Advanced Barrier Coatings for Harsh Environments

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Project ID: PD150

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Overview

Timeline:

- Project Start Date: 4/1/2015
- Project End Date: 3/31/2017

Budget:

- Phase I: $149,877
- Phase II: $998,616
- Phase IIA: $999,781

- Spent (IIA): $272,682

Barriers:

- B. Reliability and cost of gaseous hydrogen compression

Partners:

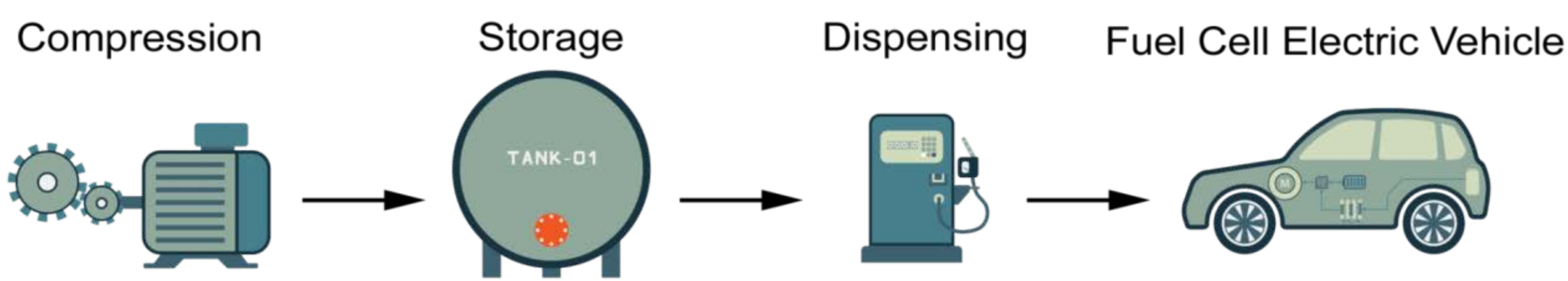
- Greene, Tweed & Co.
- Oak Ridge National Laboratory
- National Renewable Energy Laboratory
- Hydro-Pac Inc.
- PowerTech

Outline

- **Review**: Impact of seal failures on Hydrogen Compression, Storage and Dispensing (CSD)
- **Technology Concept**: Flexible barrier coatings to prevent hydrogen ingress
- **GVD Background & Technology Overview**
- **Program Goals**
- **Progress to Date**

Relevance: Impact of Seal Failures

- Plastic and elastomeric seals are integral to all areas of hydrogen compression, storage, and dispensing (CSD)
- Hydrogen ingress degrades seals
  - Temperature and pressure cycling exacerbate issues
- Wear due to friction in high pressure, high temperature operation degrades seals
  - Frequent seal replacement is required
- Seal failure is a major contributor to process down time
  - Largest cause of unscheduled maintenance
  - >25% of hydrogen leaks
  - Without improvement, redundant compression necessary



Relevance: Program Goals

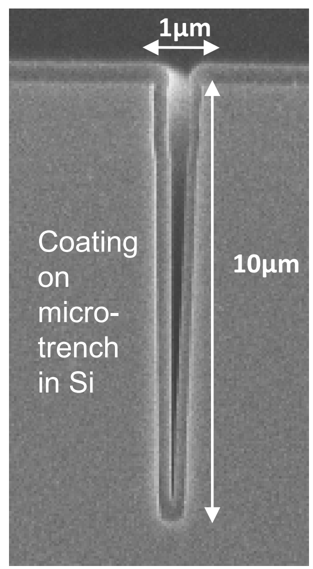
- Make tangible improvements in seal life
  - **Lubricious coatings** for **dynamic seals** reduce seal wear due to friction
  - **Barrier coatings** for **elastomeric seals** mitigate hydrogen vapor permeation
- Improved seal performance benefits operations and cost
  - **3-5x reduction** in frequency of seal maintenance
  - Help decrease hydrogen CSD cost from *$3.50/gge* to **$2.00/gge**

Approach: Polymer Vapor Deposition

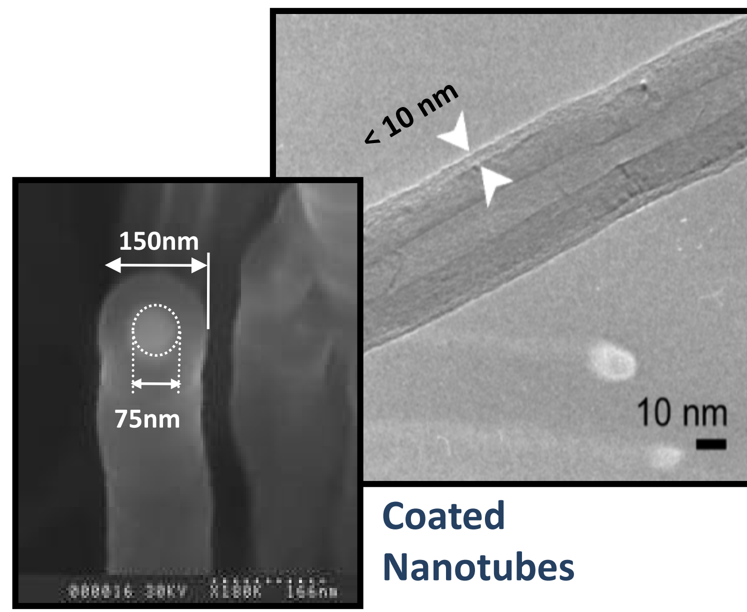
A **room-temperature coating** process which produces **thin polymer coatings** on almost any material.

- "Gentle" application
  - low temperature
  - dry process
  - single-step
- nano- to micro- meter thicknesses
- conformal on nano- and micro- structures

Water drop (dyed blue) beads up on tissue paper with hydrophobic coating

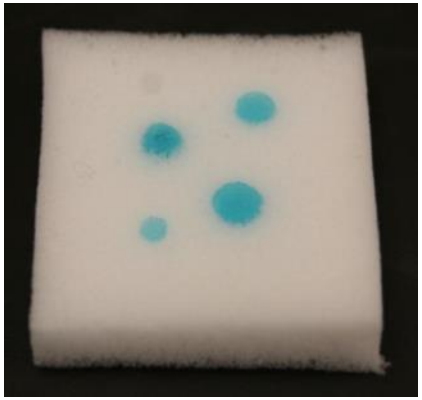


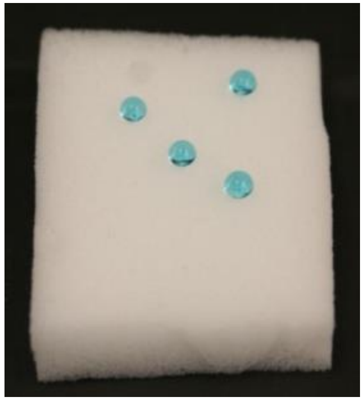
Coating on micro-trench in Si

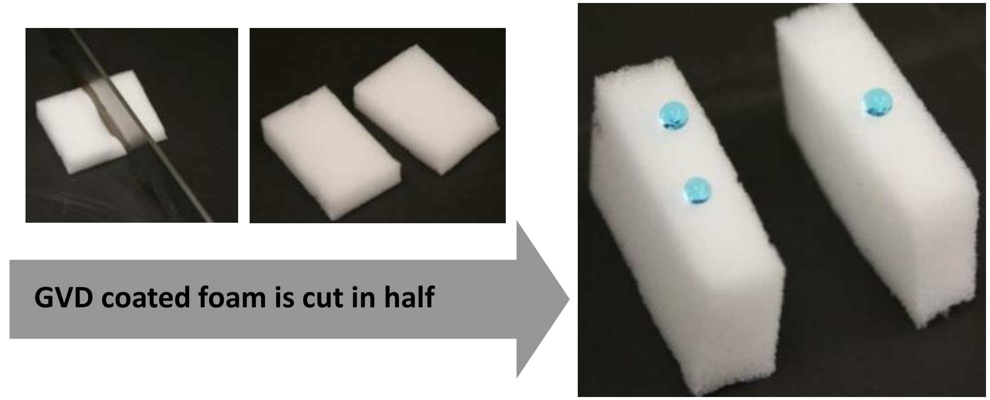


Coated Nanotubes

Approach: Conformal, Uniform Coverage





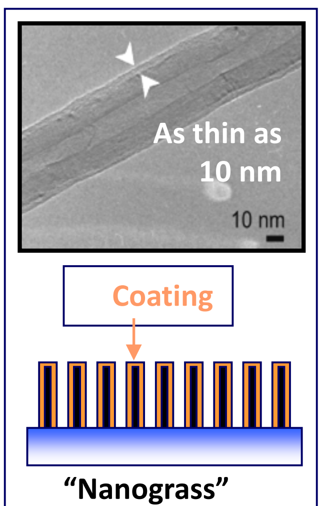


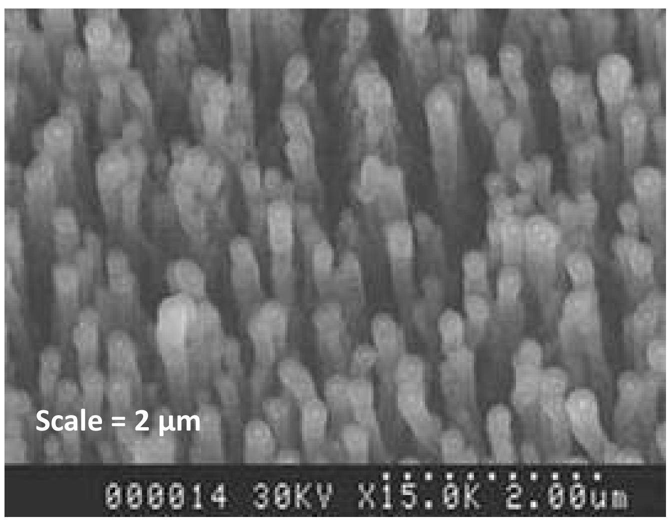
1. Water droplets soak into <u>uncoated foam</u>

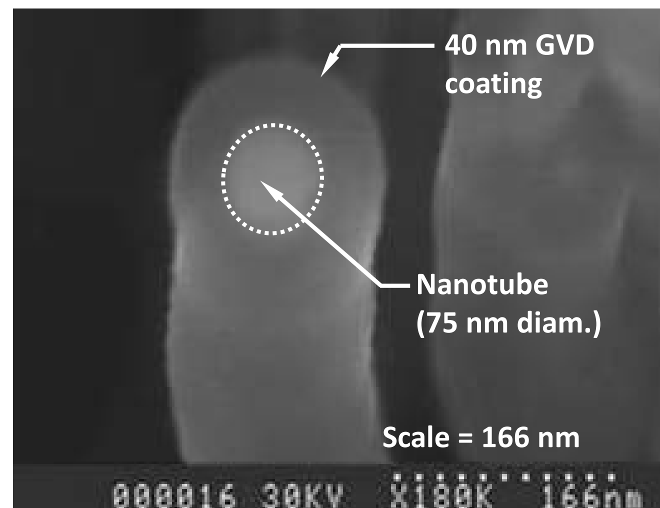
2. Water droplets bead-up on <u>GVD Coated Foam</u>

3. Water droplets bead up on the cross-sectioned foam, demonstrating the hydrophobic coating has penetrated deep into the foam.

GVD coatings are conformal down to the nano-scale

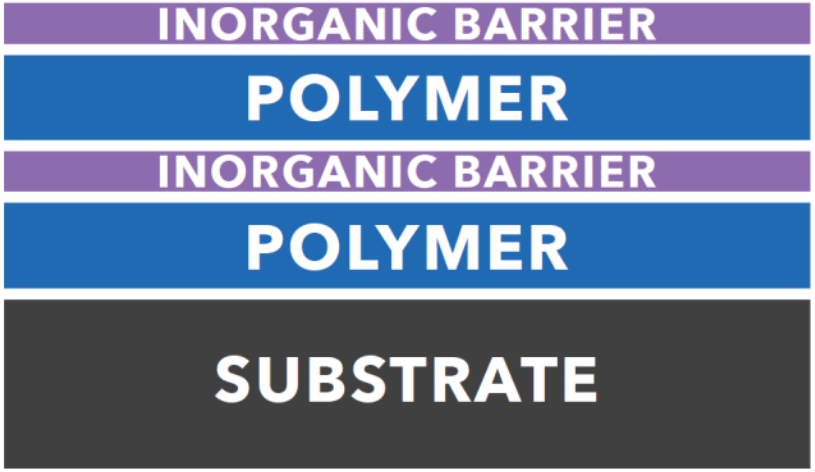






Approach: Barrier and low friction coatings

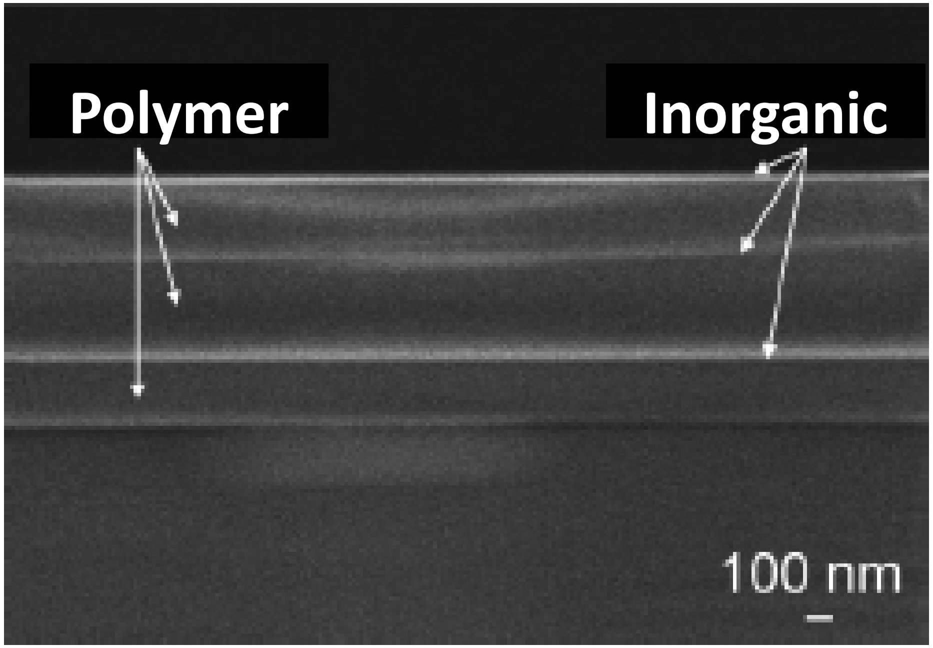
- Vapor Deposition of flexible barrier coatings to prevent hydrogen ingress into elastomeric seals
  - Thin inorganic layers provide **vapor barrier**
  - Polymer layers provide **flexibility**
- Vapor Deposition of lubricious coating to reduce wear on rigid plastic hydrogen seals
  - Thin PTFE film provides low coefficient of friction surface for reduced wear
- Vapor deposition advantages:
  - Conformal coating of **3D seal geometries**
  - Barrier layers deposit in the **same chamber** using the **same feed gas**
  - **Scalable and manufacturable** compared to competitive solutions



Barrier Coating Stack

Approach: Barrier Coating

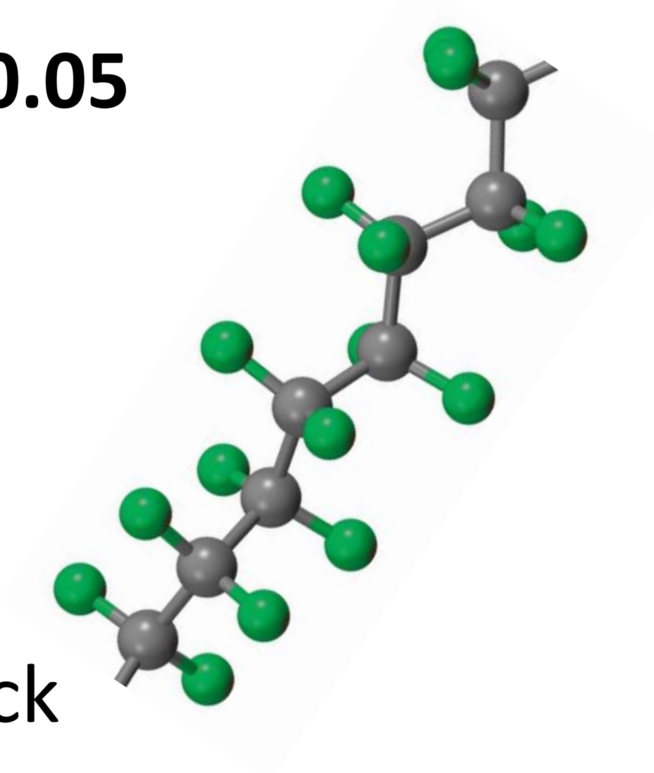
- Initial demonstration of flexible barrier coatings by GVD founder Prof. Karen Gleason at MIT
- Barrier coating flexibility
  - **Maintains gas exclusion properties after hundreds of 180° bend cycles**

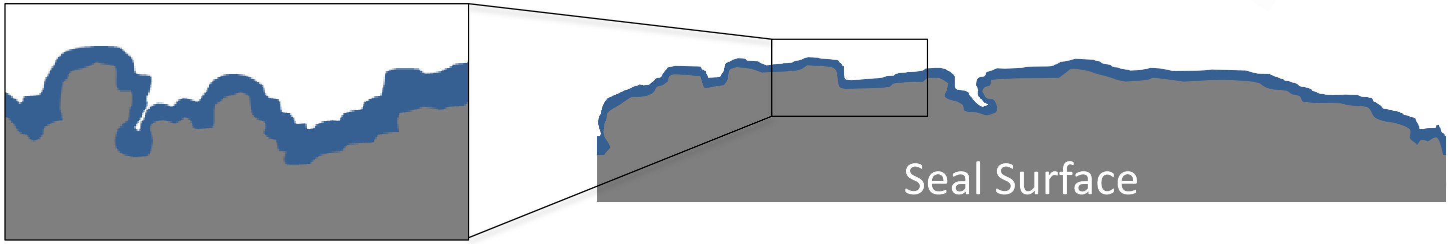


- Barrier properties of coating driven by number of bilayers (dyads)
  - Order of magnitude reduction in water vapor transmission per dyad
  - Permeability reduction of **~1,000 fold with three dyads**

Approach: Low friction coating

- Vapor deposited polytetrafluoroethylene (PTFE)
- **Low coefficient of friction, 0.03-0.05**
- High chemical resistance
- Deposited at room temperature
- Dry process, solvent-free
- Highly conformal
- 50 nanometers to 10 microns thick





Approach: Prior Work Summary

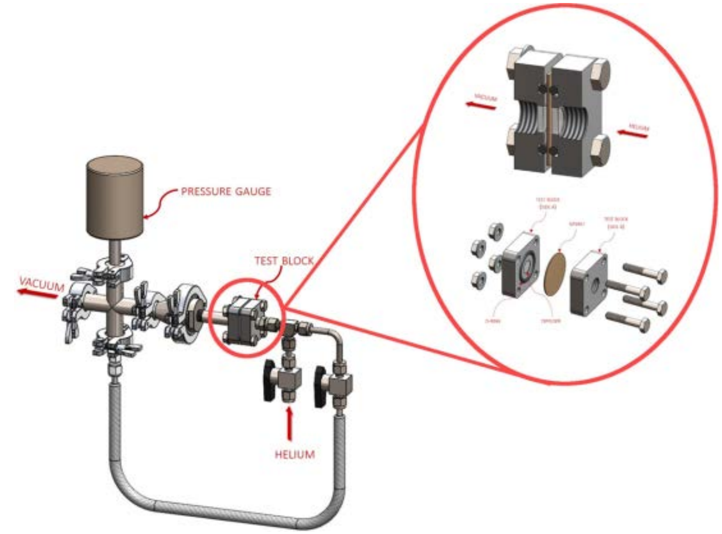
- Single monomer demonstrated as precursor for both organic and inorganic barrier coating layers
  - Required for coating cost ~10% seal cost
- Barrier coating thickness optimized at 2um with a **35% reduction in relative permeability** during preliminary helium testing
  - Helium 7X higher permeation than Hydrogen
- Pilot-scale PECVD system built for alternating deposition of polymer and inorganic layers

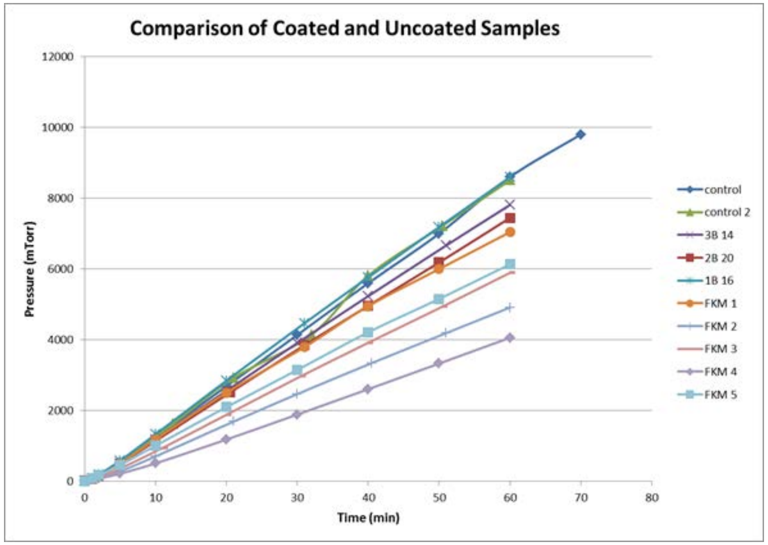
Approach: Phase IIA Objectives

- Optimize organic/inorganic barrier coatings using scaled PECVD processes
- Demonstrate a 10-fold reduction in relative hydrogen permeability of GVD barrier coatings
- Field validate a low-friction top coat of polytetrafluoroethylene (PTFE) for friction wear reduction of plastic piston-head seals
- Demonstrate improved seal life (goal of 3-5X increase) in field testing by a hydrogen compressor end user (PowerTech/NREL)

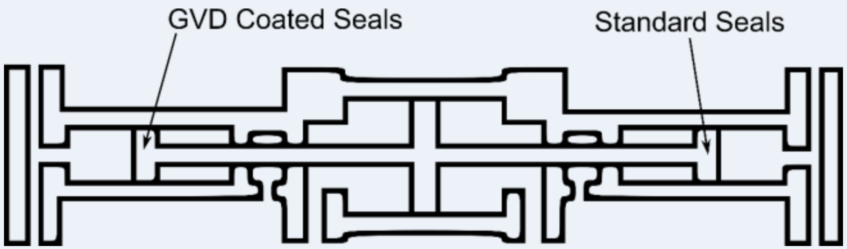
Accomplishments: Reduction is Gas Permeability

- Note: Project not evaluated at 2017 annual merit review due to timing of funding award
- In-house permeability tester developed for fast-turn evaluation of barrier coating stacks
- Optimization of organic vs inorganic coating thickness demonstrates additional 60% reduction in helium permeation
  - Total reduction now 57% vs 35%
  - Coating thickness (and approximate cost) unchanged
- Translation to hydrogen still requires demonstration



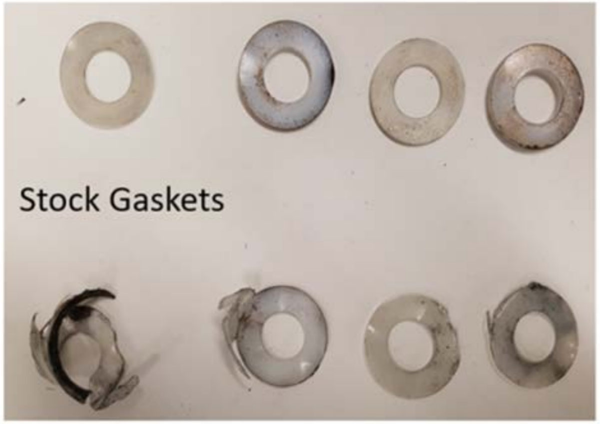


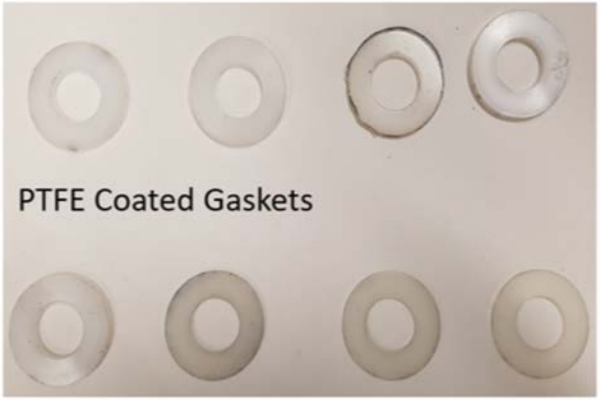
Accomplishments: Reduction in Compressor Seal Wear



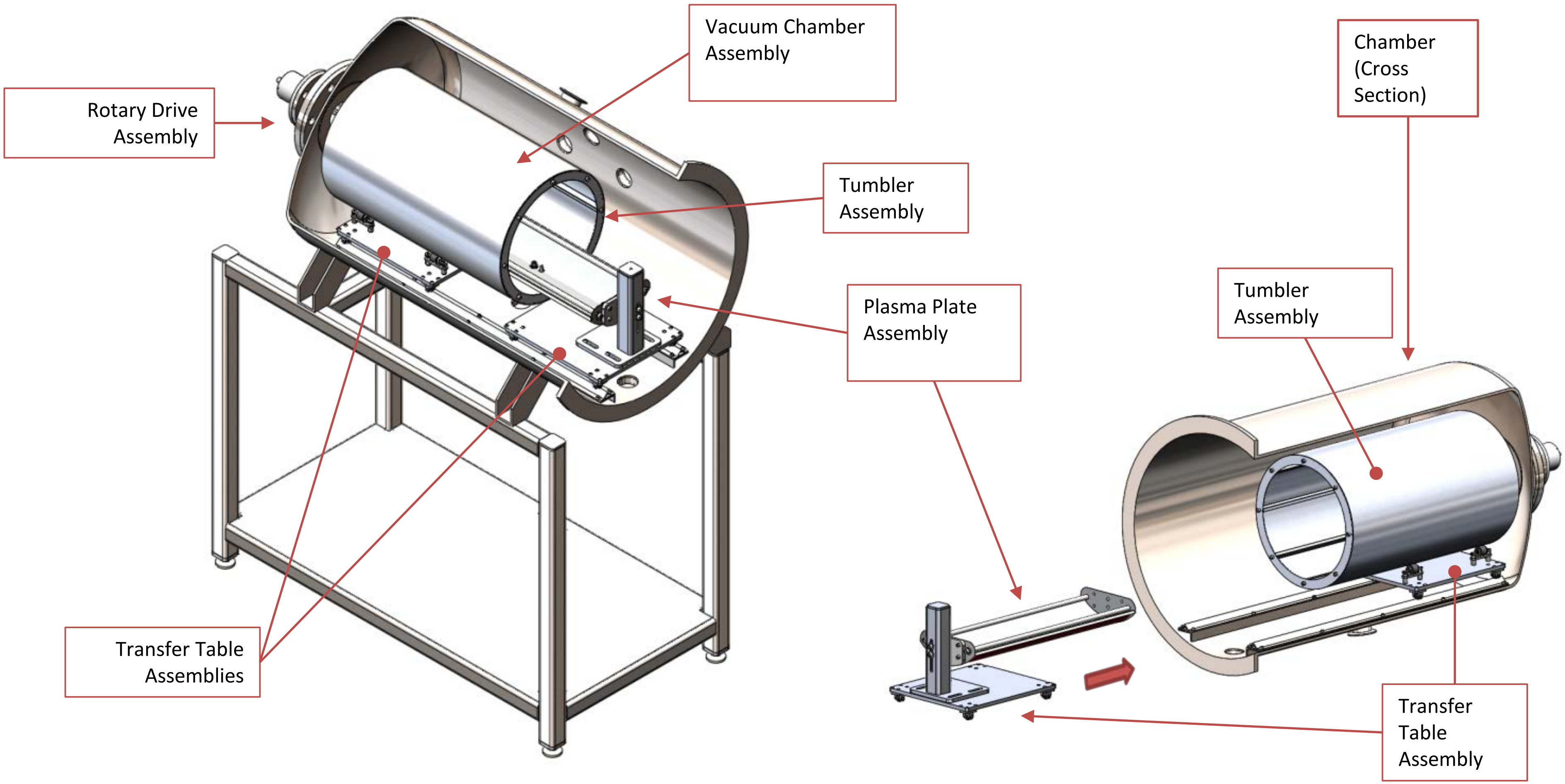
Schematic of gasket seal locations in Hydro-Pac compressors. Tested by Powertech

- Side-by-side testing of coated versus uncoated hydrogen piston gaskets
  - >70% reduction in mass loss observed
- No failure of coated gaskets during testing
  - Samples pulled at uncoated failure per protocol
  - Future testing will allow independent lifetime assessment





Accomplishments: Commercial Scale Coater Design



- Production tool fully designed for high-volume coating
- Fabrication waiting on final process parameters to ensure optimal sizing of peripherals

Collaborators

Greene, Tweed & Co.	Manufacturers of advanced seals and gaskets	Providing seal samples for experimentation & performing helium permeability tests
Oak Ridge National Lab	Leaders in evaluation of hydrogen permeability in polymers	Evaluating GVD barrier coating performance in hydrogen permeability tests
National Renewable Energy Lab	Leaders in evaluation of hydrogen CSD technologies	Evaluation of GVD coated seal lifetimes in simulated hydrogen fuel station environment
HydroPac Inc.	Manufacturers of advanced hydrogen compression equipment	Dynamic piston bore seal design details and testing.
PowerTech	Turnkey designers and manufacturers of hydrogen fueling stations	Testing the life of coated dynamic piston bore seals

Remaining Barriers and Challenges

- For technology validation:
  - Troubleshoot barrier coating deposition process
    - Particulate inclusion issues
  - Complete field and representative testing of barrier and low friction coatings
  - Optimize process parameters for a high-throughput plasma coating system based on test data
- For meeting industry technical targets and commercialization:
  - Demonstrate 10 fold reduction in hydrogen permeability
  - Demonstrate 3-5x extension of seal life in representative testing or field operation

Future Work: Testing Underway

- Hydrogen Permeability
  - Oak Ridge National Labs
  - Performed on ONRL's High Pressure Temperature Cycling (HPTC) apparatus
    - 700-875 bar on the upstream side
    - -50°C to 200°C temperature range
- Wear Reduction
  - National Renewable Energy Lab
  - Low friction PTFE coated seal tested in a double-ended single stage hydrogen compressor
    - Hydrogen compression pressure 12,500psi
      - 5k psi inlet
    - Evaluations of coated and uncoated seal lifetime to failure (10% loss in efficiency) as well as degradation profile

Any proposed future work is subject to change based on funding levels

Technology Transfer Activities

- Commercial Interest and Inquiries:
  - Hydrogen Compression & Storage
  - Hydrogen Refueling Stations
  - Downhole Oilfield
- Potential Commercial Partnerships
  - Seal manufacturers
  - Hydrogen compressor manufacturers
- Intellectual Property
  - IP established based on MIT proof of concept
  - Additional GVD patents to be submitted as required

Summary

Objective: Reduce costs to Hydrogen Fuel Cell Electric Vehicles and hydrogen processing systems associated with Hydrogen Compressor seal failure. Improve seal life 3-5X.

Relevance: Seal failure is a major contributor (>25%) to hydrogen compressor maintenance, adding significant downtime and cost to operation.

Approach: Improve seal life through two types of coatings. Barrier coatings that mitigates hydrogen ingress into the static seals, preventing premature failure. Low friction coatings that reduce wear of dynamic seals, extending seal life significantly.

Accomplishments: GVD's barrier coating has demonstrated significant reduction in helium permeation through elastomeric seal material and significant reduction in mass loss for dynamic seals. Optimized coating process for high-throughput manufacturing and constructed a prototype system.

Future Work: Demonstrate barrier performance in relevant testing environments (HPHT Hydrogen). Demonstrate reduce wear for low friction coatings in a full operational environment.

Thank you
Questions?

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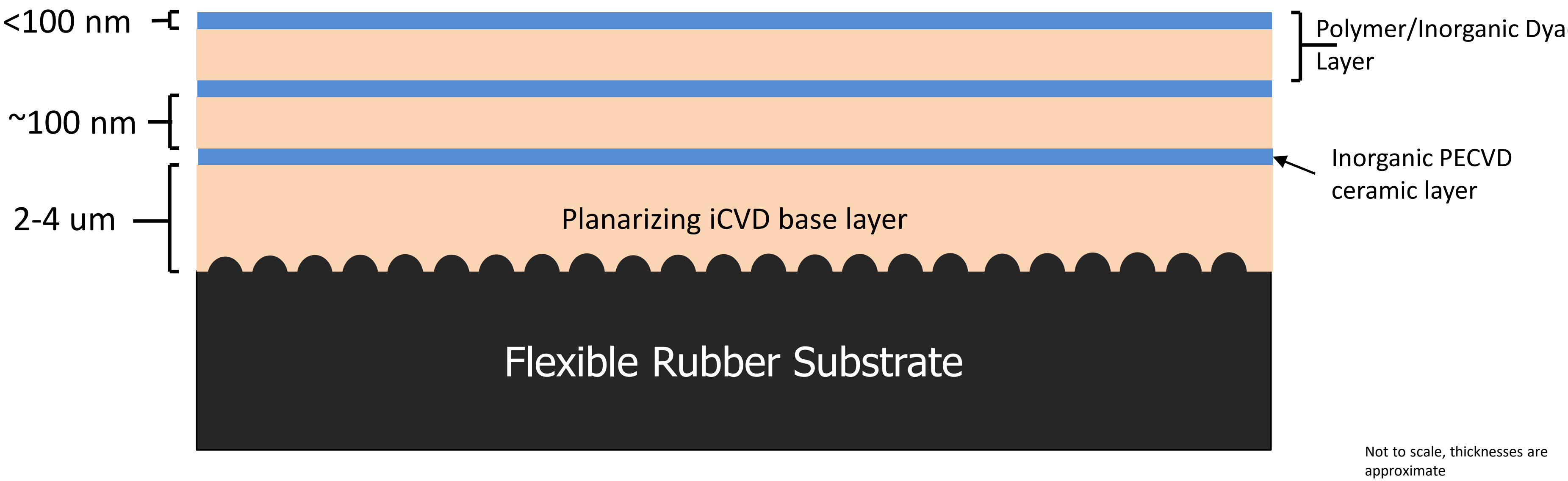
Technical Back-Up

Barrier Coating Construction



- Multiple dyads force the H_2 molecules to forge a tortuous path through nanodefects in the coating surface
- Number of dyads and coating thicknesses were optimized for maximum flexibility, planarization and minimum Hydrogen ingress

Technical Backup: Helium Permeability Testing

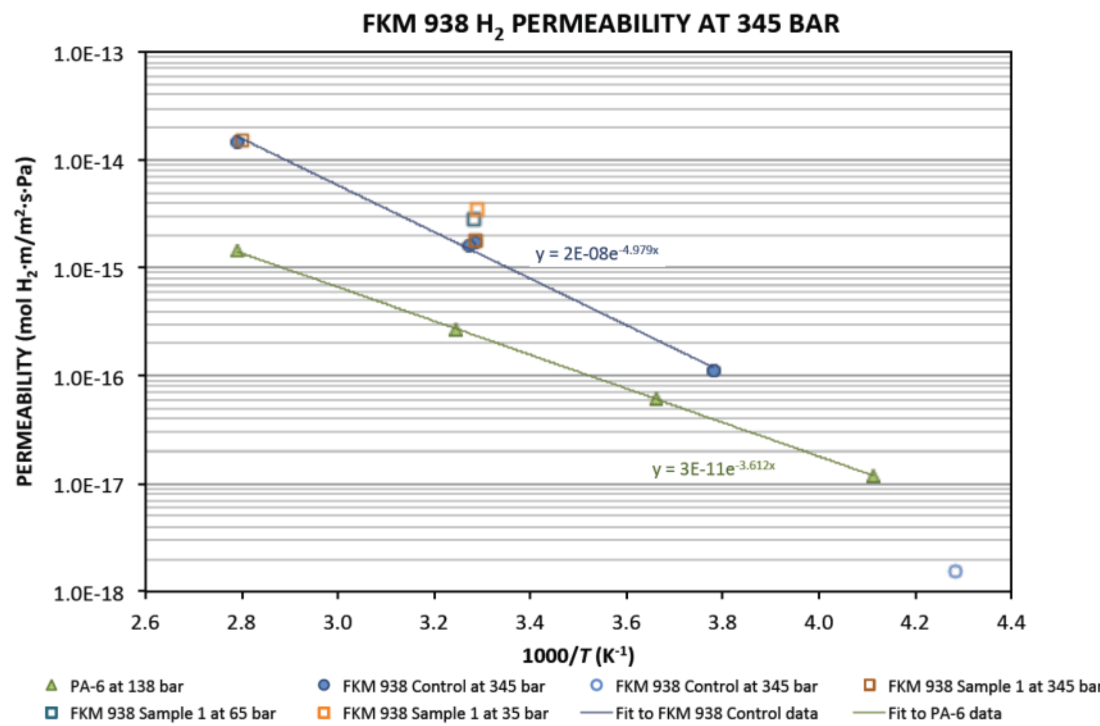
Sample	Average Permeation Reduction	Standard Deviation	SiOx/Exilis (nm/nm)	Bilayer Thickness (nm)
Neat Silicone	0.0%	-	-	-
Barrier Coating	48.8%	7.6%	100/100	2000
Barrier Coating	50.7%	3.3%	70/100	2000
Barrier Coating	54.2%	8.0%	50/100	2000
Barrier Coating	**57.3%**	9.7%	35/100	2000

- Samples prepared and sent to ORNL for H_2 testing
  - No improvement in permeability seen
  - Plan to perform helium testing at ORNL in Phase IIA for validation before further H_2 work

Technical Back-Up:
ORNL Barrier Coating Permeability Testing

Initial Testing

- 4um GVD coating on Greene Tweed FKM 2mm thick fluoroelastomer
- Initial testing shows no statistical difference in permeability
    - Test data dominated by FKM lack of permeability
    - Particulate inclusion issues also likely

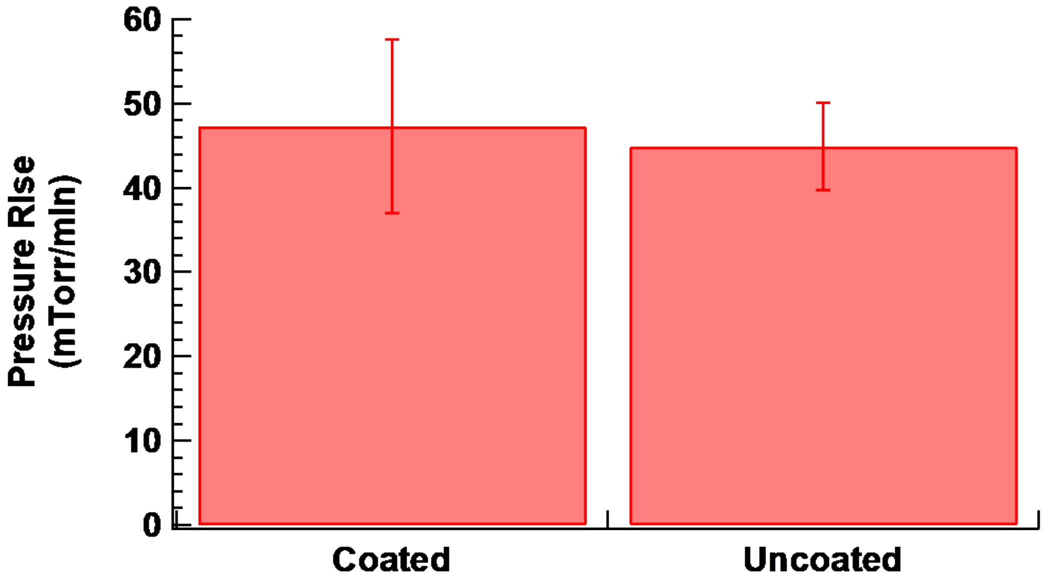


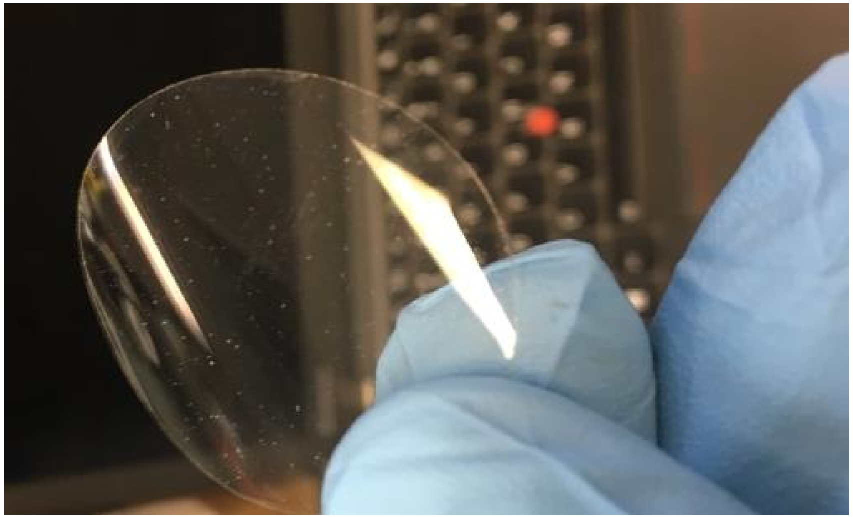
Future Planned Testing

- GVD will coat commercial Viton for testing
    - Current elastomer used as energetic seal
    - Permeability multiple orders of magnitude higher than FKM
        - Lower temp testing required
- GVD reworking pilot-scale coating system to eliminate particulate issues

Technical Backup: Particulate Inclusion Issues

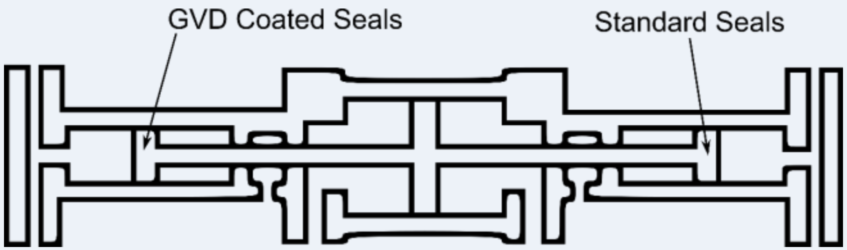
- Particles observed on samples from new deposition set-up
- Flow conditions create recirculation and particle generation
  - Developing improved flow orientation to eliminate - unsuccessful
- Return to horizontal flow with improved pumping to reduce residence time





Technical Backup: PowerTechCompressor Seal Testing

- Abbreviated Testing Procedure
  - Weigh gasket before cycling
  - Record compressor run time until failure
  - Measure weight after failure



Schematic of gasket seal locations in Hydro-Pac compressors. Tested by Powertech

Example of a Hydro-Pac seal received by GVD prior to coating.

Stock Gaskets from Hydropak

Total Initial Mass	11.76g
Total Final mass	10.95g
Ttl. Delta:	0.81g
Average Delta:	0.10g
Run Time	20.63h
Depletion rate	4.933mg/h

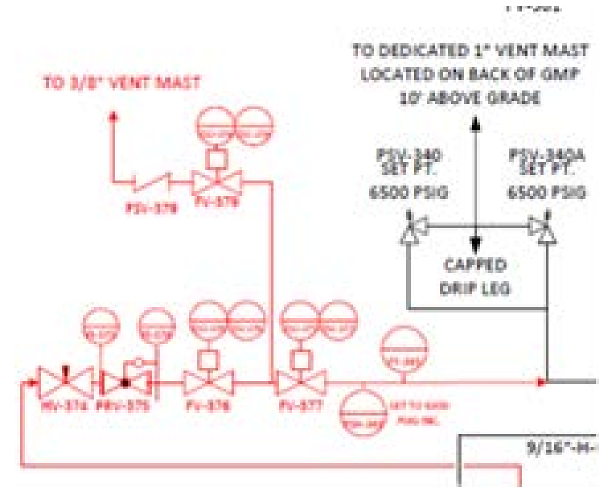
GVD Coated Hydropak Gaskets

Total Initial Mass	11.79g
Total Final mass	11.61g
Ttl. Delta:	0.18g
Average Delta:	0.02g
Run Time	20.63h
Depletion rate	1.095mg/h

$$Depletion\ Rate\ \left({}^{mg}/_{hr}\right) = \frac{Initial\ Mass\ (mg) - Final\ Mass\ (mg)}{Runtime\ (hr)}$$

Technical Backup: Seal testing at NREL

- Hydropac compressor on recirculation loop
- High wear duty cycle
  - 1 hour on/ 1 off continuous
- Metrics
  - Compressor efficiency loss
  - H_2 bypass
- Direct comparison of coated vs. uncoated
  - Will provide data on failure rate and failure mode
- Validate coating does not contaminate fuel



Critical Assumptions and Issues

Assumption: Mass loss reduction in piston seals is a good analogue for extended seal life

- Seal mass loss “cliff” after sufficient coating wear
  - Increase coating thickness
  - Redesign bulk seal material to best leverage surface lubricity
- Reduced friction changes failure mechanism
  - Analyze seal failure rate data and physical seals to understand new failure mechanism and how to mitigate

Critical Assumptions and Issues

Assumption: Technical success for coating design requirements will provide desired increase in hydrogen compressor reliability

- Mechanical damage to the barrier coating can cause premature failures
  - Develop detailed installation procedures
- Demonstration in operation is required to determine whether the technology will be useable commercially
  - Testing before commercial launch with potential early adopters