# Supported Molten-Metal Membrane (SMMM) for Hydrogen Separation

**Project ID: PD012**

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# Overview

"Supported Molten-Metal Membrane (SMMM) for Hydrogen Separation"

- **Award No.** DE-FE0001050
- **Timeline:**
  - Start Date: 9.30.2009
  - End Date: 9.29.2012
- **Budget:**
  - Govt. Share: $996,567
  - WPI Share: $249,857
  - Total: $1,246,424
- **Funding Received:**
  - FY 09: $347,814

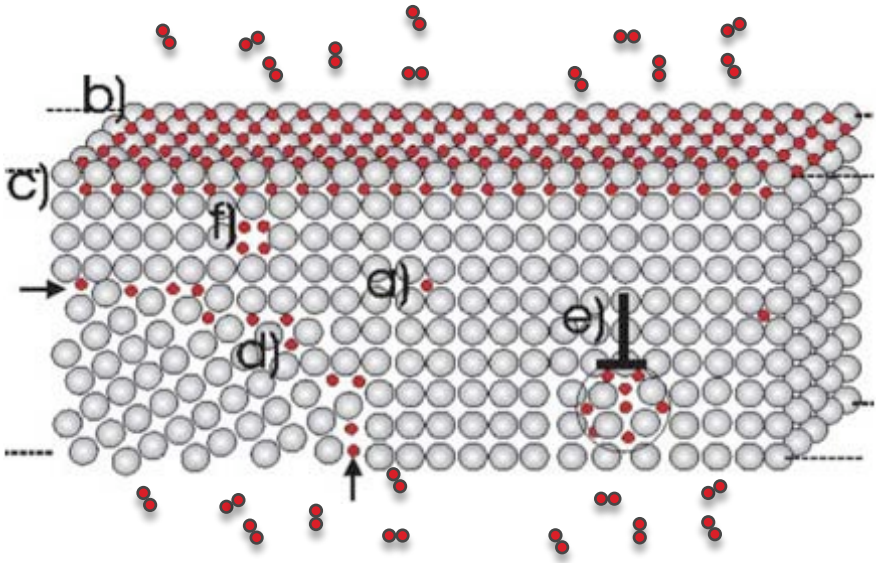
- **Project Manager:** Jason C. Hissam
- **Technical Barriers:**
  - Non-precious metals
  - Low cost
  - High $H_2$ flux & selectivity
  - CO & sulfur tolerance
- **Technical Targets:** NETL Test Protocol: 2008/1335, October, 2008

# Technical Targets

| Property | 2010 Target | 2015 Target |
|---|---|---|
| $H_2$ Flux (std $m^3/m^2.h$) | 60 | 90 |
| $H_2$ Feed Pressure, (psia) | 150 | 150 |
| $H_2$ Permeate Pressure, (psia) | 50 | 50 |
| Operating (psi) | 100 | 100 |
| Operating Temperature, *T* (ºC) | 300–600 | 250–500 |
| Pressure Tolerance, (psi) | 400 | 800–1,000 |
| Sulfur Tolerance (ppm) | 20 | >100 |
| CO Tolerance | Yes | Yes |
| WGS Activity | Yes | Yes |
| $H_2$ Purity (%) | 99.5 | 99.99* |
| Cost ($/ft$^2$) | 500 | <250 |

***Implies dense membrane!**

# Approach: Theoretical Rationale




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

$$Q_{H_2} = S \times D_H$$

Lattice Structure

- Crystalline
- Amorphous
- Molten

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

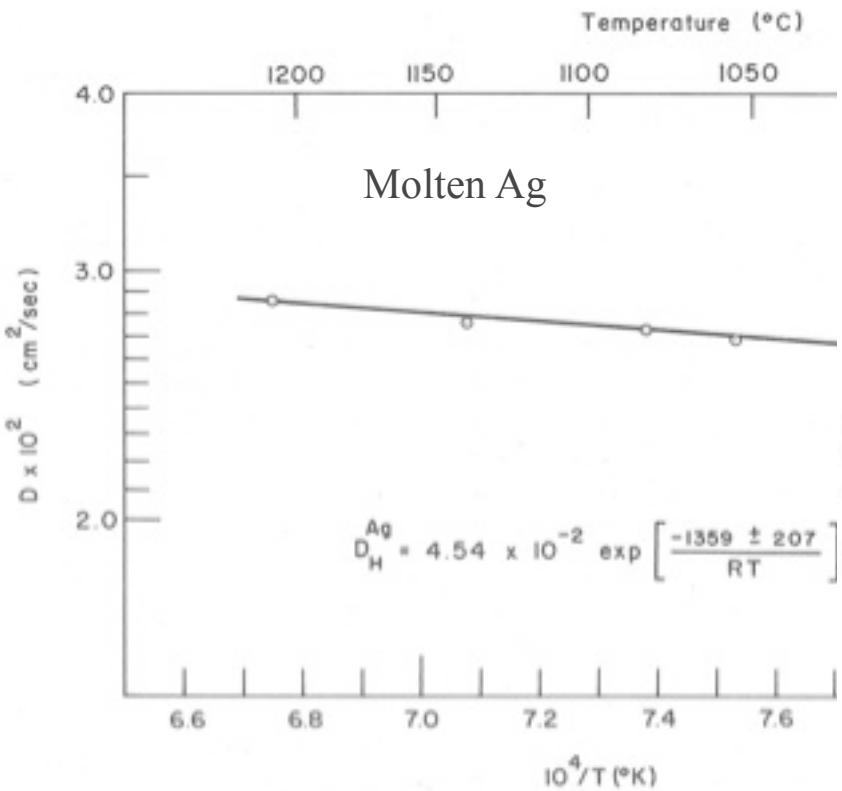
$$D_H = \left\{\frac{1}{6}\lambda^2 \nu_0 \exp\left(-\frac{\Delta S_D^{\ddagger}}{RT}\right)\right\}\exp\left(-\frac{E_D}{RT}\right)$$

# Approach: Rational $H_2$ Membrane Design

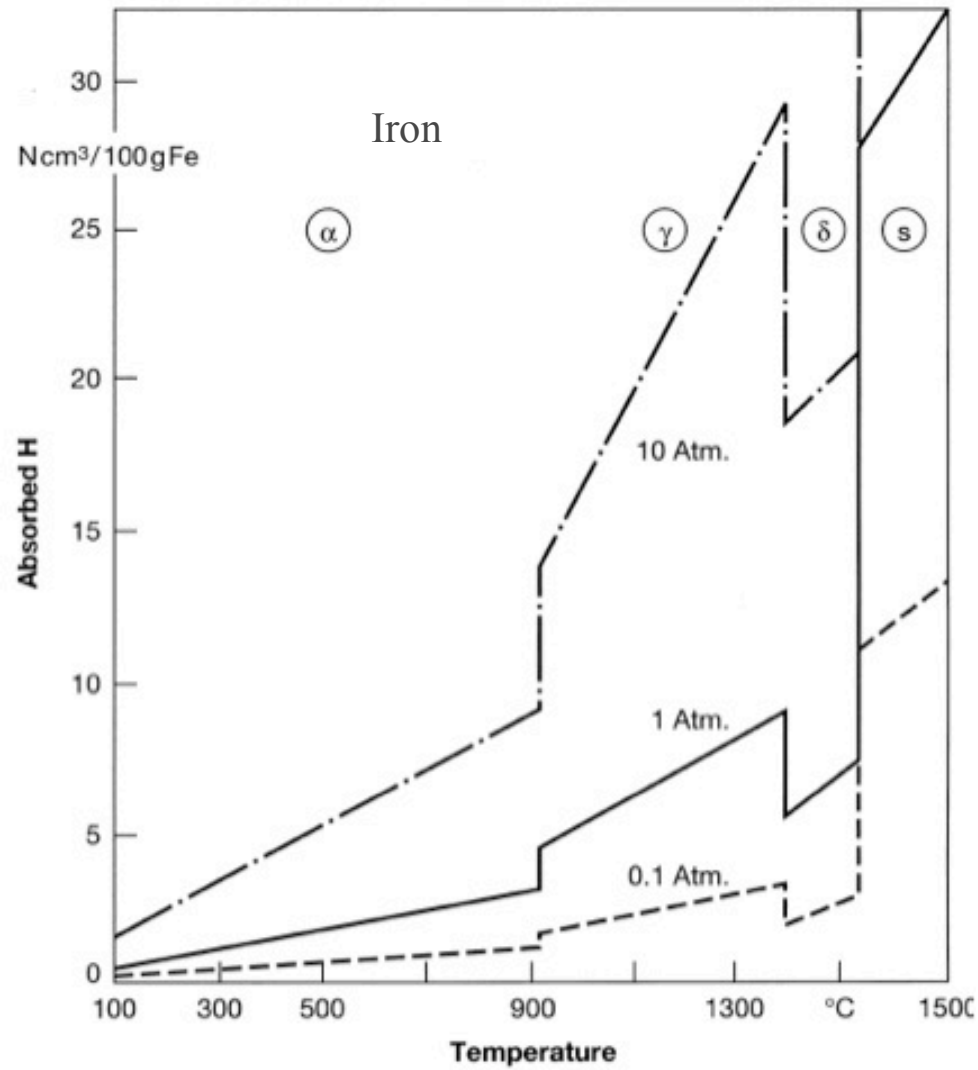
- Enhance H diffusion via a more open lattice ($M_1$)
- Enhance H dissolution via more open lattice ($M_1$)
- Enhance density of surface dissociation sites ($M_2$)
- Enhance $H_2$ dissociative adsorption via catalyst ($M_2$)

Molten metals/alloys for $M_1$!

# Approach: Higher Diffusivity & Solubility in Molten Metals

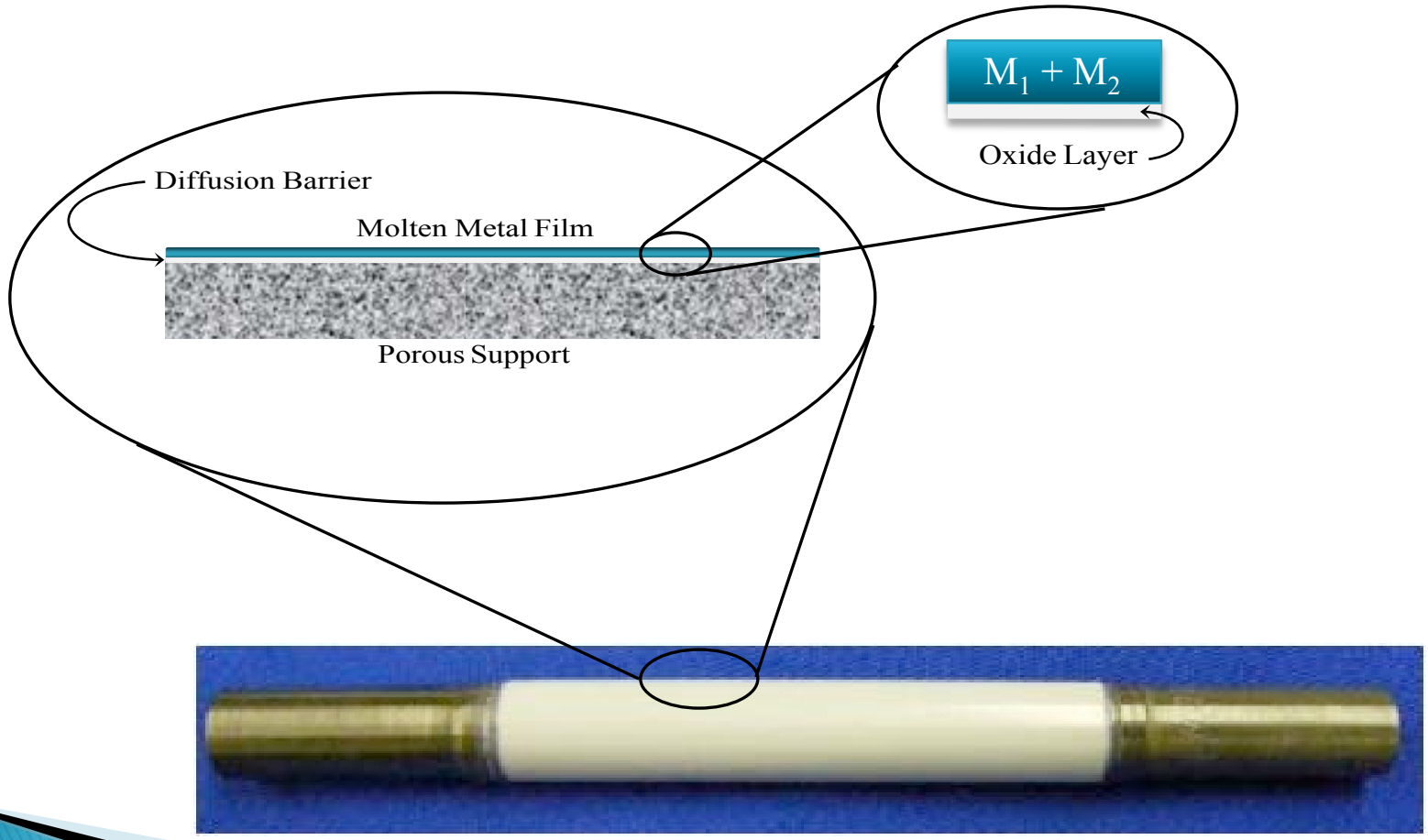



E. M. Sacris, and N. A. D. Parlee, "The Diffusion of Hydrogen in Liquid Ni, Cu, Ag, and Sn," *Metallurgica Materials Transactions B*, **1**, 3377-3382 (1970).




Woodtli, J., and Keiselbach, R., *Engng. Failure Analysis*, **7**, 427-450 (2000).

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



# 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
- $H_2$ Dissociation Activity

# Collaboration: Team Relevant Experience

- PI has extensive experience in fuel cells and $H_2$ 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

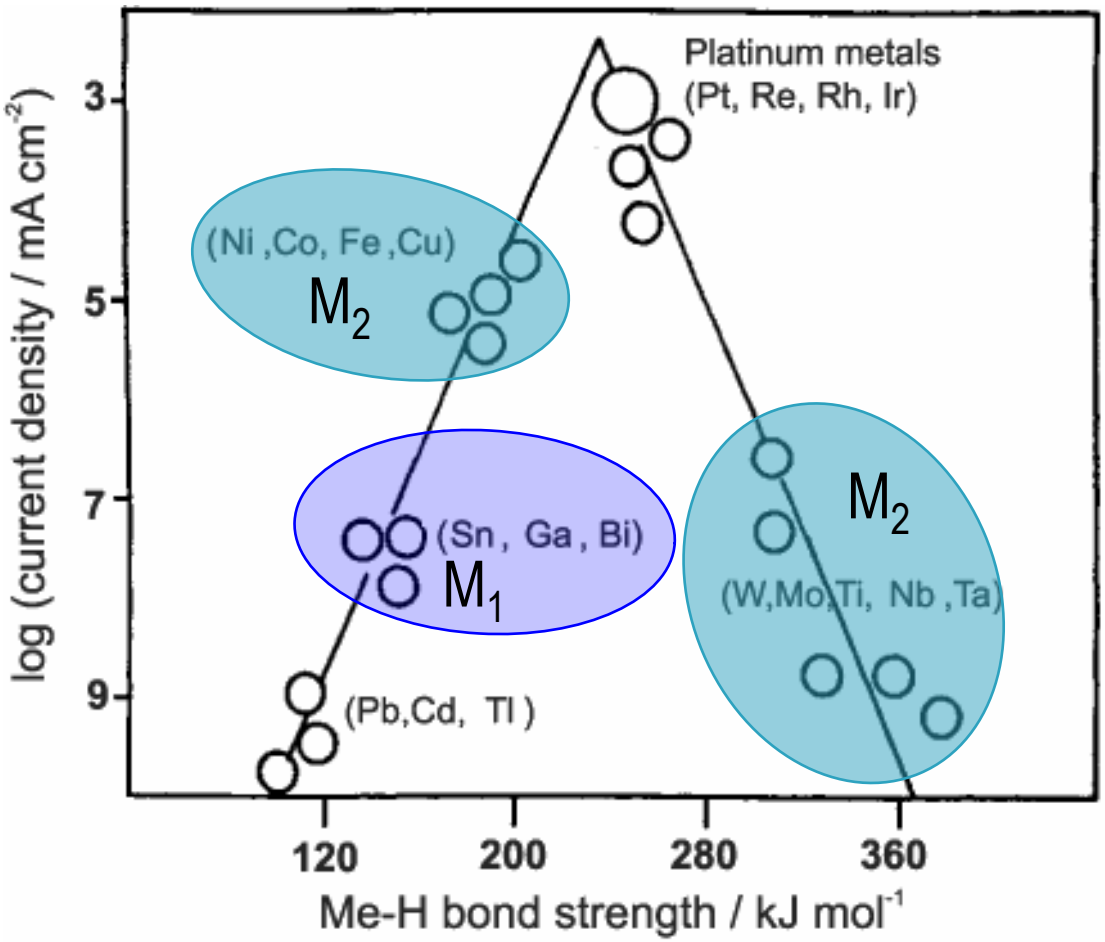
# Goal 1: Select Low Melting Metals ($M_1$)

| | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | H −259 | | | | | | | | | | | | | | | | | He −270 |
| 2 | Li 181 | Be 1278 | | | | | | | | | | | B 2300 | C 3700 | N −210 | O −218 | F −220 | Ne −248 |
| 3 | Na 98 | Mg 649 | | | | | | | | | | | Al 660 | Si 1410 | P 44.2 | S 119 | Cl −101 | Ar −189 |
| 4 | K 63 | Ca 839 | Sc 1541 | Ti 1660 | V 1890 | Cr 1857 | Mn 1244 | Fe 1535 | Co 1495 | Ni 1455 | Cu 1083 | Zn 420 | Ga 30 | Ge 937 | As 817 | Se 217 | Br −7 | Kr −157 |
| 5 | Rb 39 | Sr 769 | Y 1522 | Zr 1852 | Nb 2467 | Mo 2610 | Tc 2172 | Ru 2310 | Rh 1966 | Pd 1554 | Ag 962 | Cd 321 | In 156 | Sn 232 | Sb 631 | Te 450 | I 114 | Xe −112 |
| 6 | Cs 29 | Ba 725 | La 921 | Hf 2227 | Ta 2996 | W 3410 | Re 3180 | Os 2700 | Ir 2410 | Pt 1772 | Au 1064 | Hg −39 | Tl 304 | Pb 328 | Bi 271 | Po 254 | At 304 | Rn −71 |

Melting points of the elements /°C

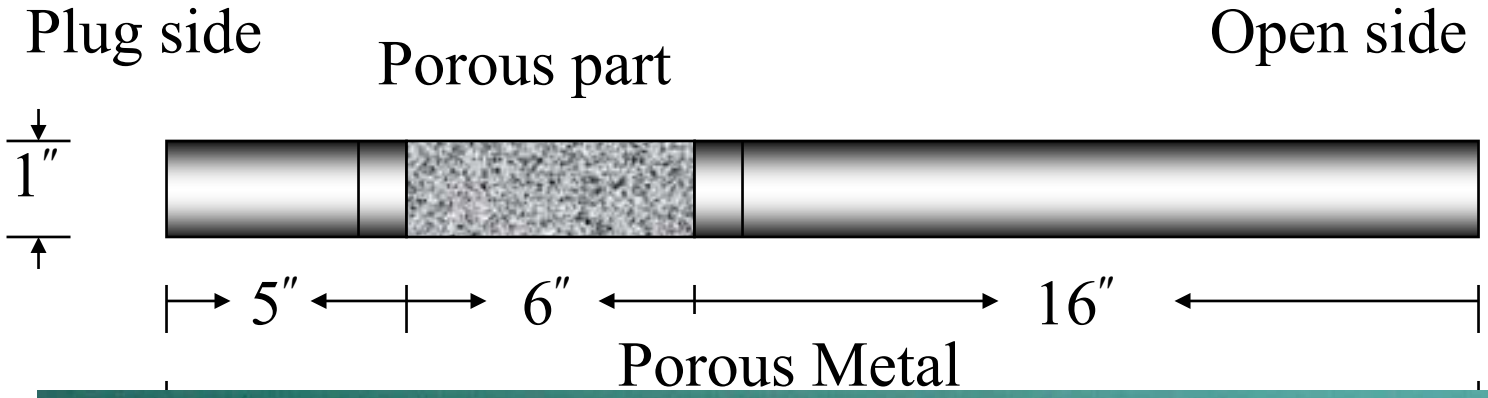
Technical Accomplishment

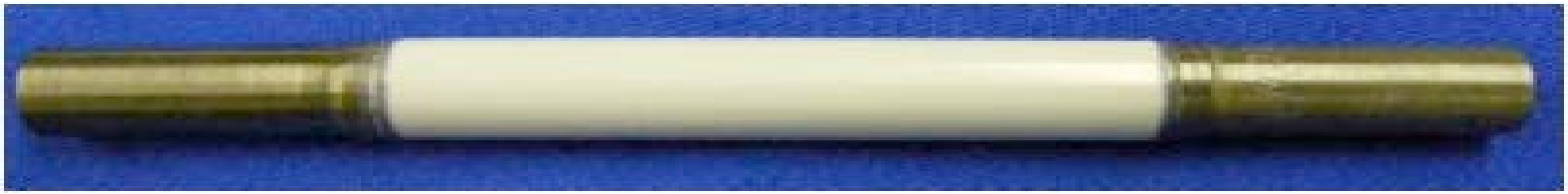
# Goal 1: Select Catalytic Component ($M_2$)




Technical Accomplishment

# Goal 2: Select Suitable Porous Support(s)





Porous Metal with Ceramic Layer

Technical Accomplishment

# Porous Support Discussion

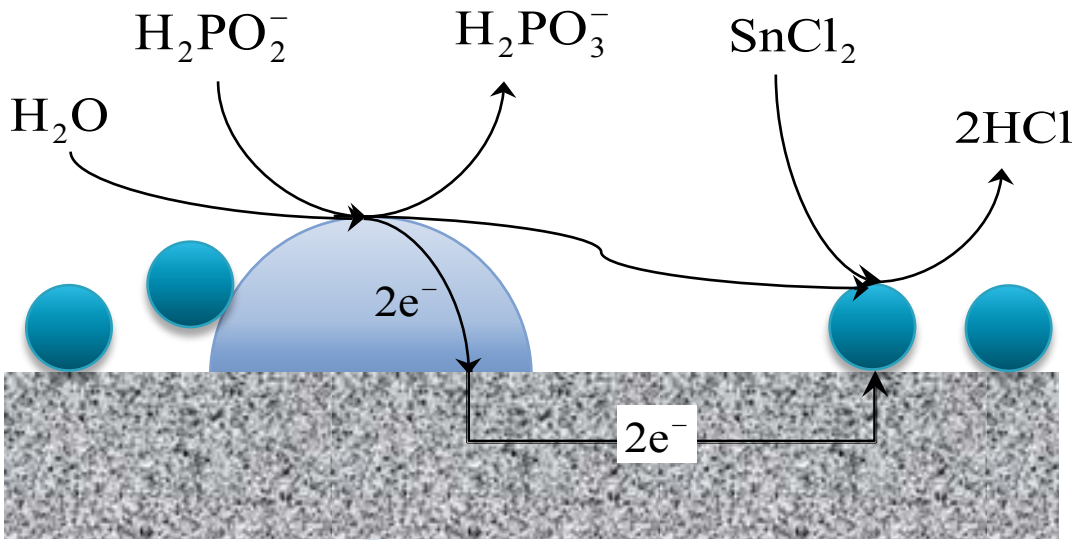
- Porous Stainless Steel (PSS)/Inconel
  - ✓Alloying?
- Porous Ceramic
  - ✓Wettability/Sealing/Fragility?
  - ✓$Al_2O_3$
  - ✓$ZrO_2$
  - ✓$TiO_2$
  - ✓SiC
  - ✓Porous Vycor® glass
- PSS/Inconel w/Oxide Layer
  - ✓Best Option?

# 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

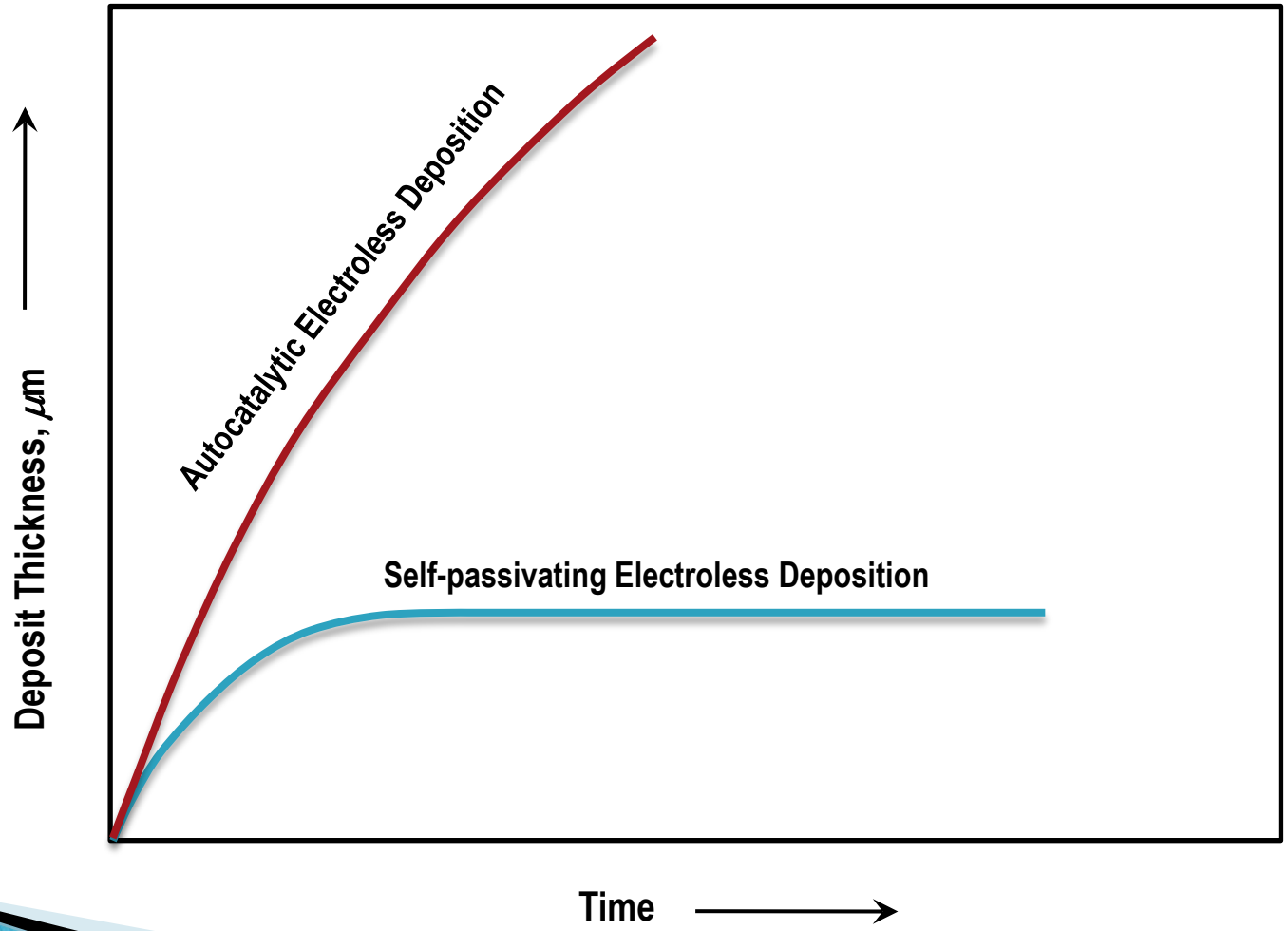



| Electrode | Reaction, $s_\rho$ | $\sigma_\rho$ |
|---|---|---|
| *Cathode*: | $Sn(Cl)_2 + 2H^+ + 2e^- \leftrightarrows Sn^0 + 2HCl$ | $+1$ |
| *Anode*: | $Na^+H_2PO_2^- + H_2O \overset{Pd}{\leftrightarrows} Na^+H_2PO_3^- + 2H^+ + 2e^-$ | $+1$ |
| *Overall*: | $Sn(Cl)_2 + NaH_2PO_2 + H_2O \leftrightarrows 2HCl + Sn^0 + NaH_2PO_3$ | |



Technical Accomplishment

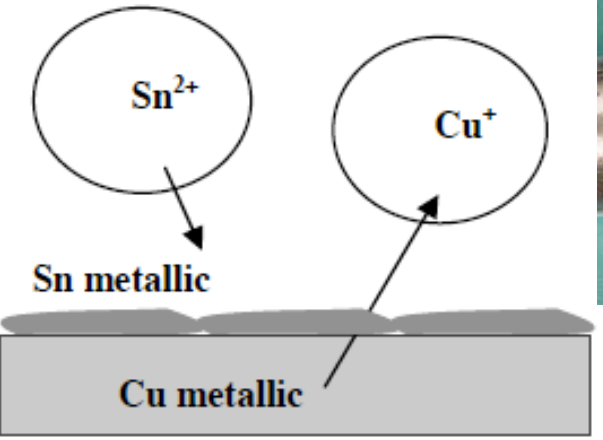
# Goal 3: Electroless Deposit Thickness



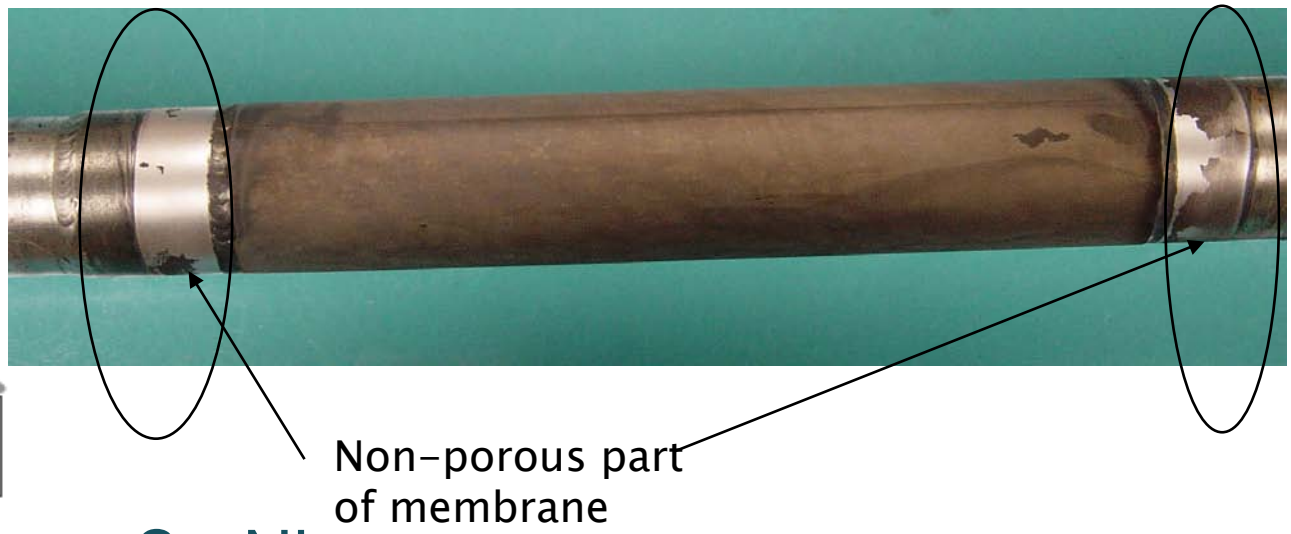

Technical Accomplishment

# Goal 3: Immersion Deposition

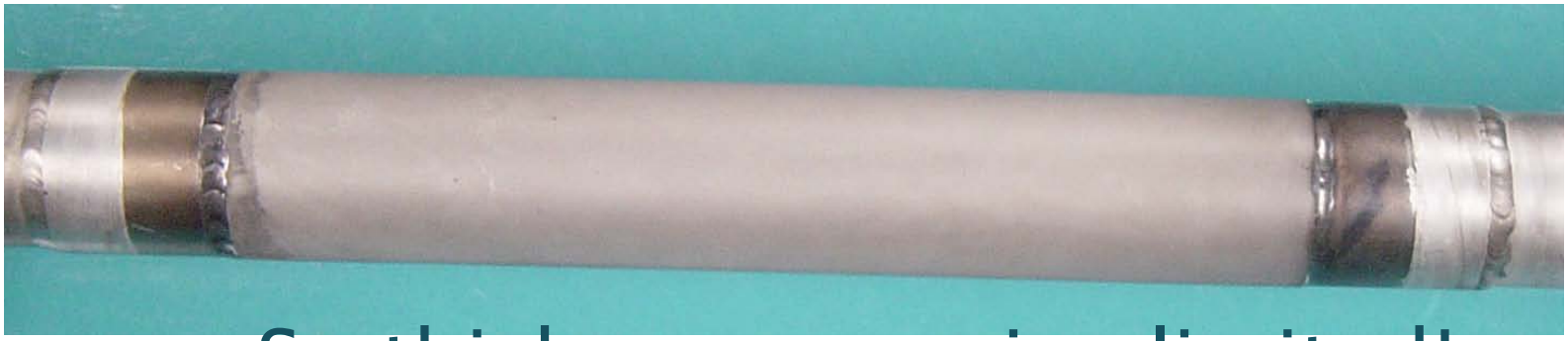
*Solution #1; acidic




Sn-Cu:




Sn-Ni:

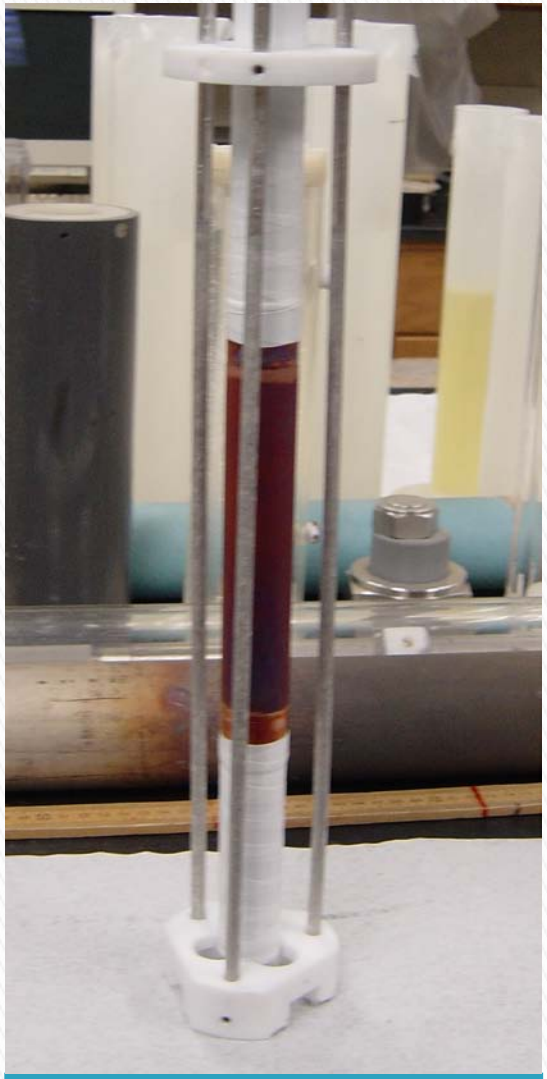


Sn thickness remains limited!

Technical Accomplishment

# Goal 3: Electroplating Apparatus

Electroplating Apparatus



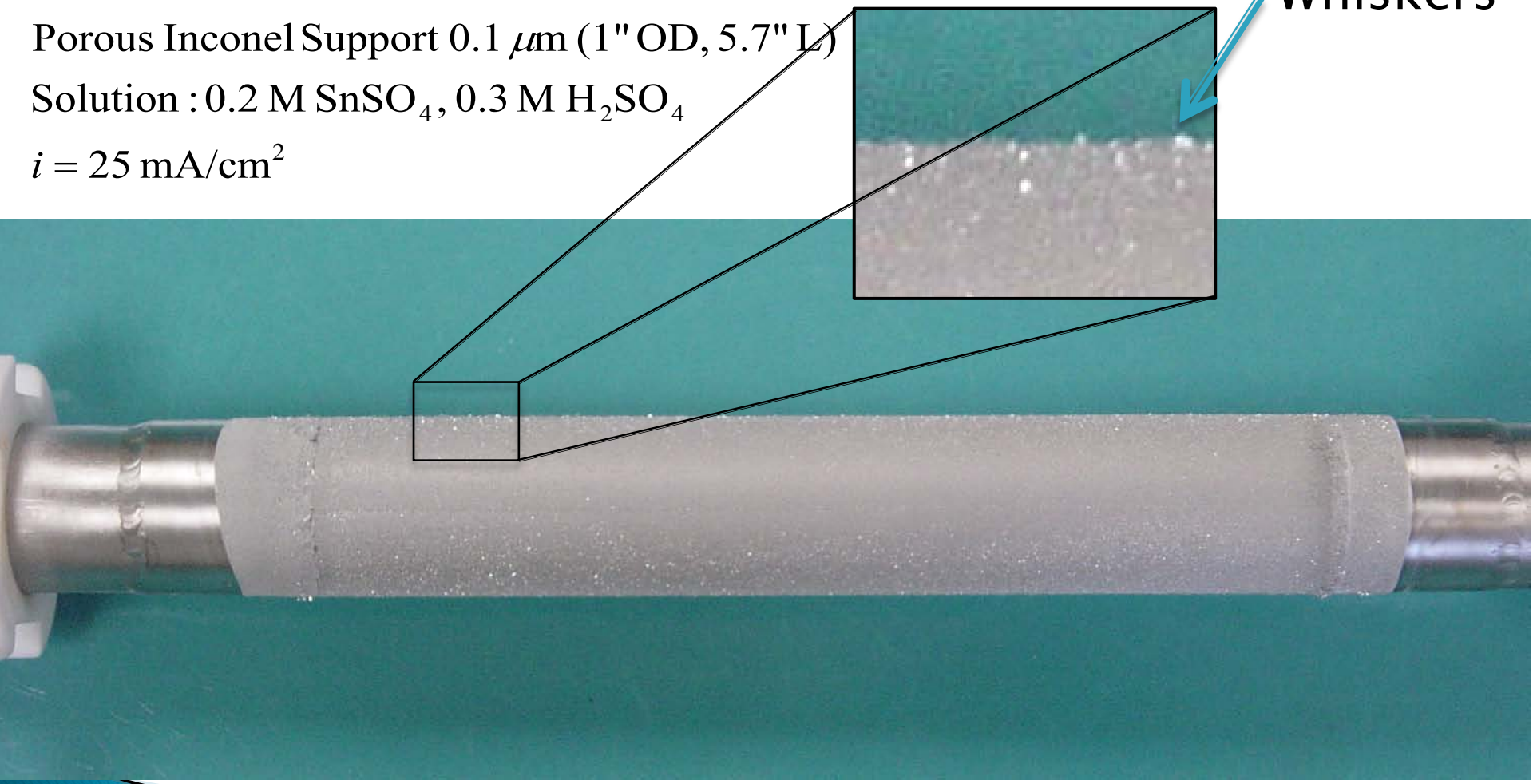
3 Sn Electrodes

# Goal 3: Electroplated Sn SMMM on Porous Inconel

Porous Inconel Support 0.1 $\mu$m (1" OD, 5.7" L)

Solution : 0.2 M $SnSO_4$, 0.3 M $H_2SO_4$

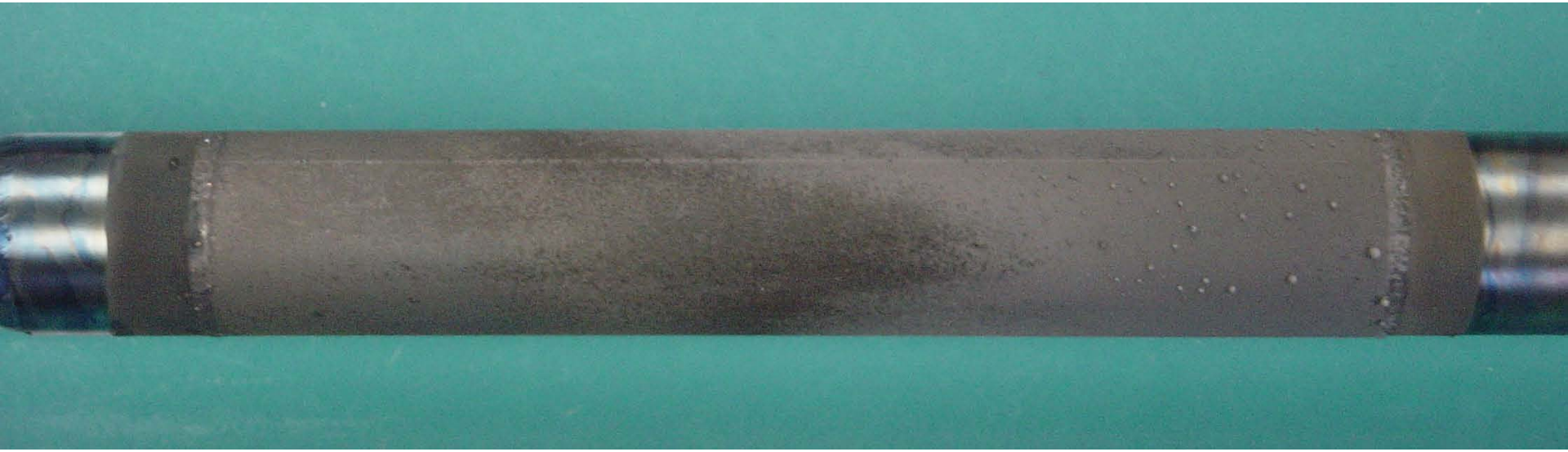
$i = 25\ \mathrm{mA/cm^2}$






Technical Accomplishment

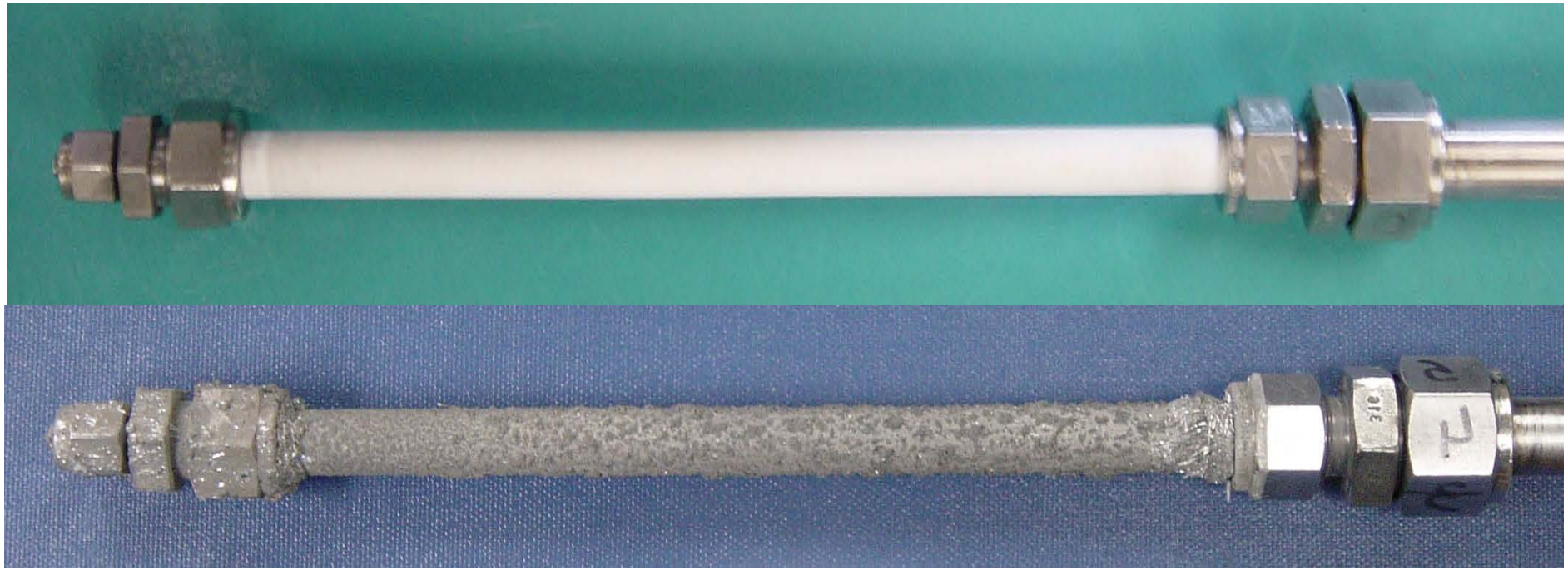
# Goal 3: 10 $\mu$m Sn/Inconel SMMM Post 600 ºC Treatment



Upon melting, Sn alloyed with Inconel to form an impermeable layer

Technical Accomplishment

# Goal 3: Porous Ceramic Support



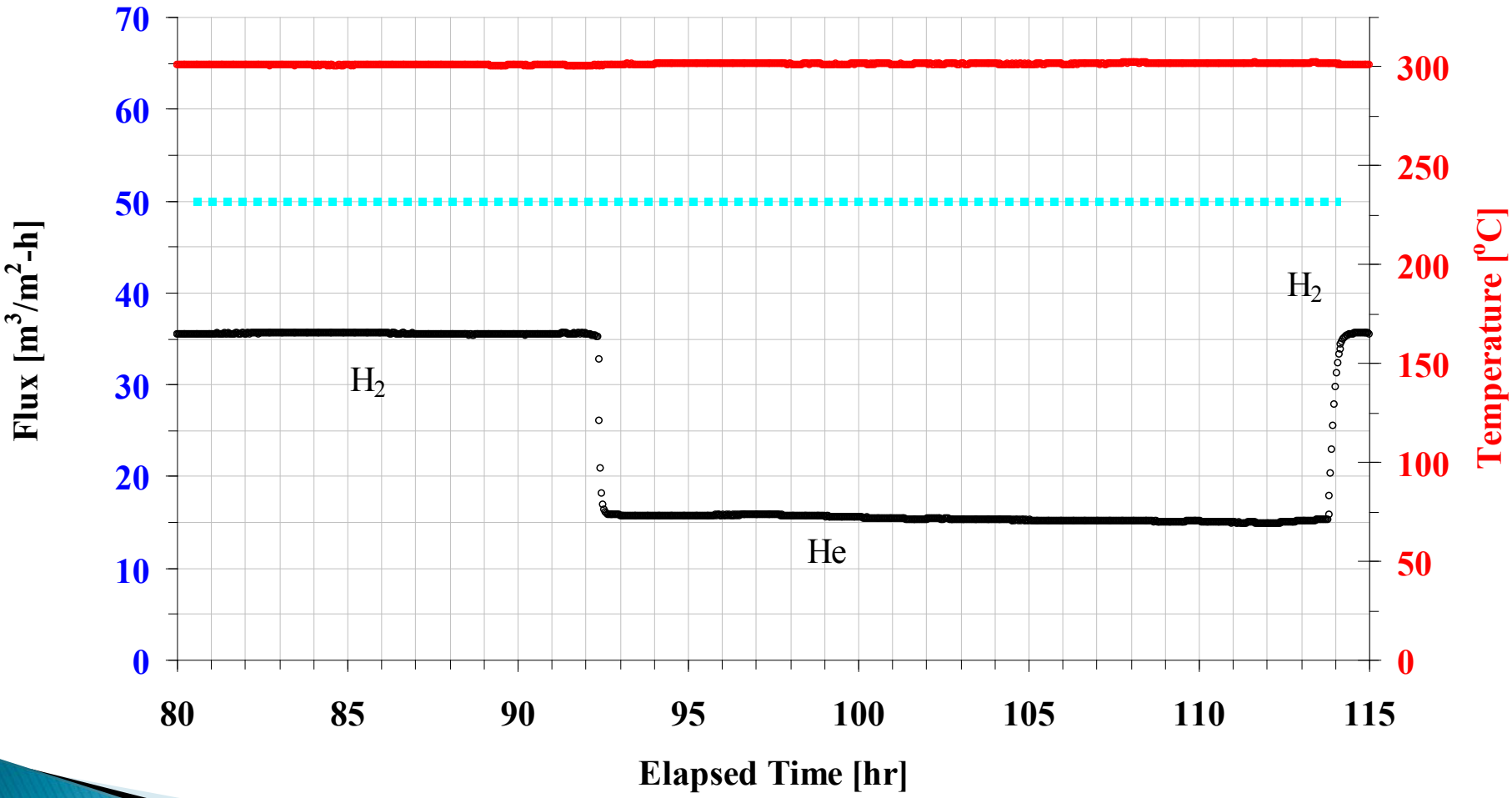


Technical Accomplishment

# Goal 3: Sn-Porous Ceramic Membrane Post-Mortem

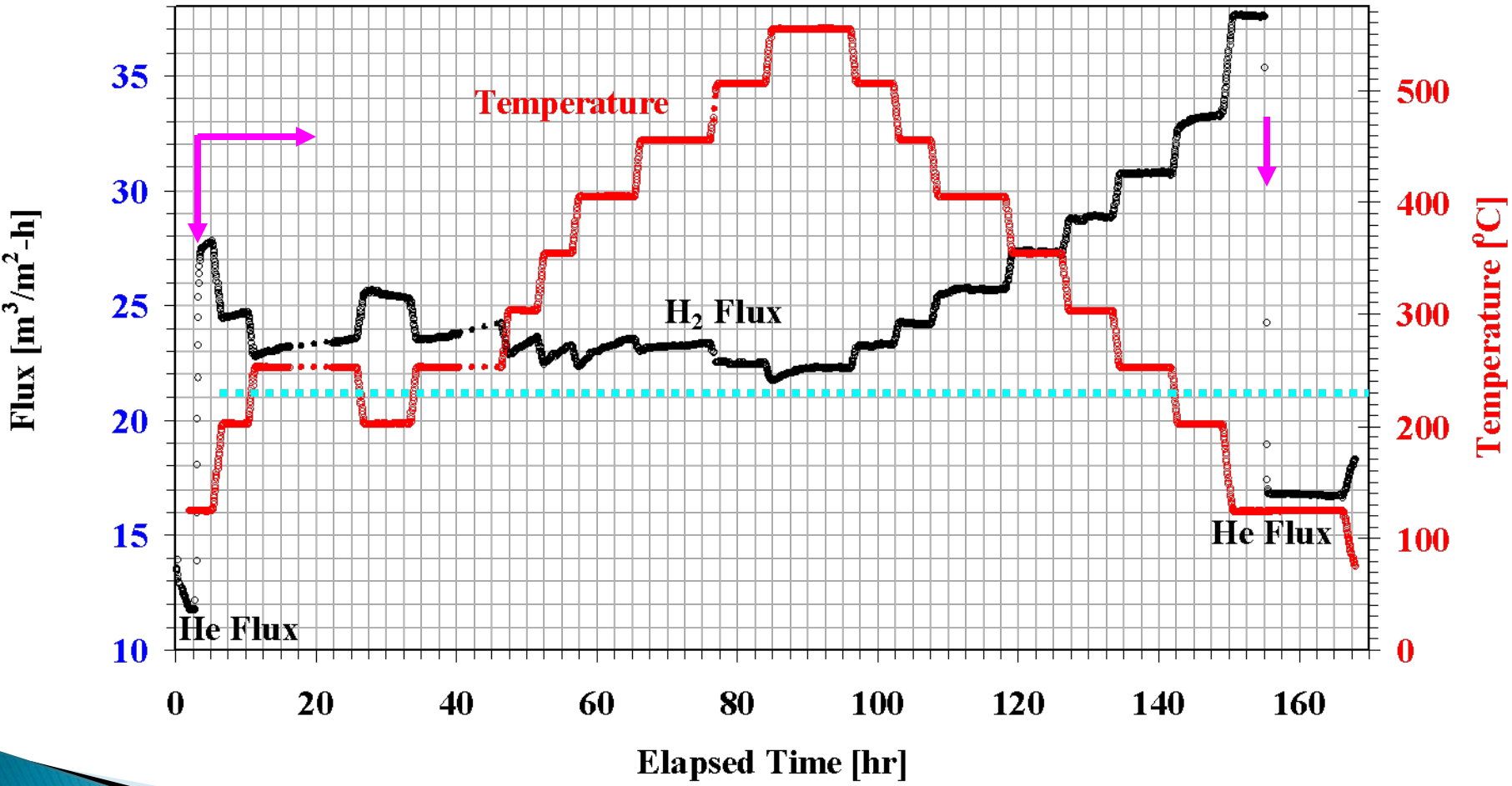
Technical Accomplishment

# Goal 3: Permeability of Sn-Porous Ceramic SMMM



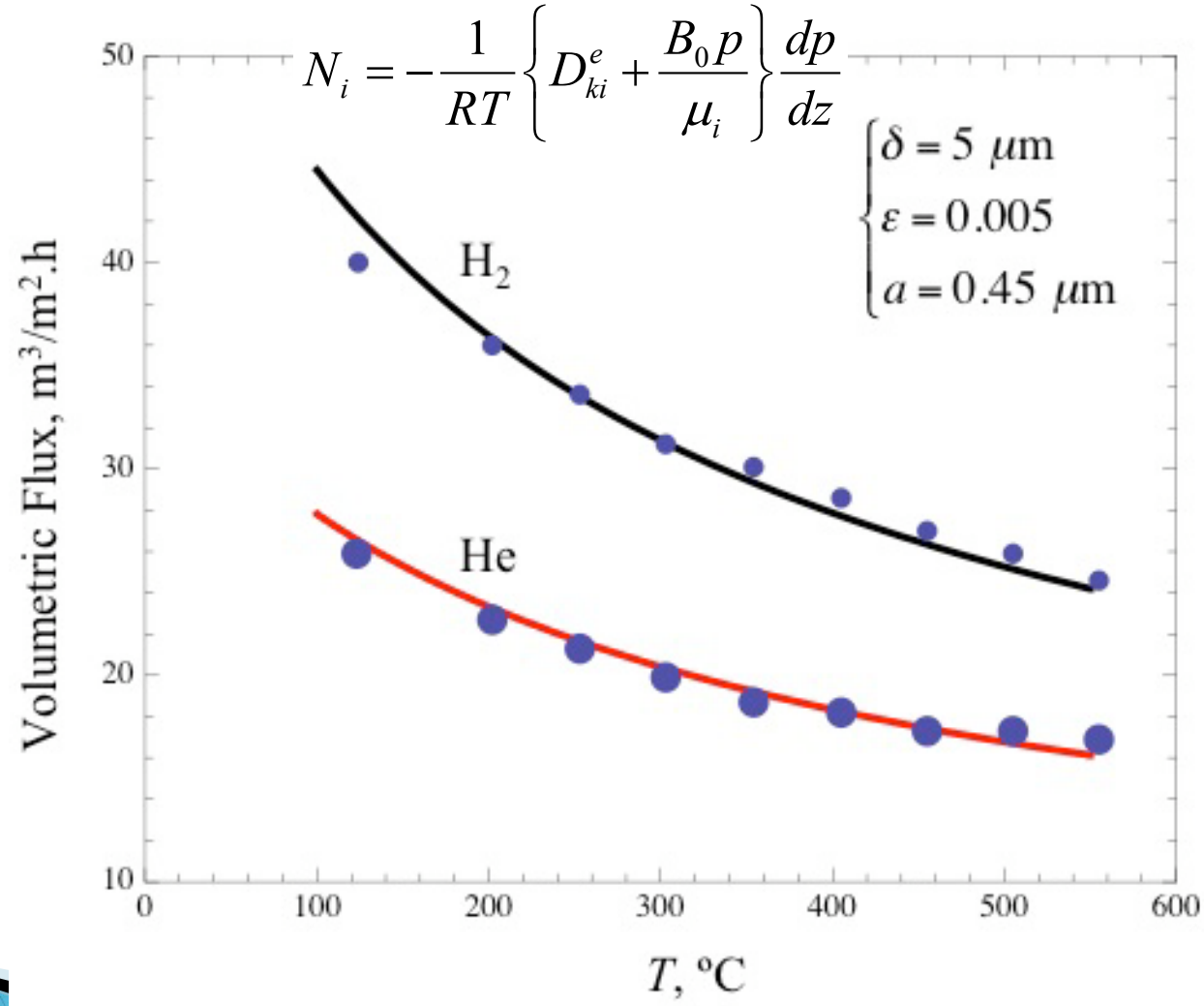

Technical Accomplishment

# Goal 3: Permeability vs Temperature




Technical Accomplishment

# Goal 3: Permeability vs Temperature: Theory




Technical Accomplishment

# 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