Advanced Barrier Coatings for Harsh Environments

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Subcontractors:

- Oak Ridge National Laboratory, Oak Ridge, TN
- National Renewable Energy Laboratory, Golden, CO

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Project End Date: April 5, 2019

Overall Objectives

- Optimize a flexible hydrogen barrier coating to be vacuum deposited onto elastomeric materials to reduce seal failure due to damage from hydrogen permeation.
- Demonstrate prolonged life of seals and gaskets in compression systems by increasing seal lubricity with a thermally initiated chemical vapor deposition polytetrafluoroethylene (PTFE) coating.
- Demonstrate feasibility of a high throughput, mass manufacturing system for coated O-rings and seals.

Fiscal Year (FY) 2018 Objectives

- Quantify materials characteristics of polymeric and oxide layers as a function of deposition conditions.
- Identify best candidate materials for barrier coating.
- Quantify improved lifetime of PTFE-coated gaskets in hydrogen compressors and dispensers.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Delivery section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan[1]:

(B) Reliability and Costs of Gaseous Hydrogen Compression

(I) Other Fueling Site/Terminal Operations

(J) Hydrogen Leakage and Sensors.

Technical Targets

This project addresses the failure of seals in hydrogen compression, storage, and delivery operations. Large pressure and temperature variations in the hydrogen station operation compromises seals and gaskets. Barrier film coatings address failures due to hydrogen permeation into elastomeric seal materials. PTFE lubricious coatings address failure due to friction wear on both hard-plastic gaskets and elastomeric seals. Results are aggregated into Table 1.

The objective of this project is to increase the lifetime of seals and gaskets, thereby reducing failures and maintenance downtime of systems. Success in this project will create significant movement toward the stated DOE goal of enabling a delivered hydrogen cost of $7/gallon gas equivalent in early markets by 2025.

FY 2018 Accomplishments

- Correlated chemical structure of gas barrier material to process conditions. Identified material with lowest defect density, greatest electrochemical stability, and best adhesion to test substrates. It is expected that these properties are aligned with good gas barrier characteristics.
- Improved the mechanical properties of the polymeric layer deposited by plasma activation

[1] https://energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22

(instead of thermal activation) so that manufacturing can be economized.

- Established protocols for lubricious coating testing with the National Renewable Energy Laboratory (NREL) to obtain continuous, quantitative comparisons of coated seals with uncoated seals in hydrogen compressors (high-temperature, high-pressure application).
- Began lifetime testing of coated O-rings in hydrogen dispensers with Takaishi Industry Co. Ltd. (low-temperature, high-pressure application).

Table 1. Progress Toward Meeting Technical Targets for Advanced Barrier Coatings for Harsh Environments

Characteristic	Units	Current Status
Average permeation reduction (helium)	Percent reduction (%)	53%
Average permeation reduction (hydrogen)	Percent (%)	N/A
Compression gasket failure (incumbent benchmarking)	Pass/fail	Pass
Dispenser seal lifetimes	Relative lifetime	Testing in progress

INTRODUCTION

In order to realize the full potential of zero-emission fuel cell electric vehicles, a critical hurdle that has yet to be overcome is achieving viable cost for hydrogen compression, storage, and dispensing. Current hydrogen systems within fuel cell electric vehicles and the supporting infrastructure to compress, store, and deliver hydrogen fuel are prone to systemic inefficiencies and poor reliability. Many of these reliability problems stem from the failure of plastic and elastomer seals (including O-rings, gaskets, and piston seals), which results in significantly increased labor costs for rebuilds and excessive equipment downtime. One cause of failure is that seal components leak and weaken as hydrogen molecules saturate these materials under conditions of extreme temperature and high hydrogen pressure. Another important mechanism of failure is simple frictional wear, which stems from insufficient lubricity and is exacerbated by extreme temperatures and pressures. Thus, there is a need for improved polymer seals with prolonged lifetimes and improved performance in extreme temperature (-40°C to 200°C) and high-pressure (>875 bar) hydrogen environments to enable reliable operation of hydrogen systems. This need has been emphasized in two recent meetings sponsored by the DOE's Fuel Cell Technologies Office [1, 2], hydrogen compressor manufacturers, fuel cell electric vehicles automakers, and two leading seal manufacturers. In this program, GVD addresses the challenges of hydrogen saturation and frictional wear, using its proprietary gas barrier coatings and lubricious coatings (Figure 1).

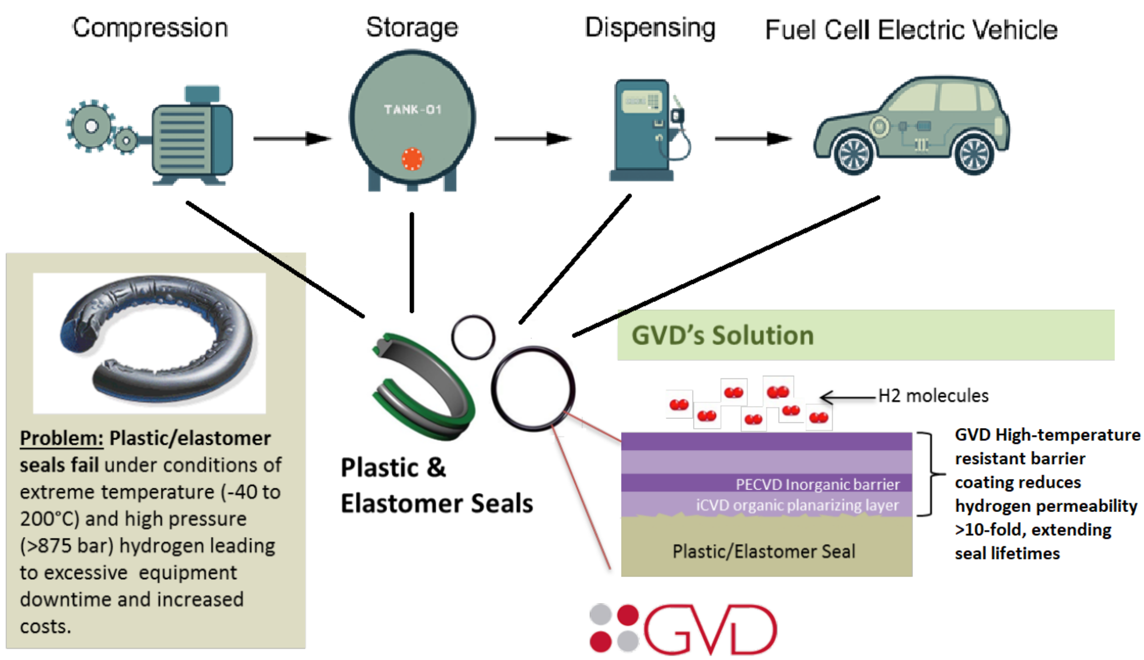

Figure 1. Plastic and elastomeric seals are central to all aspects of hydrogen generation and delivery. GVD's gas barrier and lubricious coatings promise to extend the lifetime and improve the reliability of seals in hydrogen compression, storage, and dispensing equipment.

APPROACH

This project aims to upgrade current state-of-the-art gaskets by applying a vapor deposited film on the outside of the gasket. This can be accomplished using initiated or plasma enhanced chemical vapor deposition. A glass-like oxide material is used to prevent hydrogen ingress into the sample; however, because glass is not a flexible material, it needs to be thin to prevent microfractures that compromise the coating. Dyads of thin glass-like oxides are alternated with polymeric layers to allow the material more flexibility and create a more tortuous path should any cracks form.

One application that GVD is targeting with its coatings is seals used in hydrogen compression. It is important to note that, depending on the application, seals can exhibit a wide range of different pressures and temperatures. Seals fail commonly in high-pressure compression service and must subsequently be replaced because leaks can create both economic and safety concerns. GVD is investigating coating seals with a novel PTFE material to reduce wear. As the compressors run, they heat up due to friction. This heat causes the polymeric material to expand much faster than the metal compressor housing. This expansion leads to increased wear on the plastics. When the compressor is switched to the "off" state and cools, the components constrict to room-temperature size. However, the plastics lose material from abrasion while running and fail to seal at room temperature due to a size mismatch. A PTFE coating adds lubricity to the gasket, preventing friction wear that causes material loss. GVD is partnering with NREL and Takaishi Co. Ltd. to directly test the wear rates of coated seals in industrial hydrogen compressors under harsh conditions.

RESULTS

Following promising helium permeability reduction for a multi-material gas barrier coating, GVD has carried out optimization of the two material types used in the multi-dyad barrier coatings. These are:

1. The glass-like oxide material formed by the decomposition of the precursor. The gas permeability of the oxide material depends on the extent of crosslinking, elemental composition, and surface coverage of the oxide, all of which are controlled by process conditions.
2. The polymeric material that is used as a spacer between the oxide layers. The polymeric material serves to decouple defects in the oxide layer and improve the overall flexibility of the coating, so that cracking is avoided.

Rather than using gas permeability of the complete multilayer coating as a metric for optimization, GVD optimized the two materials separately, using as metrics the properties desirable for each layer. For the oxide, these are stability, adhesion, surface coverage, and a highly crosslinked structure. For the polymeric layer, the metrics are flexibility and smoothness.

For the oxide layer, GVD used Fourier transform infrared (FTIR) spectroscopy and two electrochemical analytical tests, developed specially for this purpose, to evaluate the chemical structure, surface coverage, and stability. FTIR spectroscopy revealed that the deposition conditions explored yielded a wide range of chemical compositions and crosslinking within the film. Electrochemical testing showed that the oxide coatings were able to reject ionic species in solution, indicating that they are pinhole-free. In addition, most of the coatings, though not all, resisted electrochemical degradation, which bodes well for the long-term stability and mechanical properties of the final multilayer coating. Furthermore, there was a strong correlation between the stability and chemical structure of the films; higher levels of crosslinking and high inorganic character led to better film stability and better performance in the electrochemical tests.

One of the main thrusts of this project is the development of a plasma-deposited polymeric layer inspired by a highly flexible overcoat deposited using thermal initiation deposition. Because the oxide layer requires plasma activation, using a plasma process for the polymeric layer offers simplified and accelerated manufacturing. In earlier phases of the program, GVD arrived at a plasma-deposited material that was deemed appropriate for use. However, further testing showed that the plasma-deposited polymeric layer was more brittle than the thermally deposited material. By tuning the energy inputs, reactant mixture, and reaction times, GVD has been able to improve the flexibility of the polymeric material. This work is still ongoing, but FTIR spectroscopy has revealed that the more flexible plasma-deposited material was more similar in its chemical structure to the thermally deposited material. Higher flexibility should lead to greater cracking resistance of the overall coating.

Gaskets coated with GVD's lubricious coating were tested against uncoated gaskets in Hydropac gas compressors at NREL. In earlier phases, GVD saw promising reductions in mass loss of coated gaskets. Since then, GVD has begun testing at NREL, where more standardized testing with continuous monitoring of seal performance is possible. An aggressive testing procedure was developed to differentiate between controls and test samples. The test procedure involves repeated temperature cycling between ambient temperature and 120°C (cycle time is approximately 1 hour) in addition to real-time monitoring of leak rates. Temperature cycling is expected to maximize the degradation of seals. Real-time leak rate measurements allow for continuous, quantitative comparison between controls and seals with a lubricious coating. The test procedure was checked for repeatable temperature ramp rates and flow rates, and the first round of tests are currently underway. Testing automation introduced in 2018 has improved the repeatability and reliability of the measurements and will allow unmonitored operation of the rig to accelerate futures tests.

In addition, testing of GVD-coated O-rings is currently being carried out by Takaishi Co. Ltd. (of Japan) in low-temperature applications. GVD's lubricious coatings are being characterized for their effect on the lifetime of O-rings used in hydrogen dispenser equipment. The first round of testing is being performed presently.

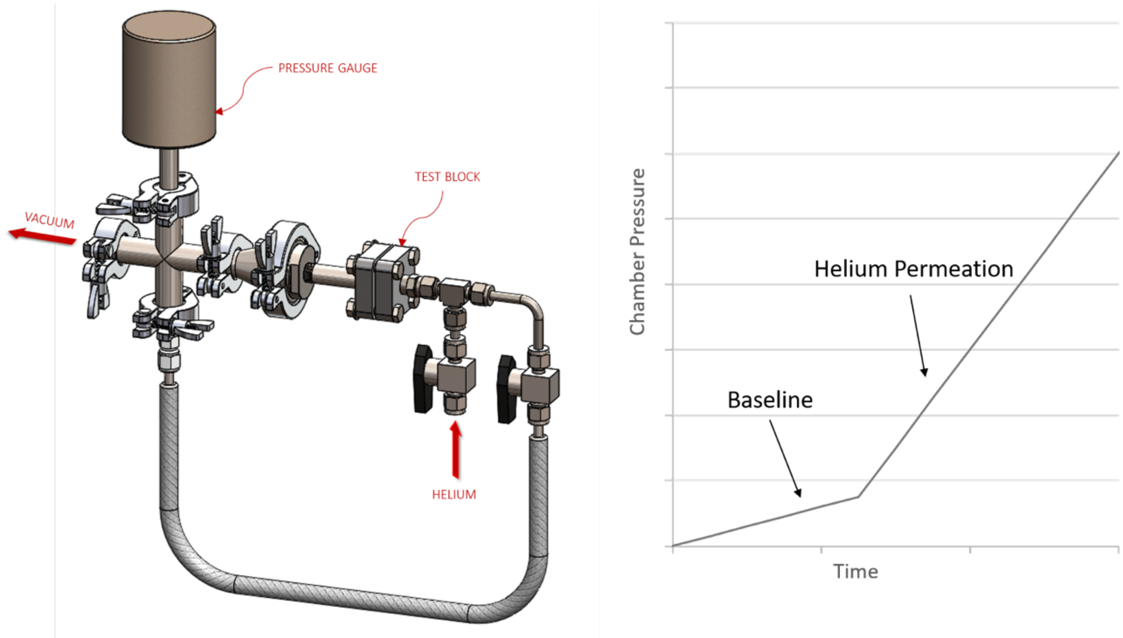

Figure 2. Schematic of the helium permeability testing setup at GVD and a theorized plot of pressure vs. time in a typical permeability measurement

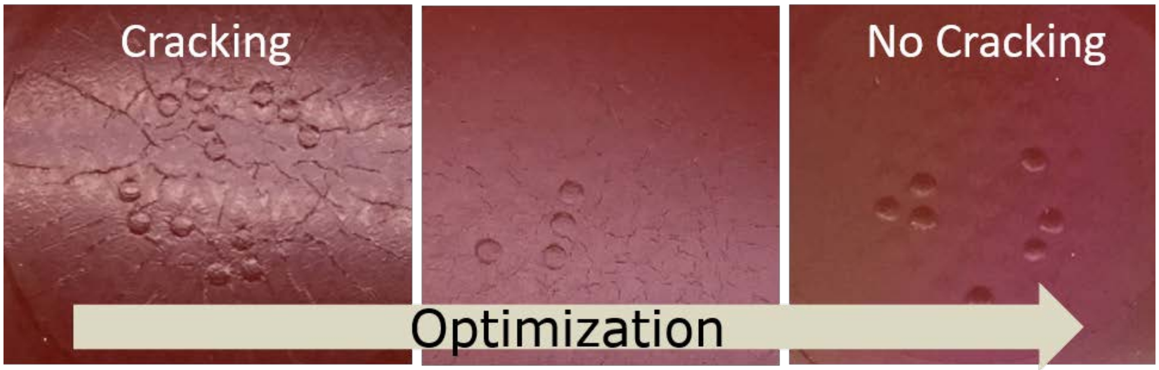

Figure 3. Effect of deposition conditions on the cracking of GVD's polymeric coating on a silicone substrate

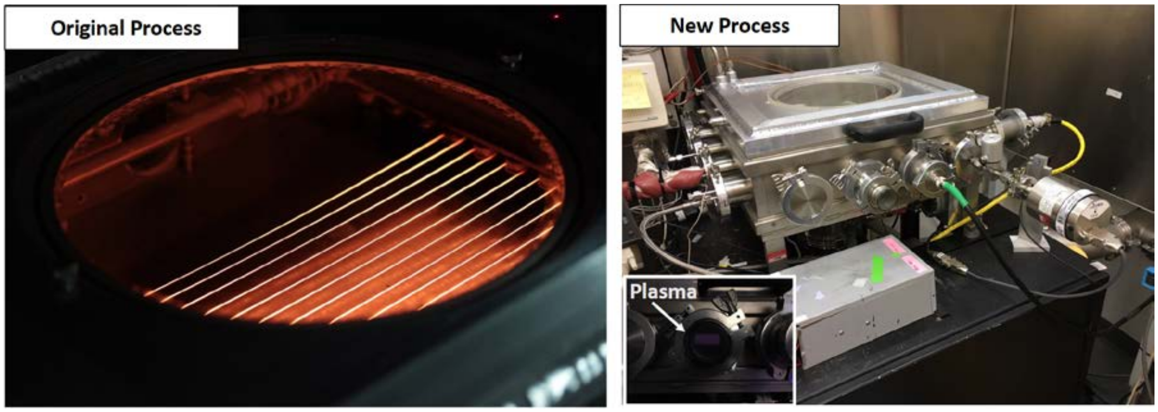

Figure 4. Image of the reactor used for the thermally initiated vapor deposition (left) and that for the plasma chemical vapor deposition process (right)

CONCLUSIONS AND UPCOMING ACTIVITIES

In 2018, GVD has identified the best potential candidate materials (determined by deposition conditions) for the oxide layer and has improved the mechanical properties of a polymeric spacer material that can be manufactured using a plasma activated process. Consequently, future tests of the hydrogen permeability at high temperatures and pressures are more likely to give positive results.

Next, GVD will optimize the geometry of the multi-material coating to achieve the greatest barrier properties and mechanical stability. The considerations include the total thickness as well as the thickness of a surface-passivation layer, a planarization layer, the subsequent oxide layers, and the subsequent polymeric layers. The barrier properties of the coating for hydrogen will then be validated, and optimized manufacturing equipment will be designed. GVD's testing of lubricious coatings for seals and gaskets with NREL will continue, as will the testing of the lubricious coating for low-temperature environments in conjunction with Takaishi Co. Ltd. Feedback from the testing currently underway will provide a starting point for optimization of the PTFE coating.

FY 2018 PUBLICATIONS/PRESENTATIONS

1. Shannan O'Shaughnessy, "Advanced Barrier Coatings for Harsh Environments," Hydrogen Storage and Delivery Tech Team, Golden, CO, February 2018.
2. Shannan O'Shaughnessy, "Advanced Barrier Coatings for Harsh Environments," DOE Hydrogen and Fuel Cells Program 2018 Annual Merit Review, Washington, DC, June 2018.

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1. "Polymer and Composite Materials Used in Hydrogen Service," Meeting Proceedings (Oct. 2012). Accessed Aug 20, 2013. http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/poly_comp_materials_proceedings.pdf.
2. S. Ahmed, E. Sutherland, *2013 Hydrogen Compression, Storage, and Dispensing Cost Reduction Workshop Final Report* (April 2013). Accessed August 21, 2013. http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/2013_csd_workshop_report.pdf.