III.4 Advanced Barrier Coatings for Harsh Environments

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Overall Objectives

- Deposit a hydrogen barrier onto elastomeric materials to reduce seal failure due to hydrogen damage.
- Increase compression system seal lubricity via a reduction in friction with an application of initiated chemical vapor deposition (iCVD) poly-tetrafluorethylene (PTFE) coatings.
- Design a high-throughput, mass manufacturing system.

Fiscal Year (FY) 2017 Objectives

- Model system testing with helium and subsequent hydrogen testing.
- Lifetime gasket testing in compressors.
- Computer-aided drawing design on a tumble coater for elastomeric gaskets.

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.

(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 variation in the hydrogen operation compromises seals and gaskets. Barrier film coatings address hydrogen ingress failure and PTFE lubricious coatings address failure due to friction wear. Results are aggregated into Table 1.

TABLE 1. Progress towards 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

This project's aim is to increase the lifetime of seals and gaskets, thereby reducing failures and maintenance downtime of systems. There are no targets outlined in the Multi-Year Research, Development, and Demonstration Plan; however, current technology requires material seal changes in fueling stations every 163 fills, whereas in the United States, the average petrol fueling station fills 200–250 cars per day. Success in this project will create significant movement toward the stated DOE goal of achieving delivery and dispensing costs of <$2/gge.

FY 2017 Accomplishments

- Improved in-house measurement capabilities and achieved a reduction in helium permeability of 53%.
- Compressor seals lost 1.30 mg/h with PTFE coating, whereas uncoated seals had a reduction of 3.45 mg/h.
- Designed a tumble coater assembly for upscale manufacturing of gasket coatings.

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INTRODUCTION

In order to realize the full potential of zero-emissions fuel cell electric vehicles, a critical hurdle that has yet to be overcome is achieving viable cost structures 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 plastic and elastomer seals (including O-rings, gaskets, and piston seals) employed in these hydrogen systems that leak and weaken as hydrogen molecules saturate within these materials under conditions of extreme temperature and high hydrogen pressure. The result is that these seals require frequent replacement, incurring significant labor costs and excessive equipment downtime. Thus, there is an urgent need for improved polymer seals that can withstand 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 DOE's Fuel Cell Technologies Office [1,2], by hydrogen compressor manufacturers, by fuel cell electric vehicle automakers, and by two leading seal manufacturers. Figure 1 shows the processes impacted by this project.

In addition, within hydrogen compressors, the wear on gaskets is a major failure point. GVD Corporation has engineered solutions to the wear problem. Increasing the lubricity of the gaskets improves the lifetime of the gaskets. This reduces downtime and equipment maintenance, one of the costliest aspects of the hydrogen fueling process.

APPROACH

This project aims to upgrade current state-of-the-art gaskets by coating a hydrogen barrier film on the outside of the gasket. This is accomplished using iCVD or plasma-enhanced chemical vapor deposition (PECVD) (Figure 2). A glass-like oxide material is coated to prevent hydrogen ingress into the sample; however, since glass is not a flexible material, it needs to be thin to prevent micro-fractures 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.

The seals that require barrier coatings come in direct contact with hydrogen at high pressures and a large temperature range. Therefore, a wide range of conditions needs to be considered. One fuel cell unit operation GVD is targeting is hydrogen compression. Since gaskets need to be replaced every 200 h of operation due to both the failure to properly seal and safety concerns, GVD is investigating coating the seals with PTFE 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

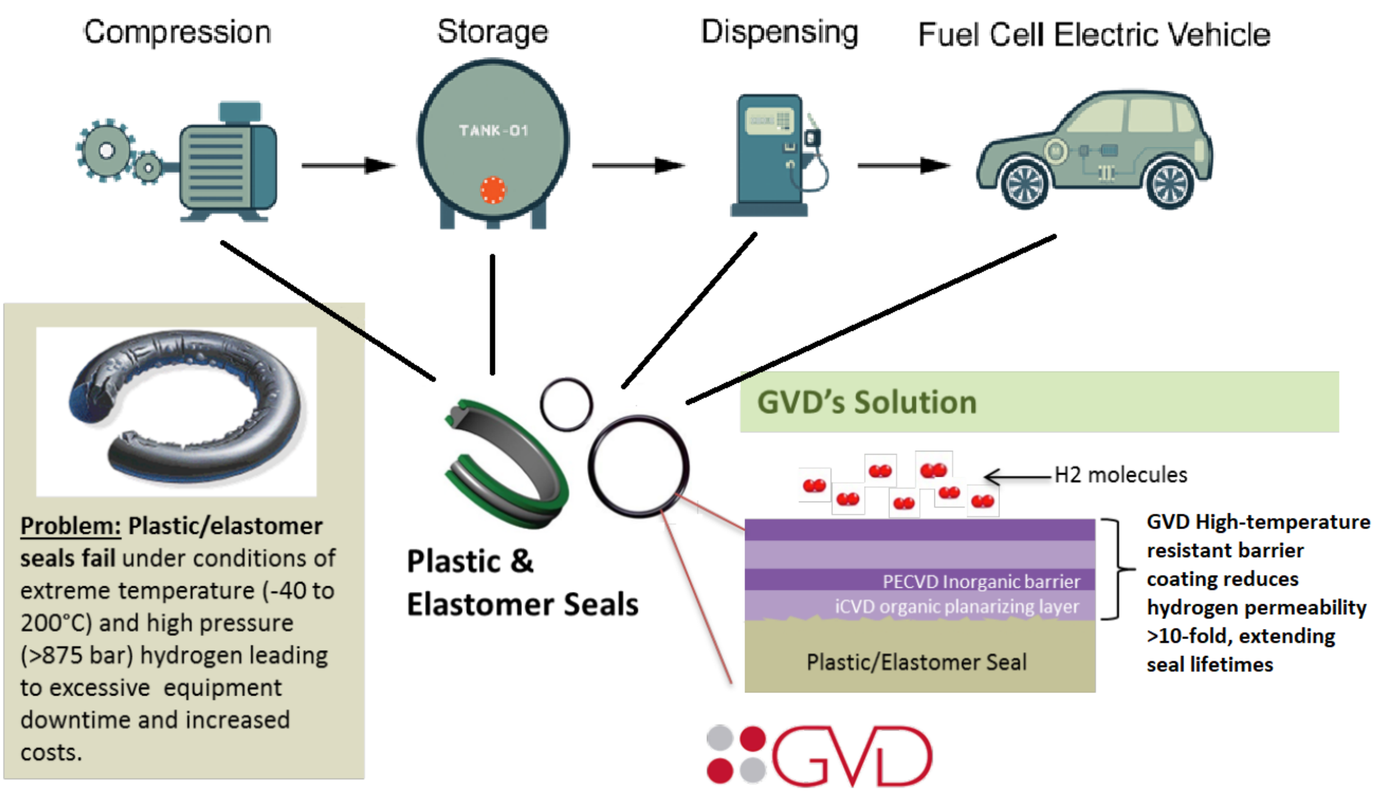

FIGURE 1. GVD's vapor-deposited, flexible, high-temperature-resistant barrier coatings are deposited on plastic and elastomer seals to prevent hydrogen permeation into the seal and thereby extend seal reliability and lifetime

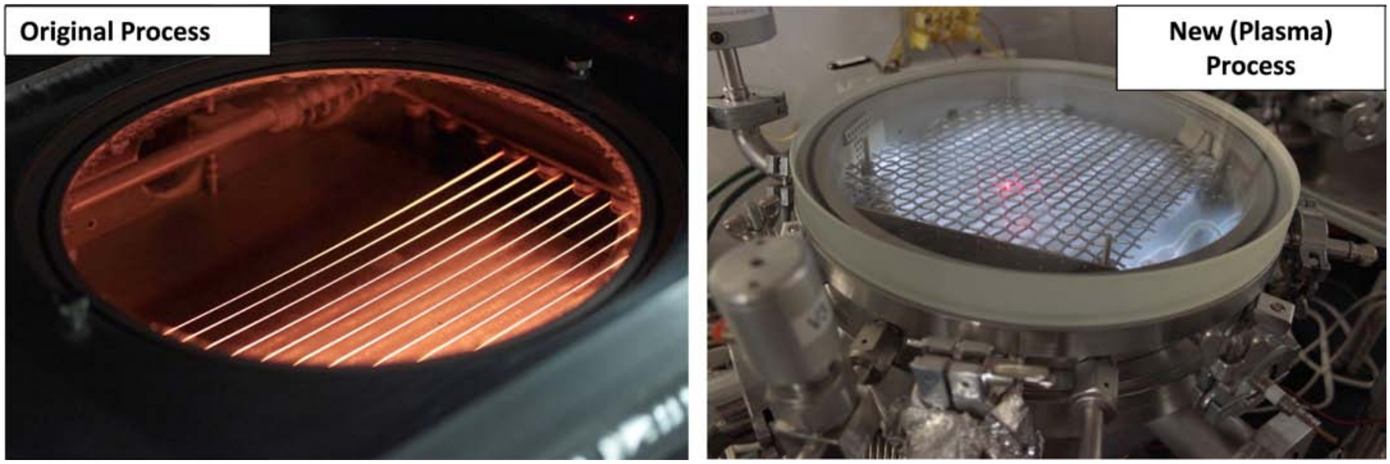

FIGURE 2. Left: iCVD process with heated filament; Right: PECVD process with radio frequency plasma

wear on the plastics. When the compressor is switched to the off state and cools, the components constrict to the 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 leading to material loss.

RESULTS

Barrier film coatings have been shown to improve permeability of helium through a silicone gasket. A special apparatus was built for high-throughput testing prior to hydrogen testing at Oak Ridge National Laboratory (ORNL). An improvement of nearly 60% was observed on custom silicone gaskets made by a leading gasket manufacturer for this project. It was observed that reducing the oxide thickness of each layer, but keeping the total oxide thickness constant, thus increasing the number of layers, leads to a reduction in the average permeability. Oxide layer thickness changes of 65 nm lead to a 25% reduction in helium permeability. See Figure 3.

Since helium has been observed to have higher diffusivity than hydrogen, these results are positive. Samples were subsequently tested at ORNL. However, the silicone samples were shown to have the hydrogen permeability with and without the coating. It is suspected that this is due to pinholes in the oxide coatings. The surface area of the test samples at ORNL is larger than that of the samples used

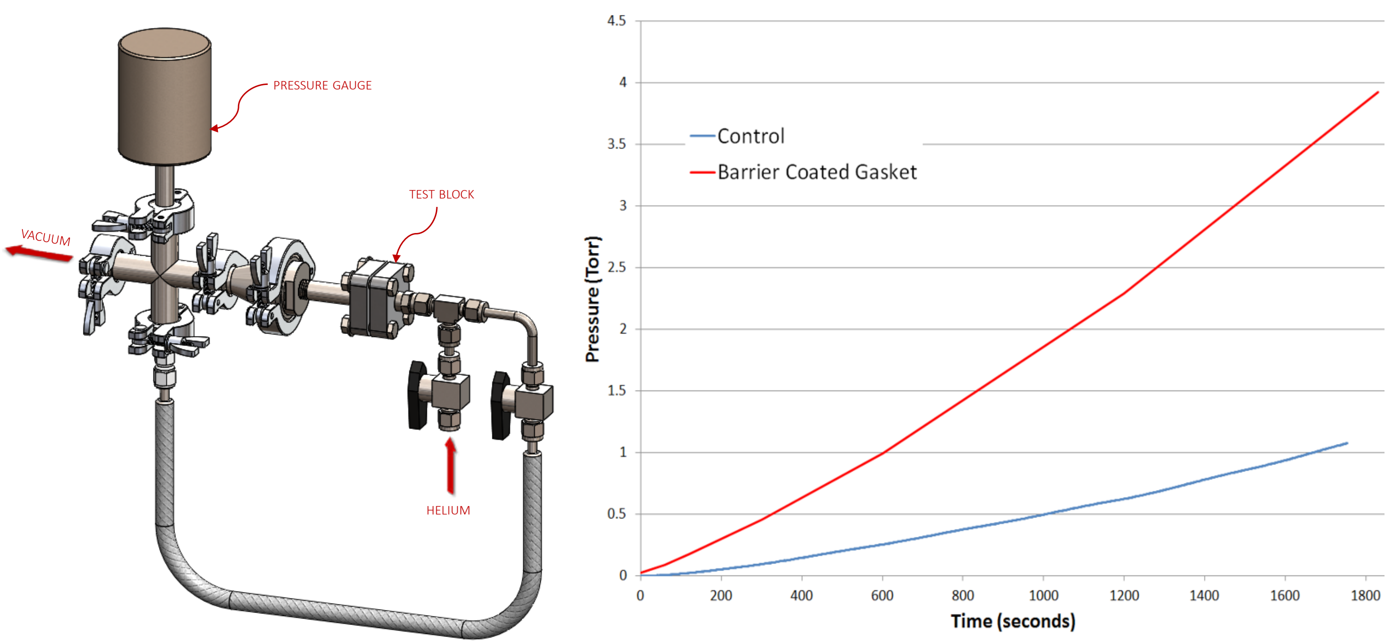

FIGURE 3. Left: Schematic of helium testing; Right: Sample graph of helium test

in the helium testing, and the increased area most likely captured more defects in the coating and negated the positive results. Efforts to coat more uniform and pinhole-free oxides layers are ongoing.

A separate effort on gaskets for compressors has promising results. The mass depletion rate of the gaskets was reduced from 3.45 mg/h to 1.30 mg/h. These gaskets passed all tests after they were removed from equipment after 177 h of run time. Unfortunately, the gaskets were removed from the compressor after a failure of another component, and while the compressor was down for maintenance, the gaskets were changed out. Therefore, a comparison of the increased running time is not available currently. A second set of gaskets has been loaded for testing. Due to the intermittent running of hydrogen compressors, a long turnaround time for results is anticipated.

Coatings are currently being done in a small research reactor. Production-level throughput would not be feasible in the current setup. A large-scale used reactor was purchased, and retrofitting has begun to transition the reactor to production-scale PECVD reactor. The design utilizes a basket that tumbles the gaskets. This allows complete 360-degree coverage of the gaskets and allows more gaskets to be coated per run. Currently, the planar systems are limited by the surface area, and samples need to be flipped to coat the back side. The tumble coater will enable reduced coating costs and increased sample throughput ultimately required to keep costs low and increase adaptation of the technology. A cross-sectional computer-aided design drawing is shown in Figure 4.

CONCLUSIONS AND UPCOMING ACTIVITIES

The project is ongoing and has been selected to be continued in a Phase IIa grant to extend this work into dispensing systems in addition to compressors and hydrogen gasketing. The oxide portion of the barrier films is undergoing ongoing improvement, and future testing with hydrogen is planned at ORNL.

Upon successful improvements to barrier properties with hydrogen, testing in dispensing systems at National Renewable Energy Laboratory will be conducted. Involvement of National Renewable Energy Laboratory is advantageous because in addition to real-world testing, GVD will also receive information on failures, which will be helpful in further designing a better coating and/or process.

Continued work with compressors will be extended in Phase IIa. Currently, coated samples are under test in compressors. A design on experiments with different PTFE densities and thicknesses has been planned to find the

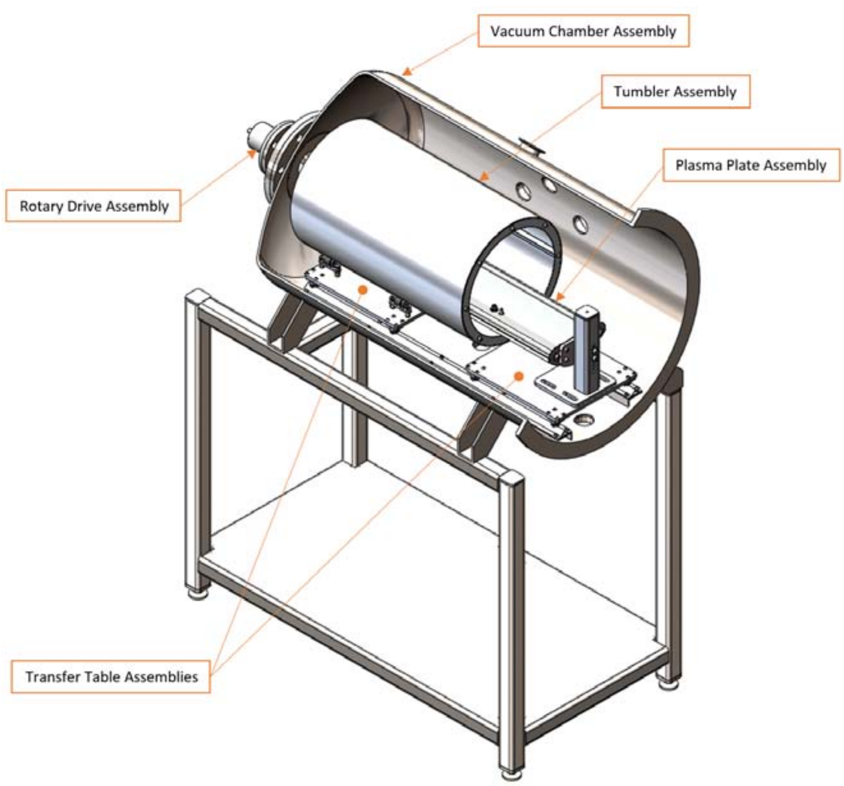

FIGURE 4. Cross sectional view of tumble coater with plasma deposition

optimal coating conditions. The first results showed that there is an improvement, but future work will quantitate and optimize the magnitude of the improvement.

FY 2017 PUBLICATIONS/PRESENTATIONS

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