# Hydrogen Material Compatibility for Hydrogen ICE

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# Overview

- **Timeline/Budget**
  - **FY 06 through FY 09 at $300K/y**
- **Barriers**
  - **Direct Injection of hydrogen requires durable, precise injection capability. This capability is affected by**
    - **impact friction at the needle/nozzle interface,**
    - **degradation of the piezoelectric ceramics used to actuate the fuel injectors, and by**
    - **sliding friction and wear of the injector materials.**
- **Partners**
  - **Westport Inc., Ford Motor Co., Argonne National Laboratory, and Oak Ridge National Laboratory**

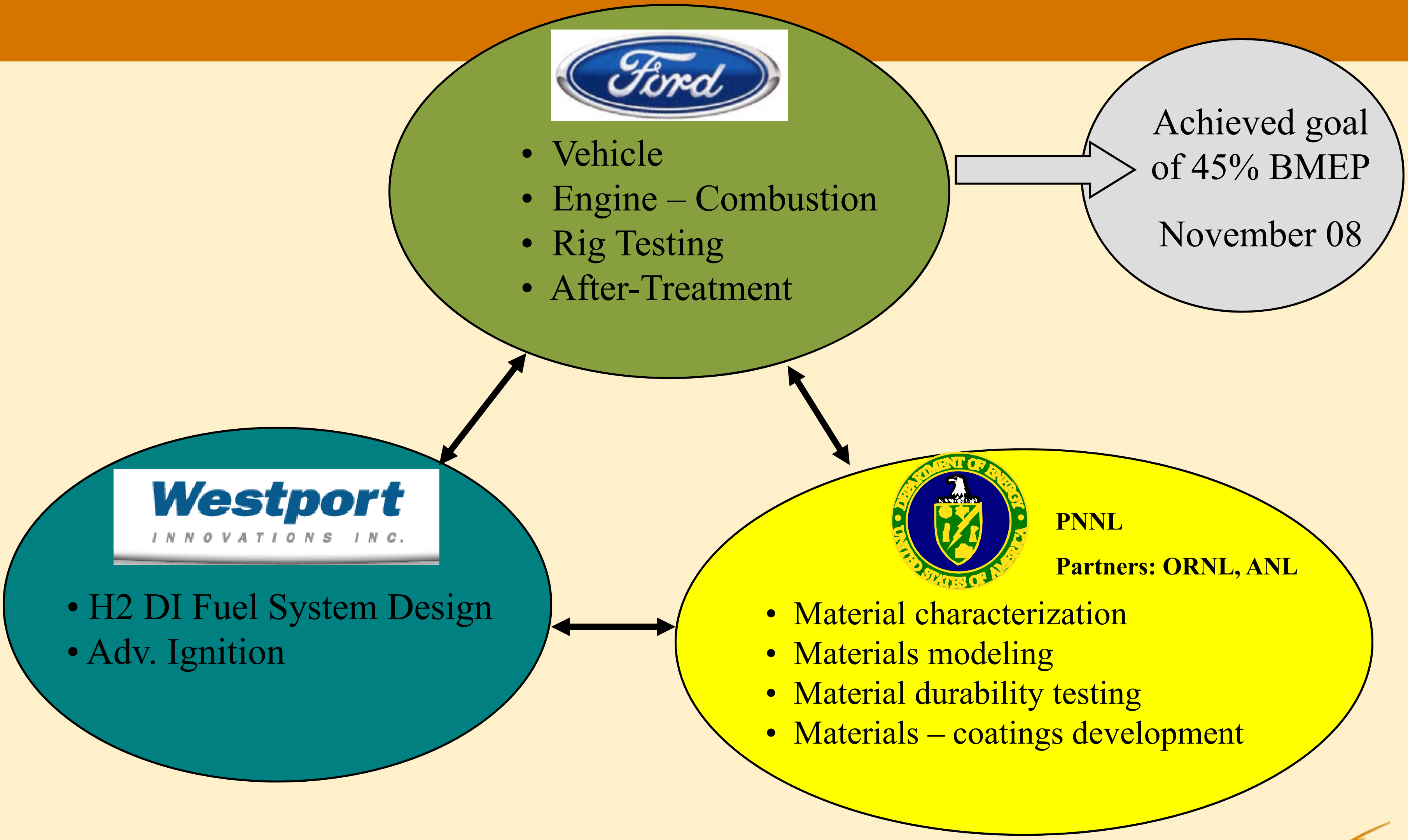
# Objectives

- **Improve the durability and performance of fuel injectors for use in direct-injection hydrogen internal combustion engines by**
  - **Evaluating failure modes of piezoelectric materials, coatings, and connectors in high-pressure hydrogen gas;**
  - **Characterizing actuator performance in hydrogen and developing new experimental methods for evaluating performance; and**
  - **Measuring the friction and wear characteristics of injector materials and coatings in hydrogen gas in order to develop better injector designs.**

# Milestones

- **September 08. Complete 100% hydrogen *in-situ* sliding wear tests to quantify injector friction coefficient and resulting material embrittlement with the goal of understanding and predicting the fundamental material degradation / aging mechanisms in hydrogen service environment. Complete.**
- **September 08. Complete 100% hydrogen *in-situ* piezo actuation tests of commercial PZT formulations, extending on the initial test plan completed in FY07. Complete.**
- **September 09. Complete material diffusion model and correlate with long-term sliding and sliding-impact data.**
- **September 09. Complete material failure analysis on sliding impact and wear samples.**
- **September 09. Complete full accelerated test method procedures that can transfer to other hydrogen related programs.**
- **September 09. Complete operation of the ORNL apparatus; quantify procedures specific to these materials**

# Program Approach:  Direct Injection Internal Combustion Engines



Ford

- Vehicle
- Engine – Combustion
- Rig Testing
- After-Treatment

Achieved goal of 45% BMEP

November 08

Westport
INNOVATIONS INC.

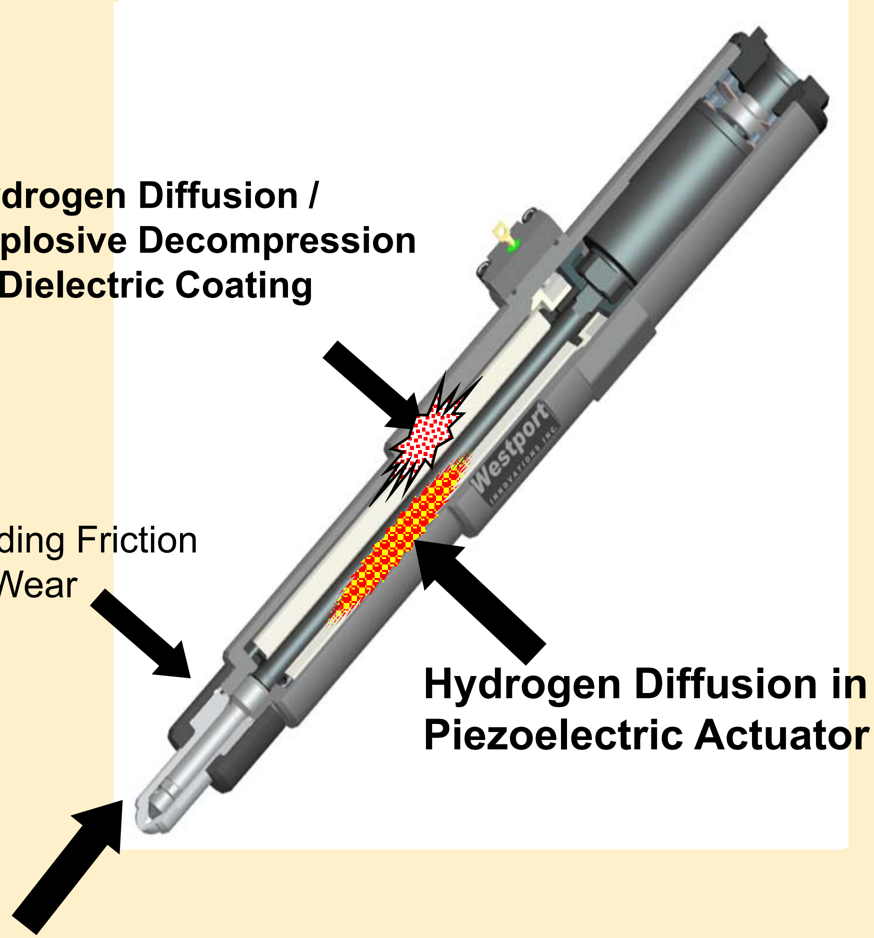
- H2 DI Fuel System Design
- Adv. Ignition

**PNNL**

**Partners: ORNL, ANL**

- Material characterization
- Materials modeling
- Material durability testing
- Materials – coatings development

# Background – Long Term Technical Challenges



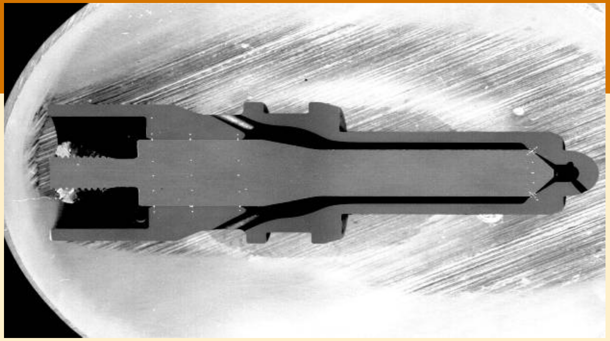
**Hydrogen Diffusion / Explosive Decompression in Dielectric Coating**

Sliding Friction & Wear

**Hydrogen Diffusion in Piezoelectric Actuator**

Impact Wear

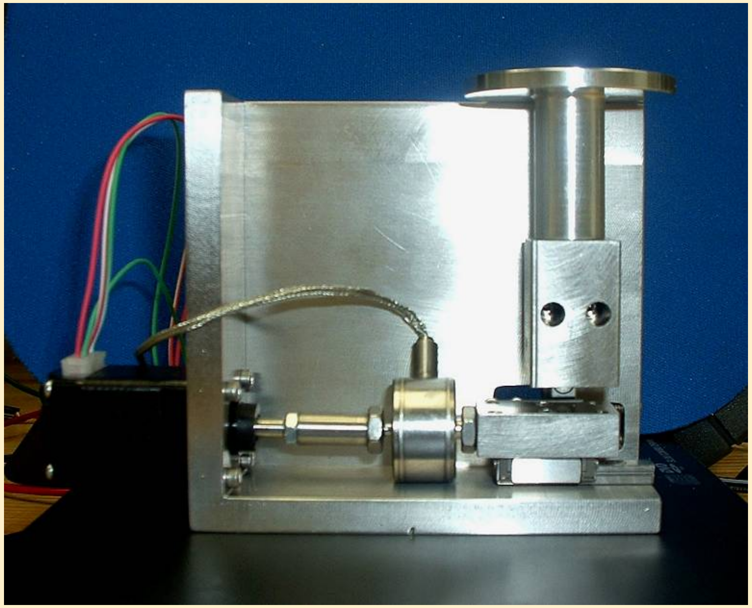
# Potential Failure Sites; Needle and Nozzle

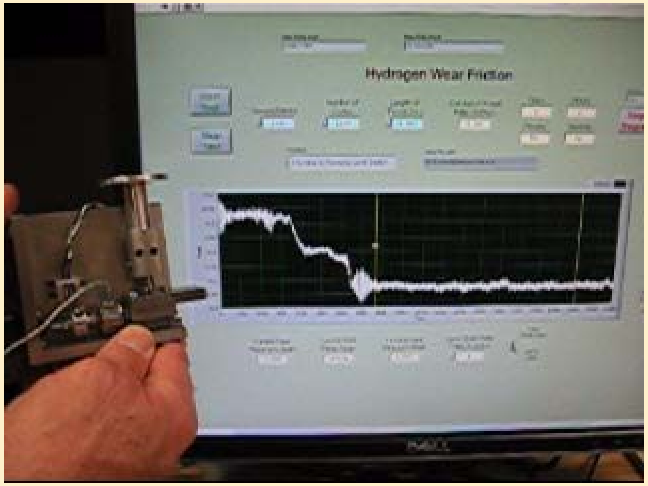


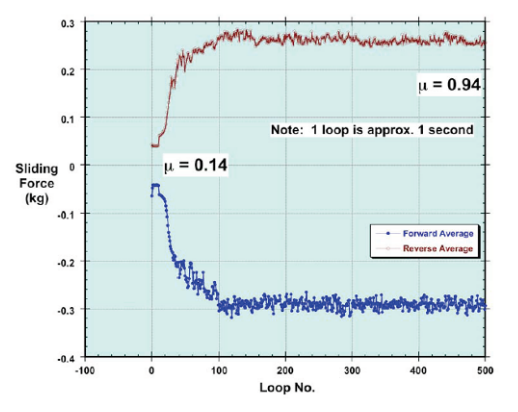
- Material selection
  - Tight clearances (~2 microns radial) mean that the onset of scuffing can lead to catastrophic failure. Scuffing resistance is affected by presence of hydrogen.
- Sliding Friction and Wear; tribology tests are conducted in hydrogen gas, and are used to evaluate tool steels and coatings.
- Coatings; Diamond-like carbon, nanolaminates
- Modeling of contact stresses, diffusion of hydrogen into nozzle materials

# Hydrogen In-Situ Friction Wear Test Apparatus

- Measure lateral (frictional) force
- Maximum operating temperature 100C
- Maximum operating pressure 350 Bar
- Stroke - minimum 0.005” inch maximum 0.1 inch
- Applied normal force 0.25 - 20 pounds
- Frequency of tests – up to 10 cycles per second
- Device runs continuously

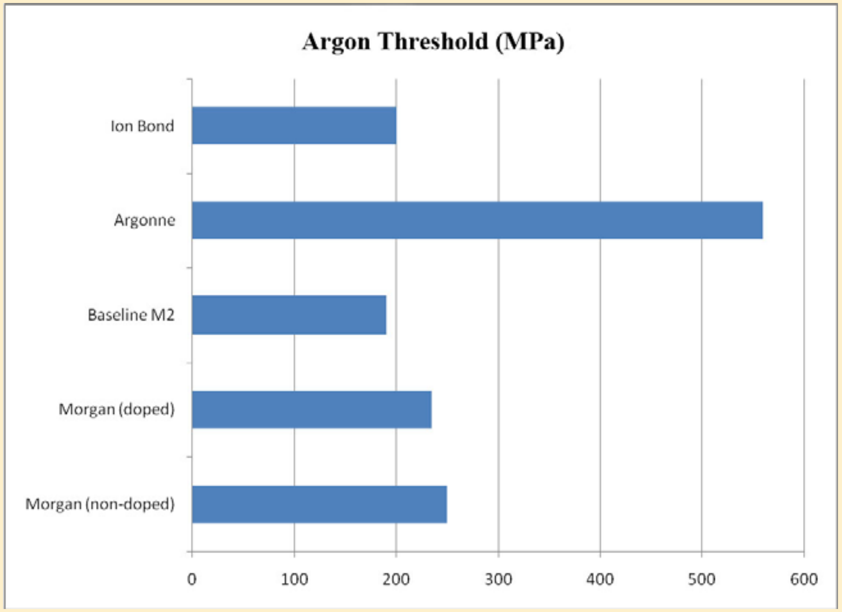






# Diamond-Like Carbon Coatings: Threshold to Scuff DLC Coatings Relative to Baseline

- **Total of 87 sliding tribology tests performed**
  - **Determine threshold for scuffing for all DLCs, base materials in pure Ar**
  - **Expose to H2 – 100 & 500 hours**
  - **Conduct tribo tests after H2 exposure – in Ar and in H2 (10 bar)**
  - **Up to this point, no 300 Bar H2 tribo tests**



# PNNL Nanolaminate Coatings

## Proposed Work

- AlN / BN
- CrN / NbN
- Other systems?

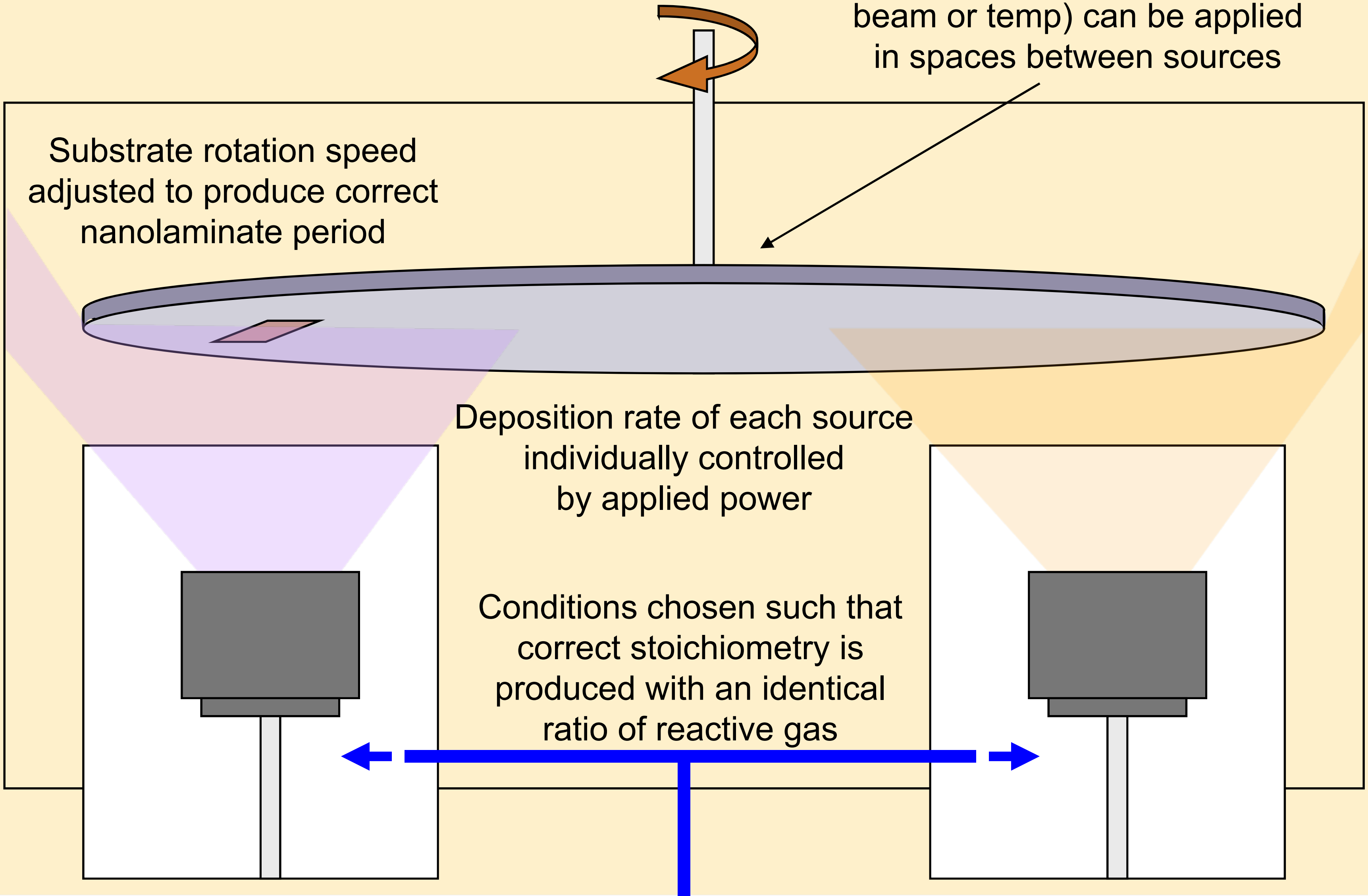
## Produced Nanolaminate Coatings

- CrN / BN;
- $Cr_2N$ / BN
- $SiC_4$ / $SiC_xN_y$
- $B_4C$ / $BC_xN_y$

## ***Rationale***

- Created by stacking different materials or phases in nanometer-scale layers
- Lattice mismatch causes strain, which counteracts applied stresses
- Ultrahard materials can be created, even from typically ductile materials
- Composite structure lends itself to the combination of hard and lubricious materials, possibly leading to a "best-of-both-worlds" scenario
- Mature technique for producing nano-structured materials

# Coating Apparatus



Energy to obtain correct microstructure or phase (ion beam or temp) can be applied in spaces between sources

Substrate rotation speed adjusted to produce correct nanolaminate period

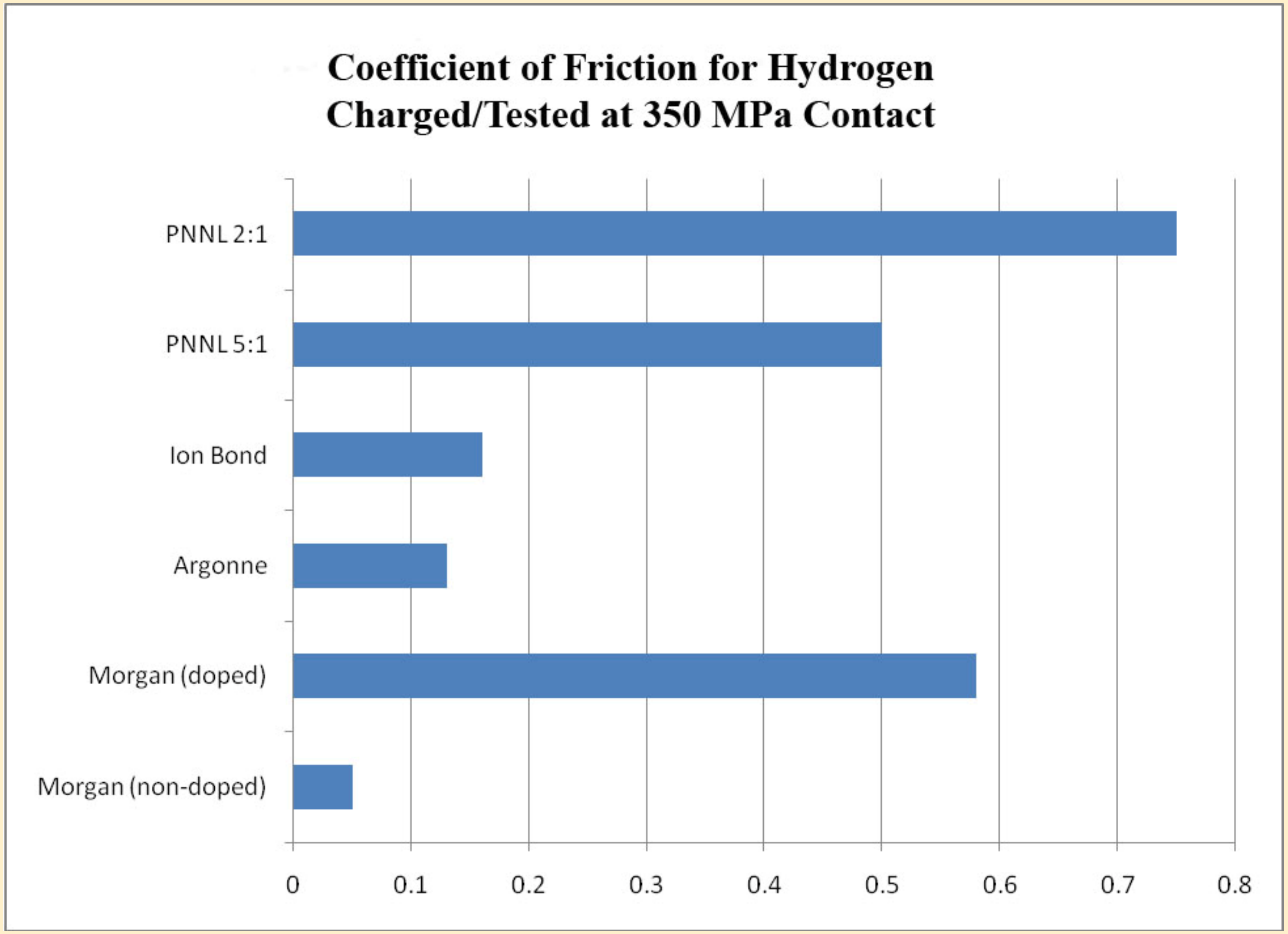
Deposition rate of each source individually controlled by applied power

Conditions chosen such that correct stoichiometry is produced with an identical ratio of reactive gas

# $Cr_xN$/BN Nanolaminate Summary

- **15 depositions (1A–1Q) to determine proper conditions for $Cr_2N$, CrN, and BN films**
- **Four depositions (1L,1P,1R,1S) of nanolaminates**
- **Nanolaminates performed poorly due to adhesion issues**
- **Revisited cleaning procedure and added the deposition of a chromium adhesion layer**
- **Four more single-layer deposition runs to test adhesion**
- **Four depositions producing** well-adhered nanolaminates:
  - **Two with 5:1 $N_2$ to Ar ratio (nominally Cr+*CrN/BN*)**
  - **Two with 2:1 $N_2$ to Ar ratio (nominally Cr+*$Cr_2N$/BN*)**

# Comparison tests at 350 MPa
## Coatings Hydrogen charged 100 hours



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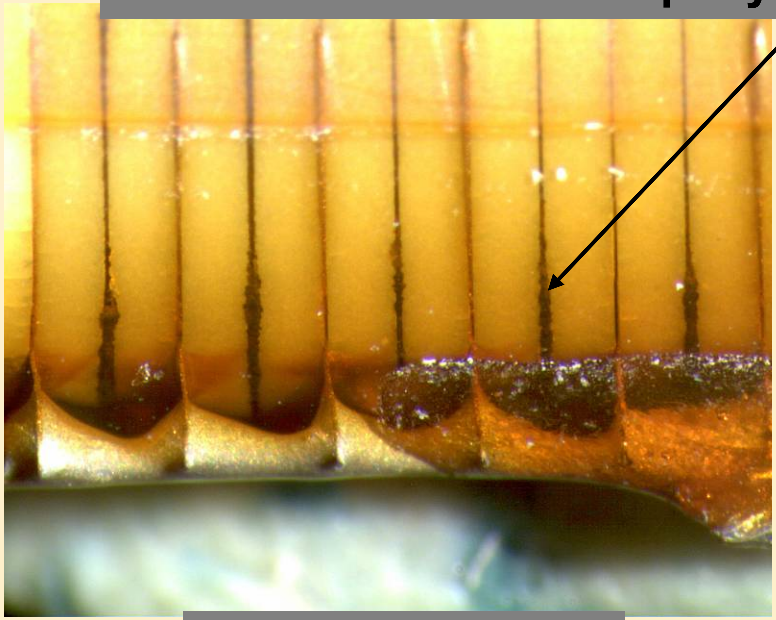
# Potential Failure Sites; Actuator

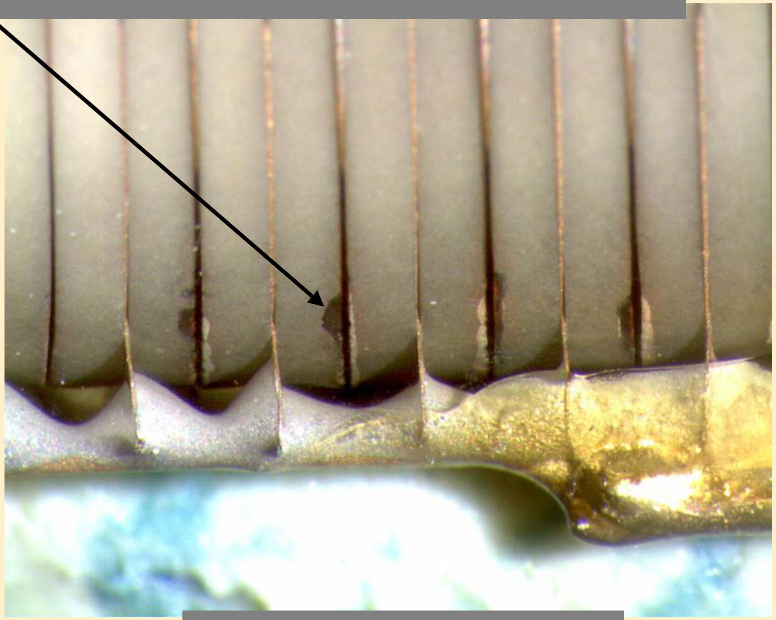
- **Actuator**
  - **Epoxy (dielectric) may break down due to elevated temperatures, hydrogen pressure, or during depressurization.**
    - **Suggested epoxy reformulation, evaluating pressure and depressurization effects.**
  - **Piezo Ceramics; hydrogen reacts with oxygen in PZT lattice to form OH-, resulting in reduced piezoelectric reaction.**
    - **Measurement of hydrogen diffusion in PZT**
    - **Modeling of the hydrogen/PZT interaction**

# Potential Failure Sites; Actuator

**Beginning of degradation (darkening) is corrosion-reaction with Cu-electrode and epoxy on alternate electrodes.**



**06-5028: 100C, $N_2$**



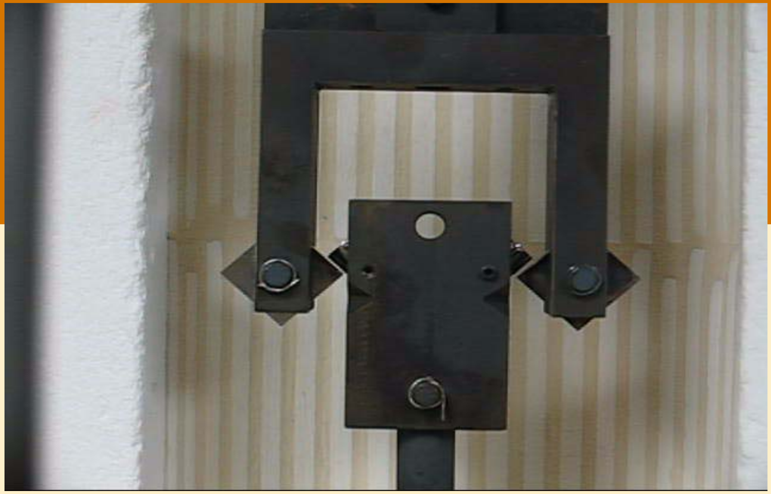
**06-5025: 100C, $H_2$**

**Main finding is that *Temperature plays major role, more important than Hydrogen*. However, high-pressure (4500 psi) hydrogen is clearly a more damaging environment at 100C.**

# Hydrogen Uptake and Transport Measurements and Modeling

- **Hydrogen uptake and transport is critical.**
  - **What is hydrogen uptake rate for PZT? Where is it trapped?**
- **Attempt to explore these issues via experimental and computational methods.**
  - **Experimental tools include:**
  - **Hydrogen charging (exposure)**
  - **Thermal desorption**
  - **Ion beam methods**
  - **Surface science tools**
  - **Nuclear Reaction Analysis (NRA) is used to probe for hydrogen in PZT and in injector materials with some depth selectivity.**

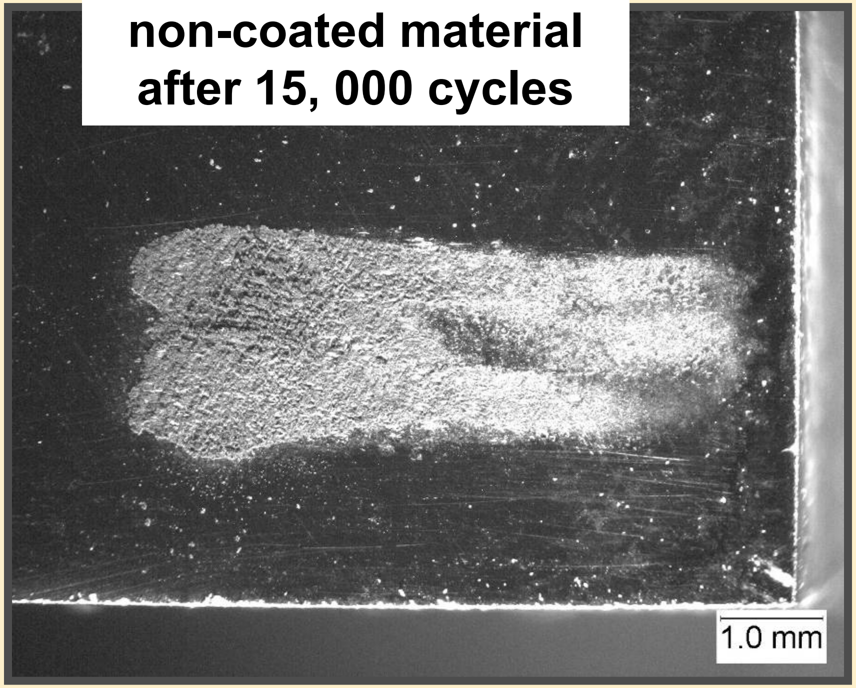
# Initial Sliding Wear Tests



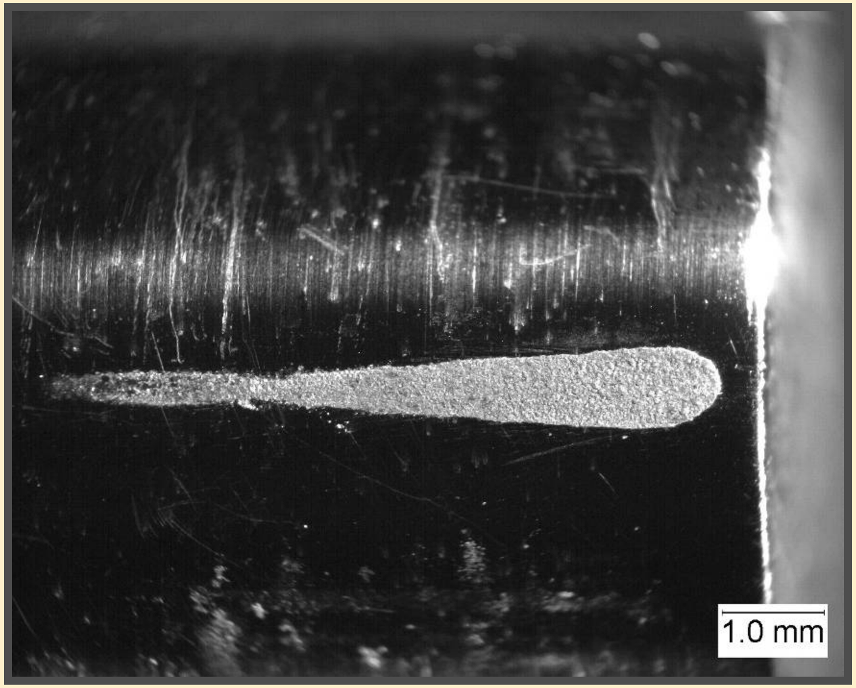
| Left block<br>matl | Right block<br>material | Load<br>(N) | Rate<br>(rpm) | Rate<br>(cyc/s) | Temp<br>(C) | Test length<br>(cyc) |
|---|---|---|---|---|---|---|
| **304** B4C/BCN 65 layer lam | **304** SiC/SiCN 65 layer lam | 29.6 | | | room | |
| **304** SiC/SiCN 65 layer lam | **304** B4C/BCN 65 layer lam | 29.6 | 115 | 1.9 | room | 5117+575 |
| **304** B4C/BCN 65 layer lam | **304** SiC/SiCN 65 layer lam | 29.6 | 115 | 1.9 | room | 4966 |
| **M2** SiC/SiCN 65 layer lam | **M2** B4C/BCN 65 layer lam | 29.6 | 115 | 1.9 | 300 | 5175 |
| **M2** B4C/BCN 65 layer lam | **M2** SiC/SiCN 65 layer lam | 29.6 | 253 | 4.2 | 300 | 10484 |
| **M2** BCN 16%N2 | **M2** SiCN 16%N2 | 29.6 | 40 / 152 | | 300 | 5014 |
| **M2** Cr+CrN/BN 2:1 N2/Ar 80 layer lam | **M2** Cr+CrN/BN 5:1 N2/Ar 80 layer lam | 29.6 | 180 | 3.0 | room | 15125 |
| **M2** Cr+CrN/BN 5:1 N2/Ar 80 layer lam | **M2** Cr+CrN/BN 2:1 N2/Ar 80 layer lam | 29.6 | 258 | 4.3 | 300 | 15000 |
| **M2** Argonne NFC DLC | **M2** Argonne NFC DLC | 29.6 | 258 | 4.3 | room | 15000 |
| **M2** Argonne NFC DLC | **M2** Argonne NFC DLC | 29.6 | 250 | 4.2 | 300 | 15157 |
| **M2** B4C/BCN 65 layer lam | **M2** SiC/SiCN 65 layer lam | 29.6 | 234-218 | ~ 3.8 | 300 | 14968 |
| **M2** SiC/SiCN 65 layer lam | **M2** B4C/BCN 65 layer lam | 29.6 | 235 | 3.9 | room | 1001 |
| Bare M2 | Bare M2 | 29.6 | 245 | 4.1 | room | 15002 |
| Bare M2 | Bare M2 | 29.6 | 245 | 4.1 | 300 | 15001 |

# Room temperature tests of non-coated M2 – 15,000 cycles

**Significant wear in non-coated material after 15, 000 cycles**

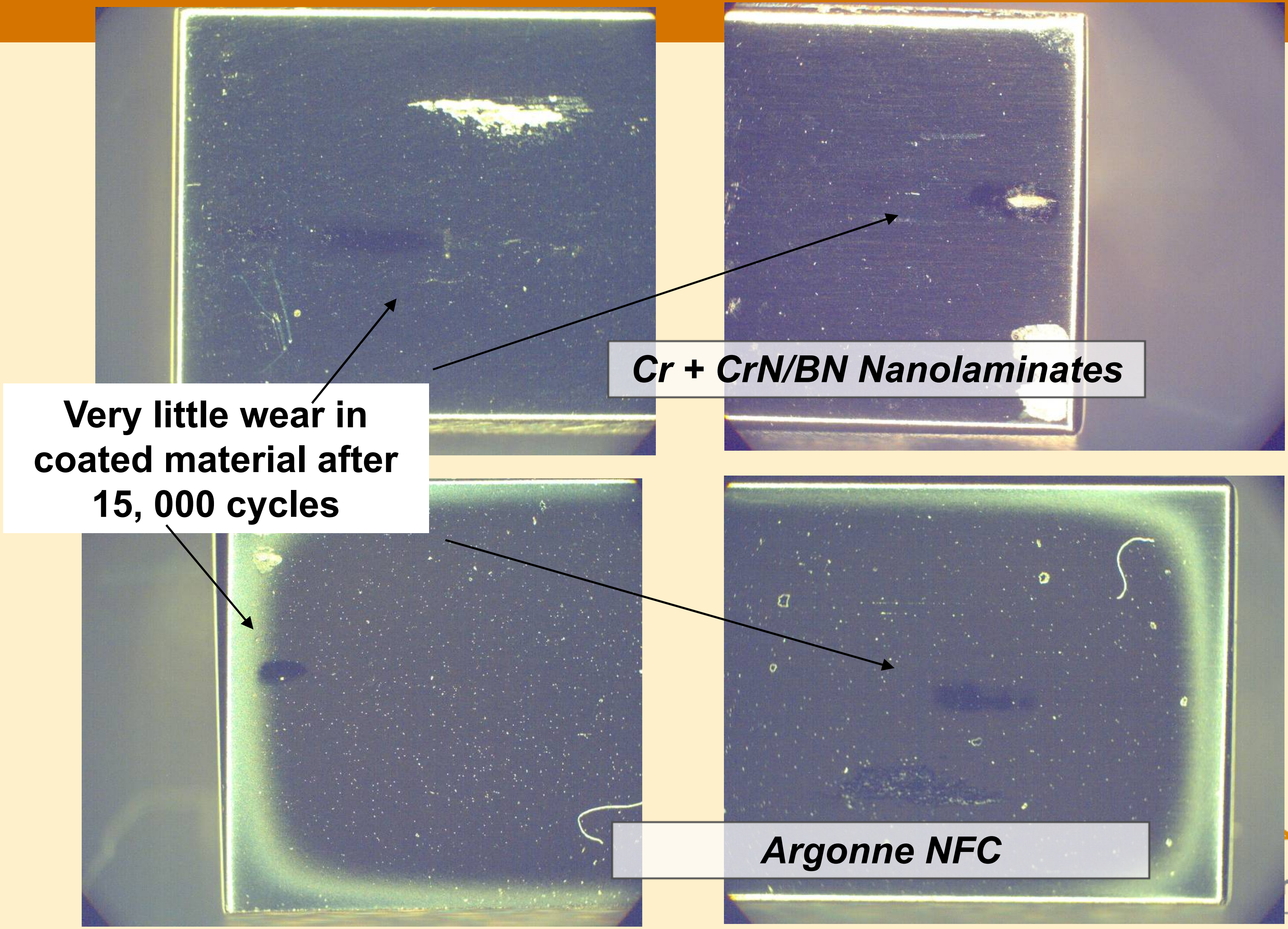


Block specimen pitted and covered with debris



Pin specimen wear zone

# Room Temperature Tests - 15,000 cycles



Very little wear in coated material after 15, 000 cycles

*Cr + CrN/BN Nanolaminates*

*Argonne NFC*

# Summary

- Sliding friction tests were conducted on bare tool steels (M2 and J10) and on surfaces coated with diamond-like carbon coatings and nanolaminate coatings. The following conclusions were obtained:
  - Diamond-like carbon coatings were shown to greatly improve scuffing resistance. A wide variation was observed between the coatings provided by three suppliers, and these differences are being explored using advanced analytical techniques.
  - PNNL has successfully created a suite of nanolaminate coatings that may be tailored to hydrogen applications, particularly where hard, impact resistant surfaces are needed.

# Summary, continued

- PNNL has worked with ORNL to further develop the sliding-impact test apparatus.  The test shows promise but it is felt that additional work will be necessary before quantitative data is obtained.

# Technical Accomplishments

- In 2008, the Ford Hydrogen Internal Combustion Engine attained 45% Brake Mean Efficiency Power, a milestone for the H-ICE Program.  PNNL efforts to eliminate direct fuel injector leakage contributed directly to this automobile industry milestone.  PNNL research and development efforts continue toward the 10000 hour durability target for injector actuators, needle-nozzle hardware, and injector system actuation accuracy.

# Work for FY ‘09

- Use advanced analytical techniques to support a model for hydrogen diffusion in piezoelectric ceramics and polymeric materials.  Use this model to assist in the development of robust actuators for hydrogen service.
- Continue testing of diamond-like carbon coatings and nanolaminate coatings charged in hydrogen up to 1000 hours.