Fabrication of Pd/Pd-alloy Films by Surfactant Induced Electroless Plating for H_2 Separation from Advanced Coal Gasification Processes

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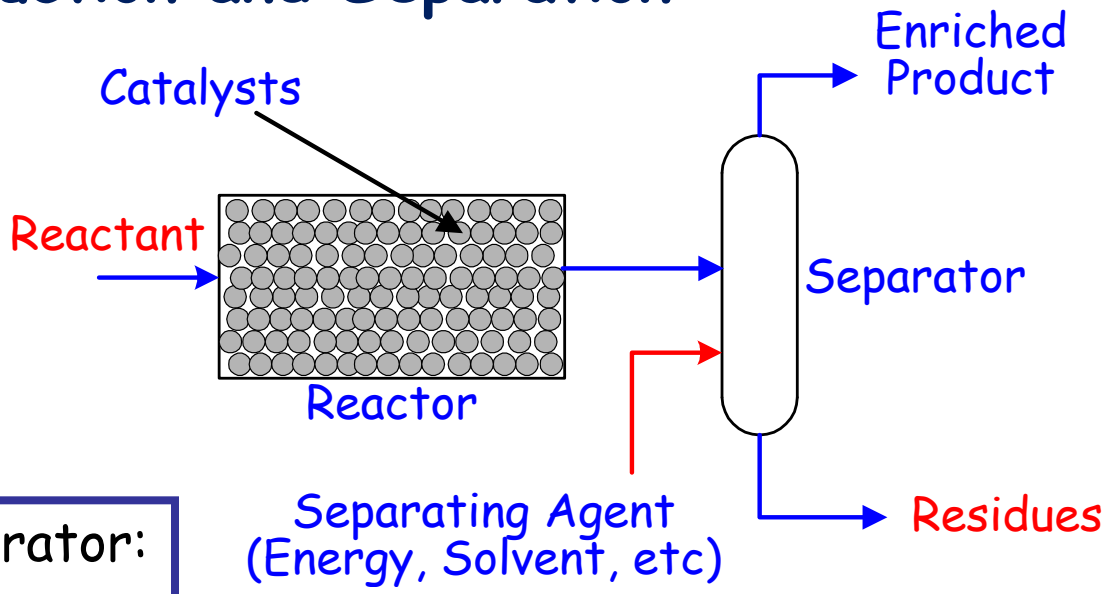
Presentation Outline

- Introduction
- Electroless Plating (EP)
- Research Objectives
- Surfactant Induced Electroless Plating (SIEP)
- Microstructure of Pd/Pd-alloy films by EP and SIEP
- H_2-Permselectivity
- Conclusions
- Acknowledgments

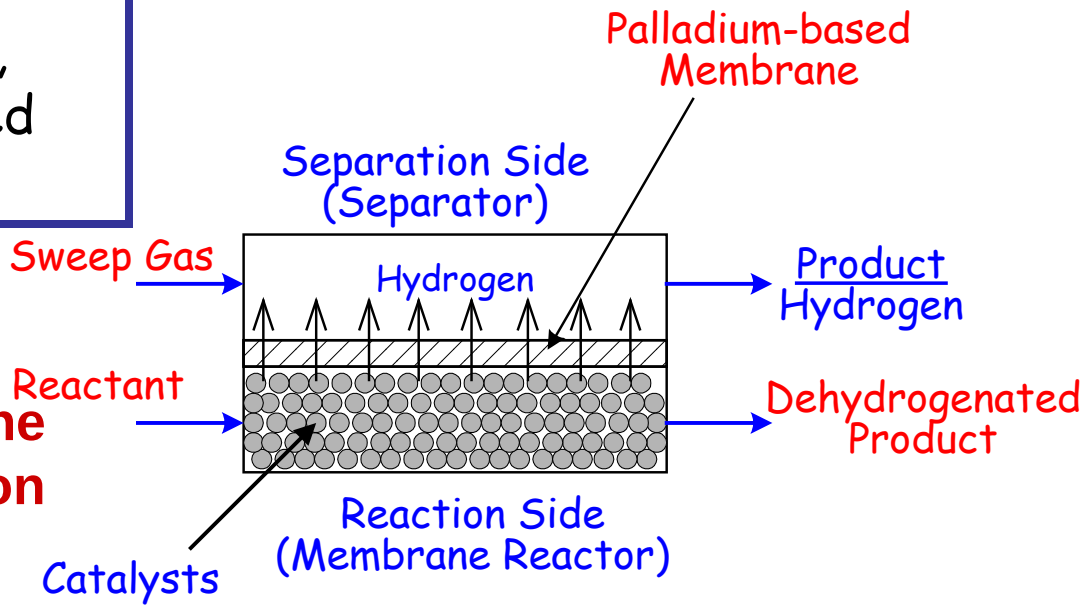
INTRODUCTION

H_2 Production and Separation

Conventional Process:
Reactor(s) and Separation Units - Complex Process, Energy and Cost Intensive

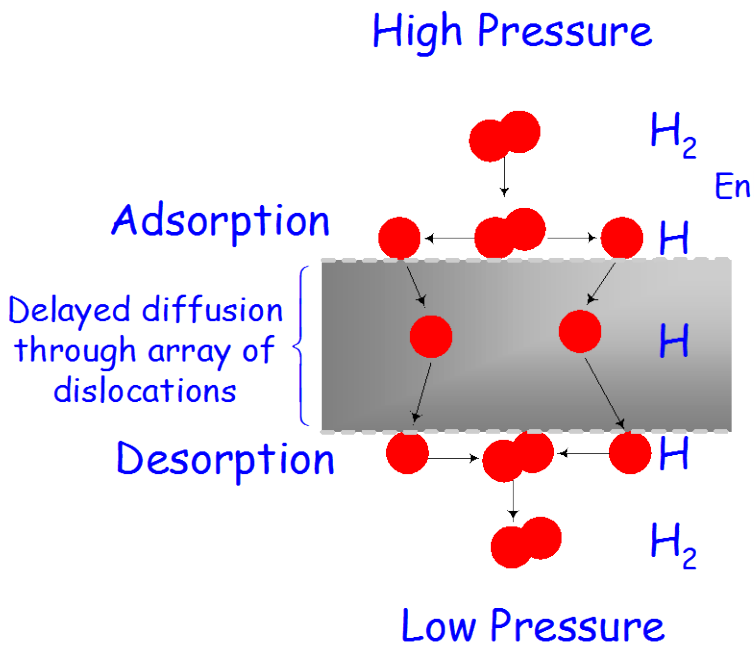


Membrane Reactor-Separator:
Modular, compact process operation - high conversion, high product purity, reduced complexity and cost



H_2-selective thin-film membrane for high temperature application is a topic of great interest.

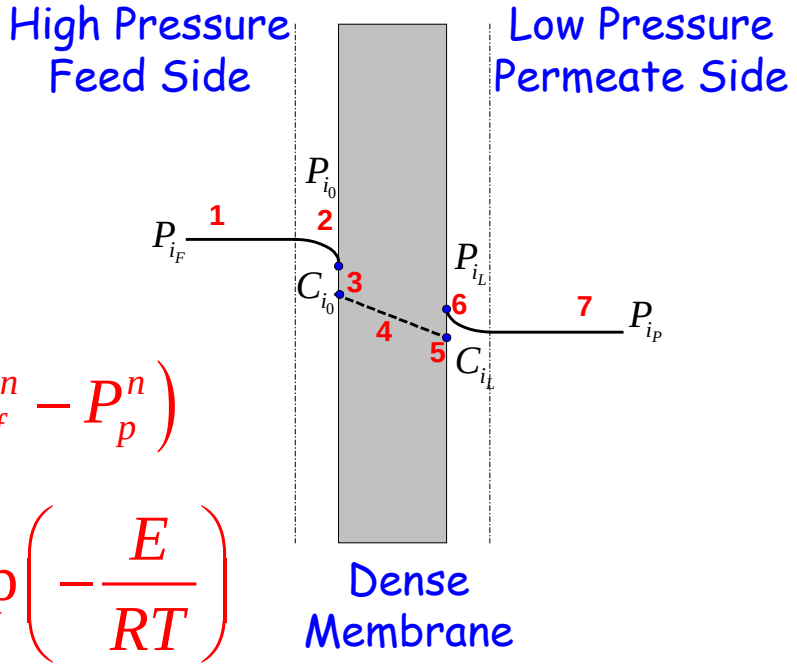
H_2 Transport in dense Pd membrane



Enhanced Adsorption at dislocated surface

$$N_H = \frac{Q_H}{t}\left(P_f^n - P_p^n\right)$$

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



H_2-flux (N_H) increases with decreasing film thickness

H_2-permeability (Q_H) increases with temperature

Fabrication of thin-film Pd- and Pd-alloy membrane is a technical challenge.

Separation and purification is critical for H_2-based energy economy. Pd/Pd-alloy membranes are viewed as serious contender for H_2-separation and purification applications at elevated temperature.

Fabrication of Pd/Pd-alloy Membranes

Wide varieties of techniques available for fabrication of thin Pd-film on porous stainless steel or ceramic support:

- Chemical vapor deposition (CVD)
- Physical vapor deposition (PVD)
- Pulsed laser deposition (PLD)
- Electro Plating
- Electroless Plating (EP)

EP is the most extensively used method in fabricating Pd/Pd-alloy membranes on micro- or meso-porous substrate surface.

ELECTROLESS PLATING (EP)

- EP is one of the most attractive technique because of its flexibility in deposition on substrates of any shape or size.
- EP of Pd is a combination of cathodic deposition of metal and anodic oxidation of reductant at the immersion potential.
- Pd-deposition is an autocatalytic process. Pd atoms deposits as solid at the solid substrate.
- Pd-deposition process strongly depends on substrate morphology and operating conditions (temperature, pH and stoichiometric concentration).

Pd-bath reactions

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

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

Autocatalytic Reaction: $2Pd[NH_3]_4^{2+} + N_2H_4 + 4OH^{-1} \rightarrow 2Pd^o +$

$[N_2] \uparrow (g) + 4H_2O + [8NH_3] \uparrow (g)$

Typical Pd EP Recipe

Senistisation Solution

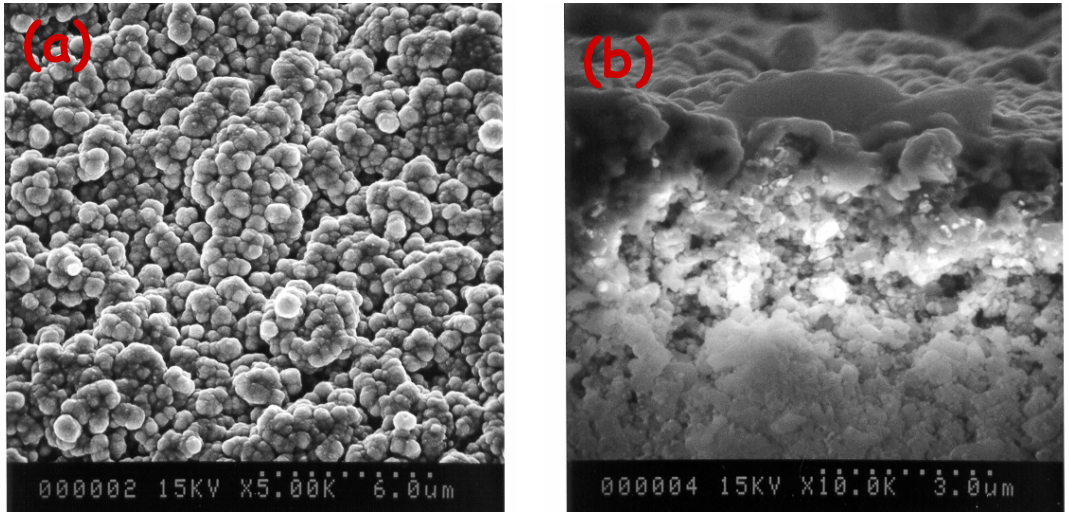
Component	Concentration
$SnCl_2 \cdot 2H_2O$	1.19 g/l
HCl	0.2 N

Activation Solution

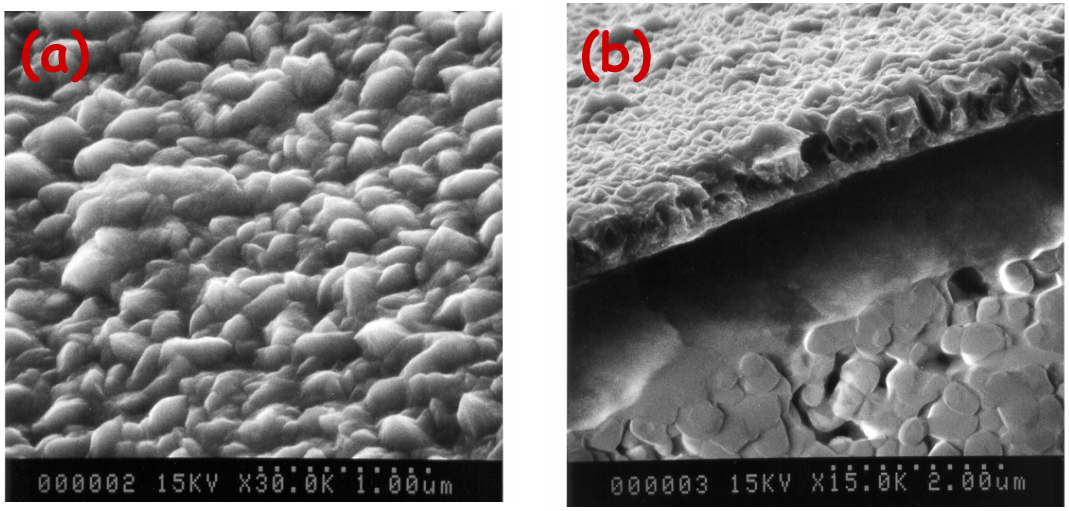
Component	Concentration
$PdCl_2 \cdot 2H_2O$	0.09 g/l
HCl	0.2 N

Pd EP Bath Solution

Component / Variables	Concentration
Tetraamine palladium nitrate(10% wt)	24.3 g/l
Ammonium hydroxide (28 % wt)	198 ml/l
Hydrazine (35% wt solution)	1.215 ml/l
EDTA	40.1 g/l
pH	10.5
Temperature	55 °C



SEM analysis of Pd-film on 0.2 μm microporous ceramic substrate: (a) Pd-film surface; and (b) Penetration of Pd across the thickness



SEM analysis of Pd-film on 0.2 μm microporous ceramic substrate: (a) Pd-film surface; and (b) Penetration of Pd-film across the thickness (film separated from the support)

EP Reactions in Ag & Cu Systems

Ag-bath reactions

Anodic Reaction: $N_2H_4 + 4OH^- \rightarrow N_2\uparrow + 4H_2O + 4e^-$

Cathodic Reaction: $4Ag[NH_3]_4^+ + 4e^- \rightarrow 4Ag^o + 8NH_3\uparrow$

Overall Reaction: $4Ag[NH_3]_4^+ + N_2H_4 + 4OH^- \rightarrow 4Ag^o + N_2\uparrow + 8NH_3\uparrow + 4H_2O$

Cu-bath reactions

Anodic Reaction: $2CH_2O + 4OH^- \rightarrow H_2\uparrow + 2HCOO^- + 2H_2O + 2e^-$

Cathodic Reaction: $Cu[NH_3]_6^{2+} + 2e^- \rightarrow Cu^o + 6NH_3\uparrow$

Overall Reaction: $Cu[NH_3]_6^{2+} + 2CH_2O + 4OH^- \rightarrow$

$Cu^o + 2HCOO^- + H_2\uparrow + 6NH_3\uparrow + 2H_2O$

- In typical EP, reaction between Pd-complex and hydrazine, results in evolution of NH_3 and N_2 as tiny gas bubbles.
- In most cases, these tiny bubbles adhered to the substrate surface and into the pores that hinder uniform deposition.

Issues in Conventional EP

- Poor control on Pd-grain size distribution
- Non-uniform film deposition
- Substrate surface morphology plays important role in the autocatalytic deposition

Modifications in EP

- Electroless plating under osmotic pressure field [Souleimanova, et al, AIChE J. 48(2): 262 (2002)].
- Intermetallic diffusion layer (barrier) & rotation of the substrate during electroless plating to reduce mass transfer resistance [Ma, et al, Annal New York Academy of Science, 984: 346 (2003)].
- Photocatlytic activation [Wu et al, Ind. Eng. Chem, Res. 39: 342 (2008)].
- PLD activation [Islam, M.A., PhD Thesis, Noth Carolina A&T State University, 2008].

RESEARCH OBJECTIVES

- Fabrication of Pd and Pd-alloy membranes on microporous stainless steel support (MPSS).
- Characterization of the Pd-composite membranes
- Study H_2-permselectivity of the Pd-and pd-alloy composite membranes

The overall goal of our work is to develop a Pd-based membrane on MPSS support by EP for H_2-separation and membrane reactor applications that will have the following attributes:

- Durable
- Defect free (no pinholes)
- Thermally stable
- High perm-selectivity for hydrogen

SURFACTANT INDUCED ELECTROLESS PLATING (SIEP)

In EP, Pd deposition occurs preferentially around the Pd seeds with release of NH_3 and N_2 gas bubble.

Autocatalytic Reaction:

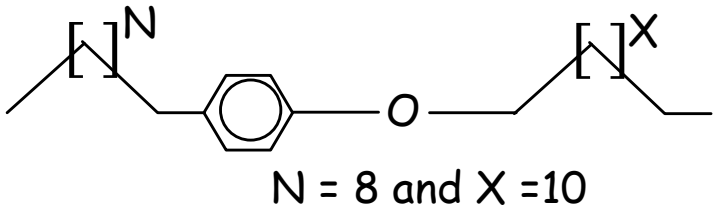
$$2\mathrm{Pd}\left[\mathrm{NH_3}\right]_4^{2+} + \mathrm{N_2}H_4 + 4OH^{-1} \rightarrow 2Pd^{o} + \left[N_2\right]\uparrow(g) + 4H_2O + \left[8NH_3\right]\uparrow(g)$$

The extent of reaction (reduction into metallic Pd) depends upon efficient removal of evolved gases (NH_3, N_2) and presence of sufficient uniform Pd seeds on the substrates.

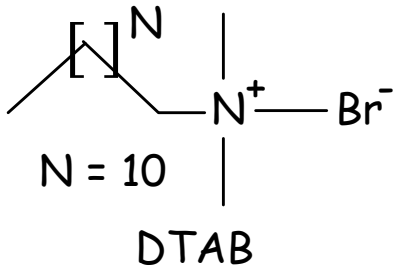
To ensure suitable film growth, surface treatment is required. Surfactant with suitable charge and concentration can be used to tailor the Pd grain size and subsequent agglomeration.

Major objective of our study is to determine if a balance between micelles collapse and retention could be used as a control to facilitate uniform nucleation and agglomeration of Pd-grains in dense membrane fabrication on microporous substrates.

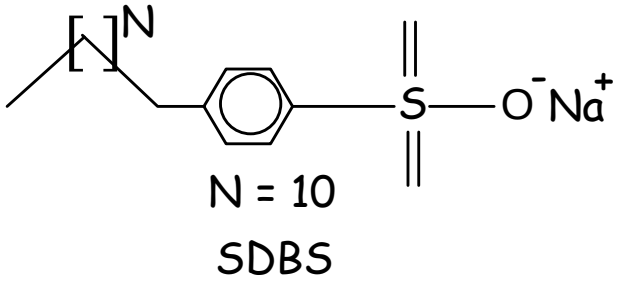
Three surfactants were used to investigate the effect of surfactant in Pd bath. The length of hydrophobic tail for each of the surfactant were very similar (around 9 to 10 carbon chain)



Polyethylene glycol ter-octaphenyl ether (Nonionic)



Dodecyltetramethylammonium bromide (Cationic)



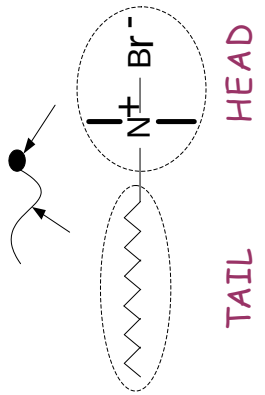
Dodecylbenzenesulfonic acid sodium salt (Anionic)

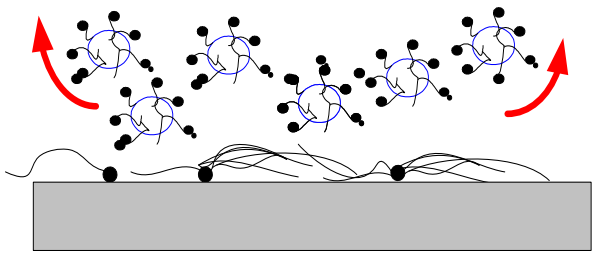
Surfactant Properties (CMC, HLB)

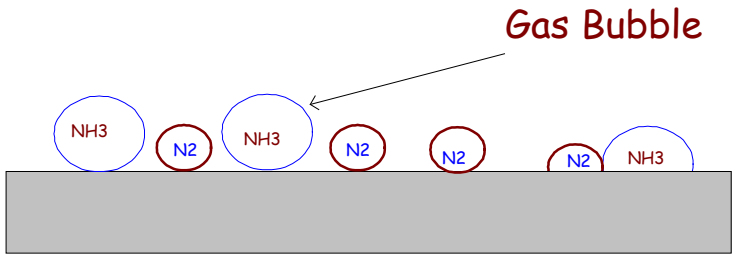
Surfactant	HLB Values	CMC (mM)
Triton X-100	14.7	0.22
DTAB	12.9	16
SDBS	13.6	1.4

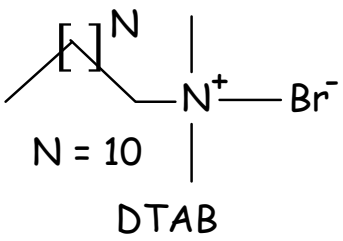
Role of Surfactant in EP

EP Autocatalytic Reaction: $2\mathrm{Pd}\left[\mathrm{NH_3}\right]_4^{2+} + \mathrm{N_2}H_4 + 4OH^{-1} \rightarrow 2Pd^o + \left[N_2\right]\uparrow(g) + 4H_2O + \left[8NH_3\right]\uparrow(g)$





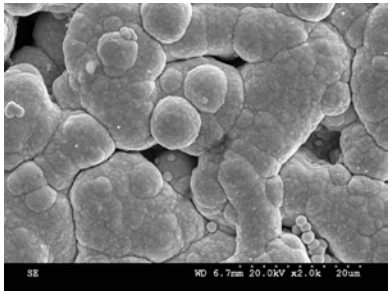




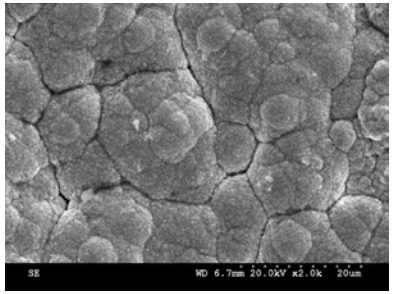
DTAB

Surfactant interactions at solid-liquid, gas-liquid and solid-gas interfaces through micelles formation

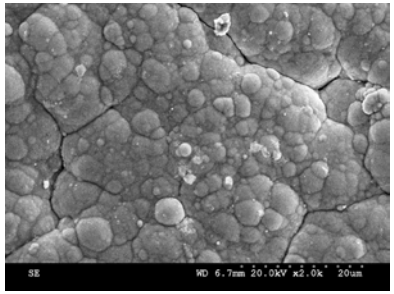
Dodecyltetramethylammonium bromide (DTAB cationic surfactant)



EP



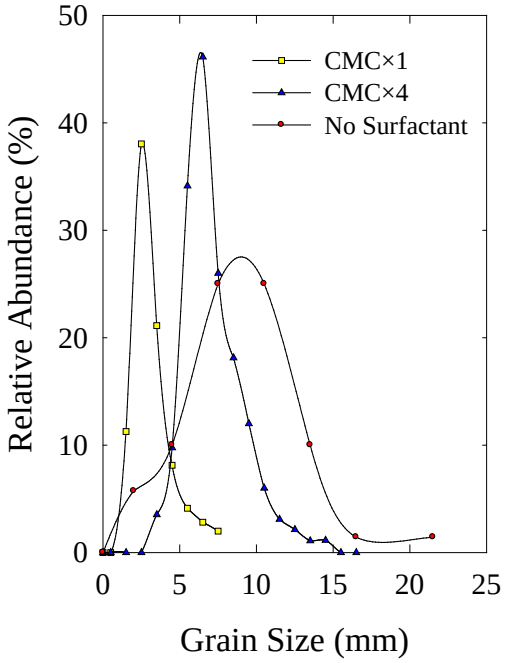
SIEP (CMC × 1)



SIEP (CMC × 4)

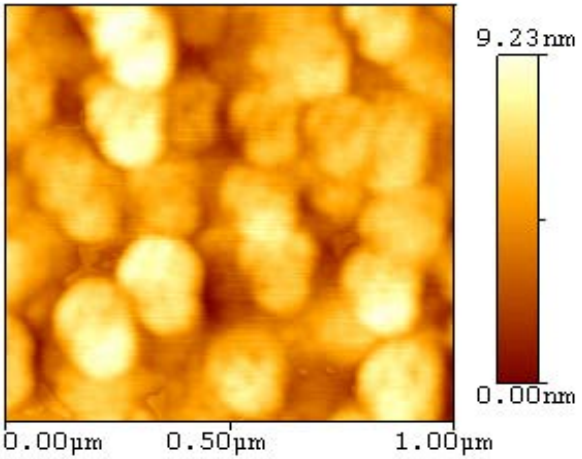
SEM images of Pd-film by CEP and SIEP with DTAB

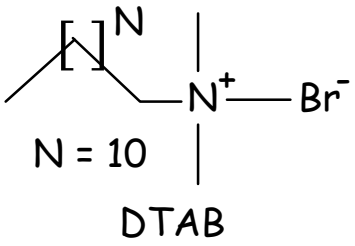
Grain size distribution



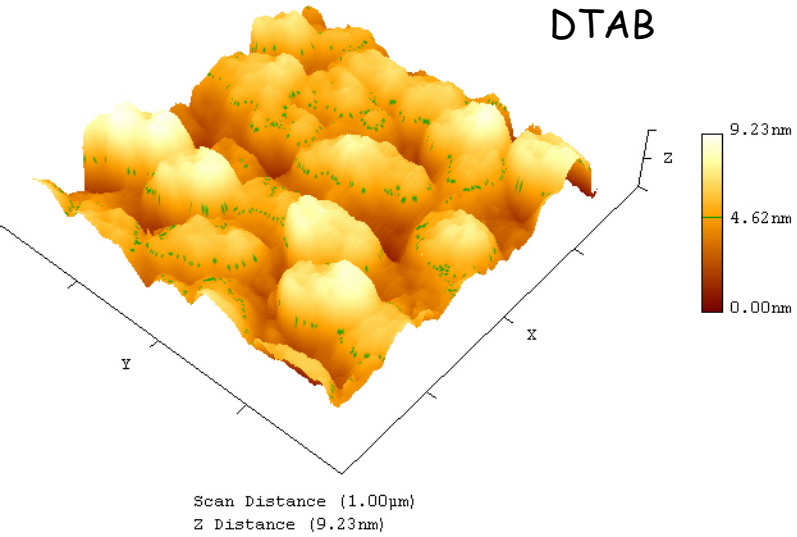
Ilias, S., and M.A. Islam, Patent Application #20100068391 (USPTO assignment date: March 18, 2010).

Interaction of DTAB in Solid Surface





DTAB



AFM images of solid surface aggregation into typical hydrophobic glass surface

AFM image shows various cylindrical long chains but repetitive structure.

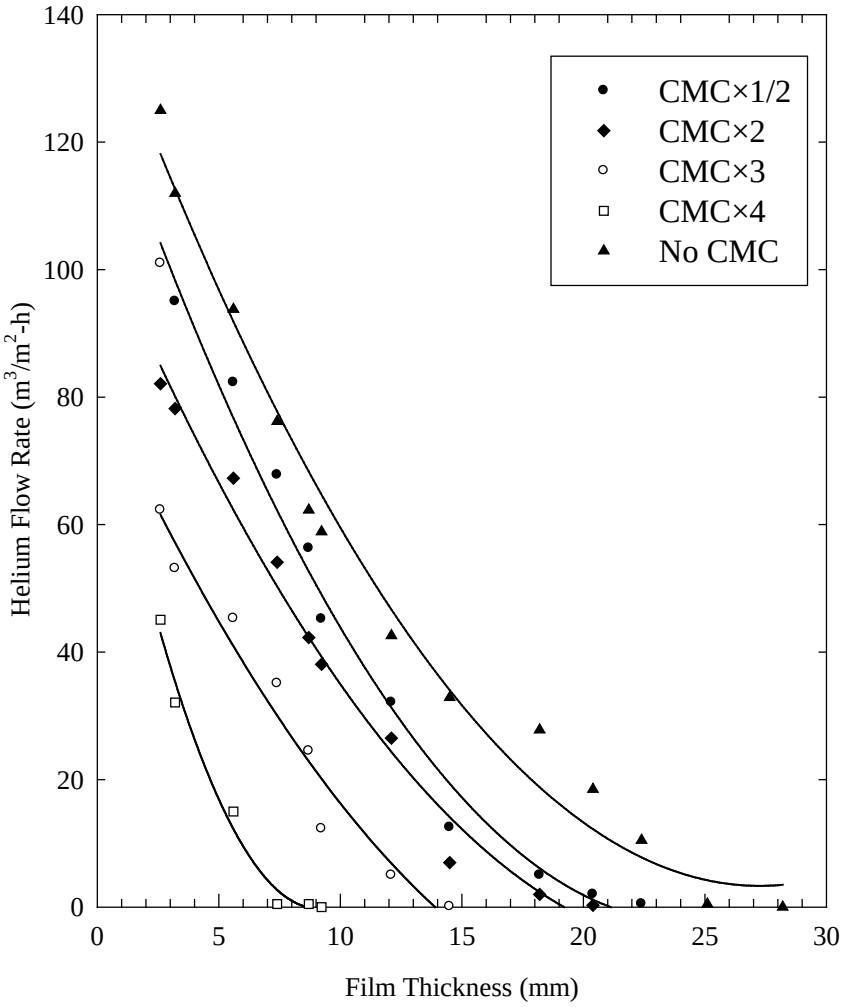
DTAB is hydrophobic in nature to be aligned around the gas-liquid interface and form various spherical or cylindrical cages like structure.

DTAB tends to form various meta-stable structures (spherical or cylindrical) at the solid-liquid interface that helps finer grain formation and subsequent coarsening of the deposited film.

DTAB contain active bromide ions in the head group (strong oxidizing agent). This head group likely to participate in the reduction process of the complex salt and favorably take part in Pd-grain formation and subsequent grain coarsening

Palladium film thickness fabricated under different CMC

Membrane Samples	DTAB (CMC)	Deposit Time (h)	Pd-film thickness (μm)	
			Weight Basis	SEM
A	0.5	22	23.0	22.5
B	2	16	17.8	18.3
C	3	13	14.0	13.5
D	4	10	8.5	8.5
E	0	28	28.5	27.5



He gas-tightness of membranes

Summary of grain distribution in Pd-film fabricated by EP and SIEP with DTAB

Surfactant	Surfactant Concentration (CMC) in mM	Surfactant Concentration in mM	Grain Size (μm)
None - CEP	N/A	N/A	5-15
SDBS - SIEP	1.4	1.4	5-15
		5.6	2-15
Triton X-100 - SIEP	0.23	0.23	10-15
		0.92	5-10
DTAB - SIEP	16	16	4-8
		64	2-4

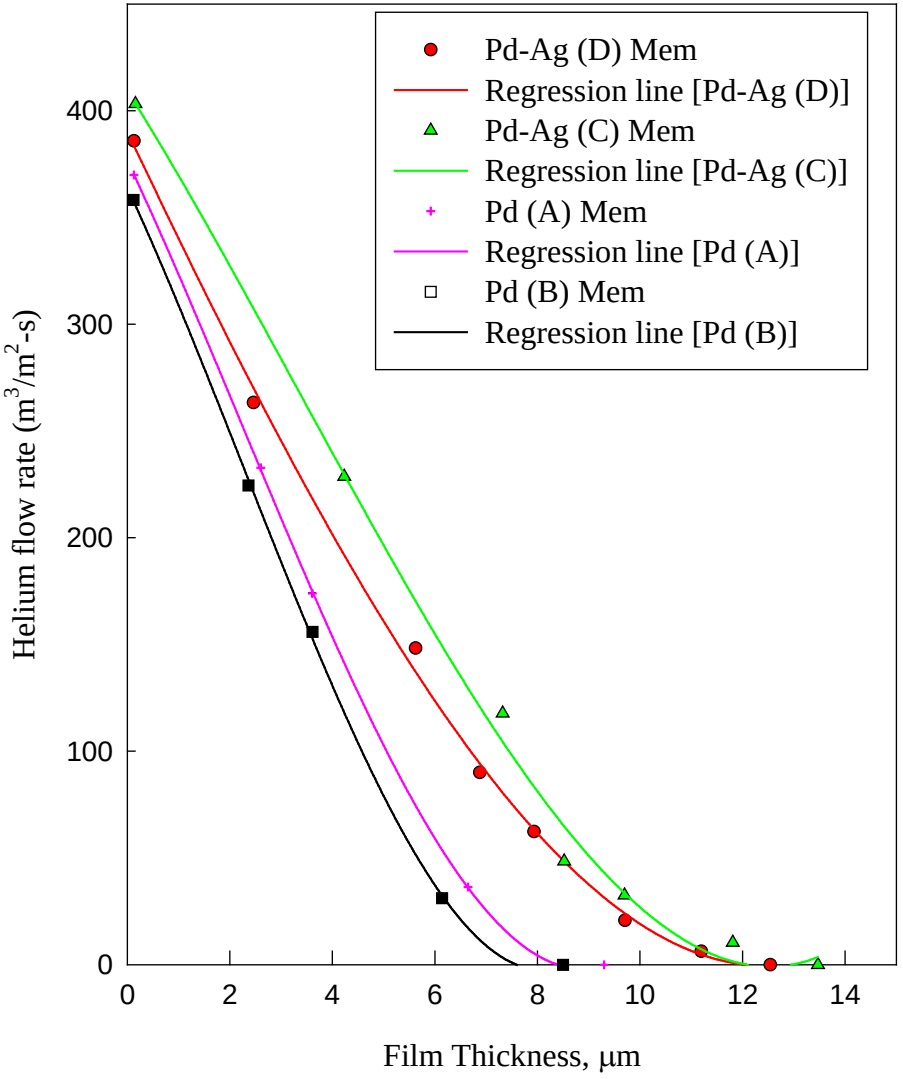
MICROSTRUCTURE ANALYSIS OF MEMBRANES BY CEP & SIEP

Membrane Support :

316L SS, 0.2 µm – Motts Corp.

Discs: 1 in dia, 0.062 in thick

Tubes: 10 cm long, 1.07 cm ID, and 0.16 cm thick



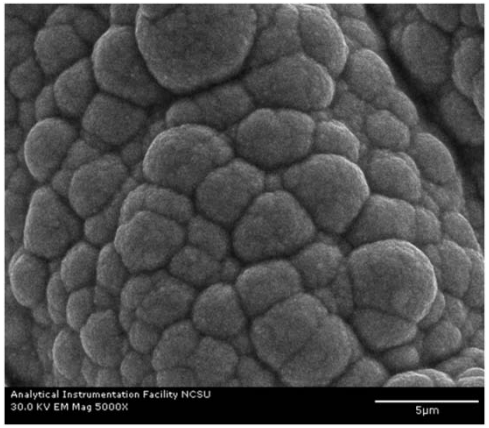
Compared to CEP, membranes fabricated by SIEP process showed superior performance.

- Thinner film thickness
- Lower deposition time
- Comparable selectivity

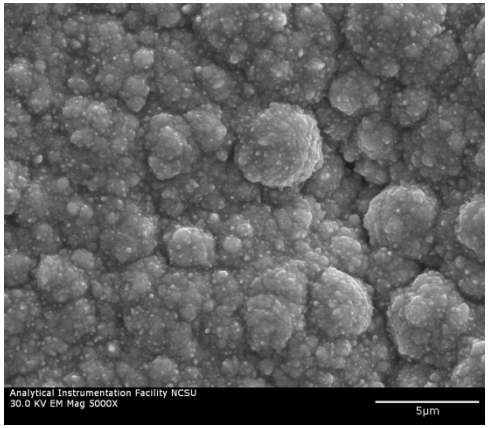
He gas-tightness of membranes

Microstructure Analysis of Membranes by CEP & SIEP

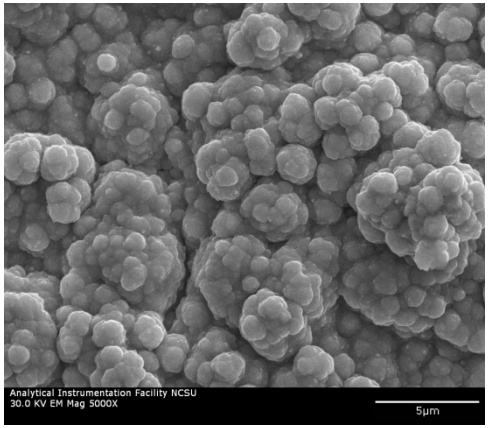
SEM images: Pd and Pd-Ag film by CEP & SIEP @ 5k & 10k



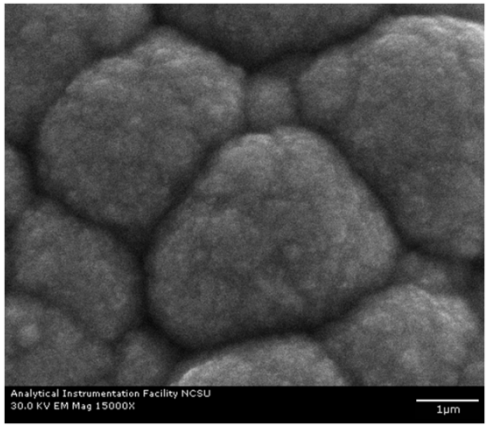
(a) Pd at 5K (CEP)



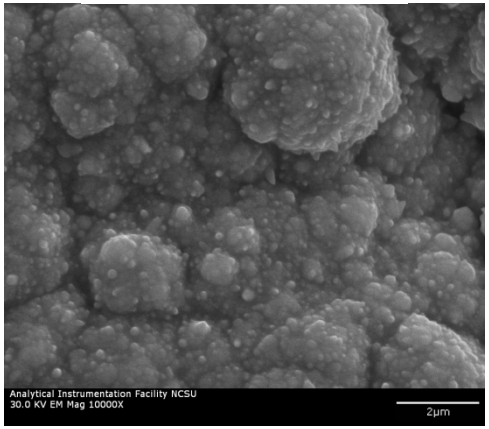
(c) Pd at 5K (SIEP)



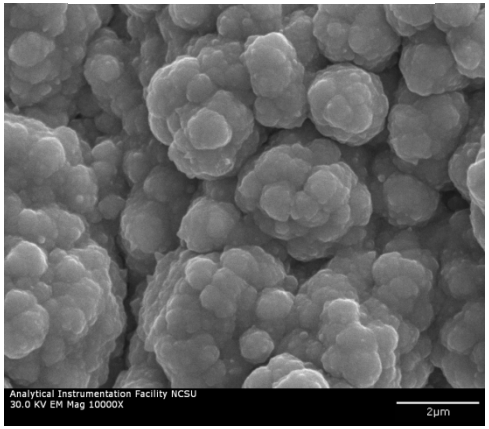
(e) Pd-Ag at 5K (SIEP)



(b) Pd at 10K (CEP)



(d) Pd at 10K (SIEP)

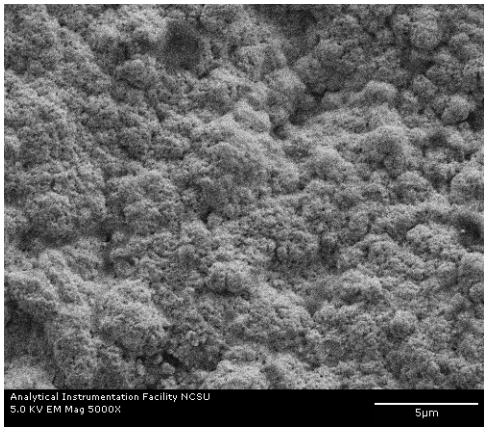


(f) Pd-Ag at 5K (SIEP)

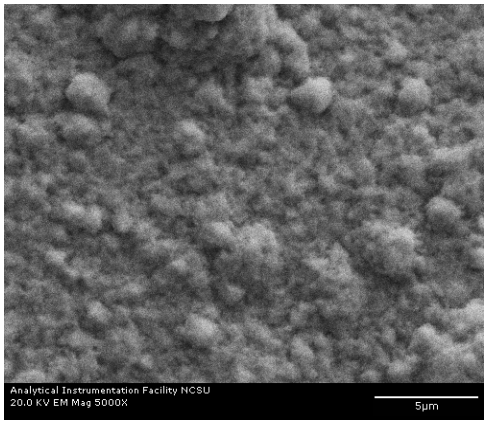
SIEP shows enhanced grain agglomeration

Microstructure Analysis of Membranes by CEP & SIEP

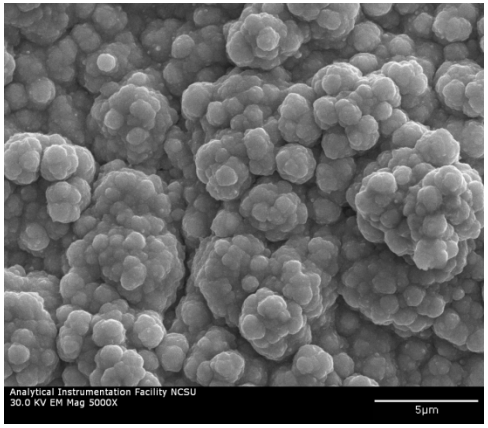
SEM images: Pd-Ag & Pd-Cu film by CEP & SIEP @ 5k & 10k



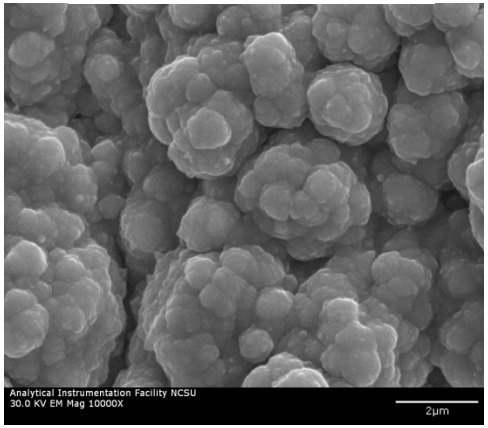
(a) Pd-Ag at 5K (CEP)



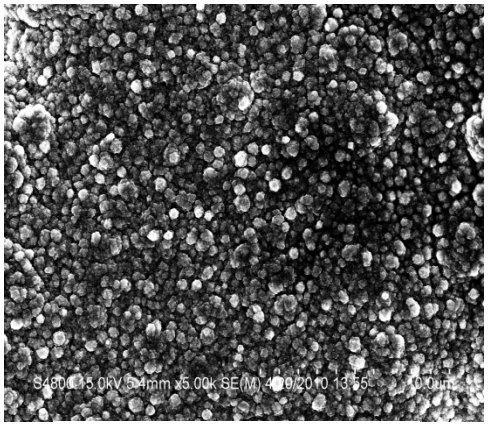
(b) Pd-Ag at 5K (CEP)



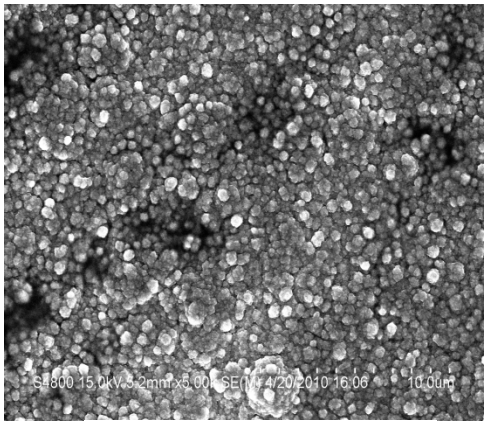
(c) Pd-Ag at 5K (SIEP)



(d) Pd-Ag at 5K (SIEP)



(e) Pd-Cu at 5K (SIEP)



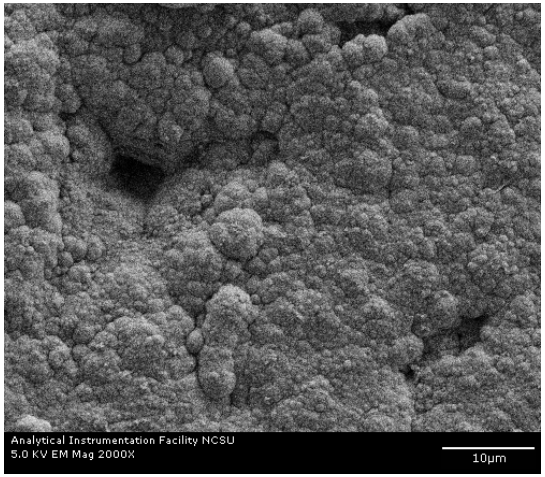
(f) Pd-Cu at 5K (SIEP)

SIEP shows enhanced grain agglomeration

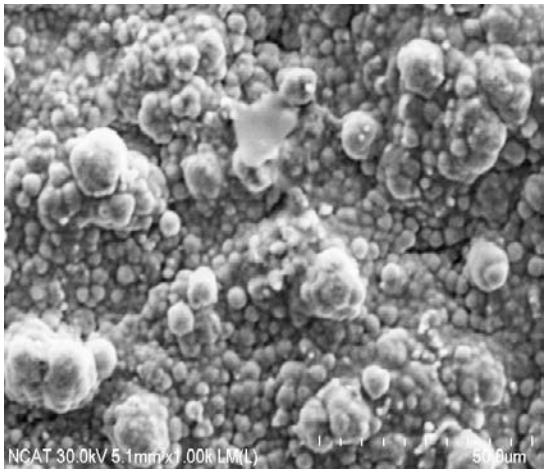
Pd-Cu film has finer grain structure

Microstructure Analysis of Membranes by CEP & SIEP

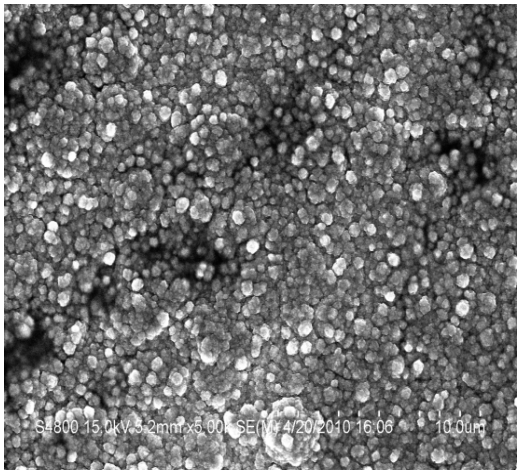
Effect of heat treatment: Pd-Cu film by CEP & SIEP



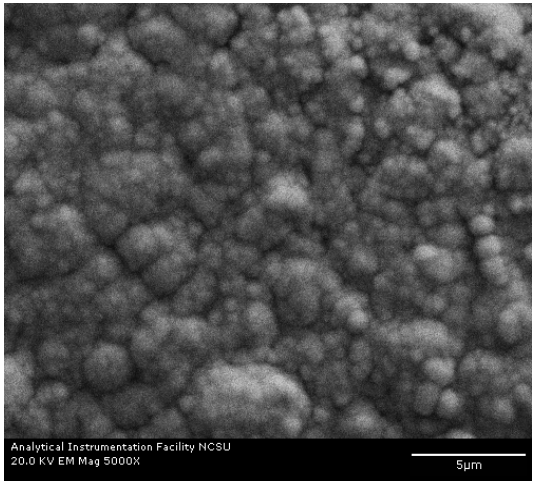
(a) Pd-Cu at 2K (CEP) WHT



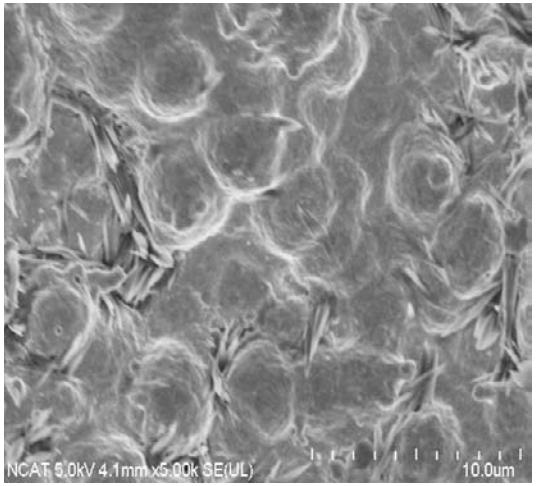
(c) Pd-Cu at 1K (CEP) HT



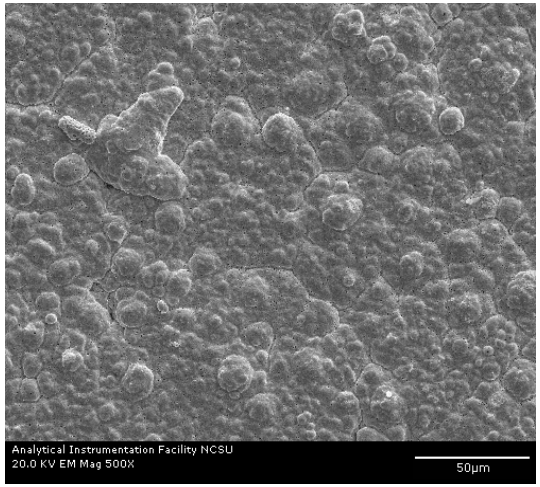
(e) Pd-Cu at 1K (SIEP) WHT



(b) Pd-Cu at 5K (CEP) WHT

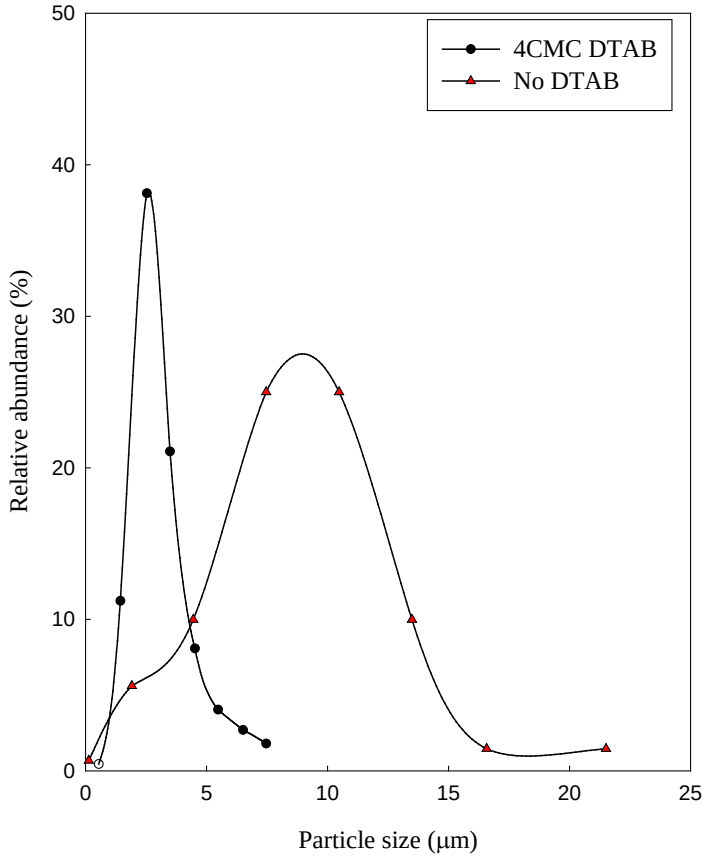


(d) Pd-Cu at 5K (CEP) HT

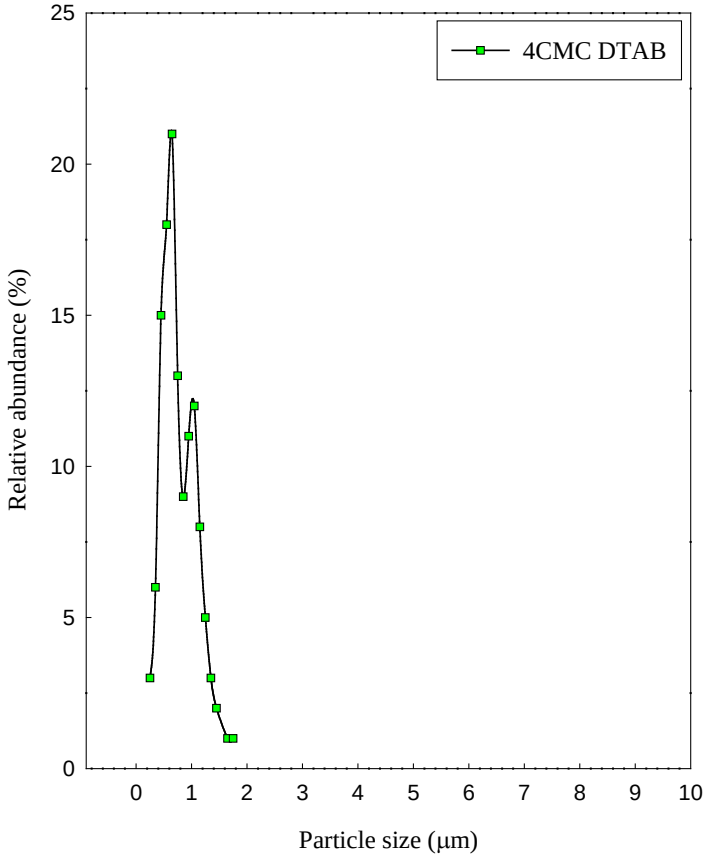


(f) Pd-Cu at 5K (SIEP) HT

Microstructure Analysis: Grain Size Distribution



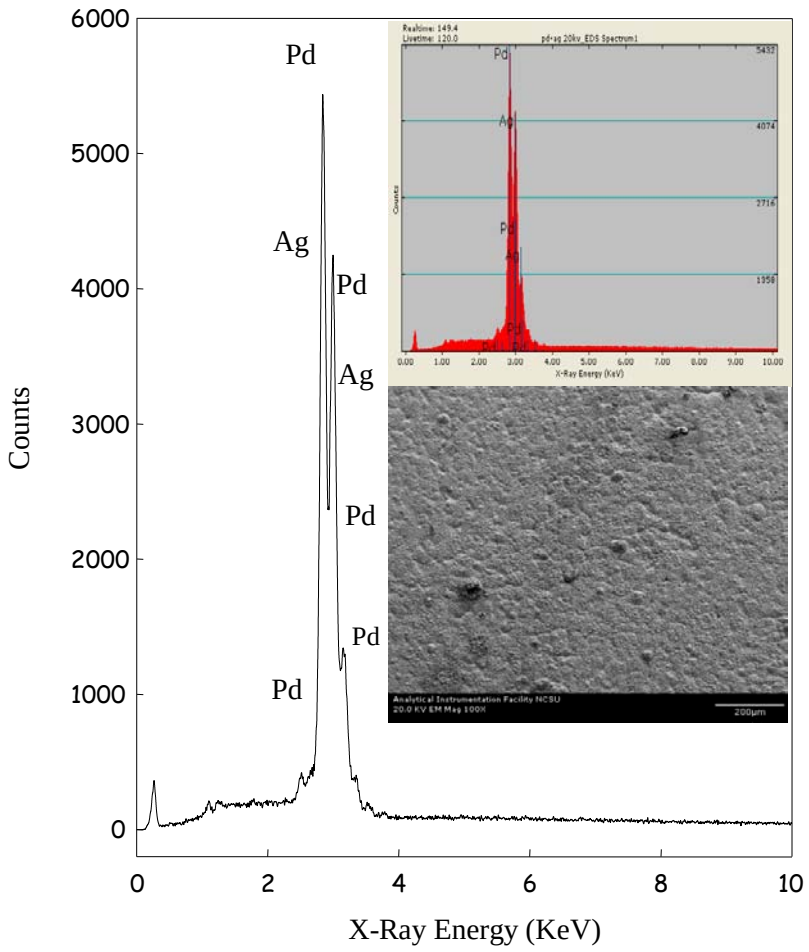
Grain size distribution of Pd film by CEP & SIEP process



Grain size distribution of Pd-Ag film by SIEP process

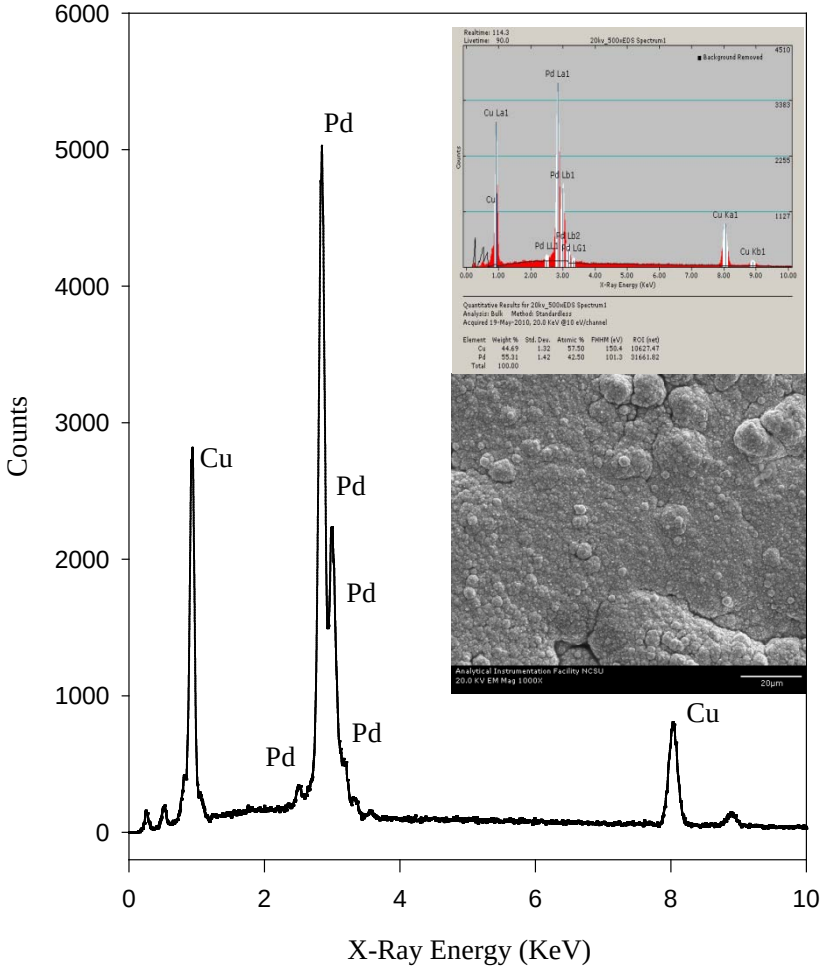
- DTAB reduces grain size from 8 to 2 μm
- Two peaks represents sequential deposition
- Reduces the grain size further (0.8 to 1.2 μm)

Microstructure: EDS Elemental Analysis



Element	Weight %	Std. Dev.	Atomic %	FWHM (eV)	ROI (net)
Ag	23.99	1.06	23.74	104	38723.85
Pd	76.01	1.88	76.26	101.9	45520.55

EDS spectrum of Pd-Ag film



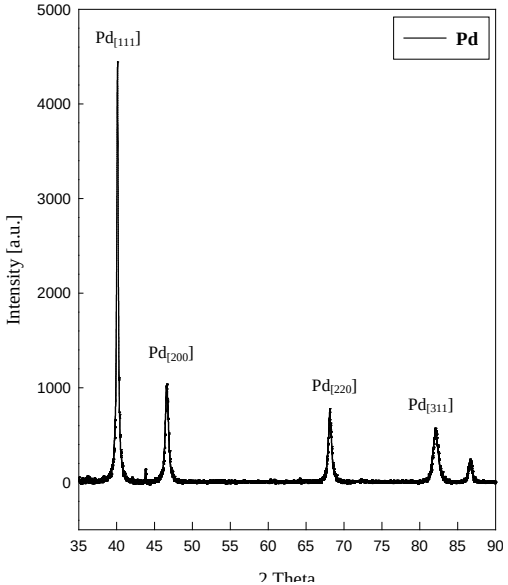
Element	Weight %	Std. Dev.	Atomic %	FWHM (eV)	ROI (net)
Cu	44.69	1.32	57.5	150.4	10627.47
Pd	55.31	1.42	42.5	101.3	31661.82

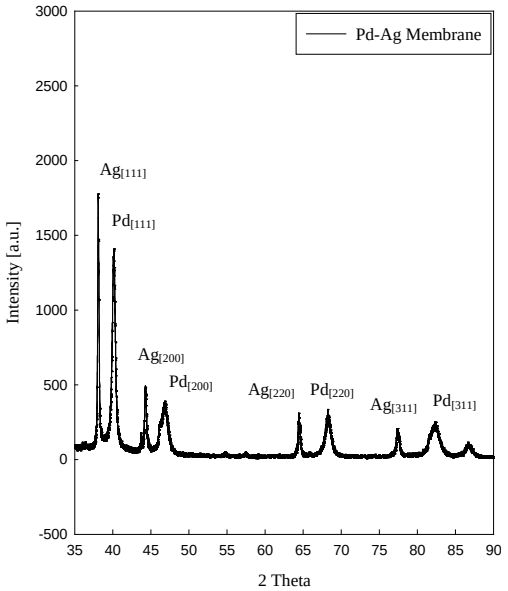
EDS spectrum of Pd-Cu film

Microstructure Analysis: XRD and SEM Images

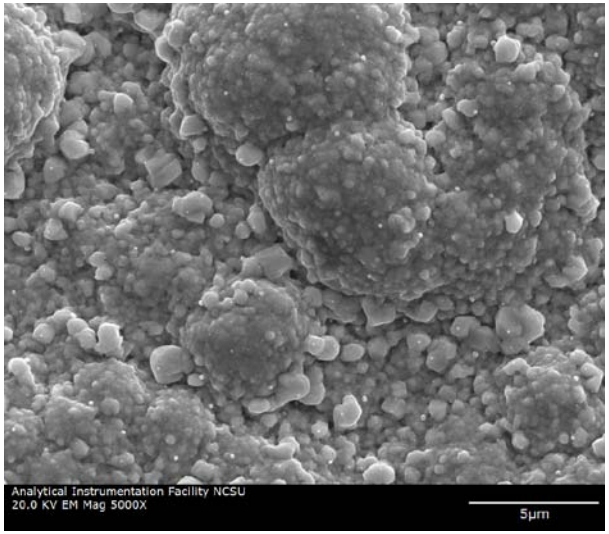
Typical XRD Pattern of Pd film by SIEP

- Give reflection peaks at characteristics plane
- Polycrystalline particles.
- Shows no impurities
- Bright dots are nucleation sites

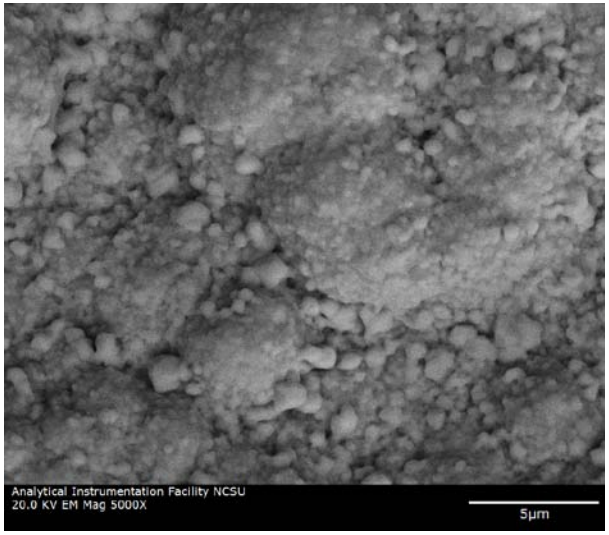




Typical XRD Pattern of Pd-Ag film by SIEP



(a) Pd-Ag at 5k (20kV) SE image



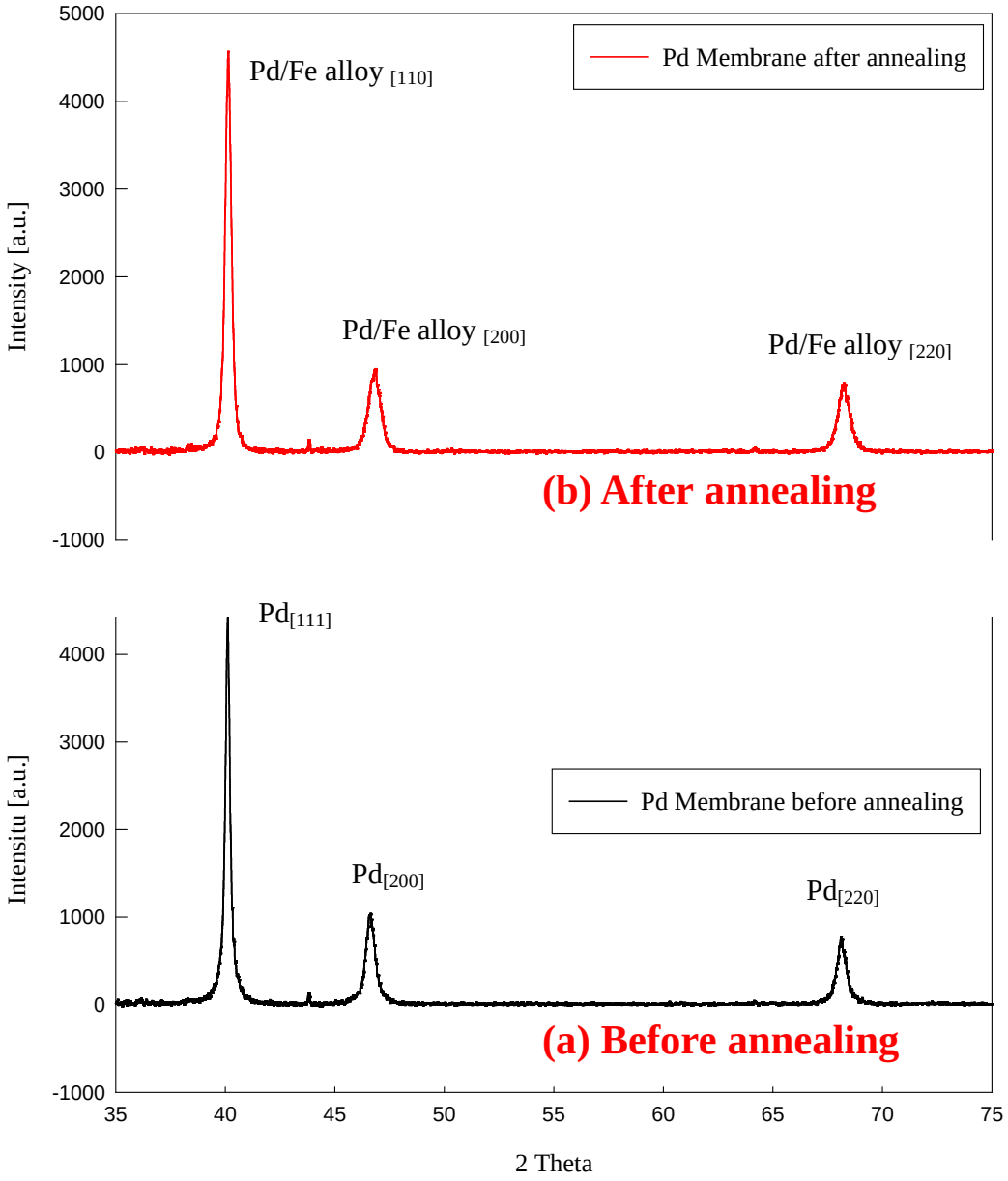
(b) Pd-Ag at 5k (20kV) BSE

Simultaneous SE & BSE images of Pd-Ag film by SIEP

Heat Treatment

Pd-MPSS Membrane by SIEP

- Pre- and Post-annealing peaks are at the same planes at [111], [200], [220], [311]
- FCC structure was observed in both occasion.
- Slight peak widening is observed due to minute amounts of Fe-diffusion in annealing
- No change in lattice parameter
- Annealing: 500°C, in H_2 environment, 18 hrs, 1 atm pressure

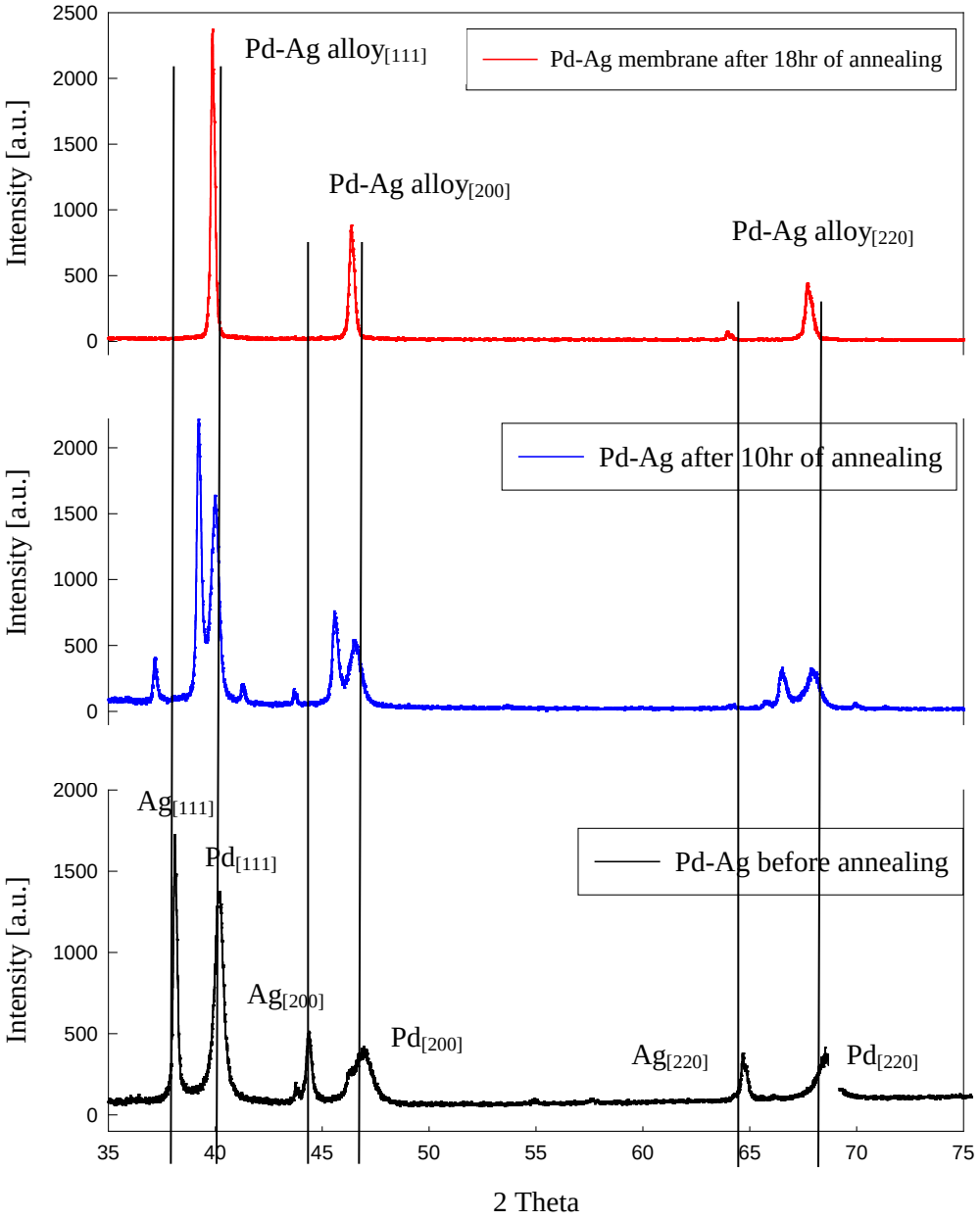


XRD Pattern: Pre- & Post-annealing

Heat Treatment

Pd/Ag-MPSS membrane by SIEP

- Pre-annealing peaks of Pd and Ag are at the characteristic planes.
- At intermediate annealing (10 hrs), peaks tends to merge to form alloy at the characteristic planes.
- After complete annealing (18 hrs), sharp alloy reflection peaks are observed in [111], [200], and [220] (intermediate positions of pure Pd & Ag).

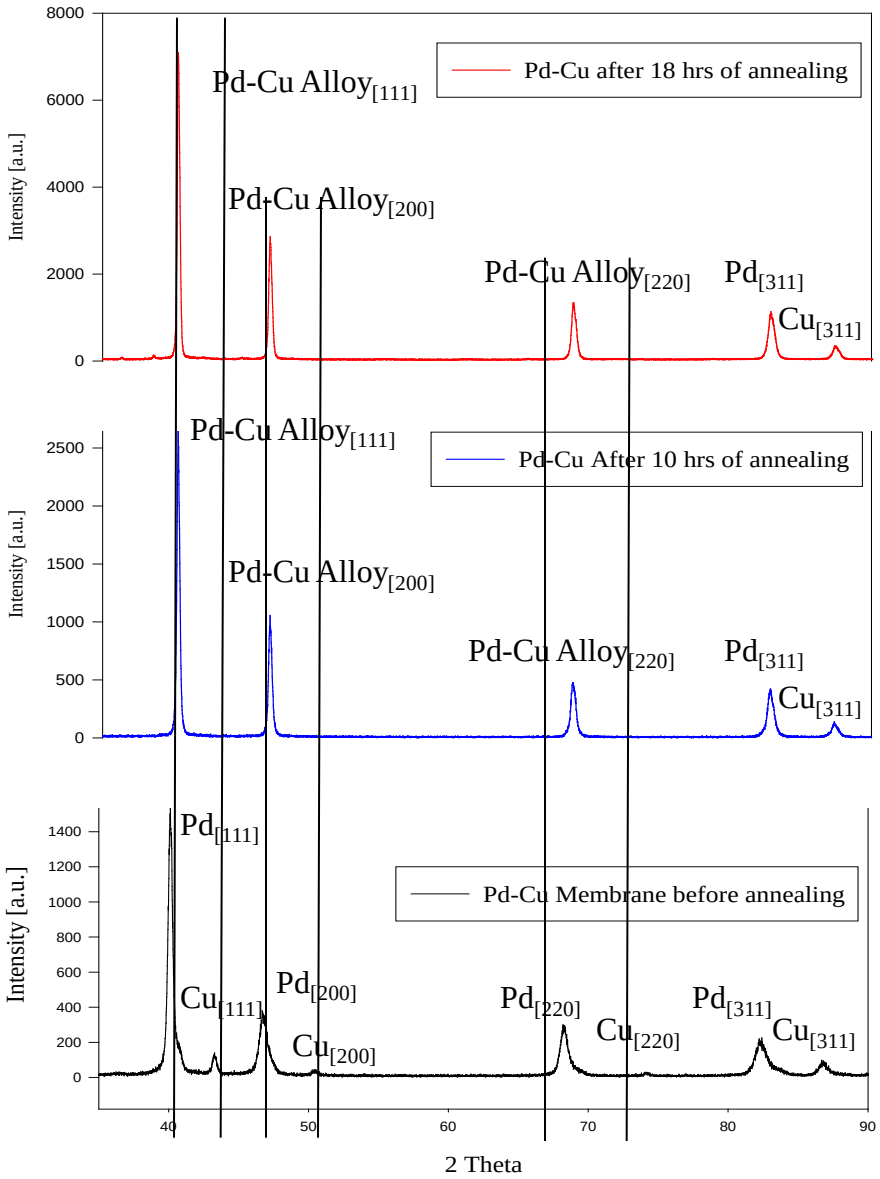


XRD Pattern: Pre- & Post-annealing

Heat Treatment

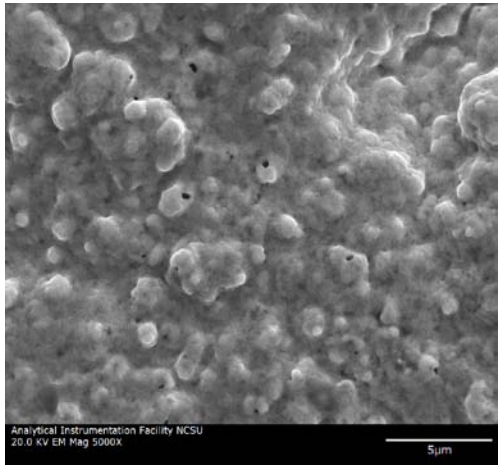
Pd/Cu-MPSS membrane by SIEP

- Pre-annealing peaks of Pd and Cu are at the characteristic planes.
- At intermediate annealing (10 hrs), peaks merge to form alloy at the characteristic planes.
- After complete annealing (18 hrs), sharp alloy reflection peaks are observed in [111], [200], and [220] (intermediate positions of pure Pd & Cu).

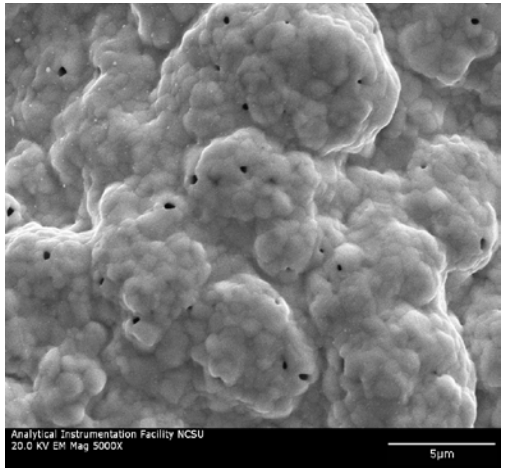


XRD Pattern: Pre- & Post-annealing

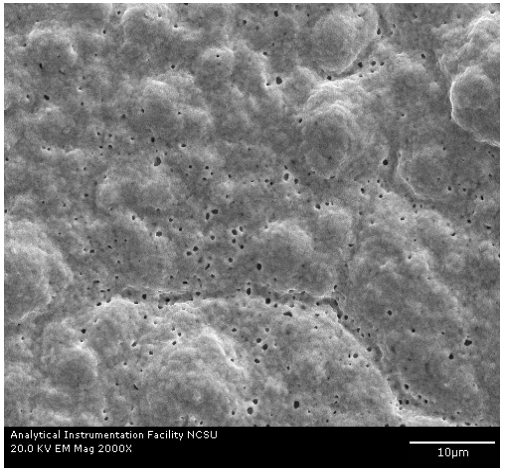
Heat Treatment: Effect on Pd, Pd-Ag & Pd-Cu Microstructures



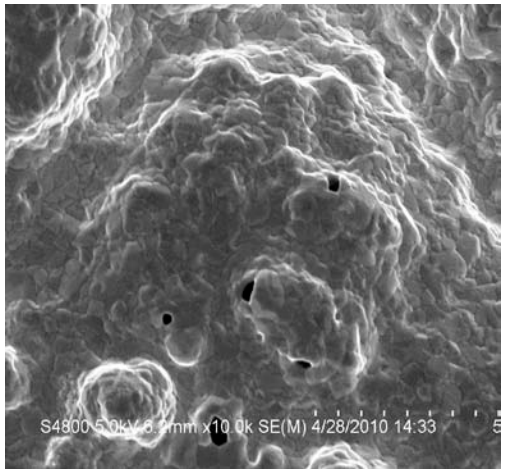
Pd membrane at 5K (AA)



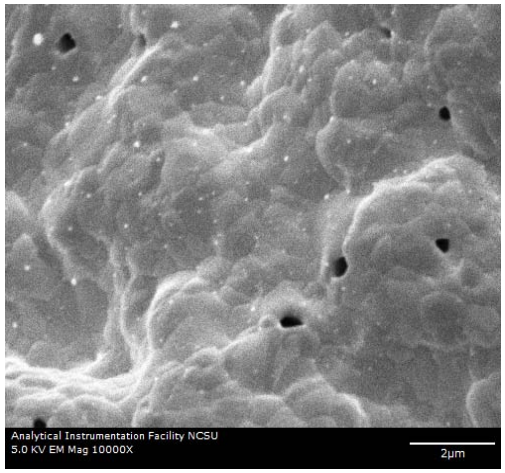
Pd-Ag membrane at 5K (AA)



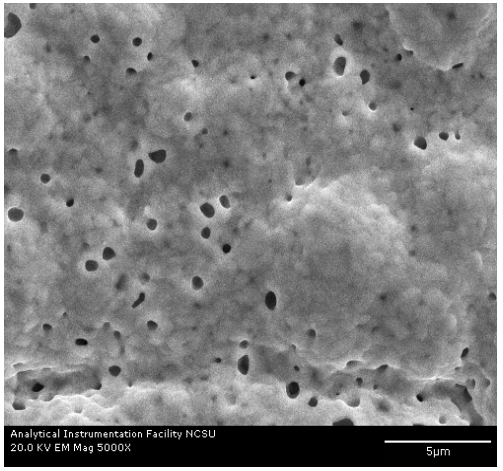
Pd-Cu membrane at 2K (AA)



Pd membrane at 10K (AA)



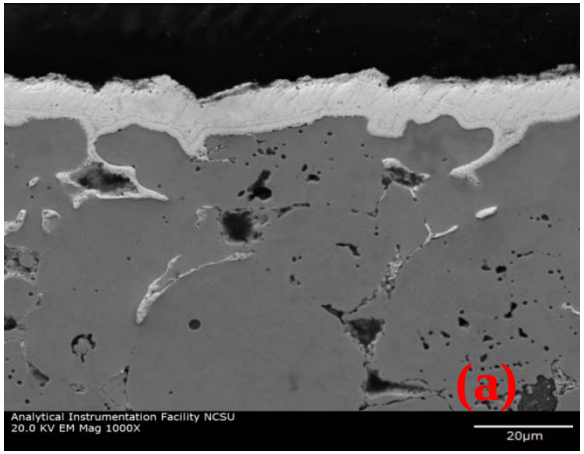
Pd-Ag membrane at 10K (AA)

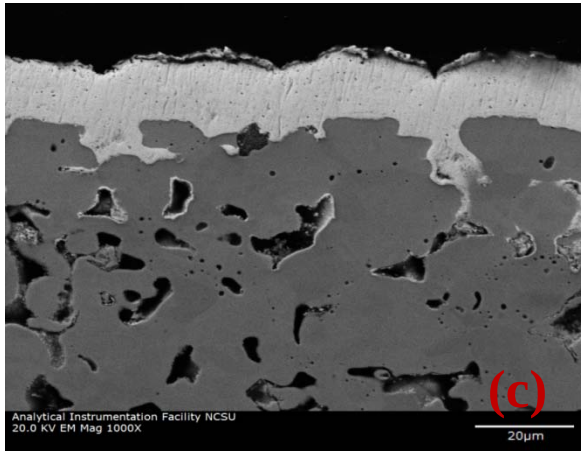


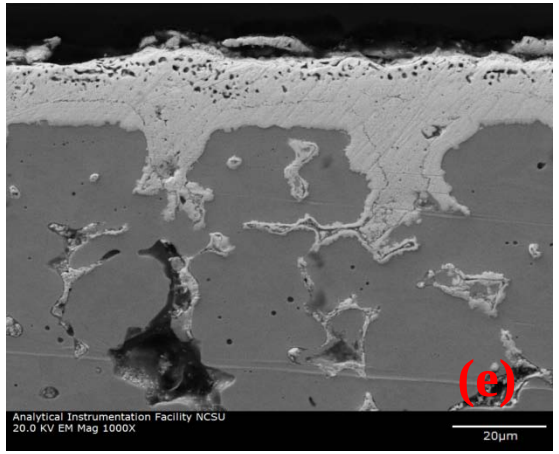
Pd-Cu membrane at 5K (AA)

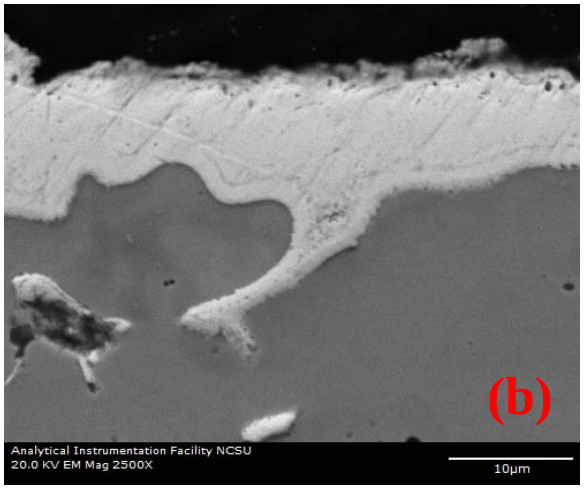
SEM images of Pd, Pd-Ag & Pd-Cu film fabricated by SIEP (AA = After Annealing)

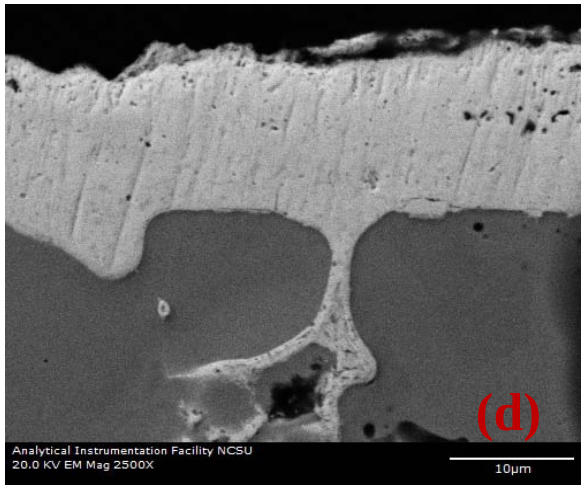
Heat Treatment: Pd, Pd-Ag & Pd-Cu film x-section

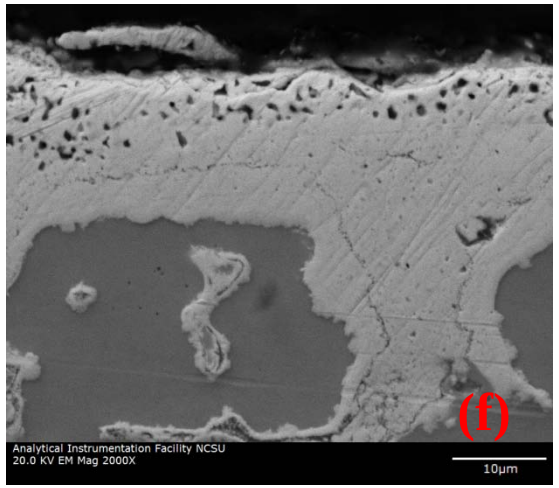








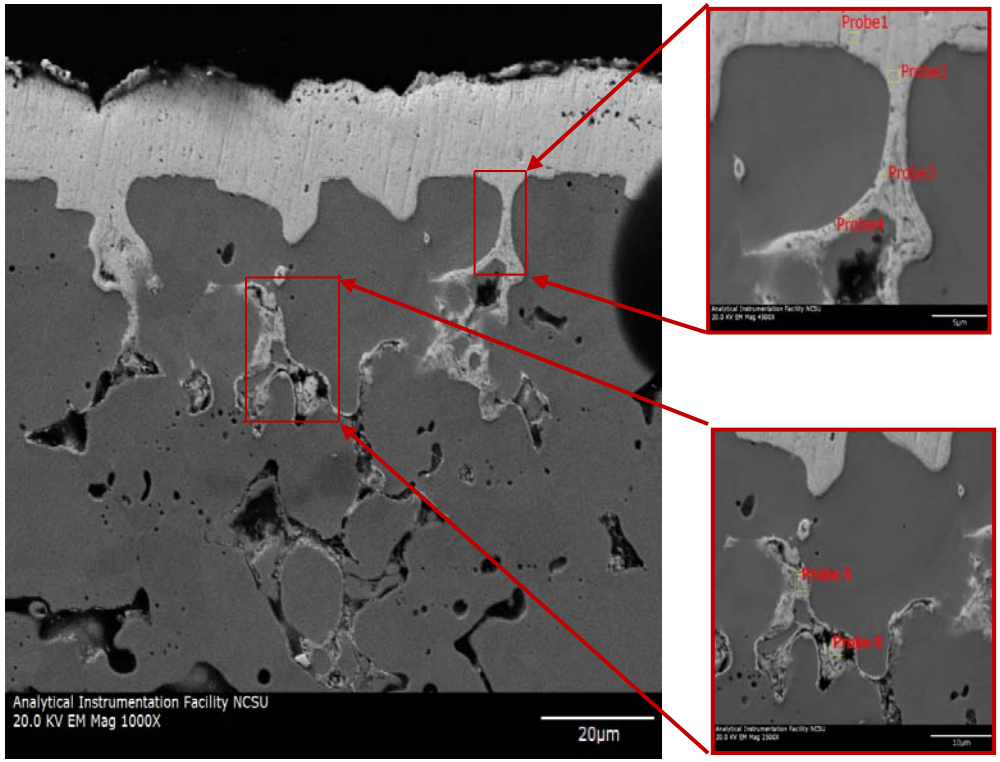




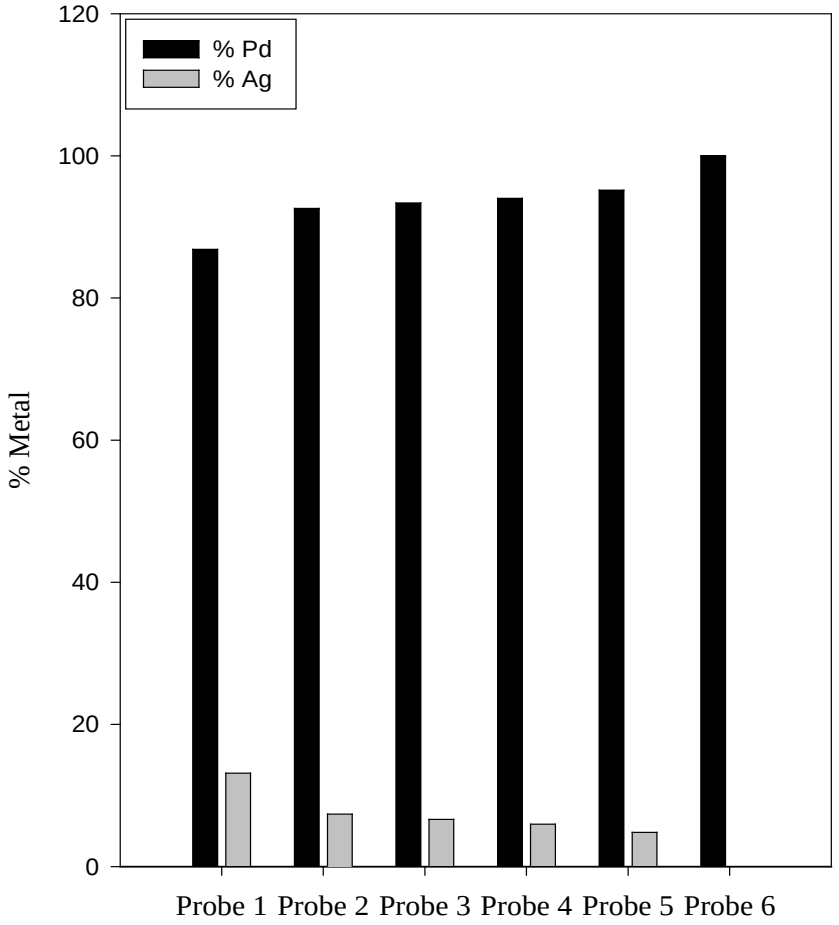
Pd X-section (a) 1K & (b) 2.5 K Pd-Ag X-section (c) 1K & (d) 2.5 K Pd-Cu X-section (e) 1K & (f) 2 K

- All recognizable pores were plugged
- Metal deposition observed far inside
- Pd membrane has thinner film than Pd-Ag & Pd-Cu film

Heat Treatment: Pore analysis of Pd-Ag film x-section

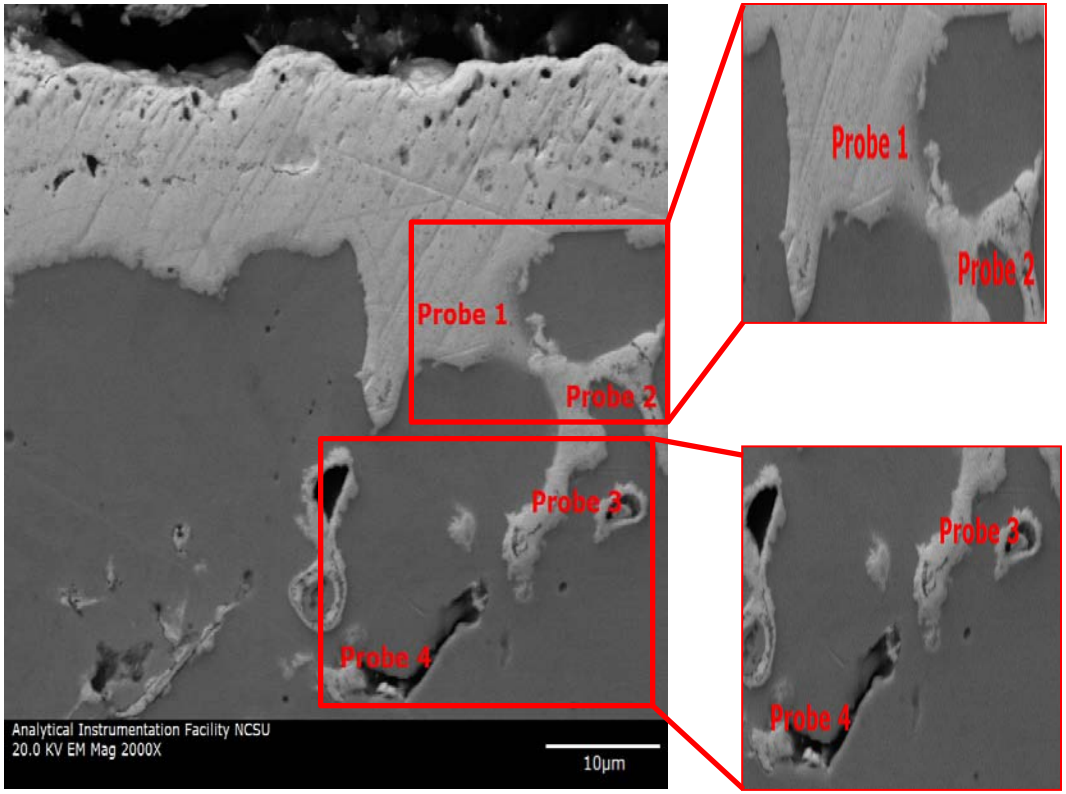


SEM images of Pg-Ag membrane cross-section: Pores plugged by metal deposition.

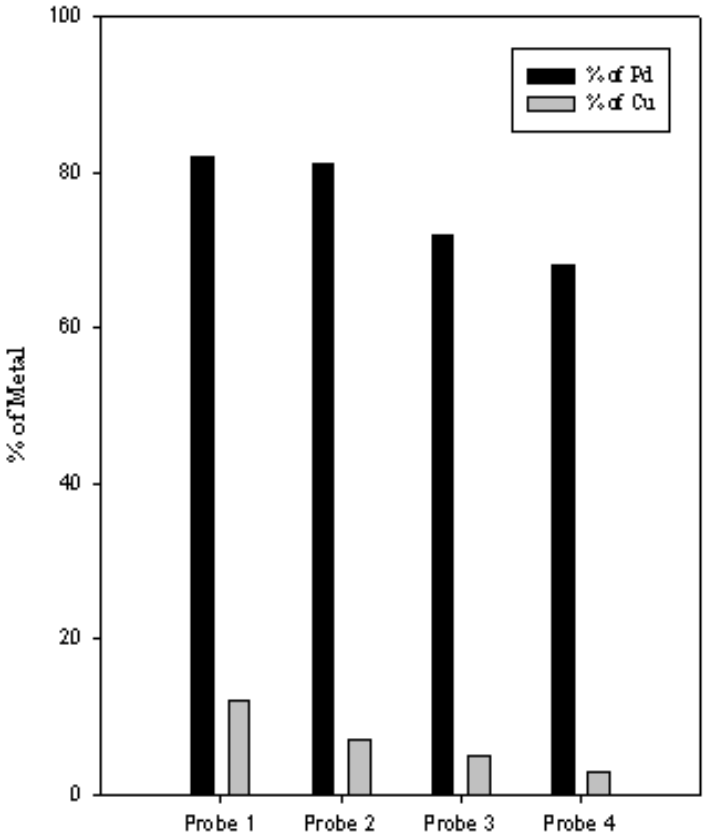


Pd-Ag membrane: Metal (Pd & Ag) distribution in the pores starting from the pore mouth to deep inside of the pore (From Probe 1 → Probe 6).

Heat Treatment: Pore analysis in Pd-Cu film x-section



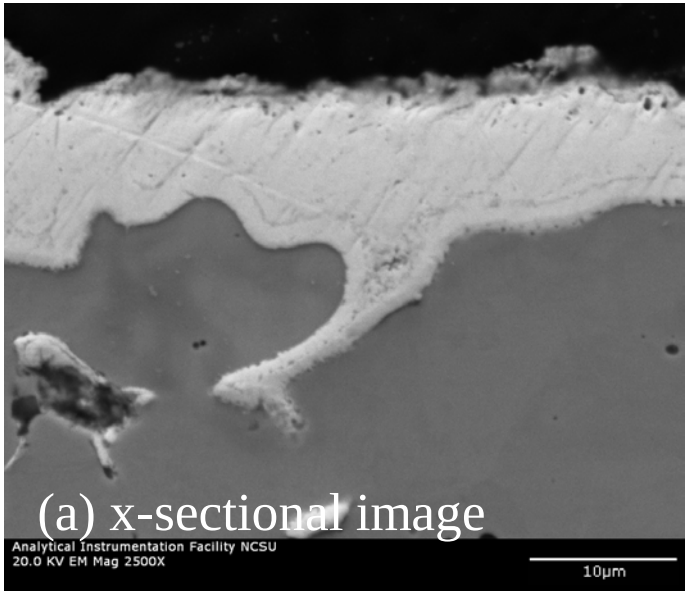
SEM images of Pg-Cu membrane x-section: Pores plugged by metal deposition.

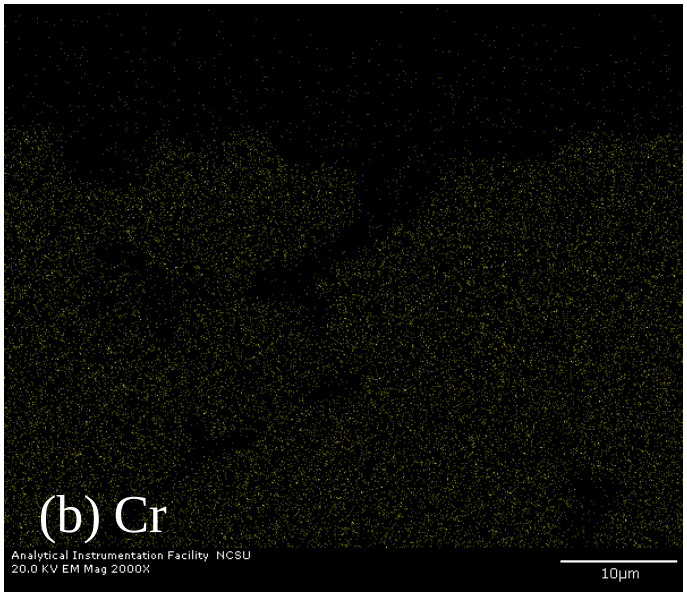


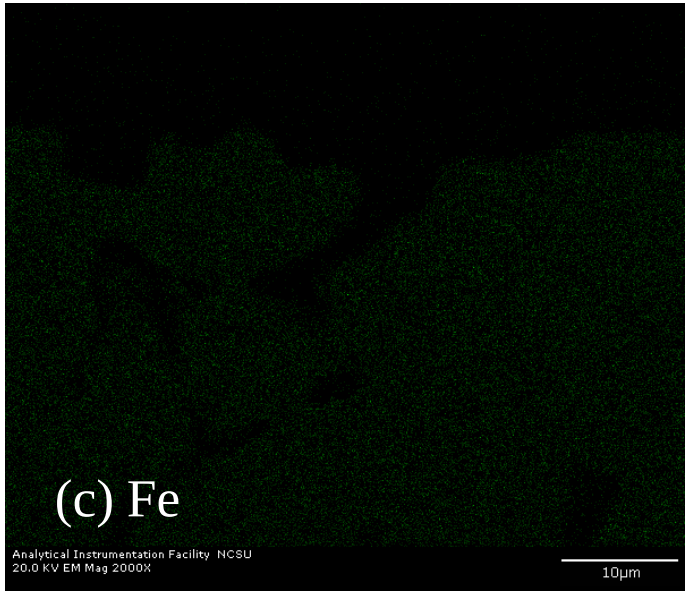
Pd-Cu membrane: Metal (Pd & Cu) distribution in the pores starting from the pore mouth to deep inside of the pore (From Probe 1 → Probe4).

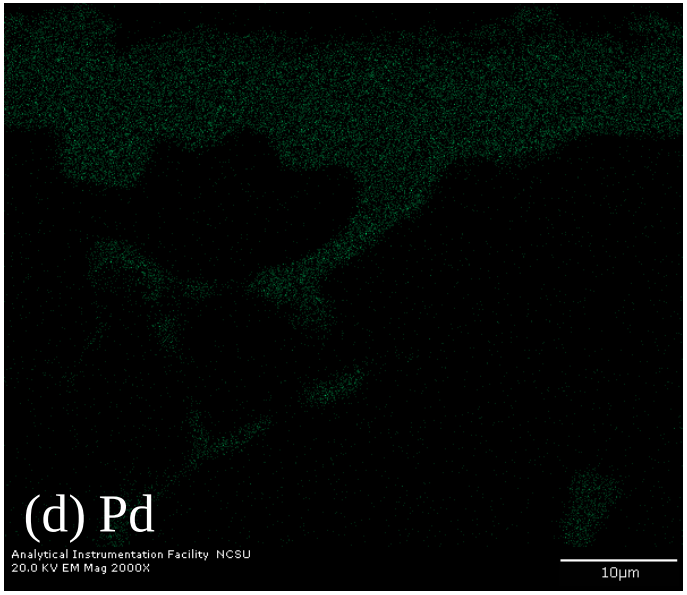
Heat Treatment: EDS mapping of Pd film

- Metal mapping provides exact shape of the film.
- Pd concentration is high on the film.
- A minor migration was observed.
- Pd deposition on the deep pores was observed.





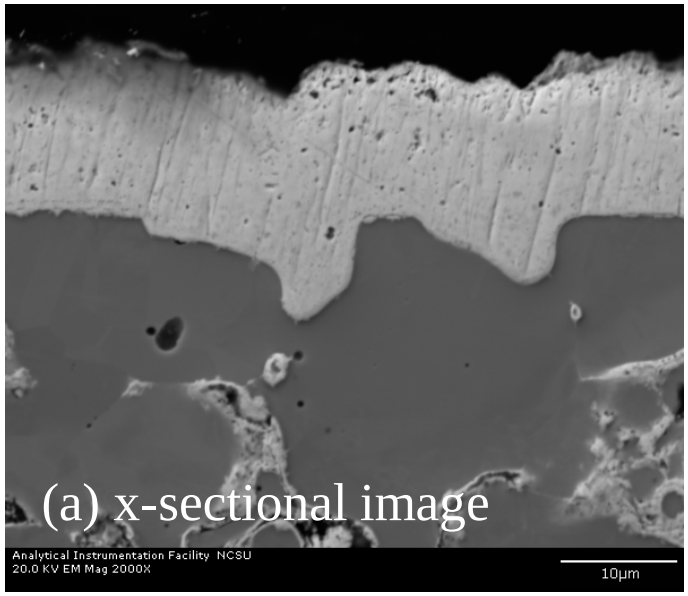


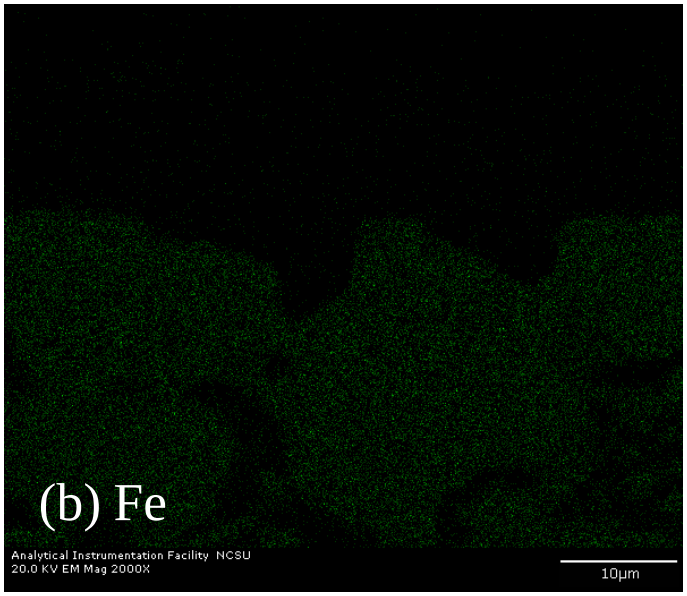


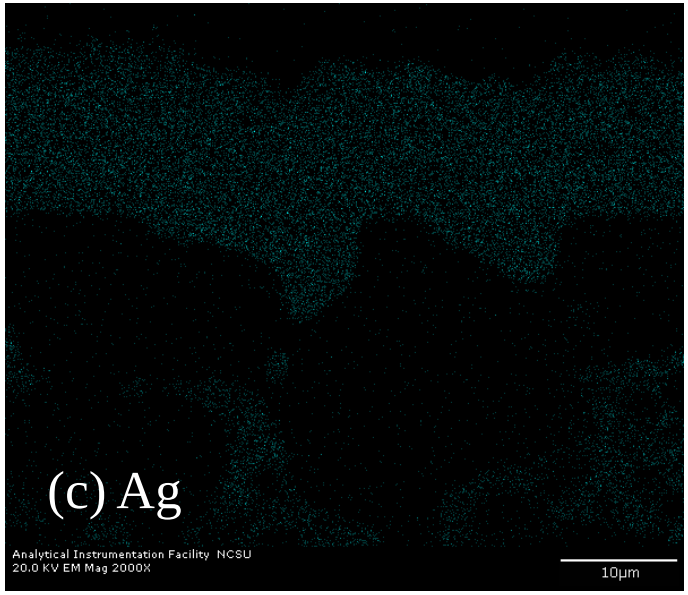
Post-annealing: Pd-MPSS membrane (SIEP)

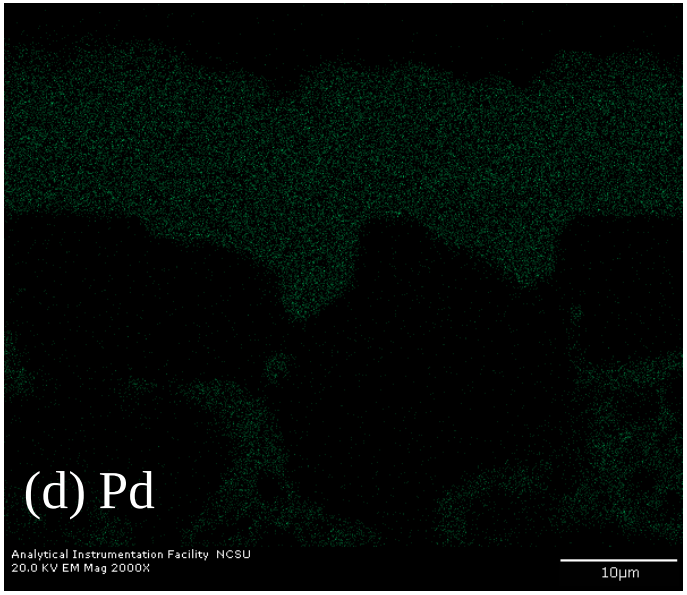
Heat Treatment: EDS mapping of Pd-Ag film

- Metal mapping forms exact shape of the film.
- Pd & Ag concentration is high on the film.
- Higher Ag migration was observed.
- Pd & Ag deposition on the deep pores was observed.





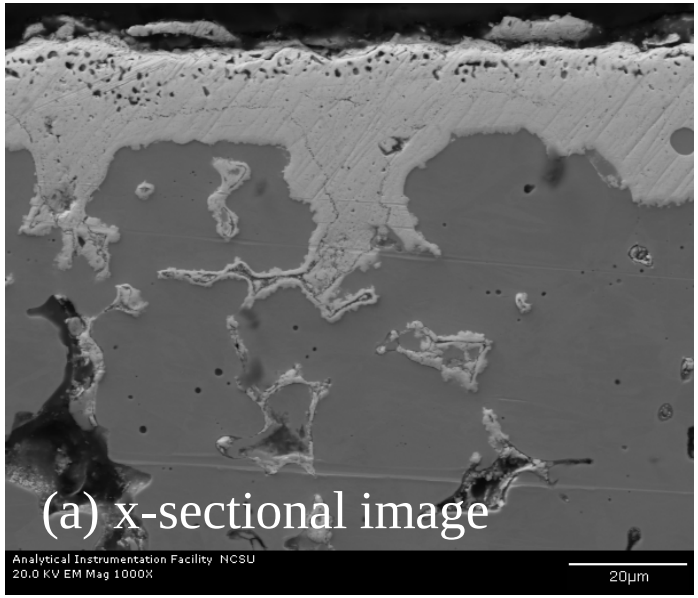


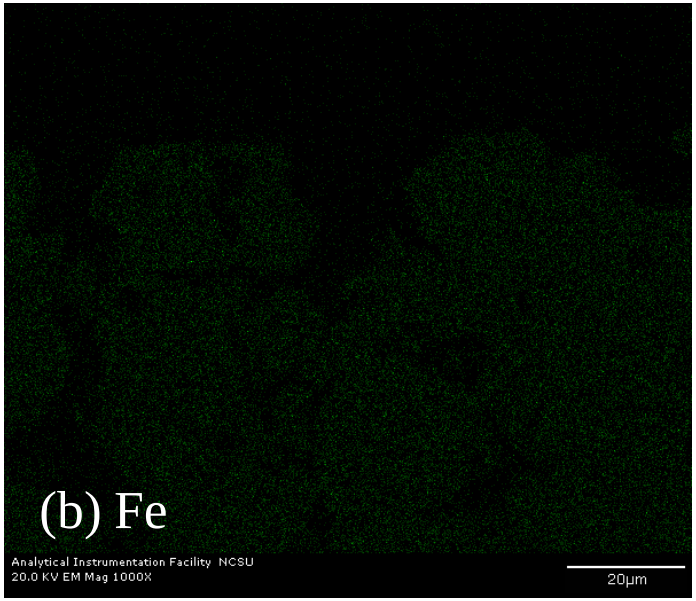


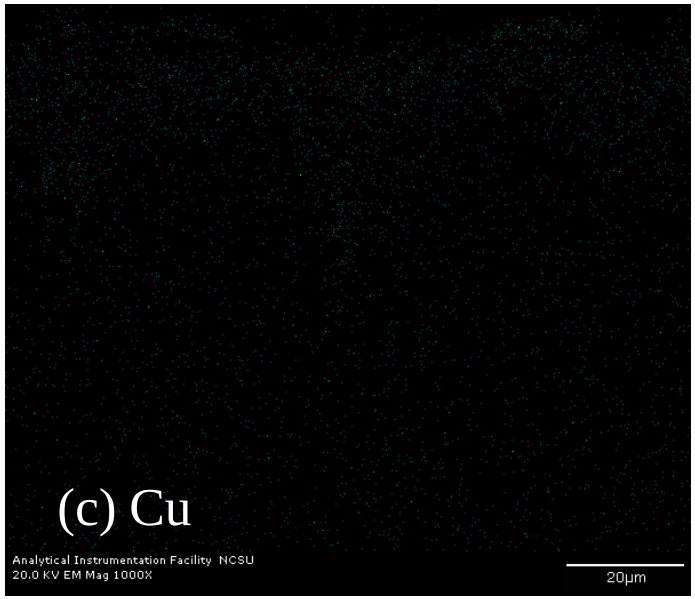
Post-annealing: Pd-Ag-MPSS membrane (SIEP)

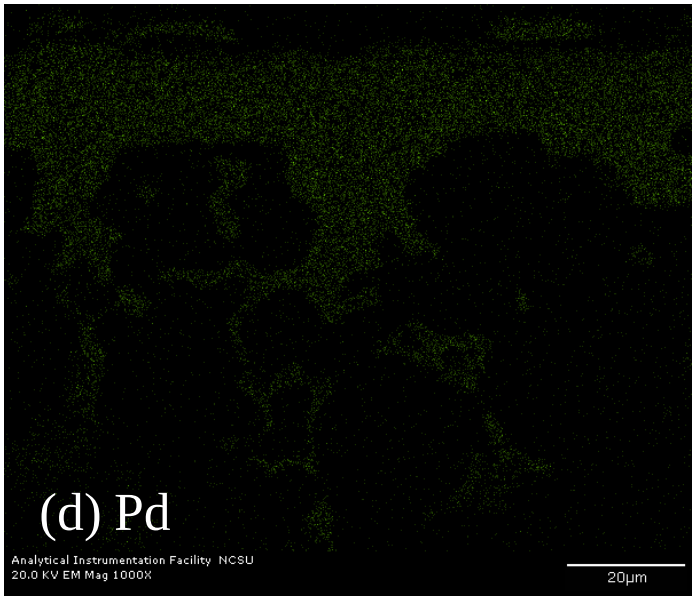
Heat Treatment: EDS mapping of Pd-Cu film

- Metal mapping forms exact shape of the film.
- Pd & Cu concentration is high on the film.
- Cu is distributed evenly from film to deep inside.
- Pd & Cu deposition on the deep pores was observed.



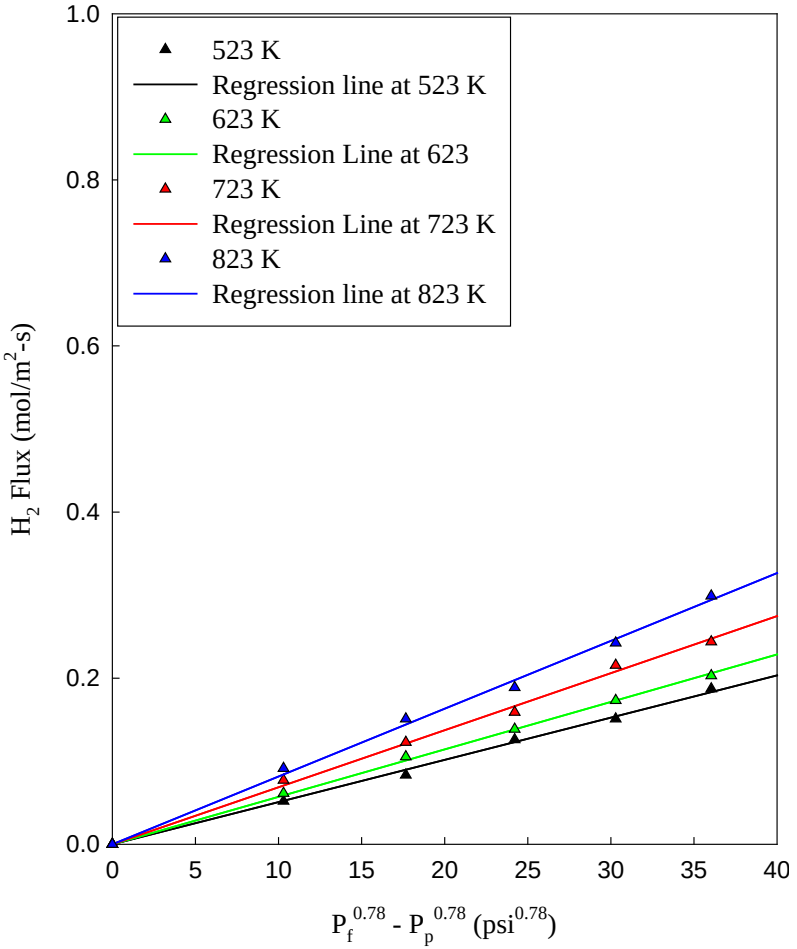




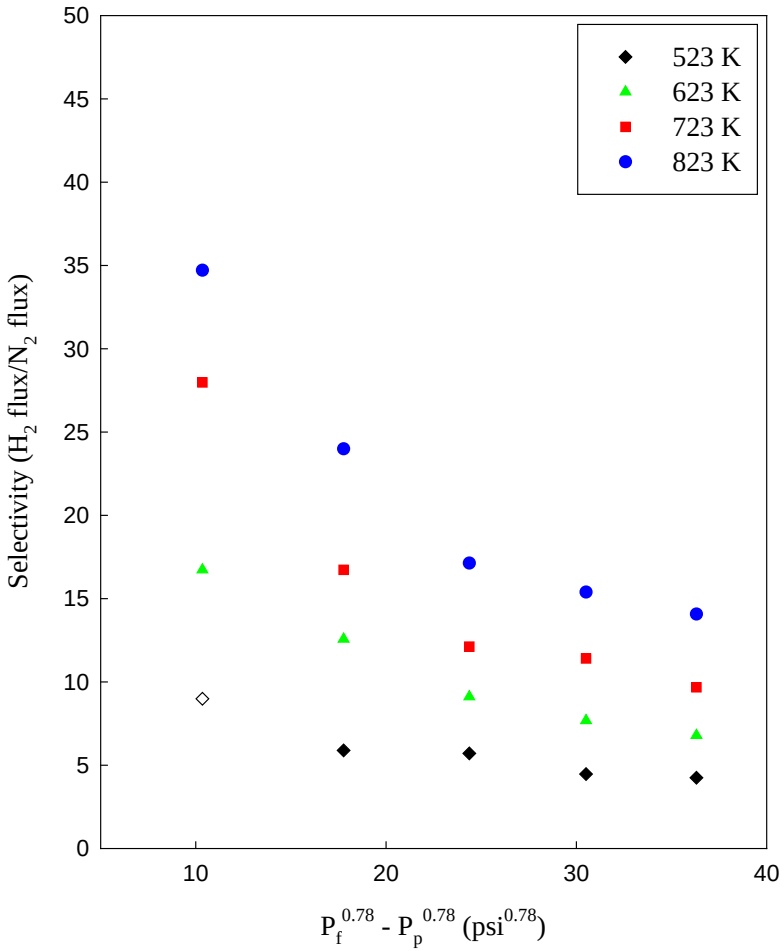


Post-annealing: Pd-Cu-MPSS membrane (SIEP)

H_2-permselectivity: Effect of intermediate heat treatment

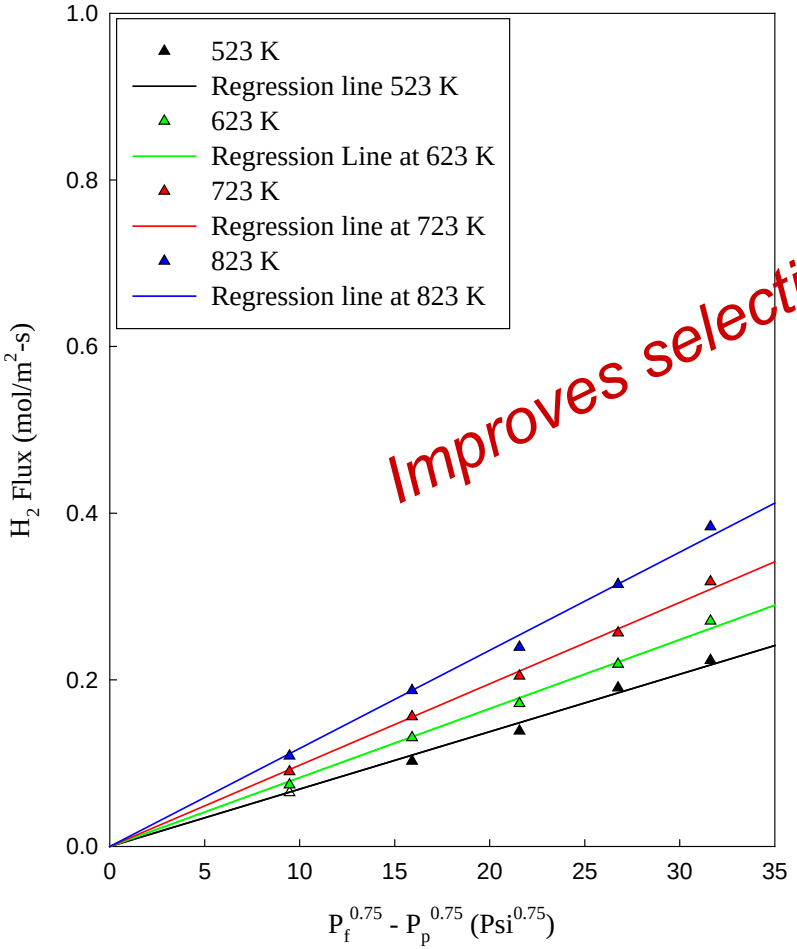


H_2 flux of Pd-Ag-MPSS membrane (without intermediate heat treatment and subsequent Pd-Ag top layer)

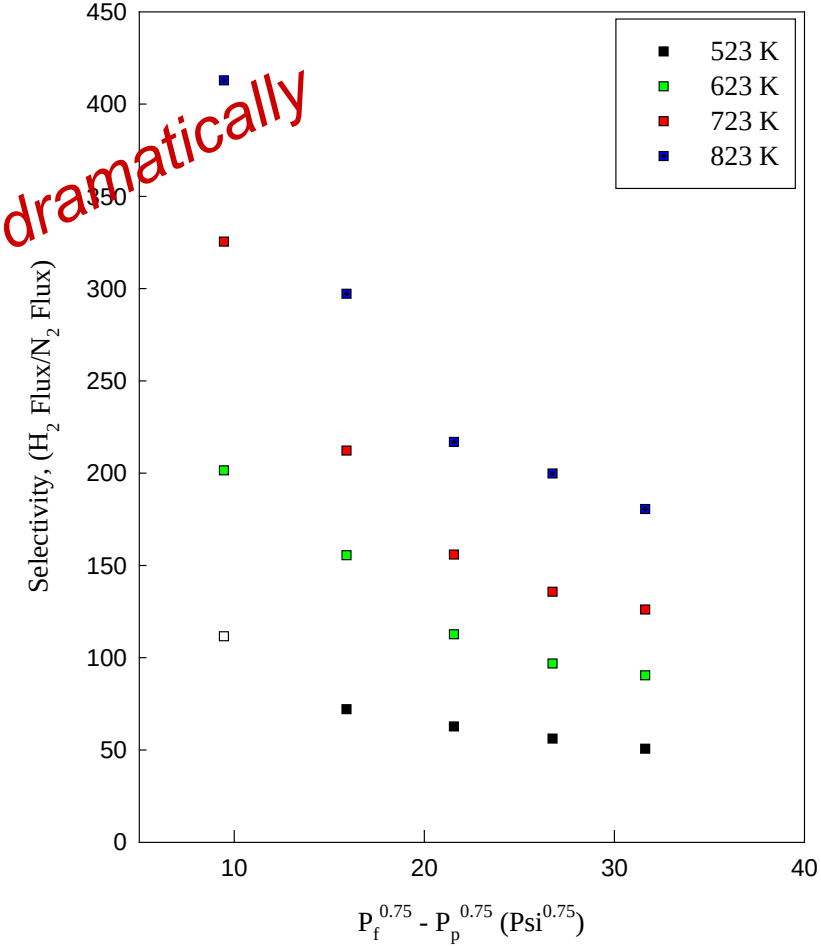


H_2/N_2 selectivity of Pd-Ag-MPSS membrane (without intermediate heat treatment and subsequent Pd-Ag top layer)

H_2-permselectivity: Effect of intermediate heat treatment



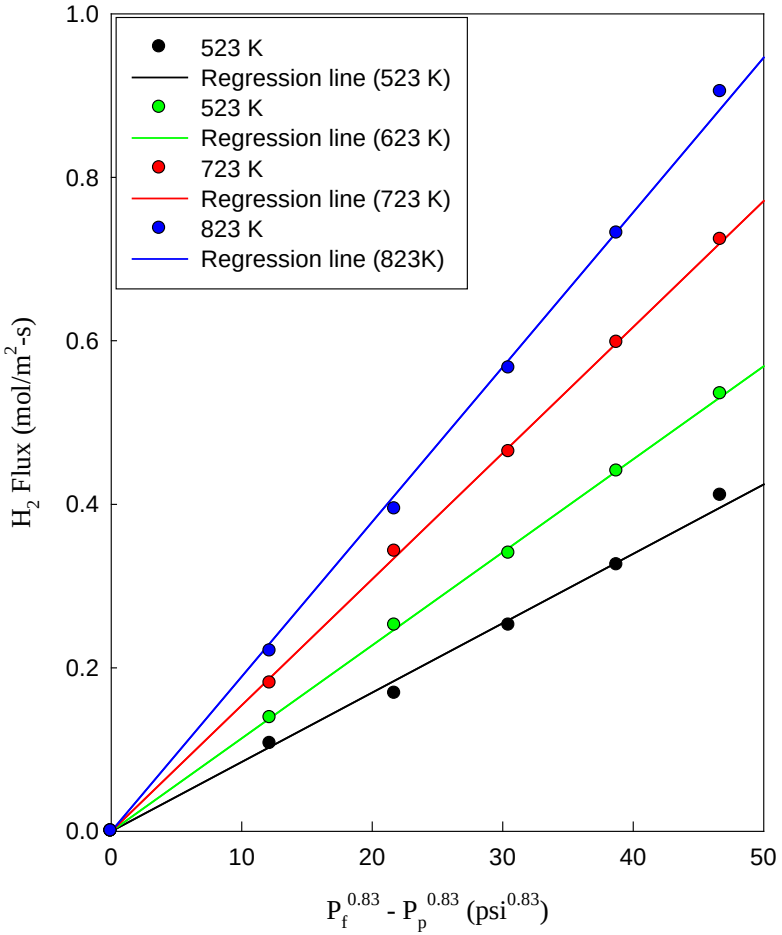
Improves selectivity dramatically



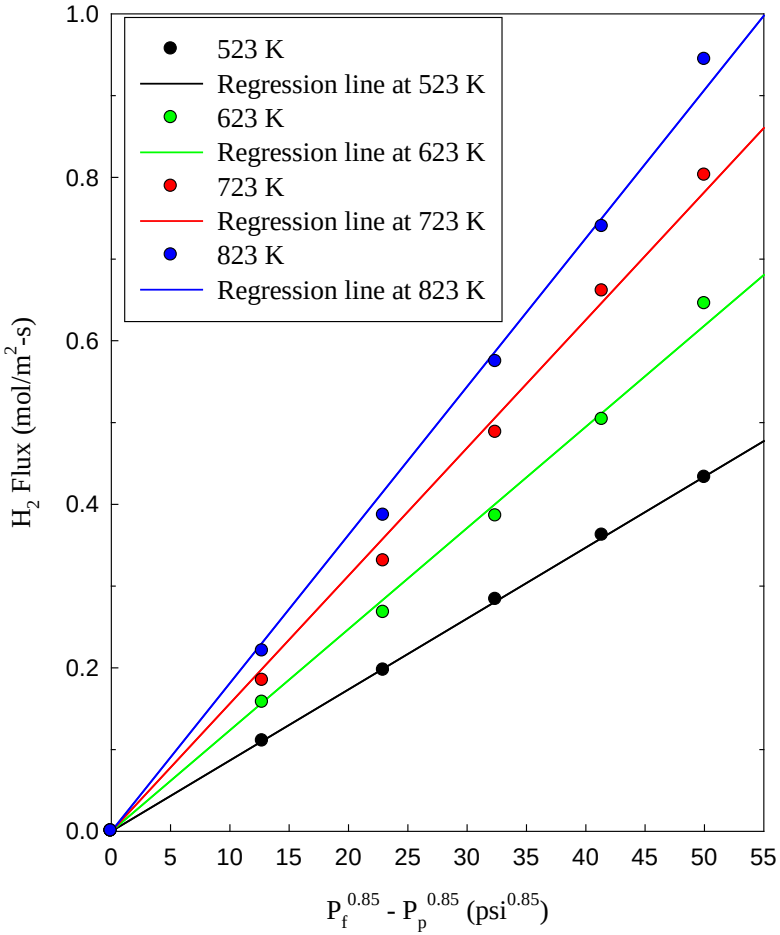
H_2 flux of Pd-Ag-MPSS membrane (after intermediate heat treatment and subsequent Pd-Ag top layer).

H_2/N_2 selectivity of Pd-Ag-MPSS membrane (after intermediate heat treatment and subsequent Pd-Ag top layer)

H_2-permeability: Pd- & Pd-Ag-MPSS membrane

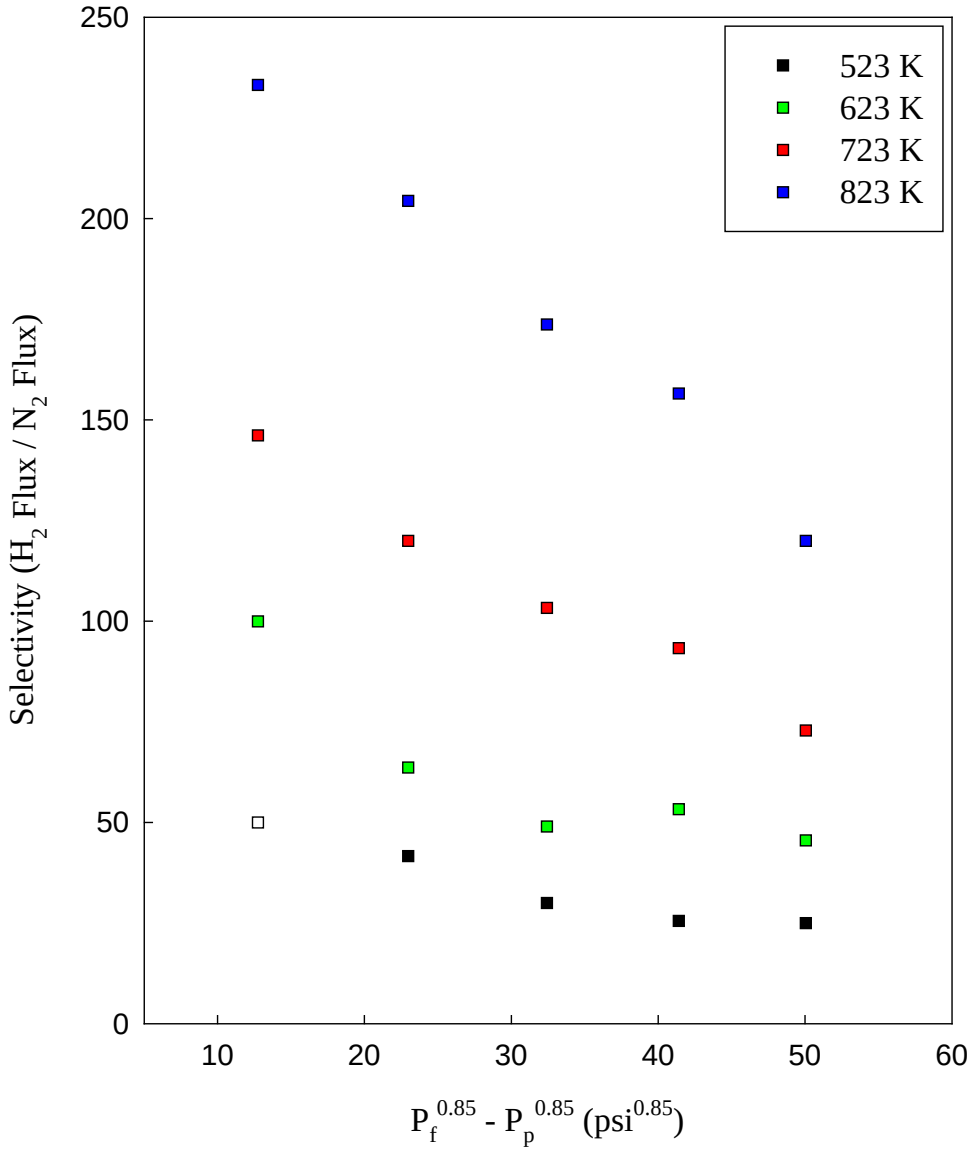


Pd-MPSS membrane (7.89 μm)



Pd-Ag-MPSS membrane (12.54 μm)

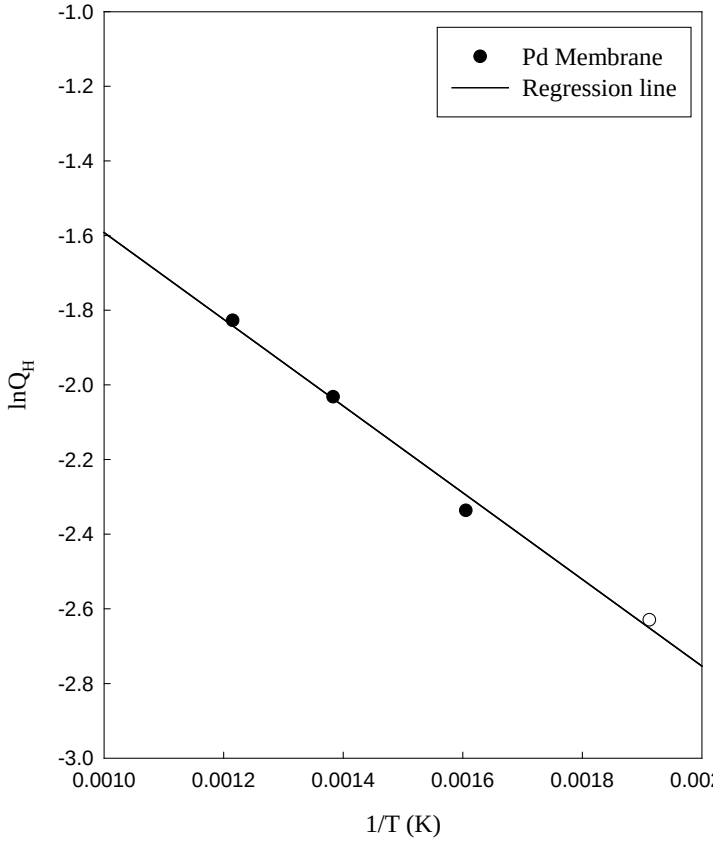
H_2-permeability: H_2/N_2 selectivity of Pd-Ag-MPSS membrane



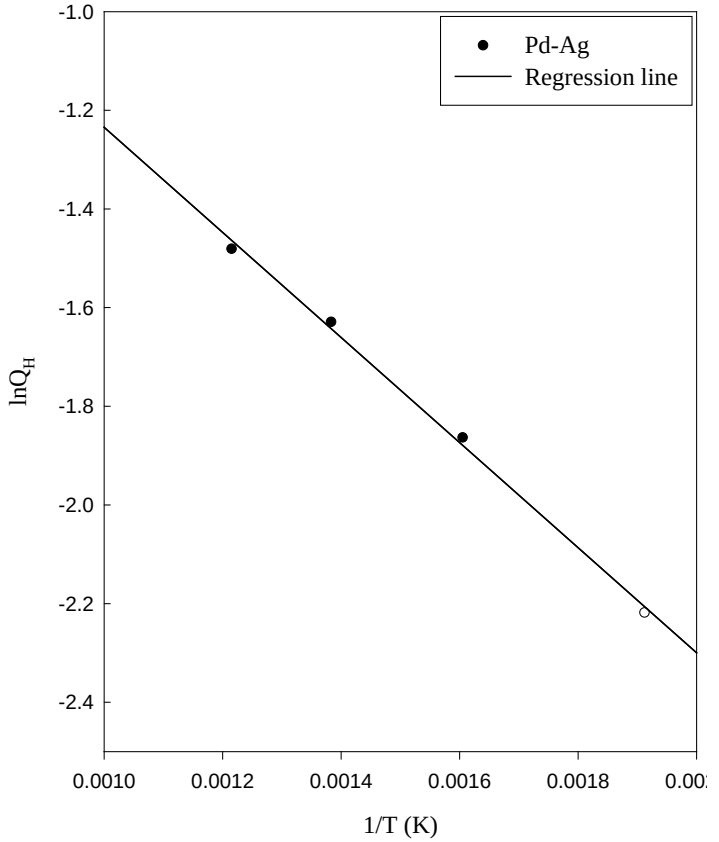
Pd-Ag-MPSS membrane (12.54 μm)

H_2 permeability: Activation energy of Pd & Pd-Ag membranes

Membrane type	Membrane thickness (µm)	Pre-exponential factor	Activation energy (E), KJ/mol
Pd	**7.89**	**0.65**	**9.7**
Pd-Ag	**12.54**	**0.84**	**8.9**



Arrhenius plot of H_2-permeability coefficients (Pd-MPSS membrane)



Arrhenius plot of H_2-permeability coefficients (Pd-Ag-MPSS membrane)

CONCLUSIONS

- The rate of Pd-deposition and surface morphology can be modified in EP by varying the choice and concentration of suitable surfactants (SIEP).
- Grain size of deposited Pd and its subsequent agglomeration to dense film can be controlled by SIEP.
- Reproducibility of membranes (thickness, plating time, grain size distribution, microstructure and permeability) by SIEP process established.
- We successfully extended SIEP to fabricate robust, defect free Pd-Ag- and Pd-Cu-MPSS membrane.
- The Pd-Ag-MPSS membrane showed comparable perm-selectivity for hydrogen with enhanced H_2 throughput.

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THANK YOU