Home of Science and Engineering Solutions

Idaho National Engineering and Environmental Laboratory

Low Permeation Liner for H_2 Gas Storage Tanks

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Objective / Relevance

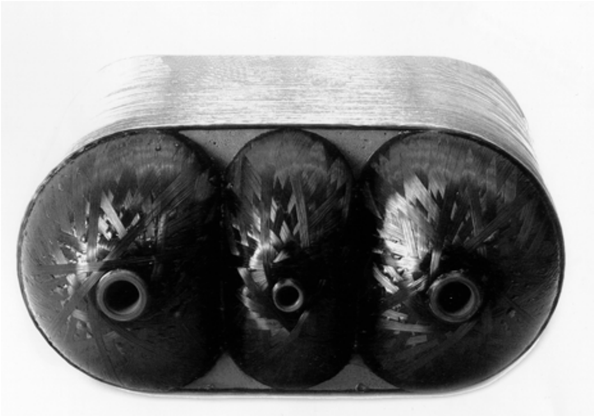
Project Objective

Greatly reduce hydrogen permeation through polymer tank liners of commercial, light-weight, composite, high-pressure hydrogen tanks.

Hydrogen Storage Relevance

Addresses On-board Storage Technical Barriers:
A. Cost B. Weight & Volume C. Durability I. Materials

Addresses Technical Targets:
1. System Cost 2. Cycle Life 3. Loss of useable hydrogen, and 4. Permeation and leakage.



"Conformable" Composite Tanks

Metric

Demonstrate measured reduction of hydrogen flux through polymer liner by a factor of 10 X as result of project.

Polymer Liners are Proposed for Composite H_2 Tanks

Examples: Nylon 6, XLPE (cross-linked polyethylene)

- ***Polymer liner advantages***
  - *Significant weight advantage over metal liner*
  - *Lower cost for “conformable” (non-cylindrical) geometries via blow or roto molding*
  - *Liner serves as a mandrel for winding composite wrap*
- ***Disadvantages***
  - *High permeability (compared to CH_4) for stored hydrogen*
  - *Loss of hydrogen & possible damage to structure*
  - *Sealing boss to polymer liner*
  - *Limited permeability data available*

Approach

Create Hydrogen Diffusion Barrier for Polymer Tank-liners

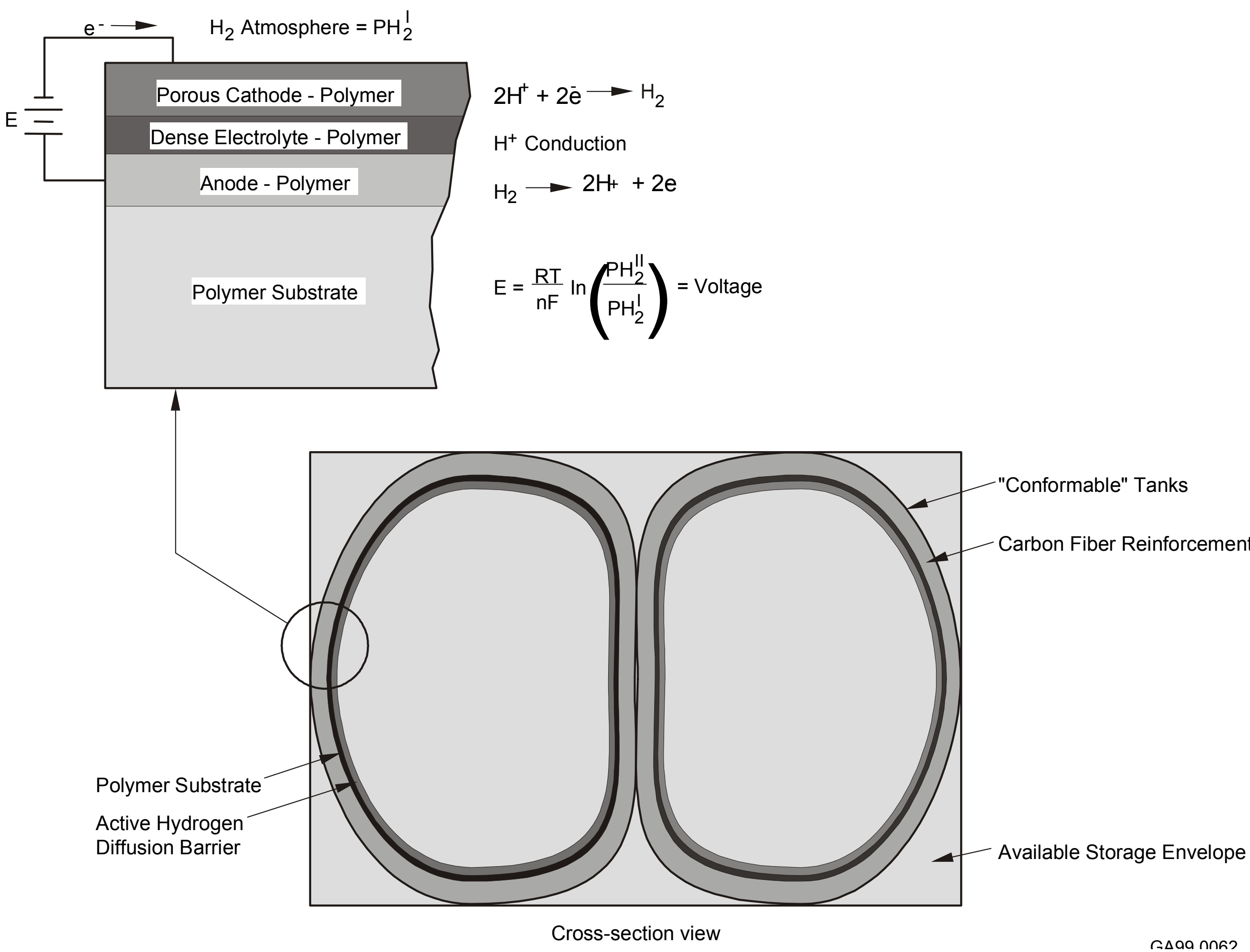
Requirements for Barrier:

- ***Low permeability of hydrogen***
- ***Adhere well to the polymer***
- ***Modulus match to polymer to prevent cracking***
- ***Apply coating inside a tank with narrow neck***
- ***No pin-holes***
- ***Low Cost and Low Weight***

“Conformable” Composite Tanks

INEEL's Active Electrochemical Diffusion Barrier Approach

Electron-conductive polymer electrodes & proton-conductive electrolyte



E = -ΔG/nF = RT/nF {ln[PH_2 (ref) /PH_2 (sub)]}

The reaction of interest is:

$$\mathbf{H_2 \rightarrow 2\,H^+ + 2\,e^-}$$

Therefore, n = 2, and for T= 300 K, and for a hydrogen pressure of 200 atm, and a postulated substrate partial pressure of hydrogen being 1x10^{-10} *atm, the applied voltage (E) would be:*

E = 0.366 volts

First Year of New Project --- On Schedule

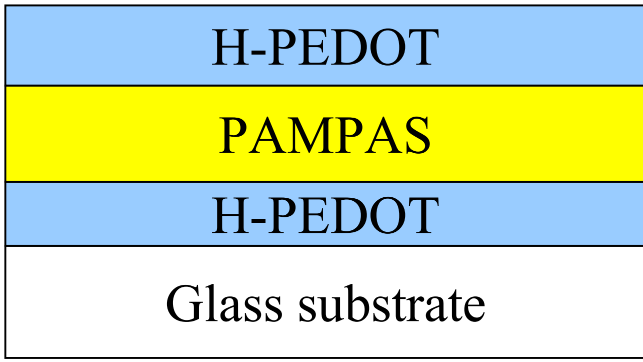
Milestones: Δ = to be accomplished, ♦ = complete

FY03 MILESTONES	O	N	D	J	F	M	A	M	J	J	A	S
Subcontract with University signed **01/03**				♦								
CRADA with Quantum signed 01/03							♦					
Task 1. Selection of Materials												
a. Electrode Candidate Polymers selected 02/03					♦							
b. Electrolyte Candidate Polymers selected 03/03						♦						
c. Catalyst Candidates selected 02/03					♦							
Task 2. Fabrication of tri-layer coatings												
a. Experiment fabrication equipment installed 04/03							♦					
b. Fabrication experiments begin 05/03								♦				
Task 3. Characterization of coating layers												
a. Determine characterization methods 06/03									Δ			
Task 4. Experiments Verification of hydrogenation protection												
a. Design of low pressure permeability device complete 02/03					♦							
b. Fabrication of low pressure permeability device complete 06/03									Δ			
c. Initial design of high pressure permeability device complete 08/03											Δ	
Report 09/03												Δ

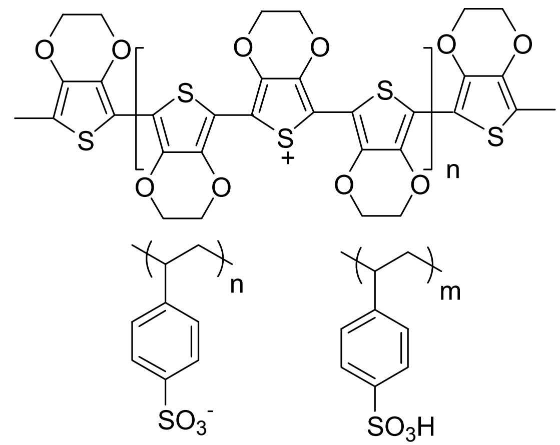
Accomplishments/Progress

- *Filed U.S. Patent Application (# 10/253,265 in Sept. 2002)*
- *Negotiated and Signed Subcontract with UCLA (Prof. Yang's Conductive Polymers Group)*
- *Negotiated and Signed CRADA (No. 03-CR-07) with Quantum Fuel Systems Technologies Worldwide, Inc. a manufacturer of composite high- pressure gas storage tanks*
- *Fabrication of tri-layer polymer coatings and fabrication of permeability measurement apparatus are well under way (see following slides)*

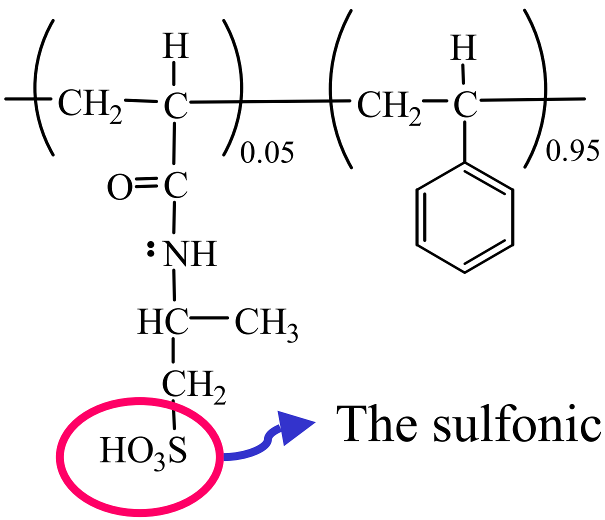
First set of candidate materials fabricated as prototype barrier



Highly-conducting PEDOT (H-PEDOT) was made by blending PEDOT with meso-Erythriol



PEDOT



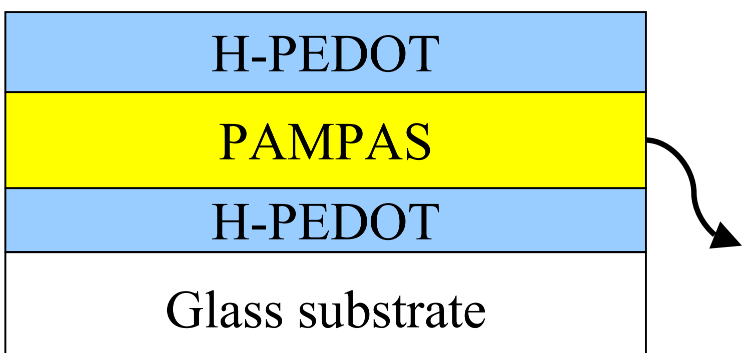
The sulfonic group here will support the proton-conductivity

Poly(2-acrylamino-2-methyl-1-propanesulfonic acid-co-styrene) (PAMPAS)

Fabrication Procedures for the Prototype Barrier

- The glass substrate was first treated by UV-ozone for 15 mins. (for surface treatment.)
- H-PEDOT was spin coated onto the substrate.
- The substrate was baked at $150^{o}C$ for 2 hours.
- After cooling, 2.5wt% PAMPAS was spin coated from toluene. (because PAMPAS is transparent, a red-dye, TPP, was added to probe survive of the film)
- The substrate was then baked at $70^{o}C$ for 30 mins.

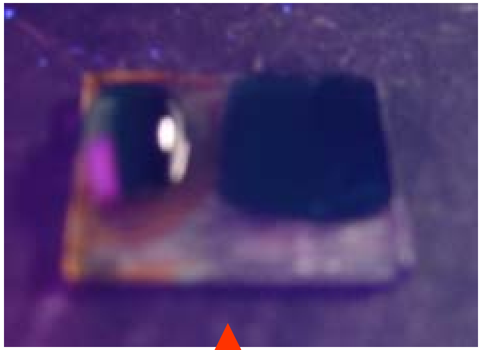
Substrates under UV light



Red-dye was add to allow the probe of PAMPAS polymer film by fluorescence.

High Contact Angle Problem

- Because PAMPAS contains 95% of styrene moieties, the film can survive after washing with water-based solvent. The washing effect due to coating of the second layer of PEDOT was minimized.
- However, the non-polar surface of PAMPAS resulted in the high contact angle while spin-coating the second layer of PEDOT. The adhesion of PEDOT and PAMPAS was very poor.
- To avoid this problem, the PAMPAS film was subjected to a UV-ozone treatment to modify the surface property before spin coating the H-PEDOT layer. A good second layer of PEDOT was then obtained.



High contact angle

Low contact angle

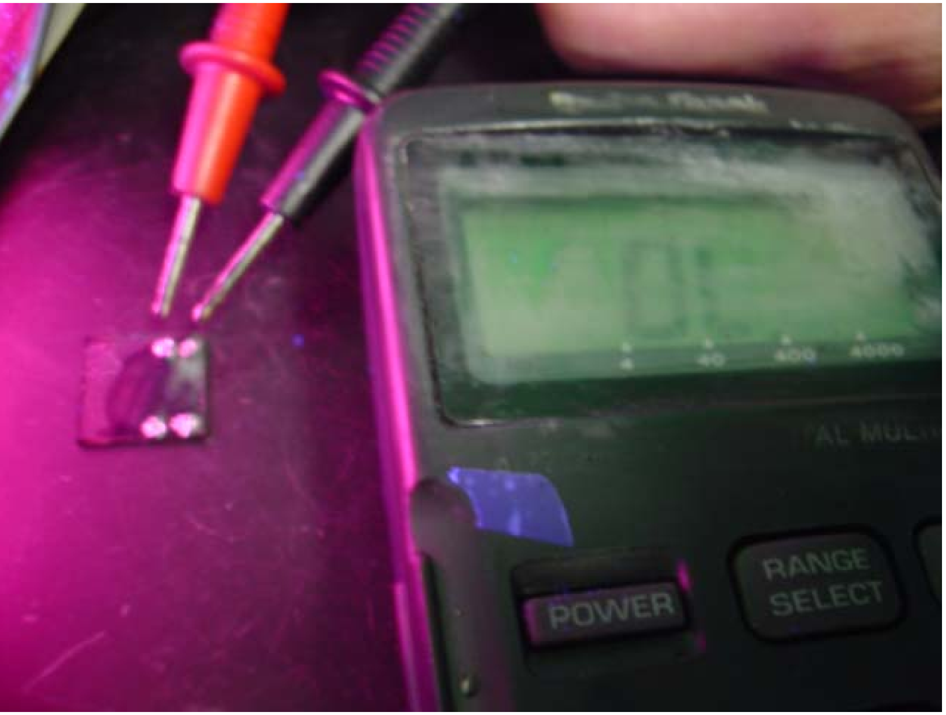
UV-Ozone Treatment Solves Contact Angle of PAMPAS Film

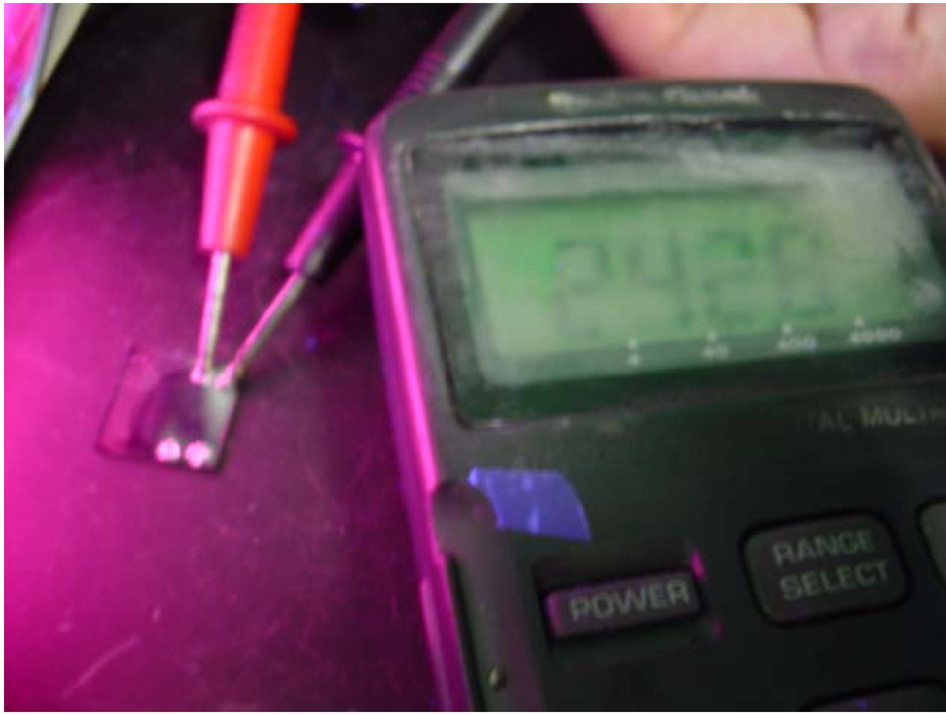
UV-Ozone Time (minutes)	Measured Contact Angle (degrees)
0.0	90.5
0.5	79.7
1.0	70.5
2.0	40.0
5.0	20.0
10.0	14.0

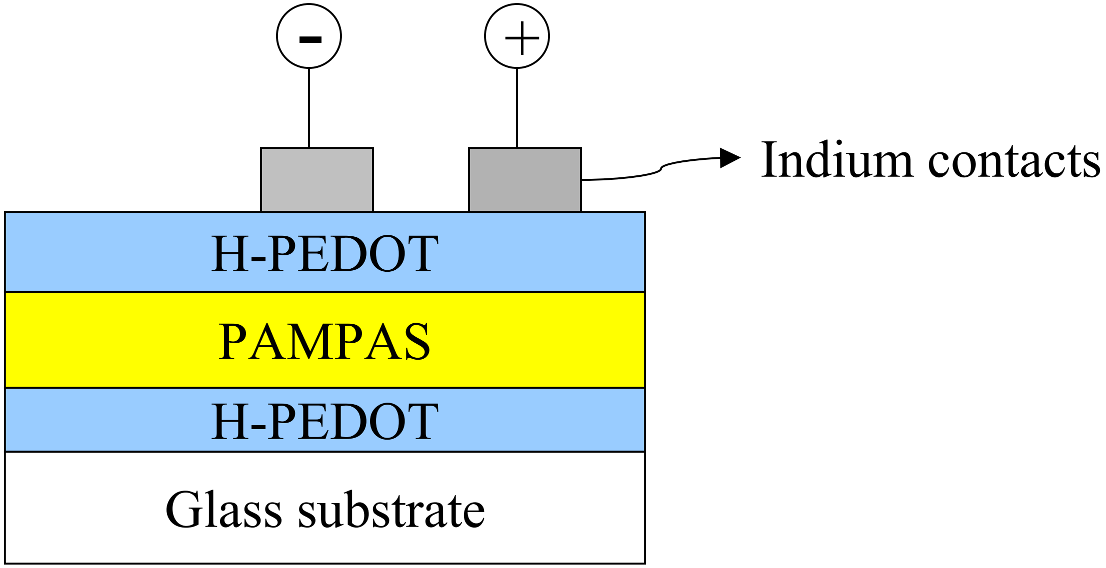
PAMPAS Solution 2.0 wt.% in Toulene   Spin Coating 1500 rpm
Baking @ 70°C for 30 minutes

Contact Angle Measurement
Cam-March Contact Angle Measurement System
Droplet size: 6.0 μL
Precision: ± 2 degrees

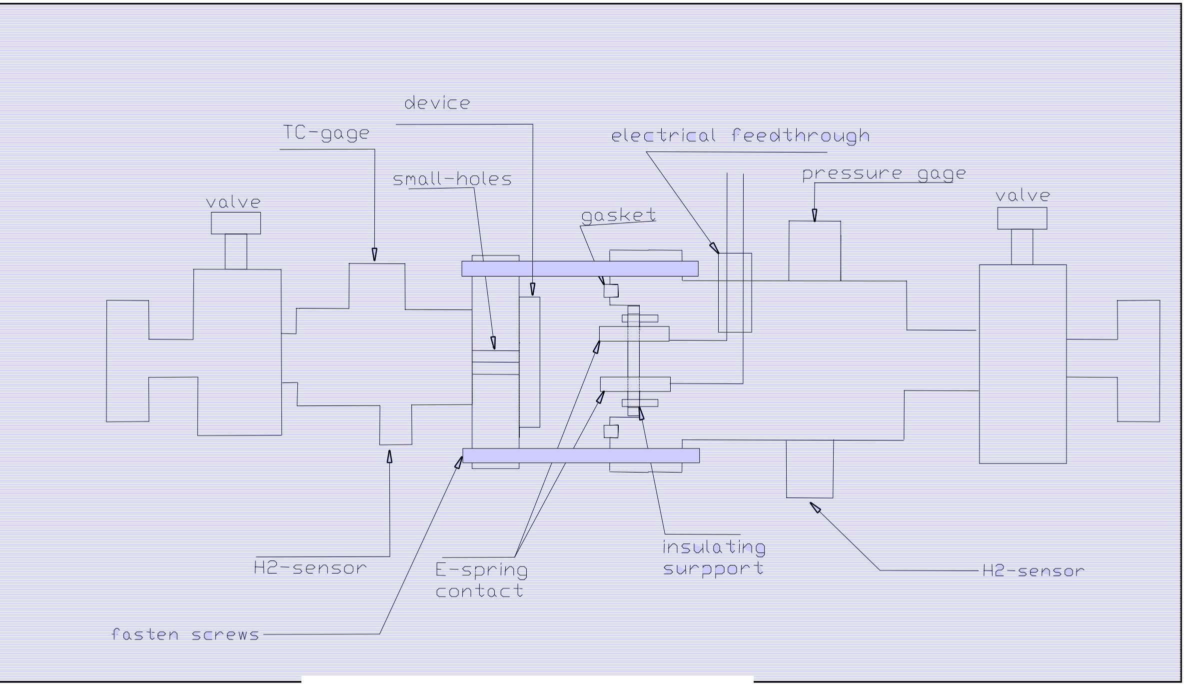
High Electronic Conductivity Demonstrated for PEDOT Electrode Layer

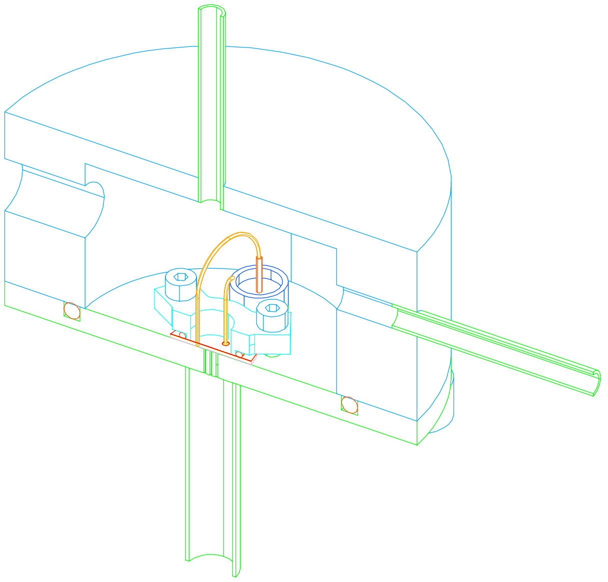




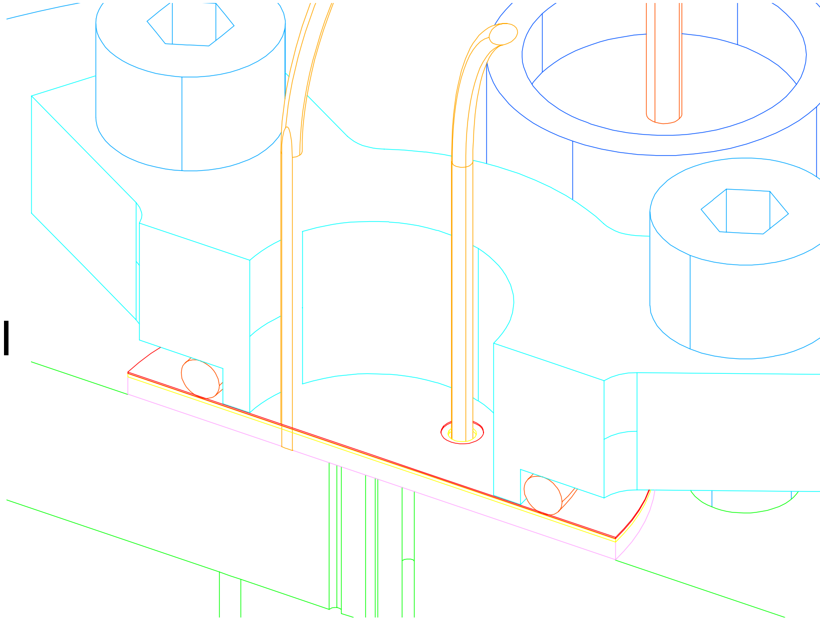


Designed a low pressure (≈100 psi) hydrogen permeability test





Schematic Drawing



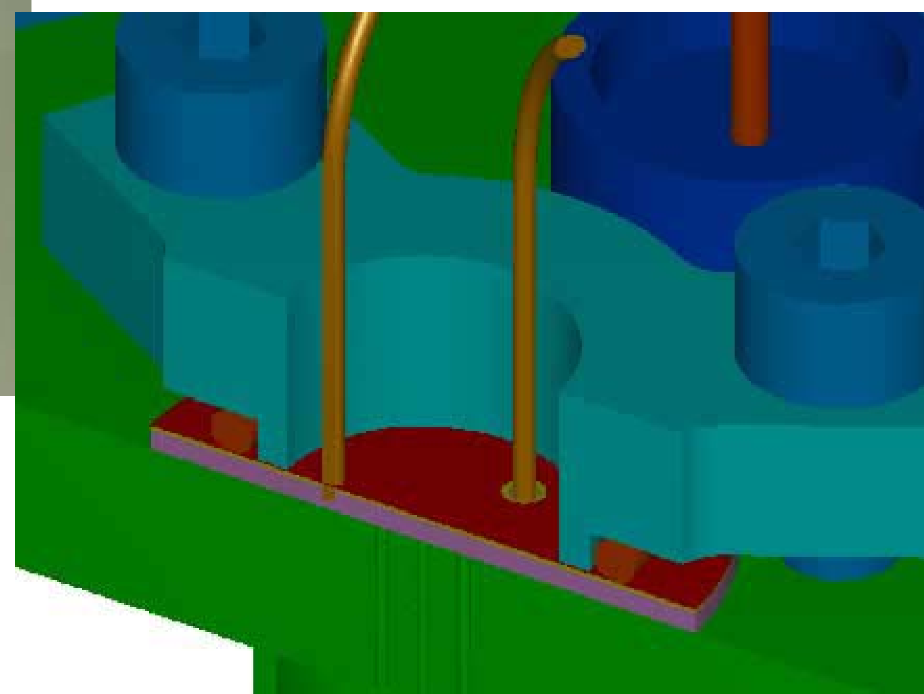
Sample Holder Detail

Fabricated the low pressure hydrogen permeability apparatus

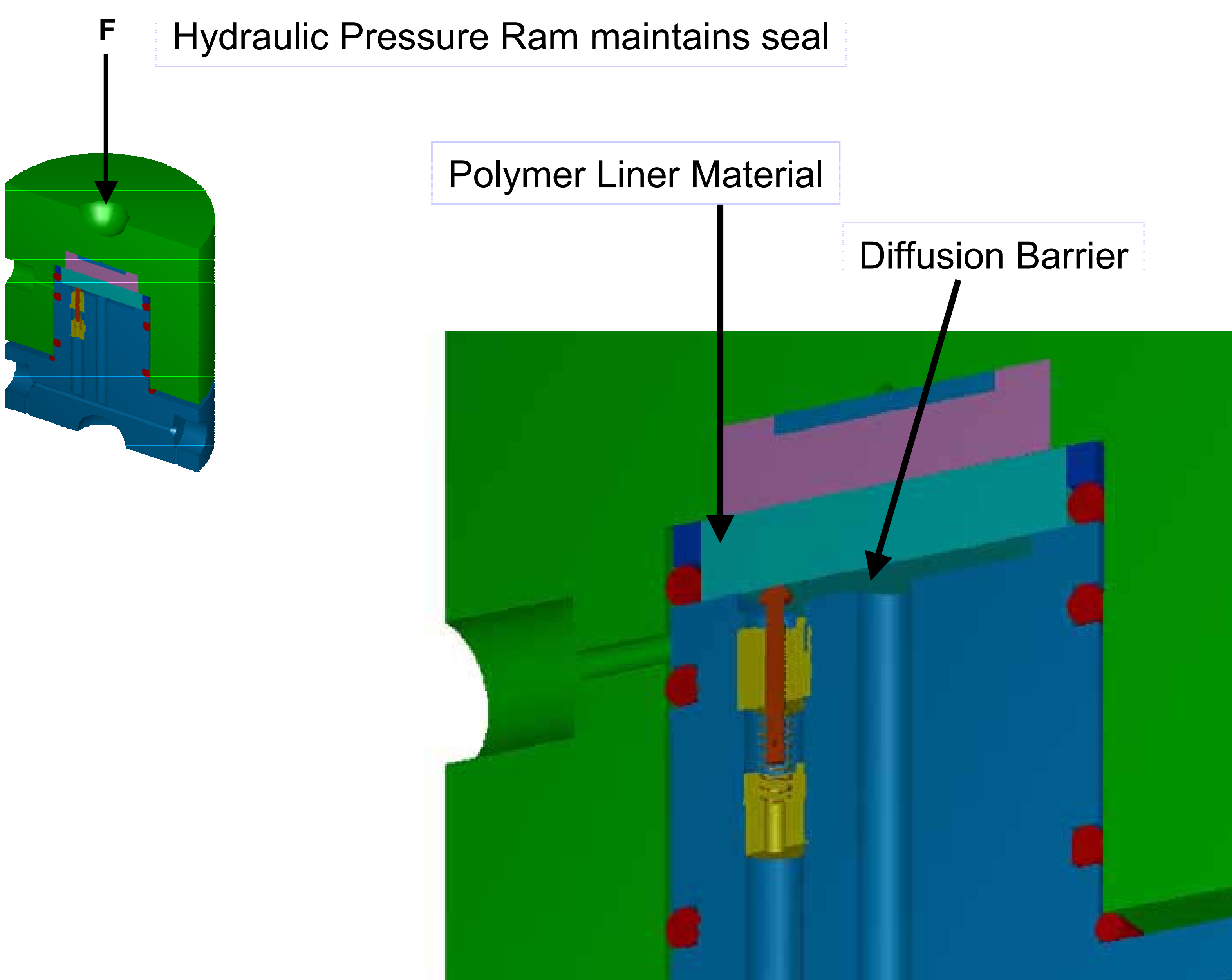
Bolts maintain chamber seal

Actual Apparatus

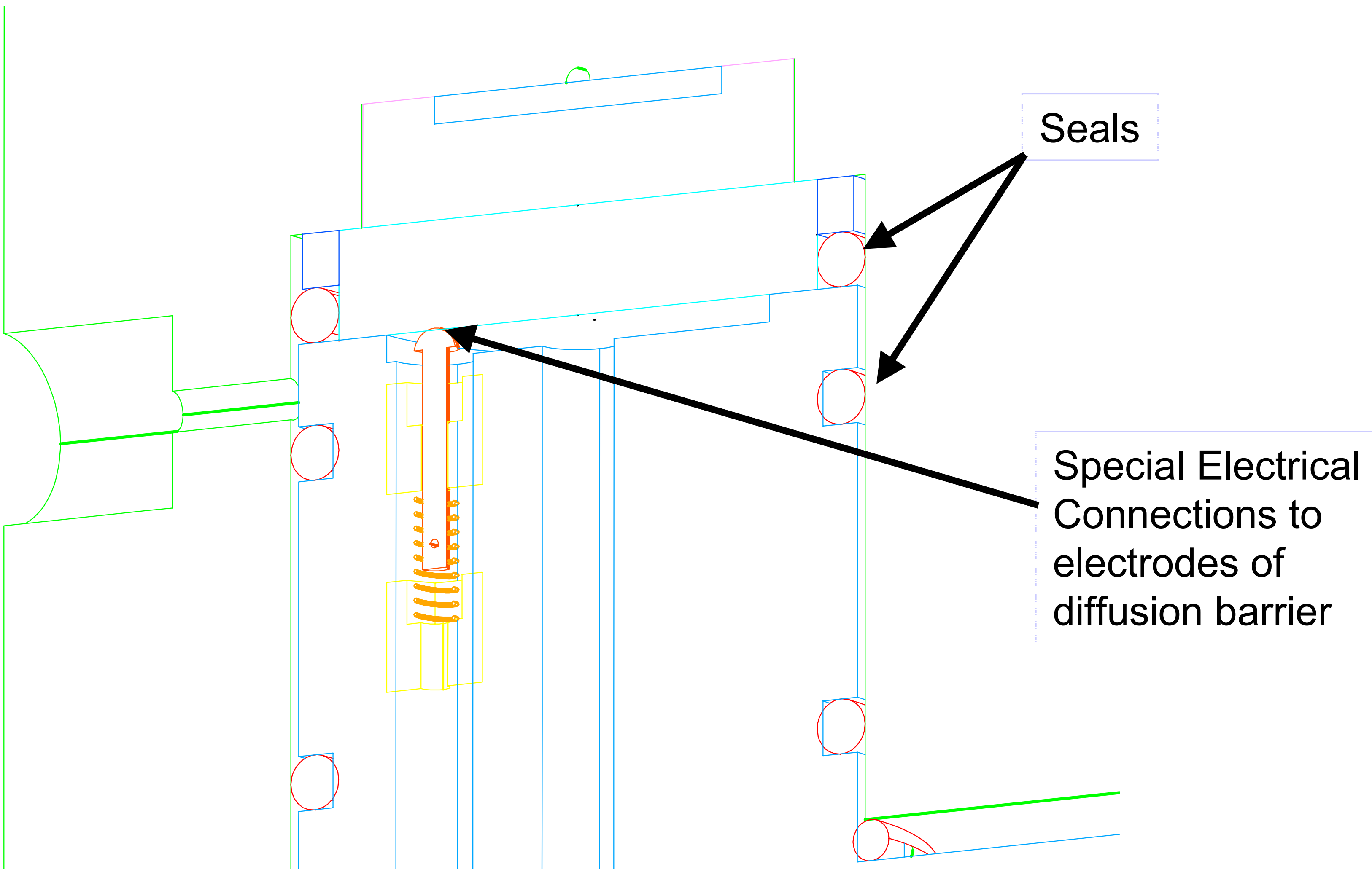
Sample Holder with
electrical connections



Initial High pressure (10,000 psi) Permeability Apparatus Design



Initial High Pressure Permeability Apparatus Design



Future work

- Measure Electrical Properties of Cell Layers. **Example: Measure the current-voltage to determine the leakage current to confirm the quality of the film. (High leakage current may suggest the existing of some pin-holes or cracks of the film.)**

- Optimize Electrolyte Layer. **PAMPSA contains very few sulfonic groups, which may limit the proton conductivity. Instead of copolymer, a polymer blend system with different weight ratio of sulfonic groups and inert (insoluble in water) polymer moieties will be tested to yield both high proton conductivity and high-resistance of the washing effect from the second layer PEDOT.**

- Permeability Testing. **Complete evaluation of hydrogen sensors. Test permeability of baseline polymer materials versus same materials with tri-layer barrier coating. Evaluate effect of catalysts. Finish design and fabricate high-pressure permeability apparatus. Perform permeability tests on tanks with barrier.**