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

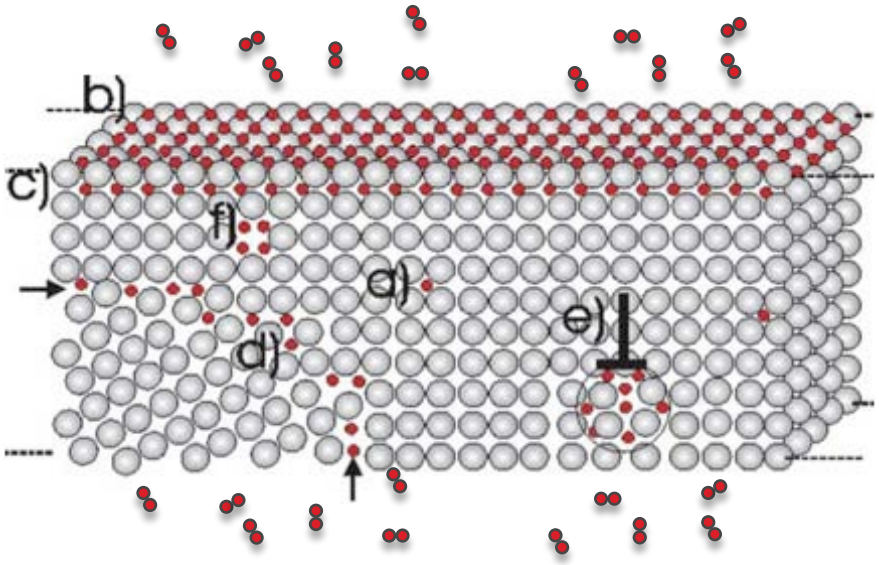
- **Project Manager:** Jason C. Hissam
- **Technical Barriers**:
  - Non-precious metals
  - Low cost
  - High H_2 flux & selectivity
  - CO & sulfur tolerance
- **Technical Targets:** NETL Test Protocol: 2008/1335, October, 2008

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

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

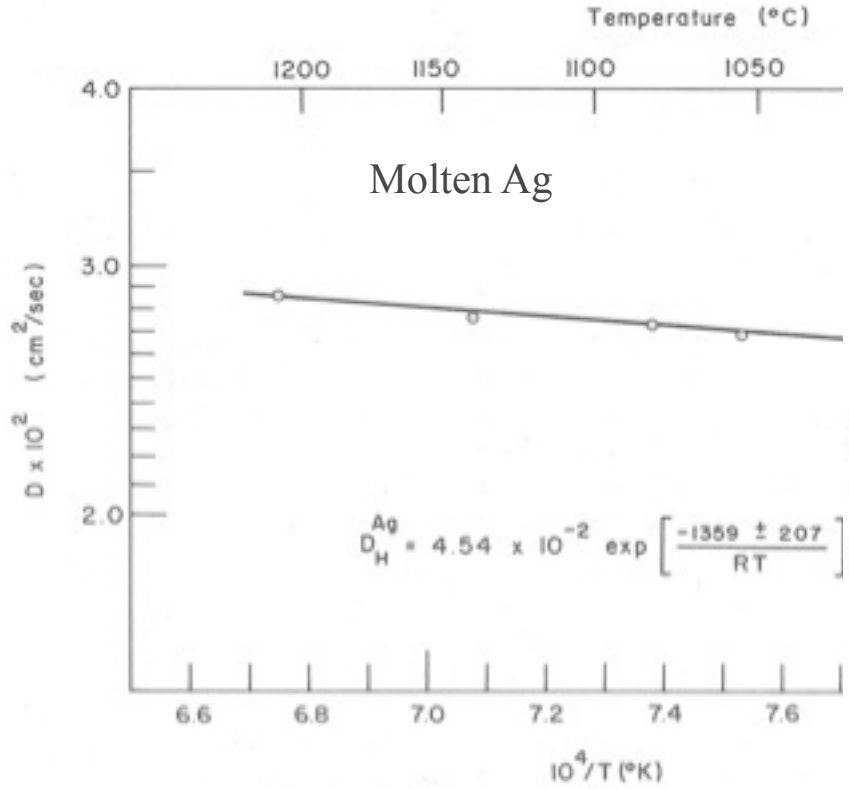
$$D_H = \left\{\frac{1}{6}\lambda^2 \nu_0 \exp\left(-\frac{\Delta S_D^{\ddagger}}{RT}\right)\right\} \exp\left(-\frac{E_D}{RT}\right)$$

Approach: Rational H_2 Membrane Design

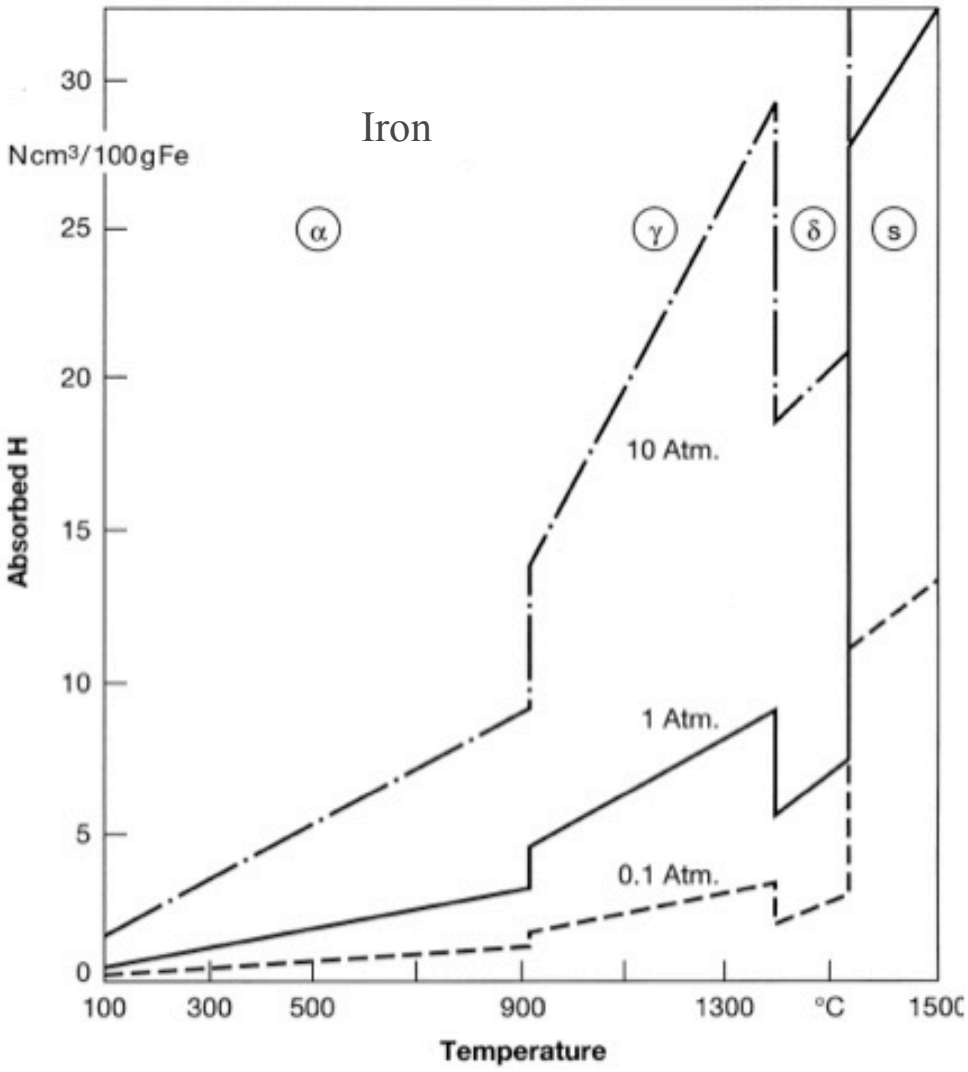
- Enhance H diffusion via a more open lattice (M_1)
- Enhance H dissolution via more open lattice (M_1)
- Enhance density of surface dissociation sites (M_2)
- Enhance H_2 dissociative adsorption via catalyst (M_2)

Molten metals/alloys for M_1!

Approach: Higher Diffusivity & Solubility in Molten Metals

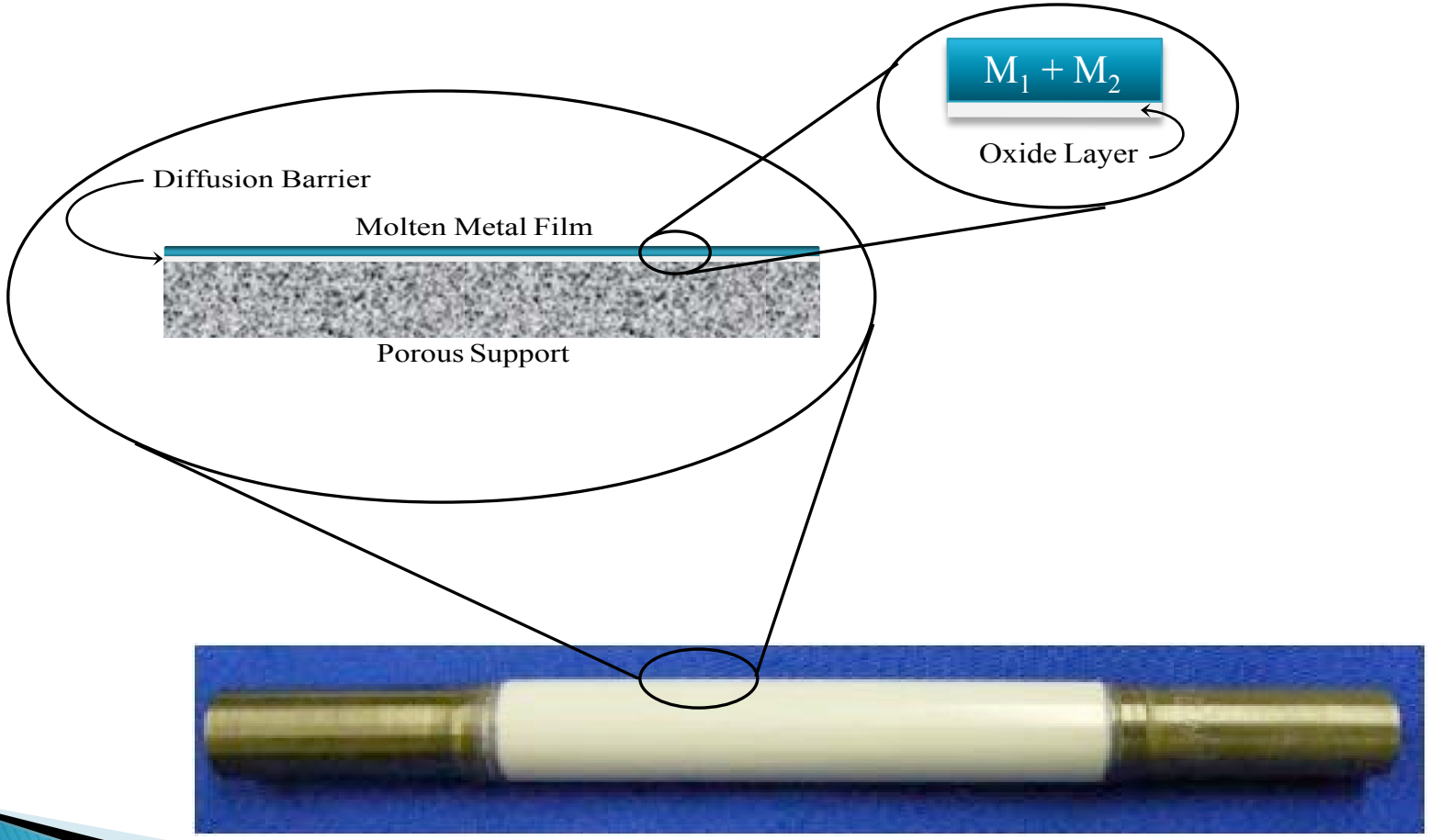


E. M. Sacris, and N. A. D. Parlee, "The Diffusion of Hydrogen in Liquid Ni, Cu, Ag, and Sn," *Metallurgica Materials Transactions B*, **1**, 3377-3382 (1970).



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

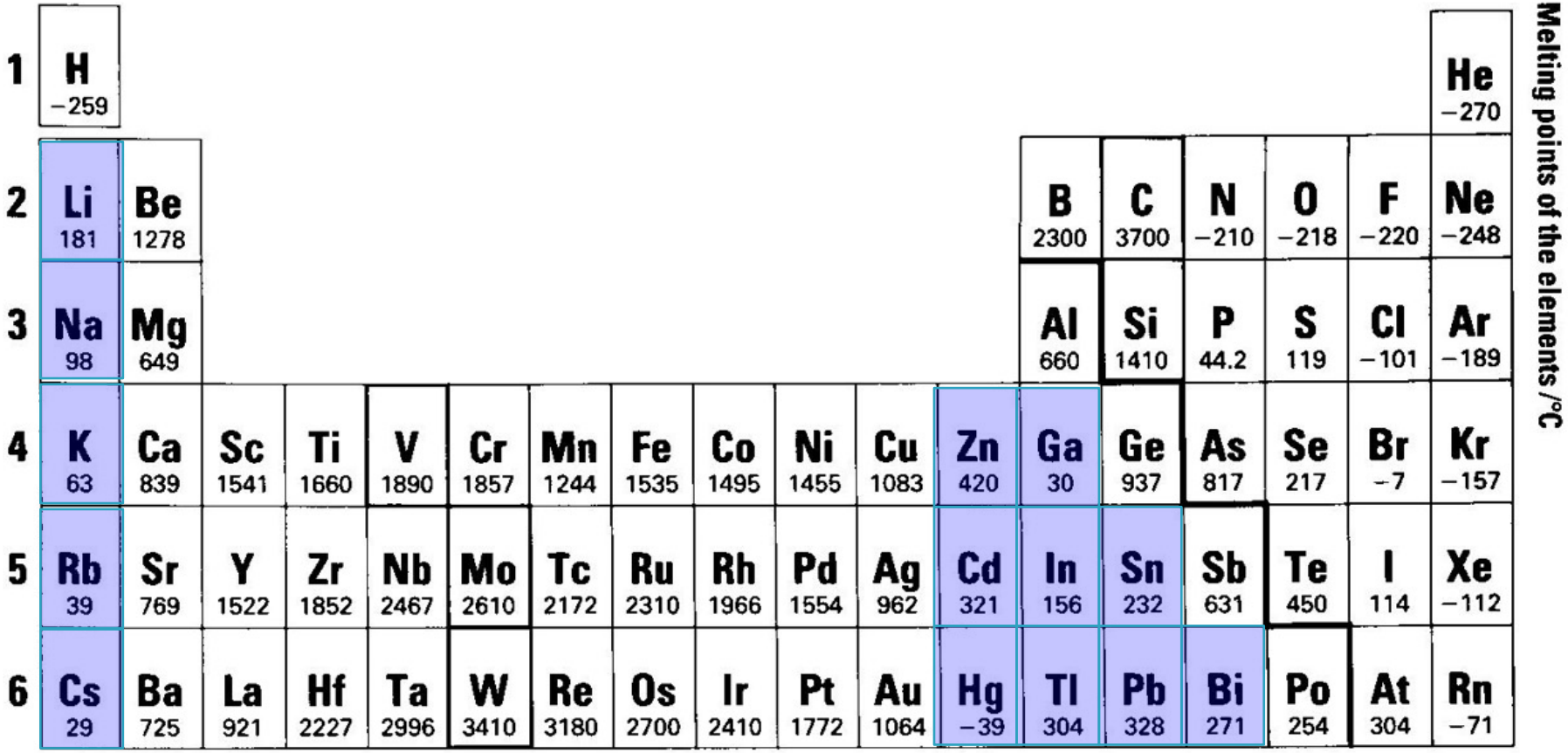
Collaboration: Team Relevant Experience

- 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)

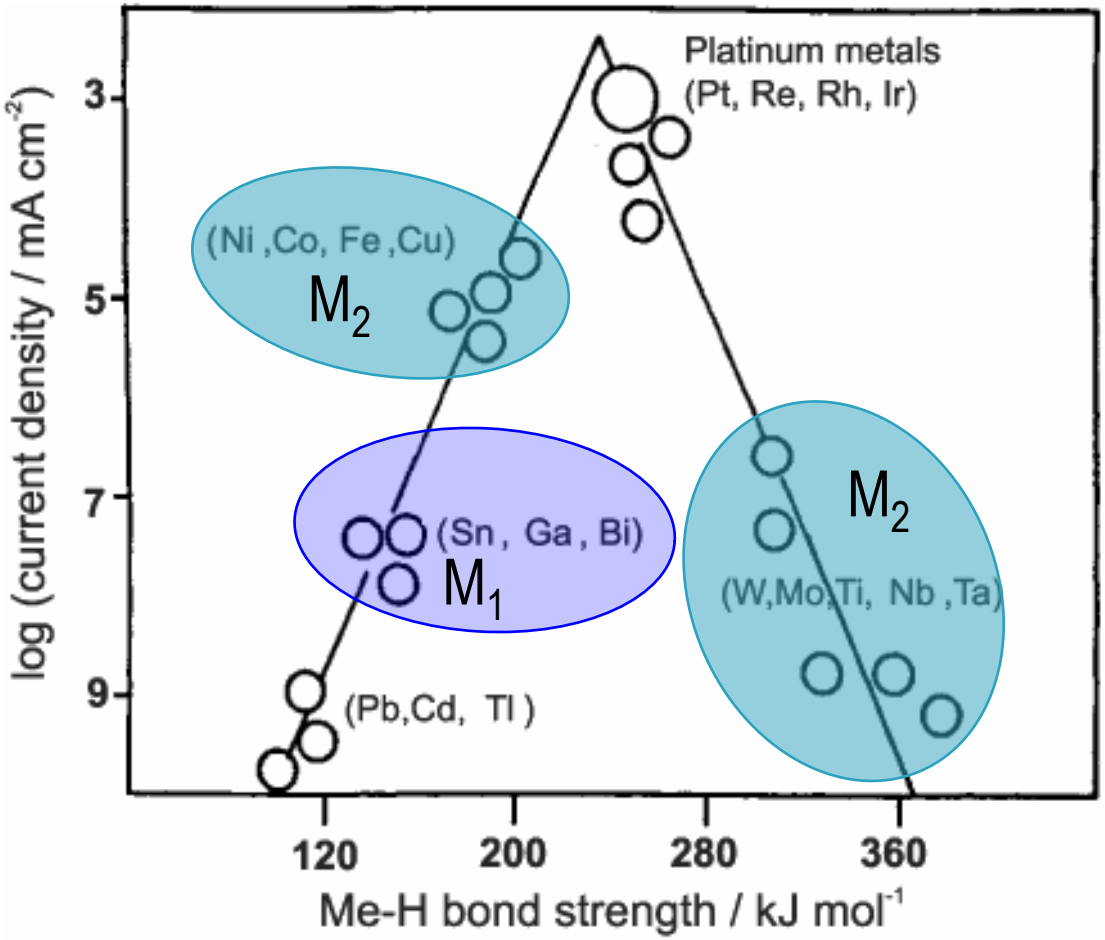
1. Select molten metal (M_1) and catalyst (M_2)
2. Select suitable porous supports (porous metal, with or without a diffusion barrier, or ceramic)
3. Develop membrane fabrication protocols
4. Establish basic feasibility of the SMMM

Goal 1: Select Low Melting Metals (M_1)



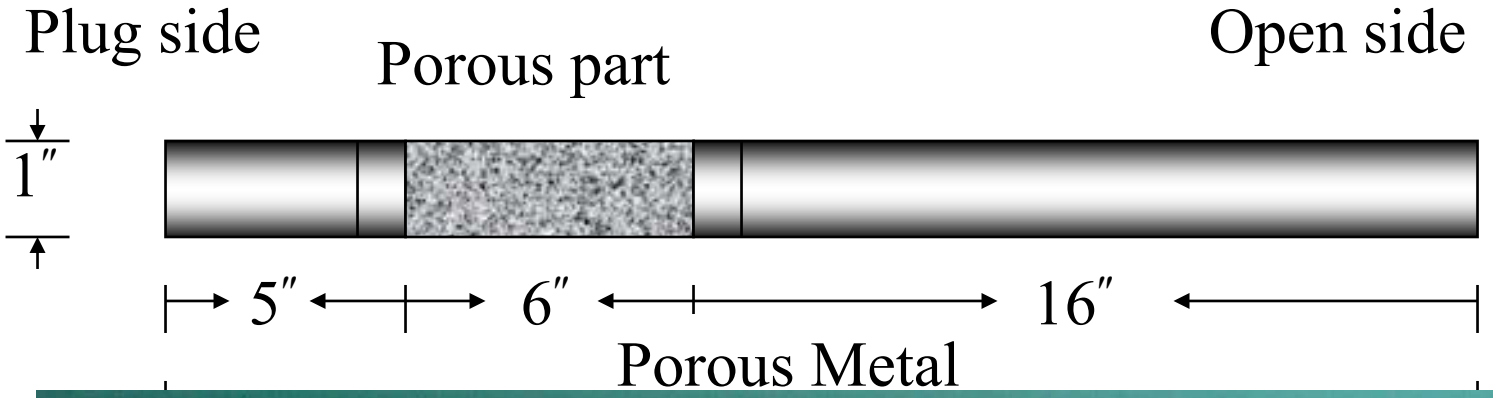
Technical Accomplishment

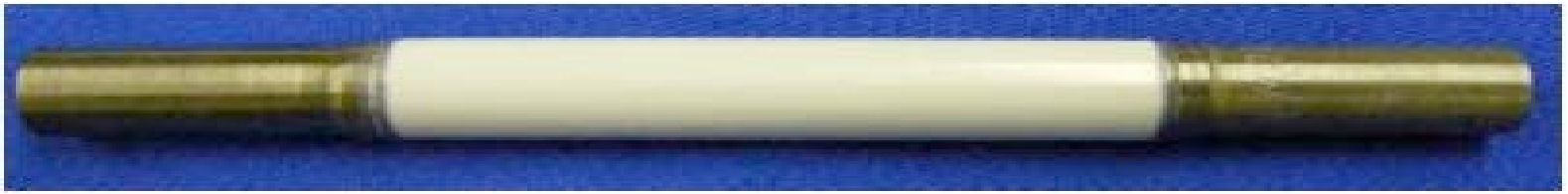
Goal 1: Select Catalytic Component (M_2)



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

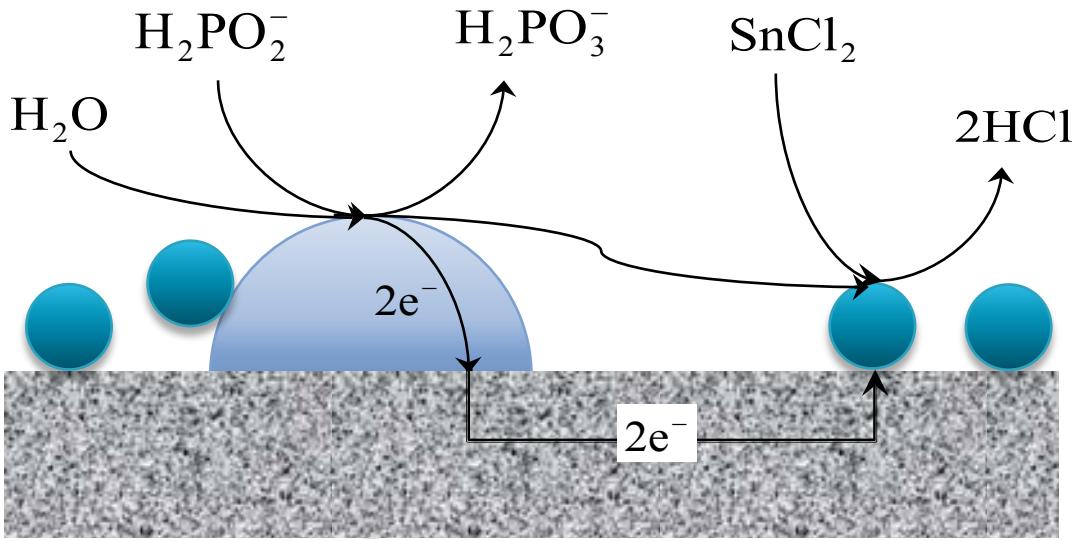
a) Electroless plating (Controllable/Complex)

b) Electroplating (Versatile/Simple)

c) Melt imbibition (Crude but quick)

Start with M_1 = Sn; No M_2;
Porous Support = Inconel

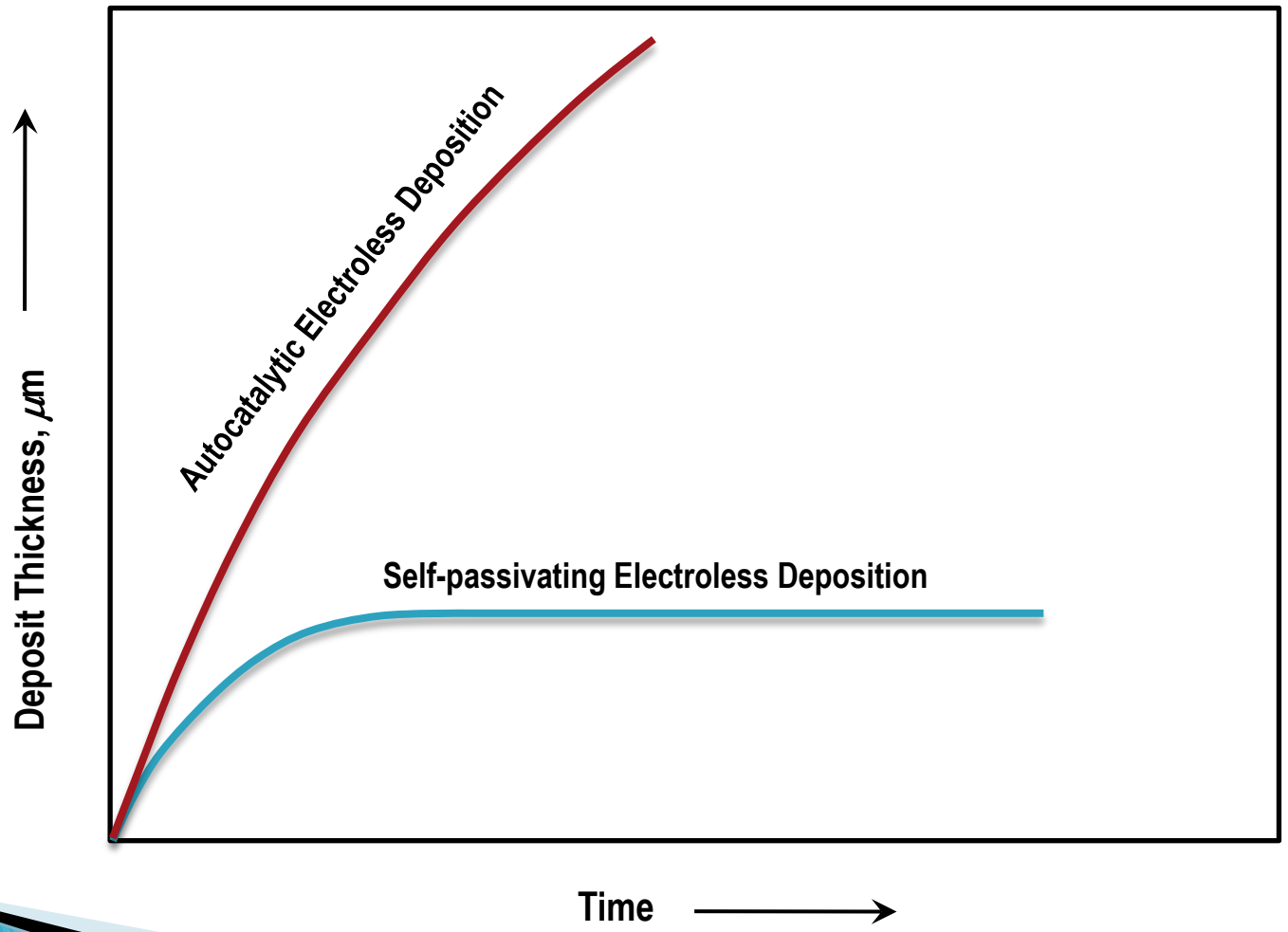
Goal 3: Catalyzed Electroless Deposition of Sn



Electrode	Reaction, s_ρ	σ_ρ
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

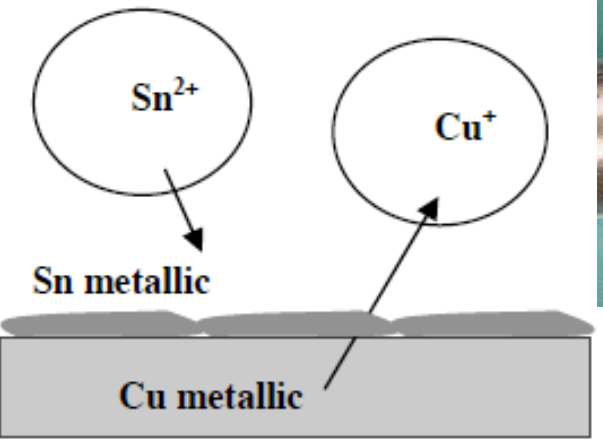
Goal 3: Electroless Deposit Thickness



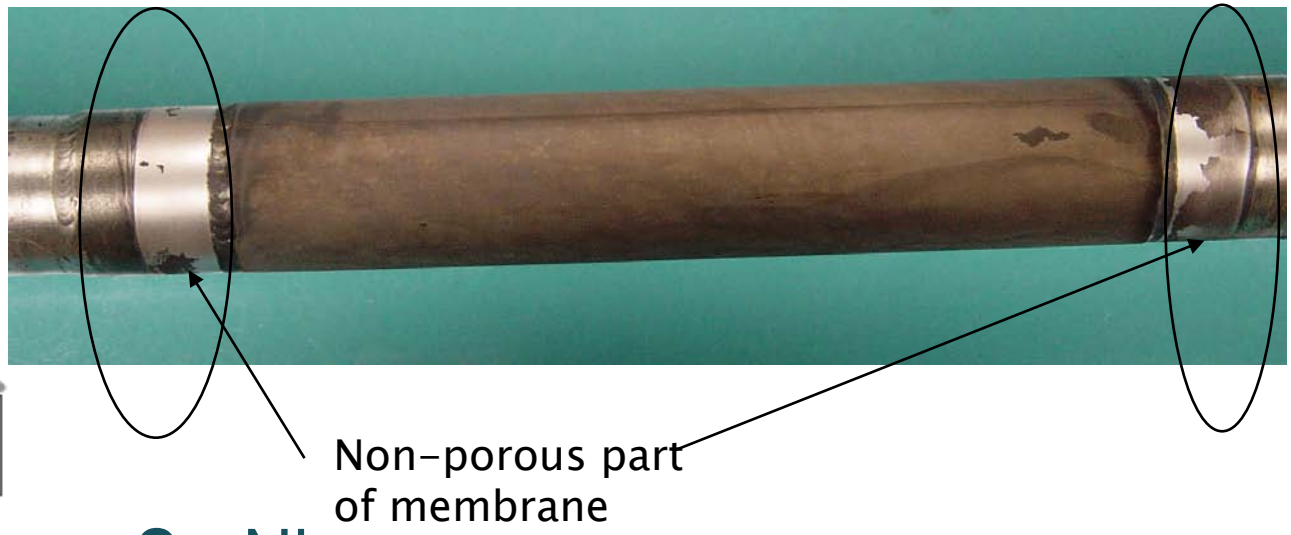
Technical Accomplishment

Goal 3: Immersion Deposition

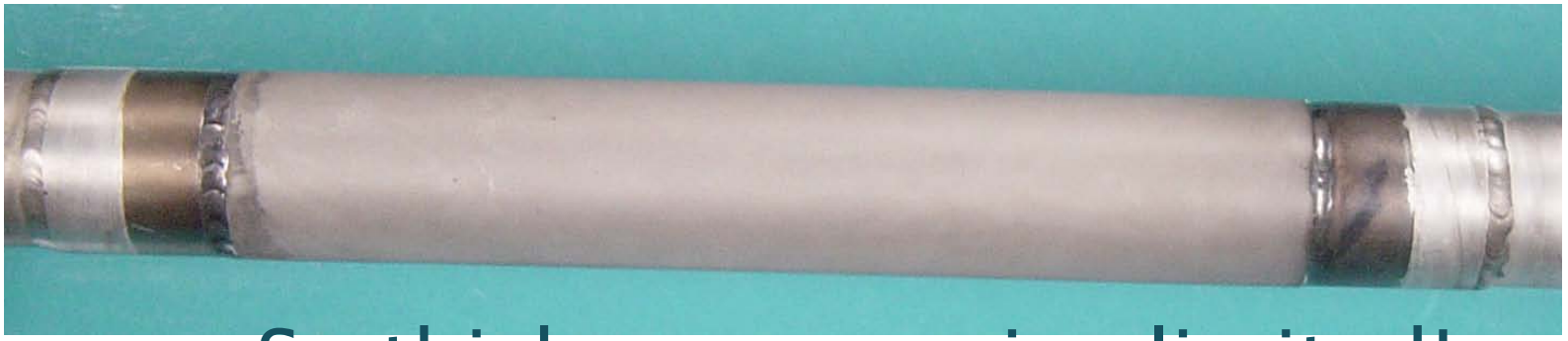
*Solution #1; acidic



Sn-Cu:



Sn-Ni:

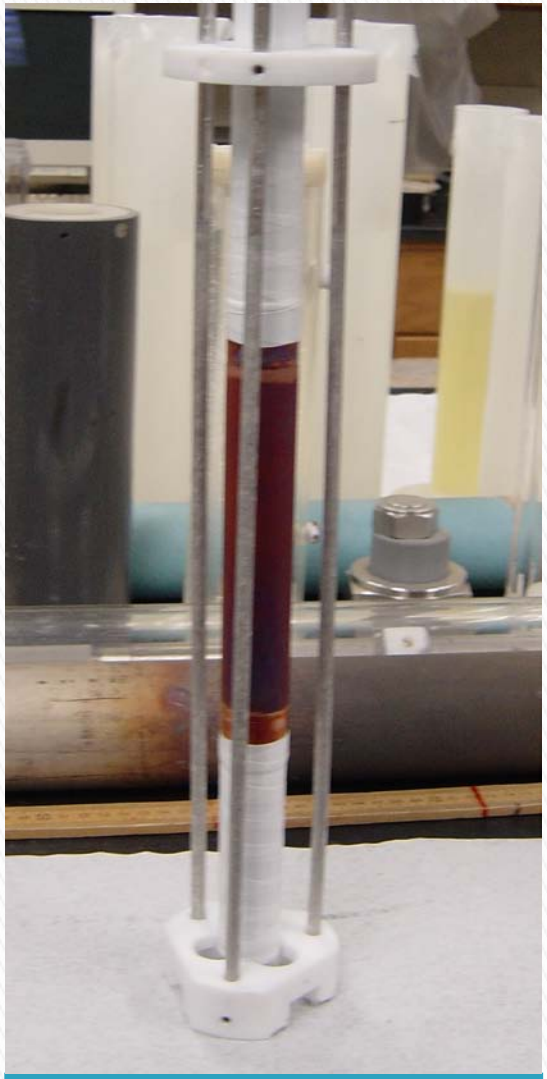


Sn thickness remains limited!

Technical Accomplishment

Goal 3: Electroplating Apparatus

Electroplating Apparatus



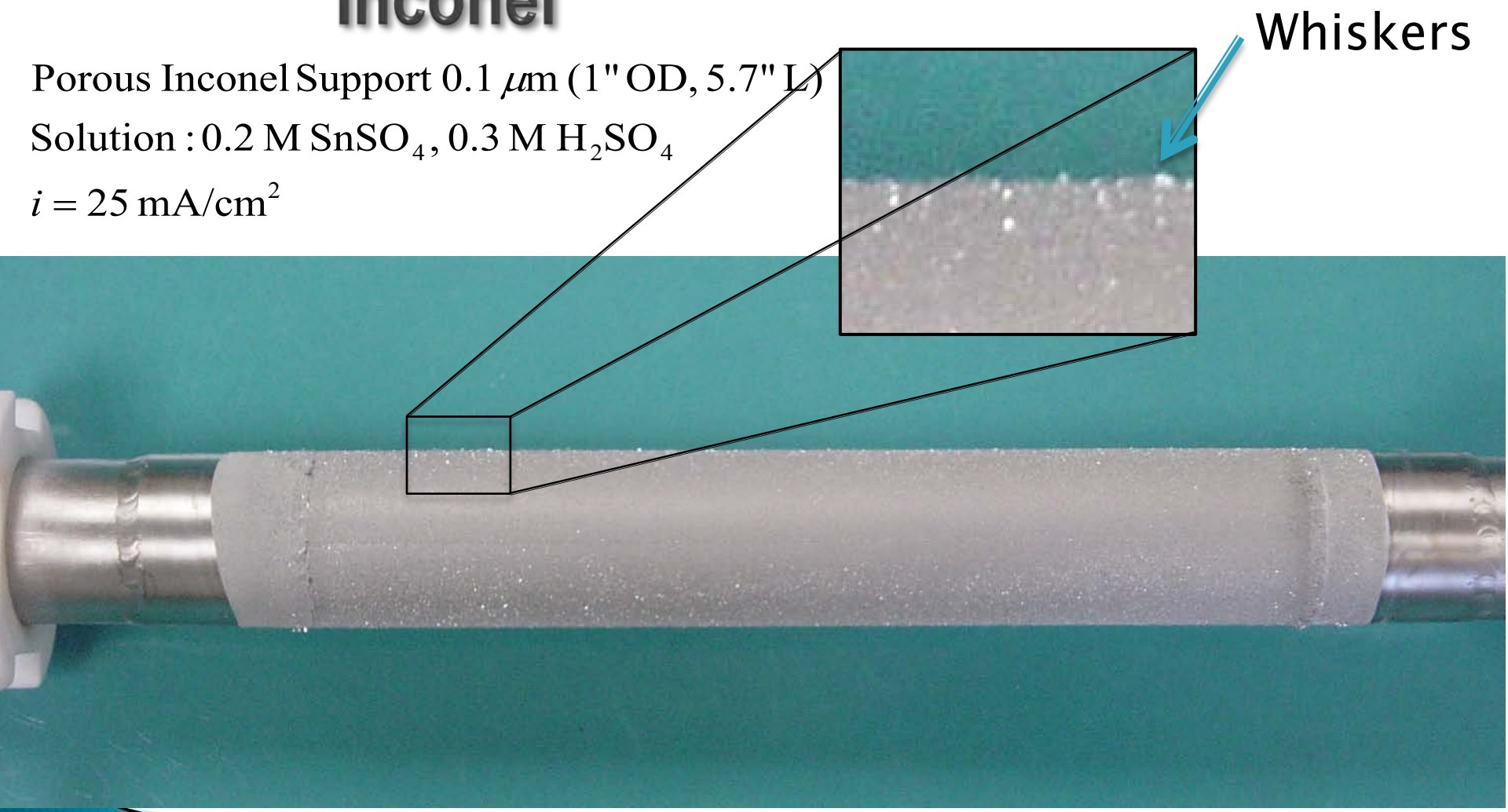
3 Sn Electrodes

Goal 3: Electroplated Sn SMMM on Porous Inconel

Porous Inconel Support 0.1 μm (1" OD, 5.7" L)

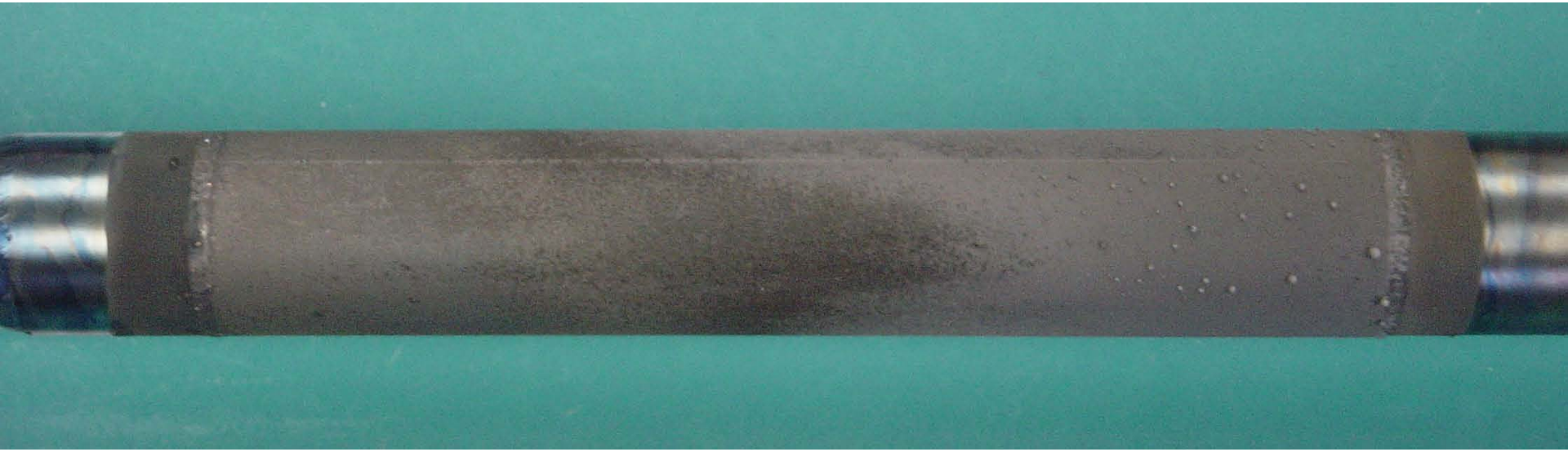
Solution : 0.2 M $SnSO_4$, 0.3 M H_2SO_4

$i = 25\ mA/cm^2$



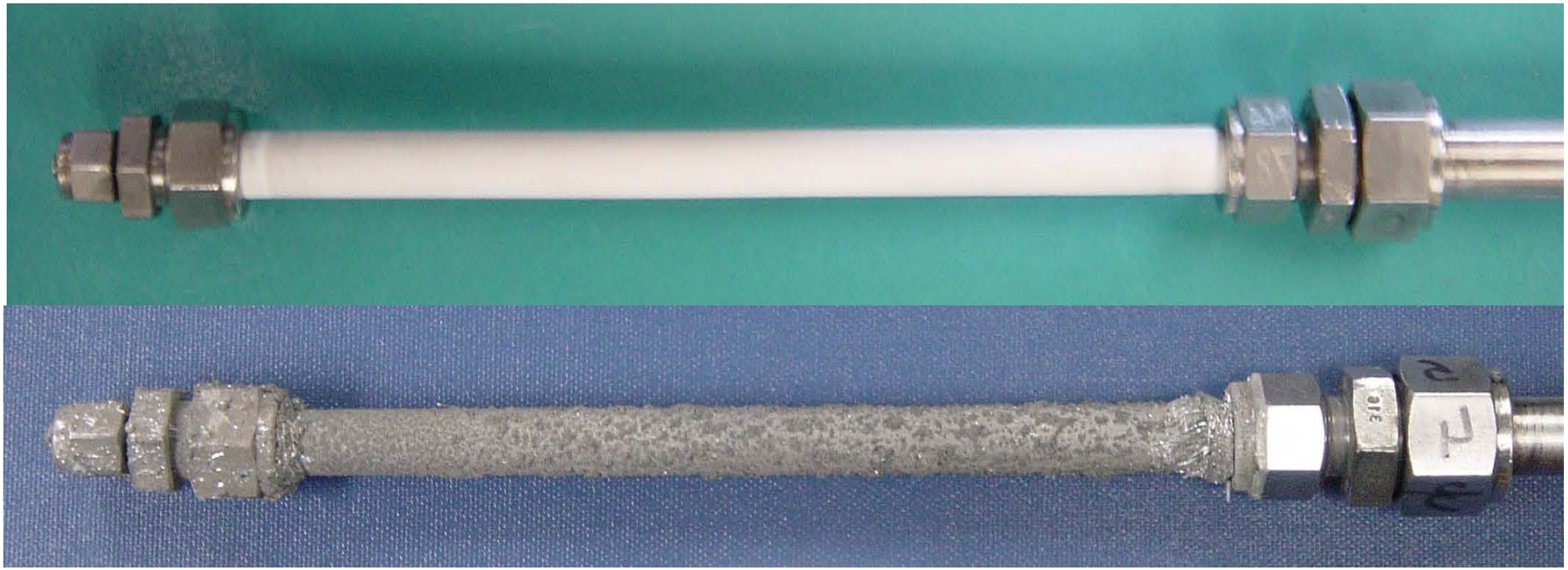
Technical Accomplishment

Goal 3: 10 μm Sn/Inconel SMMM Post 600 ºC Treatment



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

Goal 3: Porous Ceramic Support

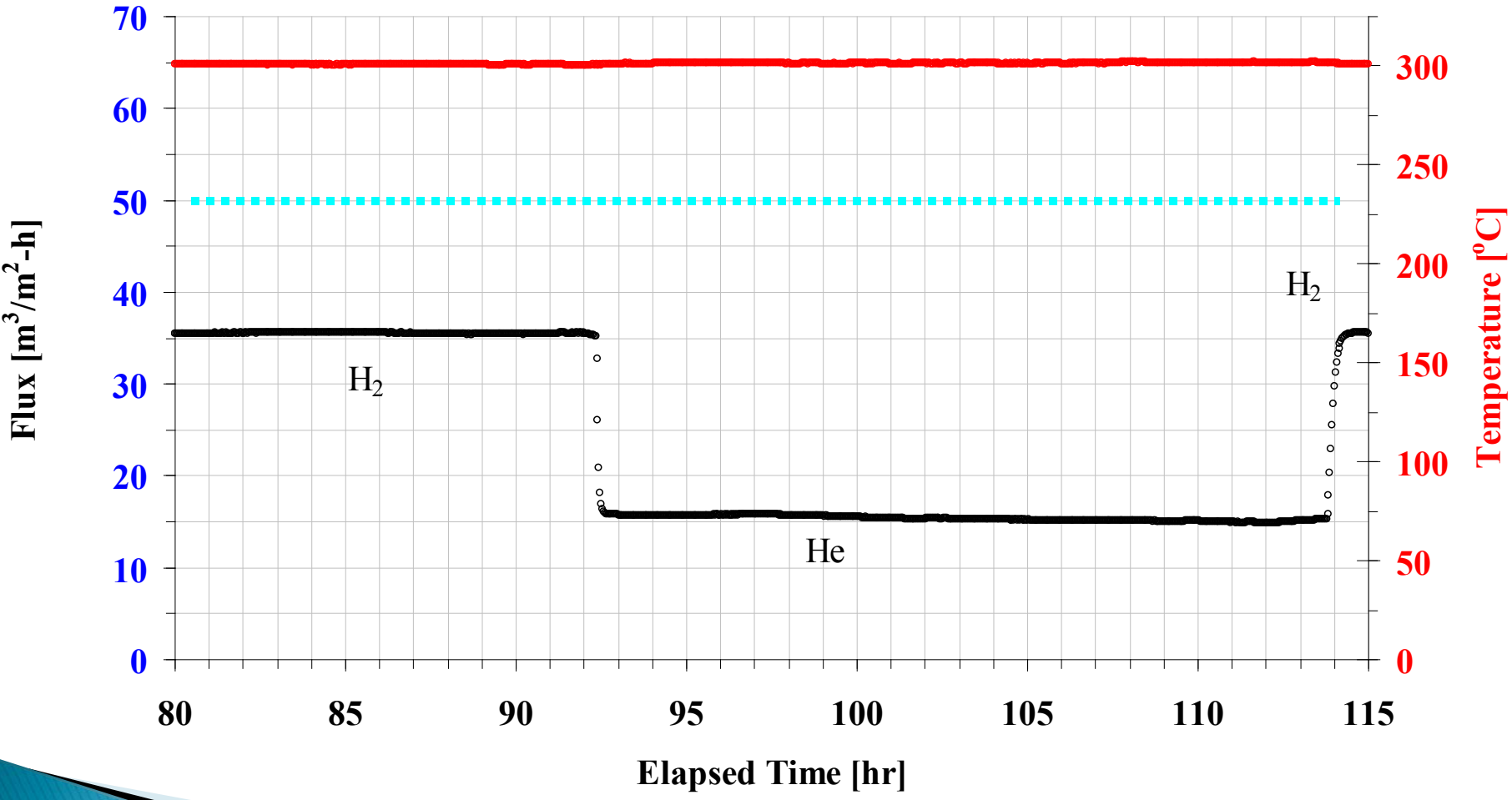


Technical Accomplishment

Goal 3: Sn-Porous Ceramic Membrane Post-Mortem

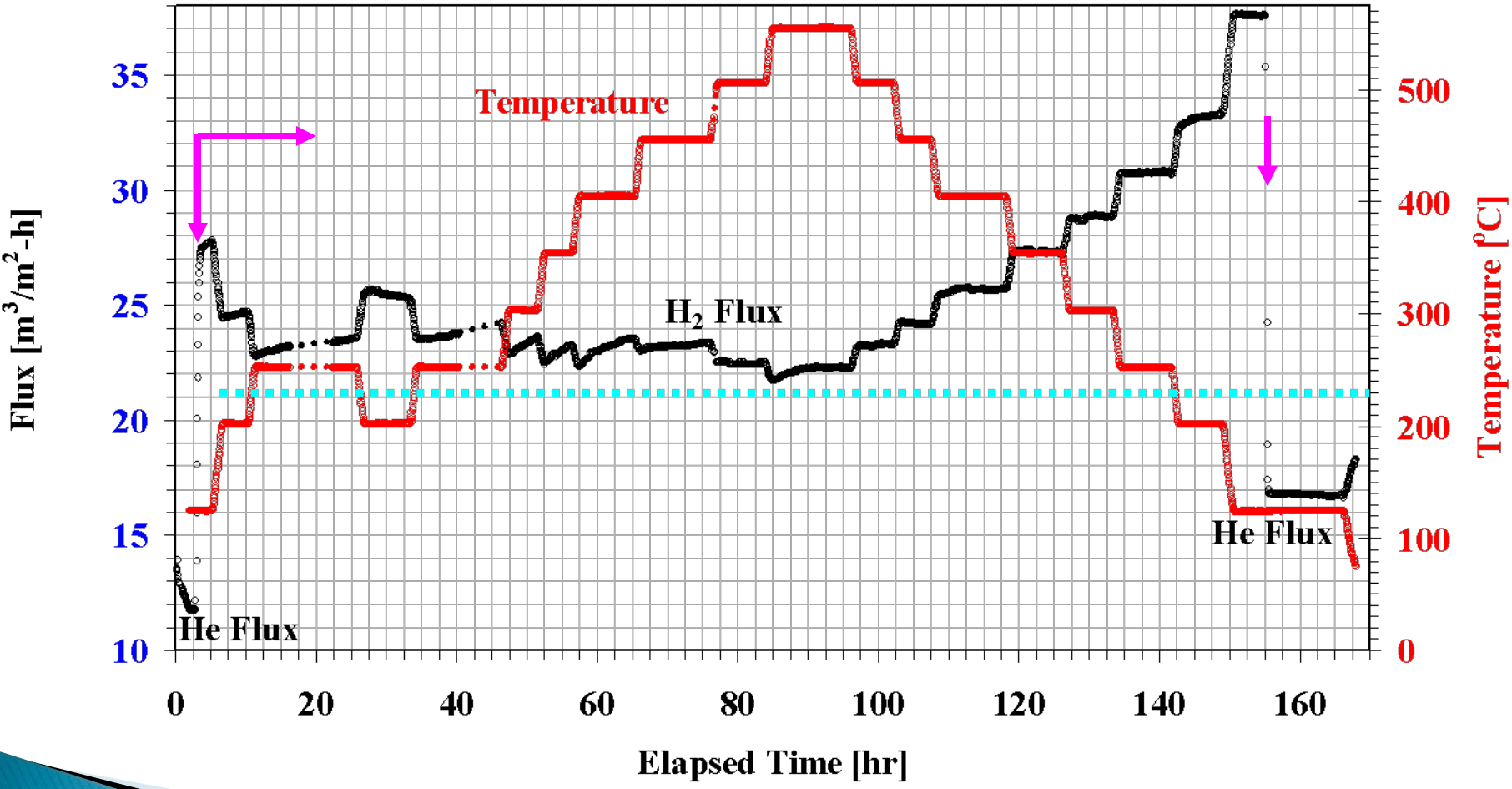
Technical Accomplishment

Goal 3: Permeability of Sn-Porous Ceramic SMMM



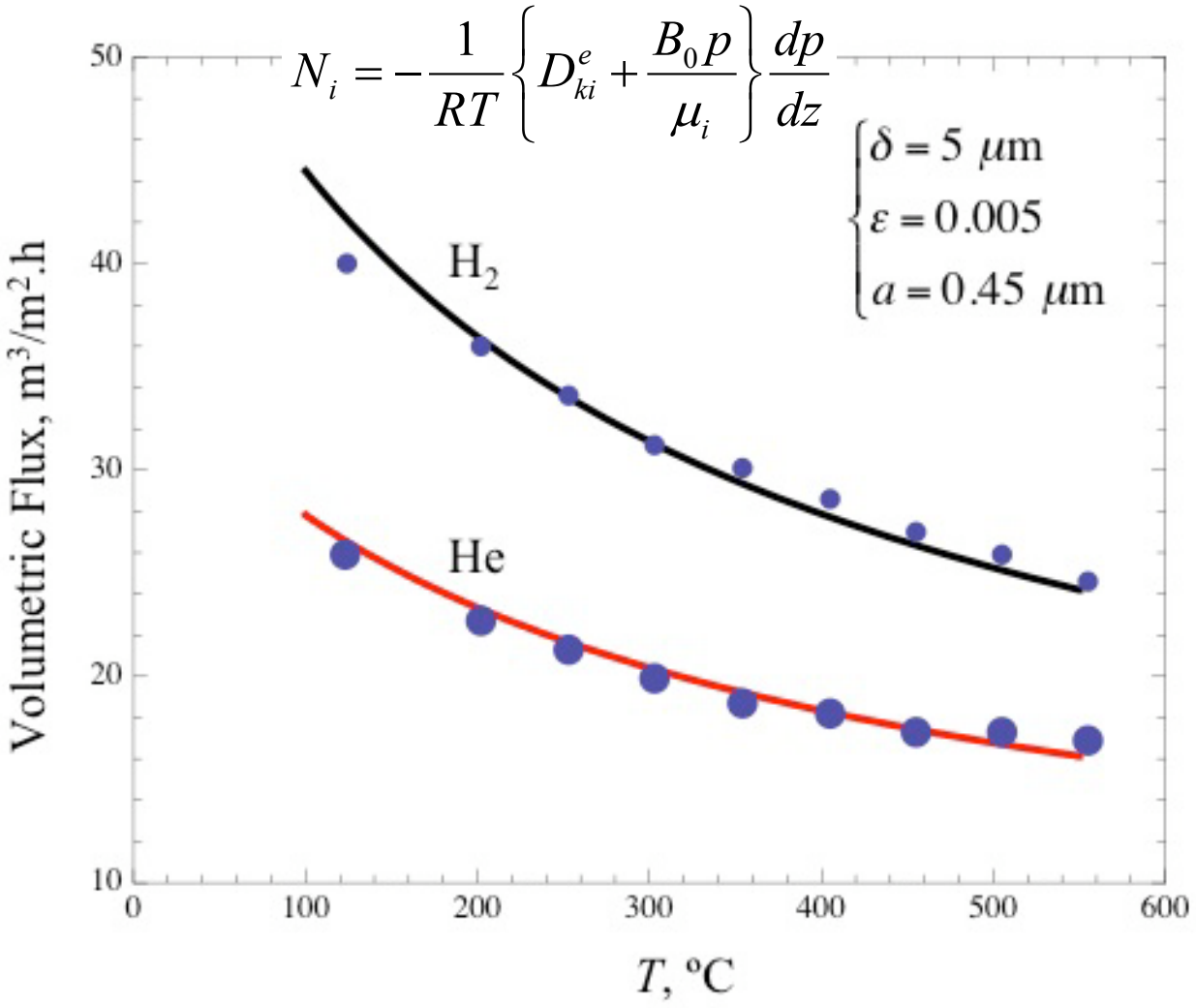
Technical Accomplishment

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