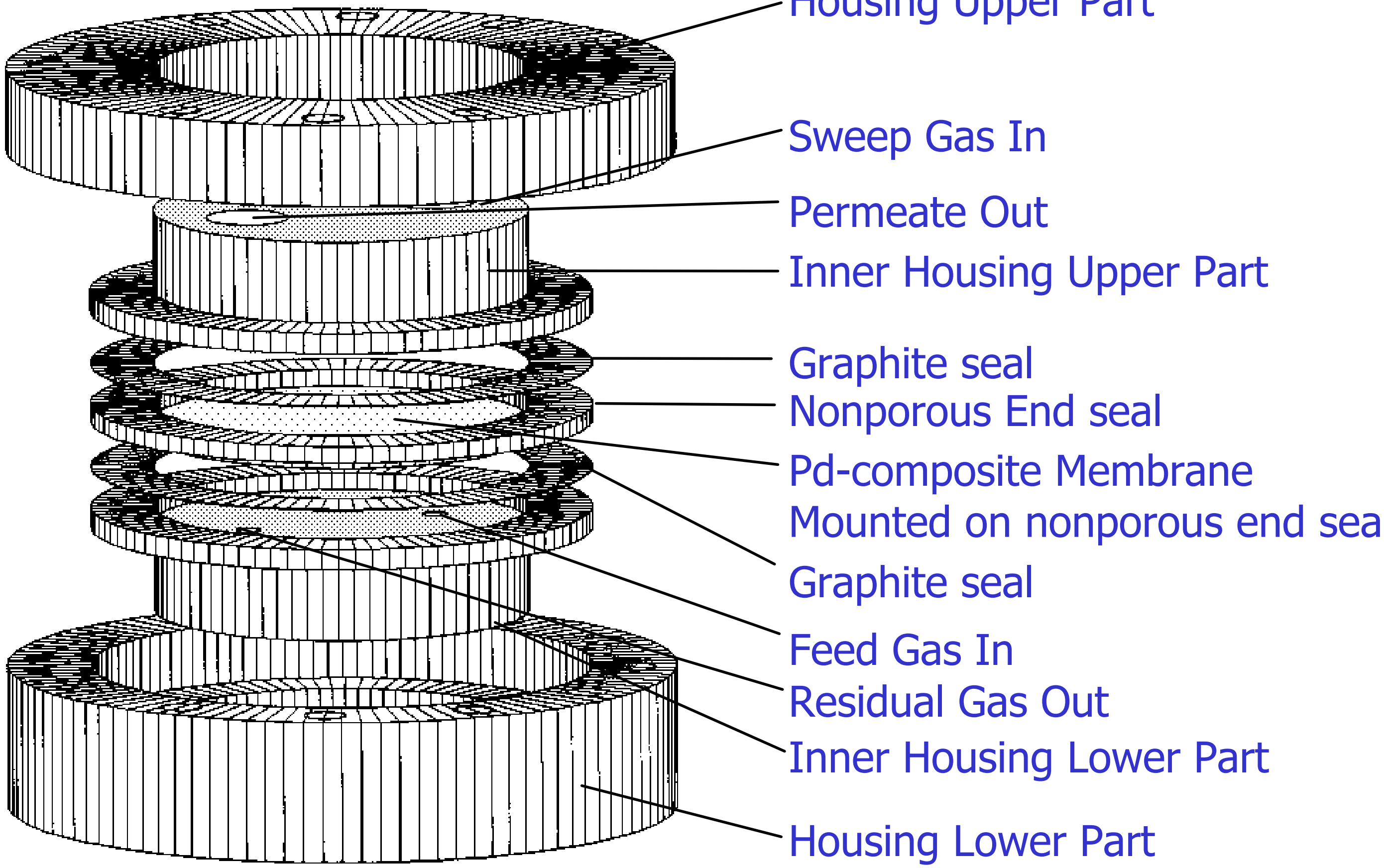
Deposited Pd (white color)

Membrane prepared using osmotic pressure field

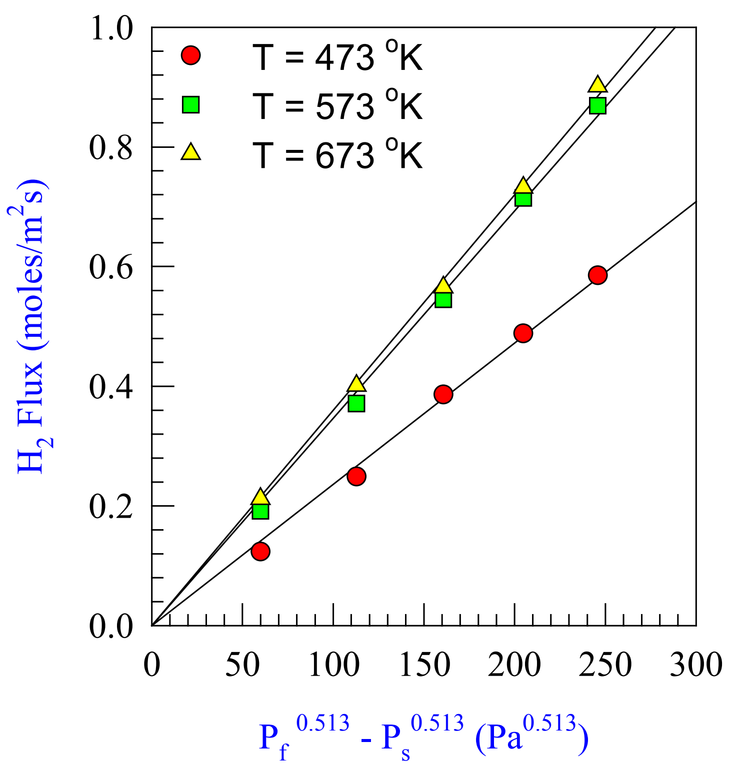
Permeability Measurement Setup



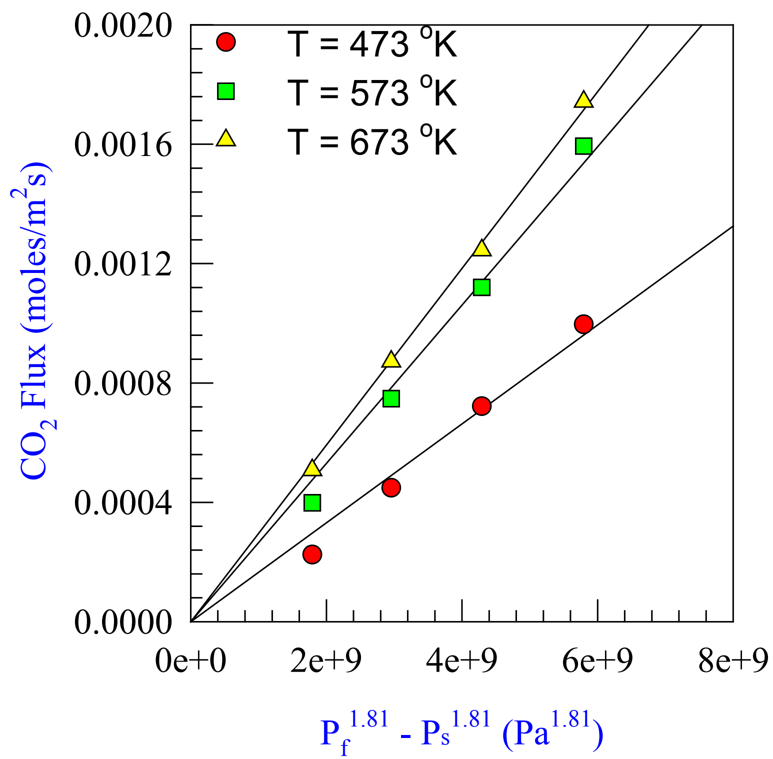
Diffusion Cell



Pd-Stainless Membrane Performance: Permeability Data



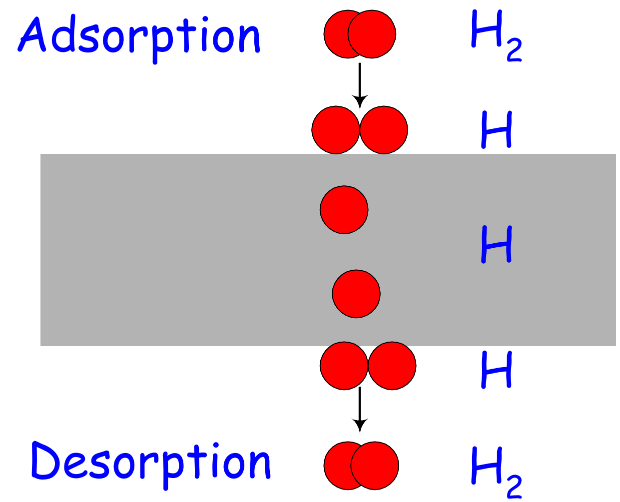
Hydrogen flux data for Pd-Stainless Membrane with 10 μm Pd-film



Carbon dioxide flux data for Pd-Stainless Membrane with 10 μm Pd-film

Hydrogen Permeation Through a Dense Metal

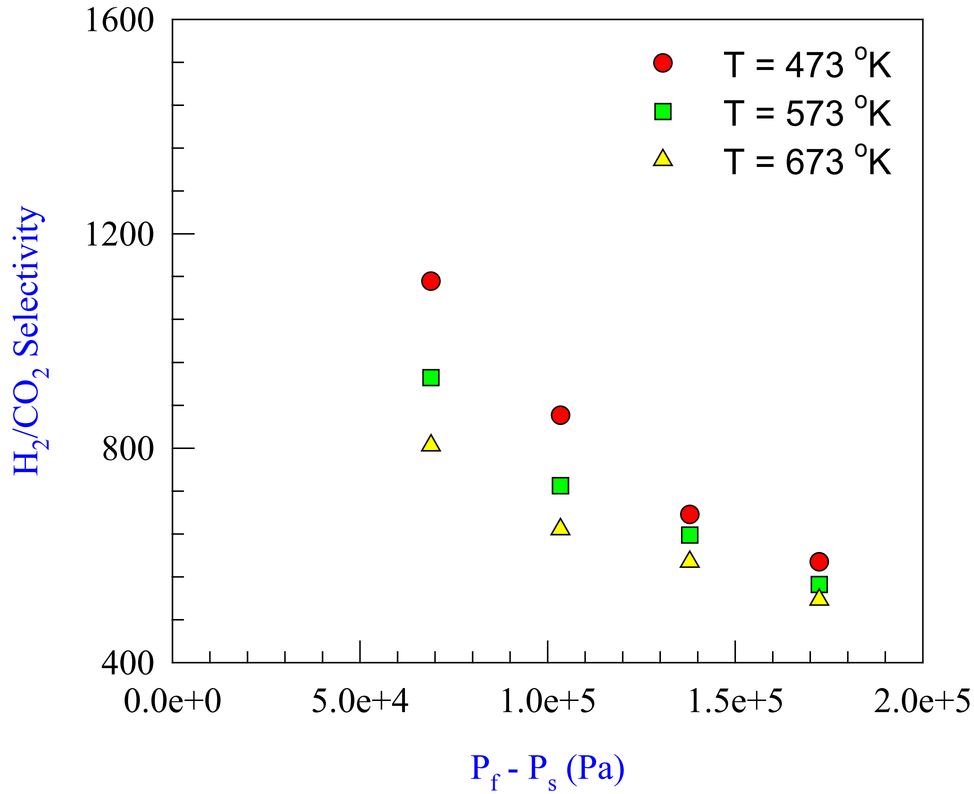
- Reversible dissociative chemsorption of molecular hydrogen on metal surface
- Reversible dissolution of surface atomic hydrogen in the bulk layers of the metal
- Diffusion of atomic hydrogen through the bulk metal
- Association of atomic hydrogen into hydrogen molecule



$$J_H = \frac{Q_H}{h}\left(P_H^n - p_H^n\right) \qquad n = 0.5 \text{ for Sievert's law}$$

$$Q_H = Q_{H_o} \exp\left(-\frac{E}{RT}\right)$$

Pd-Ceramic Membrane Performance: Selectivity Data



Hydrogen/carbon dioxide selectivity data for Pd-Stainless composite membrane with 10 μm palladium film

STEAM REFROMING OF METHANOL

Equilibrium Constant for overall reaction for non-membrane reactor:

$$K_E = \left(\frac{y_{CO_2} y_{H_2}^3}{y_{H_2O} y_{CH_3OH}} \right) P_T^3$$

Using extent of reaction (ξ), we can write:

$$K_E = \frac{(\xi)(3\xi)^3}{(1-\xi)(1-\xi)(2+2\xi)^2} P_T^2$$

$$= \frac{27\xi^4}{4(1-\xi)^2(1+\xi)^2} P_T^2$$

- Higher the total pressure, the lower the extent of reaction at equilibrium.

Overall Reaction:

$$CH_3OH + H_2O \underset{-k_R}{\overset{k_R}{\rightleftharpoons}} CO_2 + 3H_2 \qquad (1)$$

Decomposition Reaction:

$$CH_3OH \underset{-k_D}{\overset{k_D}{\rightleftharpoons}} CO + 2H_2 \qquad (2)$$

Water-Gas Shift Reaction:

$$CO + H_2O \underset{-k_W}{\overset{k_W}{\rightleftharpoons}} CO_2 + H_2 \qquad (3)$$

Reaction (2): Endothermic, to be performed at high pressure and temperature for improved catalyst use. Reaction (3): Exothermic, low temperature and pressure are needed to drive reaction.

METHANOL REFORMING: MBRANE REACTOR

In membrane reactor, hydrogen mole fraction (partial pressure) is less of a function of extent of reaction, and more of a more of a function of permeate side pressure (back pressure of hydrogen). For ideal membrane reactor, the transport resistant is minimal and the hydrogen partial pressure may be taken as hydrogen back pressure. Then for membrane reactor we can write:

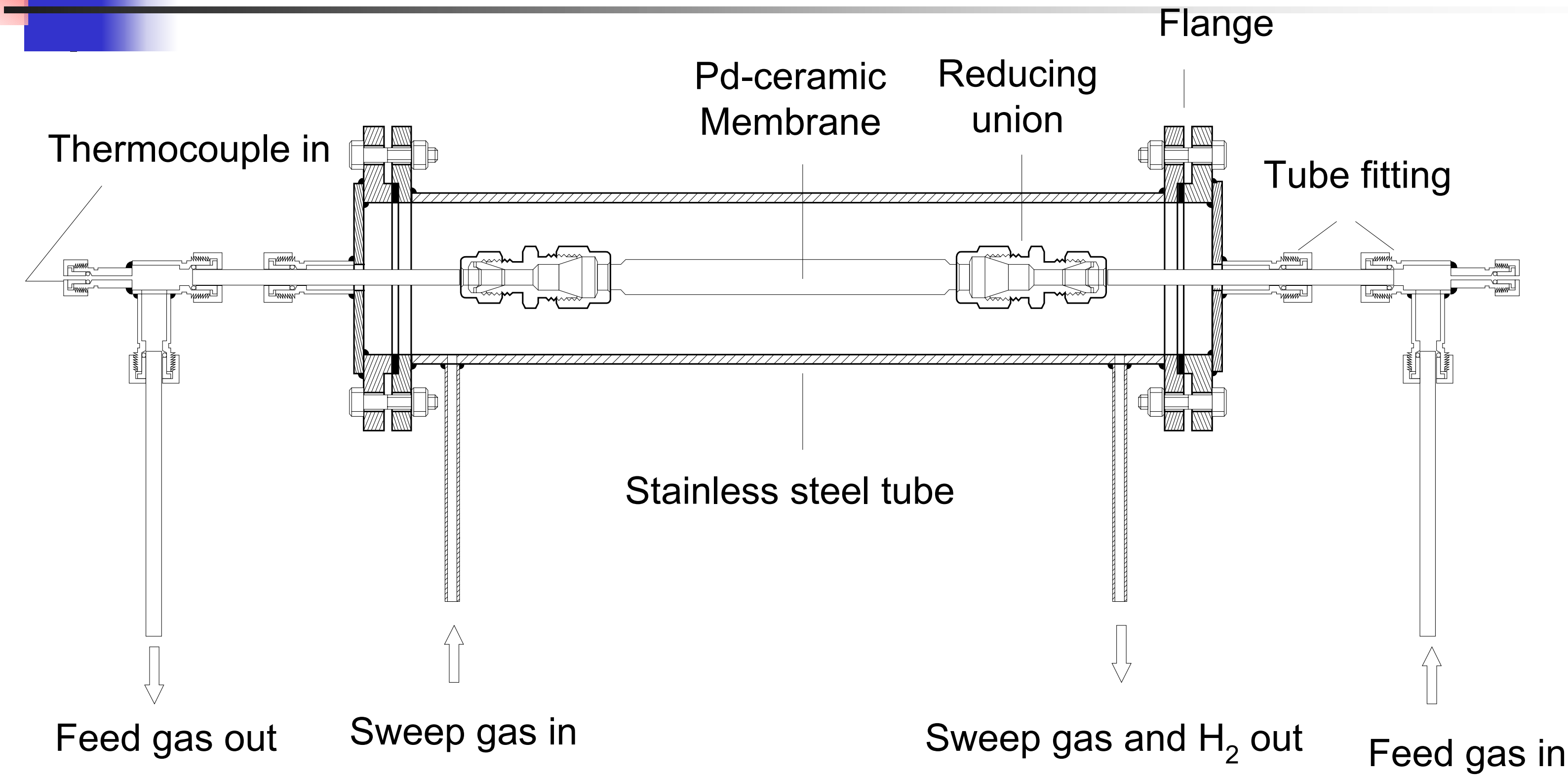
$$K_E = \frac{\beta^3 y_{CO_2}}{y_{H_2O} y_{CH_3OH} P_T}, \quad \beta = \text{hydrogen back pressure}$$

Using extent of reaction we can write:

$$K_E = \frac{\left(2-\xi+\dfrac{2-\xi}{P_T-\beta}\right)\beta^3 \xi}{(1-\xi)^2 P_T}$$

- Lowering the product hydrogen pressure, increases the reactor conversion
- The higher the total pressure, greater the conversion at equilibrium.

MEMBRANE REACTOR



- Designed and fabricated a membrane reactor in tubular configuration.
- Work is in progress to study the steam reforming of methanol in the membrane reactor.
- Based on our previous work on steam reforming of methane, we have developed 2-D pseudo-homogeneous membrane-reactor model for methanol reforming.

CONCLUSIONS

Developed a Pd-stainless-steel composite membrane by a novel electroless deposition process.

Electroless Deposition coupled with Osmotic Pressure Field for uniform and deep coating of selective metal & metal-alloy films

The membrane is thermally stable, has high perm-selectivity for hydrogen and is capable of producing pure hydrogen from a mixed gas.

The new membrane is an excellent candidate for selective separation of hydrogen in equilibrium limited dehydrogenation reactions in membrane-reactor (MBR) configuration, giving high conversion and yields by shifting equilibrium to right.

- Designed and fabricated a membrane reactor in tubular configuration.
- Developed 2-D pseudo-homogeneous membrane-reactor model for methanol reforming

CURRENT & FUTURE WORK

- Extend electroless plating deposition technique to fabricate Pd-alloy composite membranes
- Study steam reforming of methanol in the tubular membrane reactor
- Validate computational model predictions with experimental results

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Sabita Roy	Natalie Woods	Syeda J. Ahmed
M. Mondal	Joy Franklin	Katif Peay
Akilah Shelby	M.H. Khan	

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