Development of Pd–Cu Membranes for Hydrogen Separation

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Why Hydrogen Separation?

- More than 80% of hydrogen available on an industrial scale is produced by steam reforming of natural gas.*

  Reforming of natural gas (700-1100 °C, 3-25 bar, and Ni catalyst)
  \[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \]  
  (1)

  Shift reaction (Water Gas Shift)
  \[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2 \]  
  (2)

- The product gas stream contains 74% H\textsubscript{2}, 18CO\textsubscript{2}, 7% CH\textsubscript{4}, 1% CO, H\textsubscript{2}S and other by-products, which can be further purified (99.999%) by different methods, such as Pressure Swing Adsorption (PSA).

- Many applications require H\textsubscript{2} with higher purity (including PEM fuel cells).

- Dense metallic membranes offer an effective method to produce ultra pure hydrogen.

A membrane is a barrier between two phases.

It can be used to separate mixture (A&B) if one component (A) permeates through the membrane.

Pressure differential between the feed gas and permeate side is required for the gas permeation.
Palladium Membrane

Advantages:

- Separation based on the solution-diffusion mechanism
- Production of high purity hydrogen (99.999999%)
- Acceptable hydrogen permeability

Problems:

- Hydrogen embrittlement (α→β transition below 2MPa & 298 °C)
- Surface poisoning (CO, H₂S, ...)
- High cost of Pd
- Hydrogen flux needs to be improved

http://pureguard.net/cm/Library/Palladium
Alloying

Alloying Pd with other metallic elements such as Ag, Cu, Fe, Ni, Pt, Y, and ....

- Avoid $\alpha \rightarrow \beta$ phase transition
- Improve mechanical property
- Improve hydrogen permeability
- Increase resistance to the surface poisoning

Identical specimens of palladium (left) and palladium-silver (right) after 30 thermal cycles in hydrogen


![Graph showing permeability vs. temperature for different alloys](image-url)
Pd-Cu System

- Pd$_{47}$Cu$_{53}$ with bcc structure shows higher permeability than Pd at 350 °C.
- bcc phase is not thermally stable and susceptible to the surface poisoning.
- fcc phase alloys show some resistance to the surface poisoning.

_P.R. Subramanian et al. J. Phase Equilib. 1991, 12, (2), 231_
Pd-Cu-Ag Ternary Alloys

- Hydrogen Diffusivity & solubility

- Ag addition decreases the hydrogen diffusivity in both bcc and (bcc+fcc) phases.

- Ag addition increases the hydrogen solubility in both bcc and (bcc+fcc) phases.
Effect of Ag Addition on Hydrogen Diffusion

- In the bcc phase hydrogen diffusion takes place through a series of jumps between Tetrahedral Sites (T site) via PdCu$_2$/Pd$_2$Cu windows *i.e.*, Transition States (TS)

- Ag replacement for Pd or Cu in the PdCu$_2$/Pd$_2$Cu TS Increases the activation energy for the hydrogen diffusion

\[
E_a (\text{Pd}_{47}\text{Cu}_{53}) = 5.82 \text{ kJ mol}^{-1} \\
(350-400 \degree \text{C})
\]

\[
E_a (\text{Pd}_{45.8}\text{Cu}_{51.9}\text{Ag}_{2.3}) = 10 \text{ kJ mol}^{-1} \\
(350-400 \degree \text{C})
\]

Effect of Ag Addition on Hydrogen Solubility

- Ag expand the lattice parameter therefore, higher solubility can be achieved.
- Metal-H pair interaction
  Ag favours interstitial hydrogen by decreasing the binding energies of most stable O sites.

Ag-H interaction in Pd-Ag-H: -36 kJ mol\(^{-1}\)
Cu-H interaction in Pd-Cu-H: +6.5 kJ mol\(^{-1}\)
- Geometrical factor (Available free space to be occupied by hydrogen).

Binding energies in O sites predicted by CE model

*C. Ling et al. J. Memb. Sci. 2011, 371, 189*
- Hydrogen permeability is mainly controlled by hydrogen diffusion in the bcc phase.*

- Hydrogen Permeability can be improved by solubility enhancement within the fcc phase.*

### Structural Analysis

<table>
<thead>
<tr>
<th>As-rolled</th>
<th>Annealed@650 °C-96h</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Pd-Cu</td>
<td>(1) Annealed</td>
</tr>
<tr>
<td>(2) Pd-Cu-Ti</td>
<td>(2) Annealed</td>
</tr>
<tr>
<td>(3) Pd-Cu-Nb</td>
<td>(3) Annealed</td>
</tr>
<tr>
<td>(4) Pd-Cu-Ni</td>
<td>(4) Annealed</td>
</tr>
<tr>
<td>(5) Pd-Cu-V</td>
<td>(5) Annealed</td>
</tr>
<tr>
<td>(6) Pd-Cu-Y</td>
<td>(6) Annealed</td>
</tr>
<tr>
<td>(7) Pd-Cu-Zr</td>
<td>(7) Annealed</td>
</tr>
</tbody>
</table>

Pd-Cu-Zr sample shows structural stability after annealing.
Pd-Cu-M membranes (M:Y, Ti, Zr, V, Nb, and Ni)

- **Hydrogen Solubility**

  - Whilst, Ti, Nb, and V additions have no noticeable effect on hydrogen solubility, Ni addition reduces hydrogen solubility at temperatures higher than 200 °C compared to the binary Pd-Cu alloy.

  - Hydrogen solubility in Pd-Cu-Y and Pd-Cu-Zr alloys are almost doubled compared to the binary Pd-Cu alloy at temperatures higher than 200 °C.

* S. Nayebossadri, J. Speight, D. Book, To be published
Pd-Cu-M membranes (M: Y, Ti, Zr, V, Nb, and Ni)

- Hydrogen Diffusivity

- Hydrogen diffusivity in all Pd-Cu-M (M: Y, Ti, Zr, V, Nb, and Ni) alloys is lower than binary Pd-Cu alloy.

* S. Nayebossadri, J. Speight, D. Book, To be published
Pd-Cu-M membranes (M: Y, Ti, Zr, V, Nb, and Ni)

- Hydrogen Permeability @ 350 °C

- Pd-Cu-Y and Pd-Cu-Zr samples show almost similar hydrogen permeability to their binary alloys, despite their higher thickness (100 µm vs. 25µm).

* S. Nayebossadri, J. Speight, D. Book,  To be published
Pd-Cu-M membranes (M:Y, Ti, Zr, V, Nb, and Ni)

- Exposure to 1000ppm \( \text{H}_2\text{S}+\text{H}_2 \) @ 450 °C

- Hydrogen flux decreases to ~70% and ~50% of its original value for Pd-Cu-Zr and Pd-Cu alloys respectively after 8h of exposure.

- Resistance to sulphur poisoning is improved by Zr addition.

* S. Nayebossadri, J. Speight, D. Book, To be published
Pd-Cu-M membranes (M: Y, Ti, Zr, V, Nb, and Ni)

- **Post Poisoning Structural Analysis**

- Pd-Cu-Zr sample may change the local atomic composition on the surface leading to a less favourable S-surface interaction.

- Structural stability of Pd-Cu-Zr sample significantly slow down Cu segregation leading to a slower kinetics for bulk sulfidation.

* S. Nayebossadri, J. Speight, D. Book, To be published
Summary

- Hydrogen permeability in the bcc Pd-Cu alloys is mainly dominated by hydrogen diffusion.

- Hydrogen permeability in the fcc Pd-Cu alloys can be significantly improved by enhancing hydrogen solubility.

- Hydrogen solubility in the fcc Pd-Cu alloys can be significantly improved by addition of small amount (>2 at.% of Y and Zr).

- Structural stability achieved as a result of Zr addition significantly improves the resistance to the sulphur poisoning.

- We propose Pd-Cu-Zr as a new potential alloy membrane with improved permeability, thermal stability and sulphur poisoning resistance.
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Delivery of Sustainable Hydrogen (2008-13)

Hydrogen and Fuel Cell Research Hub (2012-17)

Birmingham Science City - Hydrogen Energy (2006-2016)

TSB Hydrogen Permeable Novel Membranes (HYPNOMEM) (2006-09)

www.hydrogen.bham.ac.uk
Thank you
Membrane Test Rig

- 4x Mass Flow Controllers
- Split Furnace
- PC control
- Exhaust & Downstream MFC
- Inconel Reactor
- Mass Spectrometer
- Turbo Pump