Fabrication of Pd/Pd-alloy Films by Surfactant Induced Electroless Plating for H₂ 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
- H₂-Permselectivity
- Conclusions
- Acknowledgments
**INTRODUCTION**

**H₂ 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*

*H₂-selective thin-film membrane for high temperature application is a topic of great interest.*
**H₂ Transport in dense Pd membrane**

- **H₂-flux** ($N_H$) increases with decreasing film thickness.
- **H₂-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 H₂-based energy economy. Pd/Pd-alloy membranes are viewed as serious contender for H₂-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: \[ N_2H_4 + 4OH^- \rightarrow N_2 \uparrow (g) + 4H_2O + 4e^- \]

Cathodic Reaction: \[ 2Pd[\text{NH}_3]^2+ + 4e^- \rightarrow Pd^0 + 8\text{NH}_3 \uparrow (g) \]

Autocatalytic Reaction: \[ 2Pd[\text{NH}_3]^2+ + N_2H_4 + 4OH^- \rightarrow 2Pd^0 + \]
\[ [N_2] \uparrow (g) + 4H_2O + [8\text{NH}_3] \uparrow (g) \]
**Typical Pd EP Recipe**

### Senistisation Solution

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnCl$_2$ · 2H$_2$O</td>
<td>1.19 g/l</td>
</tr>
<tr>
<td>HCl</td>
<td>0.2 N</td>
</tr>
</tbody>
</table>

### Activation Solution

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>PdCl$_2$ · 2H$_2$O</td>
<td>0.09 g/l</td>
</tr>
<tr>
<td>HCl</td>
<td>0.2 N</td>
</tr>
</tbody>
</table>

### Pd EP Bath Solution

<table>
<thead>
<tr>
<th>Component / Variables</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetraamine palladium nitrate (10% wt)</td>
<td>24.3 g/l</td>
</tr>
<tr>
<td>Ammonium hydroxide (28% wt)</td>
<td>198 ml/l</td>
</tr>
<tr>
<td>Hydrazine (35% wt solution)</td>
<td>1.215 ml/l</td>
</tr>
<tr>
<td>EDTA</td>
<td>40.1 g/l</td>
</tr>
<tr>
<td>pH</td>
<td>10.5</td>
</tr>
<tr>
<td>Temperature</td>
<td>55 °C</td>
</tr>
</tbody>
</table>
SEM analysis of Pd-film on 0.2 μm microporous ceramic substrate: (a) Pd-film surface; and (b) Penetration of Pd across the thickness.
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.

**EP Reactions in Ag & Cu Systems**

### Ag-bath reactions

**Anodic Reaction:** \( \text{N}_2\text{H}_4 + 4\text{OH}^- \rightarrow \text{N}_2 \uparrow + 4\text{H}_2\text{O} + 4\text{e}^- \)

**Cathodic Reaction:** \( 4\text{Ag}[\text{NH}_3]_4^+ + 4\text{e}^- \rightarrow 4\text{Ag}^0 + 8\text{NH}_3 \uparrow \)

**Overall Reaction:** \( 4\text{Ag}[\text{NH}_3]_4^+ + \text{N}_2\text{H}_4 + 4\text{OH}^- \rightarrow 4\text{Ag}^0 + \text{N}_2 \uparrow + 8\text{NH}_3 \uparrow + 4\text{H}_2\text{O} \)

### Cu-bath reactions

**Anodic Reaction:** \( 2\text{CH}_2\text{O} + 4\text{OH}^- \rightarrow \text{H}_2 \uparrow + 2\text{HCOO}^- + 2\text{H}_2\text{O} + 2\text{e}^- \)

**Cathodic Reaction:** \( \text{Cu}[\text{NH}_3]_6^{2+} + 2\text{e}^- \rightarrow \text{Cu}^0 + 6\text{NH}_3 \uparrow \)

**Overall Reaction:** \( \text{Cu}[\text{NH}_3]_6^{2+} + 2\text{CH}_2\text{O} + 4\text{OH}^- \rightarrow \text{Cu}^0 + 2\text{HCOO}^- + \text{H}_2 \uparrow + 6\text{NH}_3 \uparrow + 2\text{H}_2\text{O} \)
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

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

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
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:

\[
2\text{Pd}\left[\text{NH}_3\right]_4^{2+} + \text{N}_2\text{H}_4 + 4\text{OH}^{-1} \rightarrow 2\text{Pd}^{0} + \left[\text{N}_2\right] \uparrow (g) + 4\text{H}_2\text{O} + \left[8\text{NH}_3\right] \uparrow (g)
\]

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)

- Triton X-100 (Nonionic)  
  \[
  \begin{align*}
  &\text{Polyethylene glycol ter-octaphenyl ether} \\
  \text{N} = 8 \text{ and } \text{X} = 10 \\
  \end{align*}
  \]

- SDBS (Anionic)  
  \[
  \begin{align*}
  &\text{Dodecylbenzenesulfonic acid sodium salt} \\
  \text{N} = 10 \\
  \end{align*}
  \]

- DTAB (Cationic)  
  \[
  \begin{align*}
  &\text{Dodecyltetramethylammonium bromide} \\
  \text{N} = 10 \\
  \end{align*}
  \]

**Surfactant Properties (CMC, HLB)**

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>HLB Values</th>
<th>CMC (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triton X-100</td>
<td>14.7</td>
<td>0.22</td>
</tr>
<tr>
<td>DTAB</td>
<td>12.9</td>
<td>16</td>
</tr>
<tr>
<td>SDBS</td>
<td>13.6</td>
<td>1.4</td>
</tr>
</tbody>
</table>
Role of Surfactant in EP

EP Autocatalytic Reaction: \[\text{EP}: 2\text{Pd}\left[\text{NH}_3\right]_4^{2+} + \text{N}_2\text{H}_4 + 4\text{OH}^{-} \rightarrow 2\text{Pd}^0 + \left[\text{N}_2\right]_{\uparrow}^{\text{(g)}} + 4\text{H}_2\text{O} + \left[8\text{NH}_3\right]_{\uparrow}^{\text{(g)}}\]

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

Dodecyltetramethylammonium bromide (DTAB cationic surfactant)

Grain size distribution

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

AFM images of solid surface aggregation into typical hydrophobic glass surface

Interaction of DTAB in Solid 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

<table>
<thead>
<tr>
<th>Membrane Samples</th>
<th>DTAB (CMC)</th>
<th>Deposit Time (h)</th>
<th>Pd-film thickness ((\mu)m)</th>
<th>Weight Basis</th>
<th>SEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.5</td>
<td>22</td>
<td>23.0</td>
<td>22.5</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>2</td>
<td>16</td>
<td>17.8</td>
<td>18.3</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>3</td>
<td>13</td>
<td>14.0</td>
<td>13.5</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>4</td>
<td>10</td>
<td>8.5</td>
<td>8.5</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>0</td>
<td>28</td>
<td>28.5</td>
<td>27.5</td>
<td></td>
</tr>
</tbody>
</table>

He gas-tightness of membranes
Summary of grain distribution in Pd-film fabricated by EP and SIEP with DTAB

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Surfactant Concentration (CMC) in mM</th>
<th>Surfactant Concentration in mM</th>
<th>Grain Size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None - CEP</td>
<td>N/A</td>
<td>N/A</td>
<td>5-15</td>
</tr>
<tr>
<td>SDBS - SIEP</td>
<td>1.4</td>
<td>1.4</td>
<td>5-15</td>
</tr>
<tr>
<td></td>
<td>5.6</td>
<td></td>
<td>2-15</td>
</tr>
<tr>
<td>Triton X-100 - SIEP</td>
<td>0.23</td>
<td>0.23</td>
<td>10-15</td>
</tr>
<tr>
<td></td>
<td>0.92</td>
<td></td>
<td>5-10</td>
</tr>
<tr>
<td>DTAB - SIEP</td>
<td>16</td>
<td>16</td>
<td>4-8</td>
</tr>
<tr>
<td></td>
<td>64</td>
<td></td>
<td>2-4</td>
</tr>
</tbody>
</table>
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
Microstructure Analysis of Membranes by CEP & SIEP

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

SIEP shows enhanced grain agglomeration
Microstructure Analysis of Membranes by CEP & SIEP

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

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
(b) Pd-Cu at 5K (CEP) WHT
(c) Pd-Cu at 1K (CEP) HT
(d) Pd-Cu at 5K (CEP) HT
(e) Pd-Cu at 1K (SIEP) WHT
(f) Pd-Cu at 5K (SIEP) HT
Microstructure Analysis: Grain Size Distribution

Grain size distribution of Pd film by CEP & 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)

Grain size distribution of Pd-Ag film by SIEP process
Microstructure: EDS Elemental Analysis

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Std. Dev.</th>
<th>Atomic %</th>
<th>FWHM (eV)</th>
<th>ROI (net)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>23.99</td>
<td>1.06</td>
<td>23.74</td>
<td>104</td>
<td>38723.85</td>
</tr>
<tr>
<td>Pd</td>
<td>76.01</td>
<td>1.88</td>
<td>76.26</td>
<td>101.9</td>
<td>45520.55</td>
</tr>
</tbody>
</table>

**EDS spectrum of Pd-Ag film**

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Std. Dev.</th>
<th>Atomic %</th>
<th>FWHM (eV)</th>
<th>ROI (net)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>44.69</td>
<td>1.32</td>
<td>57.5</td>
<td>150.4</td>
<td>10627.47</td>
</tr>
<tr>
<td>Pd</td>
<td>55.31</td>
<td>1.42</td>
<td>42.5</td>
<td>101.3</td>
<td>31661.82</td>
</tr>
</tbody>
</table>

**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

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 H₂ 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 tend 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**

![XRD Pattern Diagram](attachment:image.png)
Heat Treatment: Effect on Pd, Pd-Ag & Pd-Cu Microstructures

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

- 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 Pd-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 Pd-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 → Probe 4).
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)**
**H₂-permselectivity: Effect of intermediate heat treatment**

**H₂ flux of Pd-Ag-MPSS membrane**
(after intermediate heat treatment and subsequent Pd-Ag top layer).

**H₂/N₂ selectivity of Pd-Ag-MPSS membrane**
(after intermediate heat treatment and subsequent Pd-Ag top layer)

Improves selectivity dramatically.

Pf \(0.75 - \) Pp \(0.75\) (Psi\(0.75\))

H₂ flux of Pd-Ag-MPSS membrane

H₂/N₂ selectivity of Pd-Ag-MPSS membrane
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)
**H₂ permeability: Activation energy of Pd & Pd-Ag membranes**

<table>
<thead>
<tr>
<th>Membrane type</th>
<th>Membrane thickness (µm)</th>
<th>Pre-exponential factor</th>
<th>Activation energy (E), KJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>7.89</td>
<td>0.65</td>
<td>9.7</td>
</tr>
<tr>
<td>Pd-Ag</td>
<td>12.54</td>
<td>0.84</td>
<td>8.9</td>
</tr>
</tbody>
</table>

![Arrhenius plot of H₂-permeability coefficients (Pd-MPSS membrane)](image1)

![Arrhenius plot of H₂-permeability coefficients (Pd-Ag-MPSS membrane)](image2)
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\textsubscript{2} throughput.
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- Syed Z. Islam (MSChE candidate for July 2012)
- M. Saiful Islam (MSChE, July 2011)
- Jasmine Taylor (BSChE, May 2011)
- M. Mizanur Rahman (MSChE, July, 2010)
- M.A, Islam (PhD, Dec 2009)

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