Supported Molten-Metal Membrane (SMMM) for Hydrogen Separation

Project ID: PD012

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## Overview

“Supported Molten–Metal Membrane (SMMM) for Hydrogen Separation”

<table>
<thead>
<tr>
<th>Award No.</th>
<th>DE–FE0001050</th>
</tr>
</thead>
<tbody>
<tr>
<td>Timeline:</td>
<td></td>
</tr>
<tr>
<td>Start Date: 9.30.2009</td>
<td>End Date: 9.29.2012</td>
</tr>
<tr>
<td>Budget:</td>
<td></td>
</tr>
<tr>
<td>Govt. Share: $996,567</td>
<td>WPI Share: $249,857</td>
</tr>
<tr>
<td>Total: $1,246,424</td>
<td></td>
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<tr>
<td>Funding Received:</td>
<td>FY 09: $347,814</td>
</tr>
<tr>
<td>Project Manager:</td>
<td>Jason C. Hissam</td>
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<tr>
<td>Technical Barriers:</td>
<td>Non-precious metals</td>
</tr>
<tr>
<td></td>
<td>Low cost</td>
</tr>
<tr>
<td></td>
<td>High H₂ flux &amp; selectivity</td>
</tr>
<tr>
<td></td>
<td>CO &amp; sulfur tolerance</td>
</tr>
</tbody>
</table>
# Technical Targets

<table>
<thead>
<tr>
<th>Property</th>
<th>2010 Target</th>
<th>2015 Target</th>
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<tbody>
<tr>
<td>H₂ Flux (std m³/m².h)</td>
<td>60</td>
<td>90</td>
</tr>
<tr>
<td>H₂ Feed Pressure, (psia)</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>H₂ Permeate Pressure, (psia)</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Operating (psi)</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Operating Temperature, T (ºC)</td>
<td>300–600</td>
<td>250–500</td>
</tr>
<tr>
<td>Pressure Tolerance, (psi)</td>
<td>400</td>
<td>800–1,000</td>
</tr>
<tr>
<td>Sulfur Tolerance (ppm)</td>
<td>20</td>
<td>&gt;100</td>
</tr>
<tr>
<td>CO Tolerance</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>WGS Activity</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>H₂ Purity (%)</td>
<td>99.5</td>
<td>99.99*</td>
</tr>
<tr>
<td>Cost ($/ft²)</td>
<td>500</td>
<td>&lt;250</td>
</tr>
</tbody>
</table>

*Implies dense membrane!
Approach: Theoretical Rationale

\[ N_{H_2} = (Q_{H_2}) \left( \frac{p_{H_2,f}^{1/2} - p_{H_2,p}^{1/2}}{\delta} \right) \]

\[ Q_{H_2} = S \times D_H \]

\[ S = c_t (K_A) (K_H) = c_t (K_{A,0} K_{H,0}) \exp \left( - \frac{\Delta H_A^0 + \Delta H_H^0}{RT} \right) \]

\[ D_H = \left\{ \frac{1}{6} \lambda^2 v_0 \exp \left( - \frac{\Delta S_D^+}{RT} \right) \right\} \exp \left( - \frac{E_D}{RT} \right) \]

**Lattice Structure**
- Crystalline
- Amorphous
- Molten

2010 DOE Hydrogen Program Review
Approach: Rational H₂ Membrane Design

- Enhance H diffusion via a more open lattice ($M_1$)
- Enhance H dissolution via more open lattice ($M_1$)
- Enhance density of surface dissociation sites ($M_2$)
- Enhance H₂ dissociative adsorption via catalyst ($M_2$)

Molten metals/alloys for $M_1$!

**Approach:** Proposed Supported Molten-Metal Membrane (SMMM)

![Diagram showing the structure of a supported molten-metal membrane with labeled components: Porous Support, Diffusion Barrier, Molten Metal Film, Oxide Layer, $M_1 + M_2$.]
Relevance: SMMM Potential Advantages & Disadvantages

- Cheaper/abundant metals
- Broader temperature range
- Lack of
  - Thermal mismatch
  - Sintering
  - Hydrogen embrittlement
  - Pin holes
- Improved CO tolerance
- Improved S tolerance

- Molten Metal/Support Interactions
  - Wettability
  - Alloying with Substrate
- Membrane Stability
  - Chemical
  - Physical
- H₂ Dissociation Activity
Collaboration: Team Relevant Experience

- PI has extensive experience in fuel cells and H₂ catalysis, and has developed the technique of Supported Molten–Metal Catalysis (SMMC)
  - Guidance in selection of molten metals/alloys
  - Guidance in permeation modeling
- Co–PI is a leading researcher in Pd/Pd–alloy membranes
  - Guidance in selection of porous supports
  - Guidance in developing fabrication protocol
Goals of Phase I (9.30.09 – 9.29.10)

1. Select molten metal ($M_1$) and catalyst ($M_2$)
2. Select suitable porous supports (porous metal, with or without a diffusion barrier, or ceramic)
3. Develop membrane fabrication protocols
4. Establish basic feasibility of the SMMM
Goal 1: Select Low Melting Metals (M₁)

Technical Accomplishment
Goal 1: Select Catalytic Component ($M_2$)

Graph showing the relationship between Me-H bond strength (kJ mol$^{-1}$) and log (current density / mA cm$^{-2}$). The graph includes various metal elements grouped into different categories:(Ni, Co, Fe, Cu), (Sn, Ga, Bi), (W, Mo, Ti, Nb, Ta) and Platinum metals (Pt, Re, Rh, Ir).
Goal 2: Select Suitable Porous Support(s)

Plug side | Porous part | Open side

- 1”
- 5” 6” 16”

Porous Metal

Porous Ceramic

Porous Metal with Ceramic Layer
Porous Support Discussion

- Porous Stainless Steel (PSS)/Inconel
  - Alloying?
- Porous Ceramic
  - Wettability/Sealing/Fragility?
  - $\text{Al}_2\text{O}_3$
  - $\text{ZrO}_2$
  - $\text{TiO}_2$
  - SiC
  - Porous Vycor® glass
- PSS/Inconel w/Oxide Layer
  - Best Option?
Goal 3: Develop Fabrication Protocols

a) Electroless plating (Controllable/Complex)
b) Electroplating (Versatile/Simple)
c) Melt imbibition (Crude but quick)

Start with $M_1 = Sn$; No $M_2$;
Porous Support = Inconel
## Goal 3: Catalyzed Electroless Deposition of Sn

### Reaction Diagram

- **H₂PO₂⁻**
- **H₂PO₃⁻**
- **SnCl₂**
- **H₂O**
- **2HCl**

### Electrode Reactions

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Reaction, $s_ρ$</th>
<th>$σ_ρ$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cathode</strong></td>
<td>$\text{Sn(Cl)}_2 + 2\text{H}^+ + 2e^- \rightleftharpoons \text{Sn}^0 + 2\text{HCl}$</td>
<td>+1</td>
</tr>
<tr>
<td><strong>Anode</strong></td>
<td>$\text{Na}^+\text{H}_2\text{PO}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{Na}^+\text{H}_2\text{PO}_3^- + 2\text{H}^+ + 2e^-$</td>
<td>+1</td>
</tr>
<tr>
<td><strong>Overall</strong></td>
<td>$\text{Sn(Cl)}_2 + \text{NaH}_2\text{PO}_2 + \text{H}_2\text{O} \rightleftharpoons 2\text{HCl} + \text{Sn}^0 + \text{NaH}_2\text{PO}_3$</td>
<td></td>
</tr>
</tbody>
</table>

### Technical Accomplishment
Goal 3: Electroless Deposit Thickness

- Autocatalytic Electroless Deposition
- Self-passivating Electroless Deposition
Goal 3: Immersion Deposition

*Solution #1; acidic

Sn-Cu:

Non-porous part of membrane

Sn-Ni:

Sn thickness remains limited!

Technical Accomplishment
Goal 3: Electroplating Apparatus

Electroplating Apparatus

3 Sn Electrodes
Goal 3: Electroplated Sn SMMM on Porous Inconel

Porous Inconel Support 0.1 μm (1" OD, 5.7" L)
Solution: 0.2 M SnSO$_4$, 0.3 M H$_2$SO$_4$

$i = 25$ mA/cm$^2$
Goal 3: 10 µm Sn/Inconel SMMM Post 600 °C Treatment

Upon melting, Sn alloyed with Inconel to form an impermeable layer
Goal 3: Porous Ceramic Support
Goal 3: Sn-Porous Ceramic Membrane Post-Mortem

Technical Accomplishment
Goal 3: Permeability of Sn-Porous Ceramic SMMM

![Graph showing permeability of Sn-Porous Ceramic SMMM with Flux [m³/m²-h] on the y-axis, Elapsed Time [hr] on the x-axis, and Temperature [°C] on the right side. The graph shows different flux values for H₂ and He over time.](image-url)
Goal 3: Permeability vs Temperature

- Flux [m^3/m^2-h]
- Temperature [°C]
- Elapsed Time [hr]

He Flux
H2 Flux
Temperature
Goal 3: Permeability vs Temperature: Theory

\[ N_i = -\frac{1}{RT} \left\{ D_{ki}^e + \frac{B_0 P}{\mu_i} \right\} \frac{dp}{dz} \]

\[
\begin{align*}
\delta &= 5 \, \mu m \\
\epsilon &= 0.005 \\
a &= 0.45 \, \mu m
\end{align*}
\]

Volumetric Flux, m³/m²·h
Proposed Work (for Remaining Phase I)

1. Alternate Supports
   a. Porous Stainless Steel with Oxide Layer
   b. Other Porous Ceramic Supports

2. Alternate Molten Metals
   a. $M_1$: In, Ga, Bi
   b. $M_2$: Ni, Cu, Co, Ag, W, Mo, Nb

3. SMMM Feasibility and Permeation Studies
Conclusions

1. Steady progress made toward goals of Phase I
2. Identified candidates for molten metals/supports
3. Developed electroless/electroplating methodologies for SMMM fabrication
4. Porous metal supports likely not suitable due to alloying with molten metals
5. Sealing and fragility an issue with ceramic supports
6. Work planned to
   - Fabricate SMMM on PSS with Oxide Layer
   - Establish feasibility
   - Study Performance characteristics
   - Incorporate $M_2$ to enhance SMMM permeability