2010 DOE Vehicle Technologies Program Review
Hydrogen Materials Compatibility for the H-ICE

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Project ID # **PM019**

Overview

Timeline

- Project start date: FY 06
- Project end date: FY 10
- Percent complete: 90 percent

Budget

- Funding received in FY09: $300K
- Funding for FY10: $300K

Partners

- Westport Innovations
- Ford Motor Co. (FY06-FY09)

Barriers

- Barriers addressed
  - 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.

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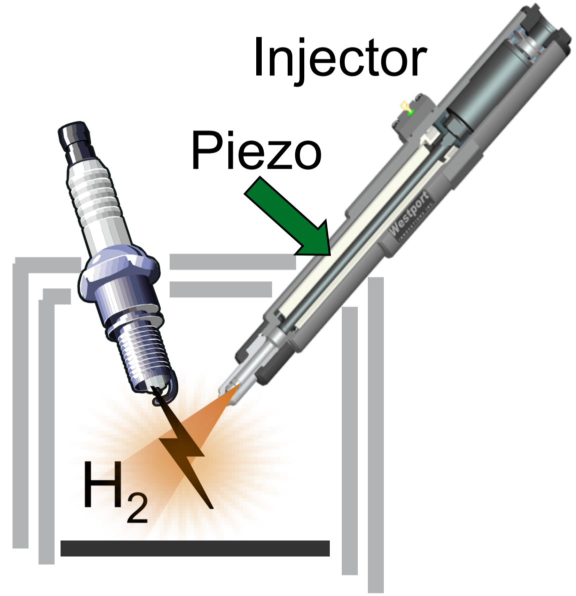
Relevance:
Direct Injection HICE Technology

- Hydrogen is a clean burning fuel for vehicle or stationary power
- Hydrogen internal combustion (HICE) engines fill short term need while fuel cells are perfected.
- While ICE is a mature, efficient technology, hydrogen materials compatibility is a challenge.
- For direct HICE engines, a piezoelectric actuator injects the hydrogen into the engine resulting in lower pollution and ~ 20% higher efficiency than port injection.



- Piezoelectric devices fail in high pressure hydrogen atmospheres limiting device reliability, as with FERAM (ferroelectric RAM)
- Basic understanding of hydrogen behavior in piezoelectrics is needed
- Improved Coatings for reduced friction and wear are required

Relevance:
Objectives

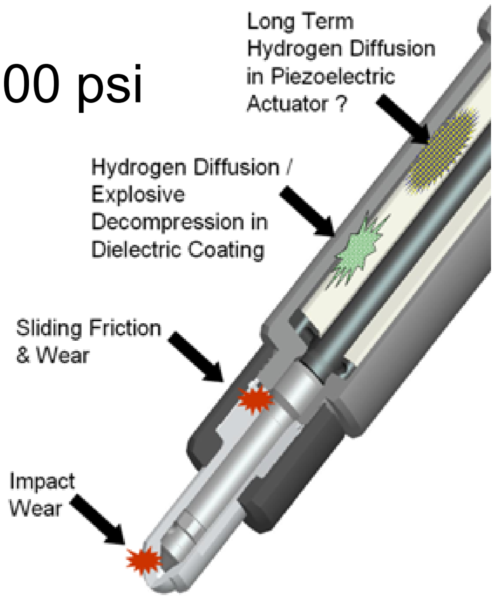
- Improve the durability and performance of fuel injectors for use in direct-injection hydrogen internal combustion engines by evaluating failure modes of piezoelectric materials, coatings, and connectors in high-pressure hydrogen gas
- Characterizing actuator performance in hydrogen and developing new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

Milestones

- **M1**—Establish a model for hydrogen absorption and desorption in lead zirconate titanate (PZT) (and/or BaTiO3) at various temperatures and hydrogen pressures under conditions relevant to injector applications. Verify key parameters using ion scattering techniques, including Elastic Recoil Detection Analysis (ERDA) and Nuclear Reaction Analysis (NRA). (May 1, 2010)
- **M2**—Use Quasi-elastic Neutron Scattering (QENS) to develop a diffusion model for hydrogen in various piezoelectric materials as a function of temperature and use this model to predict the failure of PZT (and/or BaTiO3) actuators under conditions relevant to injector applications. (Sep 30, 2010)
- **M3**—Produce novel coatings on prototypic injector components. Characterize and evaluate the essential characteristics of the coatings in anticipated service conditions. (Sep 30, 2010)

Overall Approach

- Long term Goal: Advance injector Technology by addressing critical issues in
  - Hydrogen degradation in piezoelectric materials
  - Improving Impact and sliding wear and friction
- Hydrogen Degradation in Piezoelectrics
  - High Pressure Hydrogen testing at PNNL up to 5,000 psi
  - Simple thin film piezo samples to isolate effects
  - Ion scattering to measure hydrogen uptake
  - Neutron Scattering to measure hydrogen diffusion
  - Numerical Modeling to complement experiment
- Improving Sliding and Impact wear and friction
  - Development and evaluation of CrN and BN nanolaminates for improved tribological characteristics



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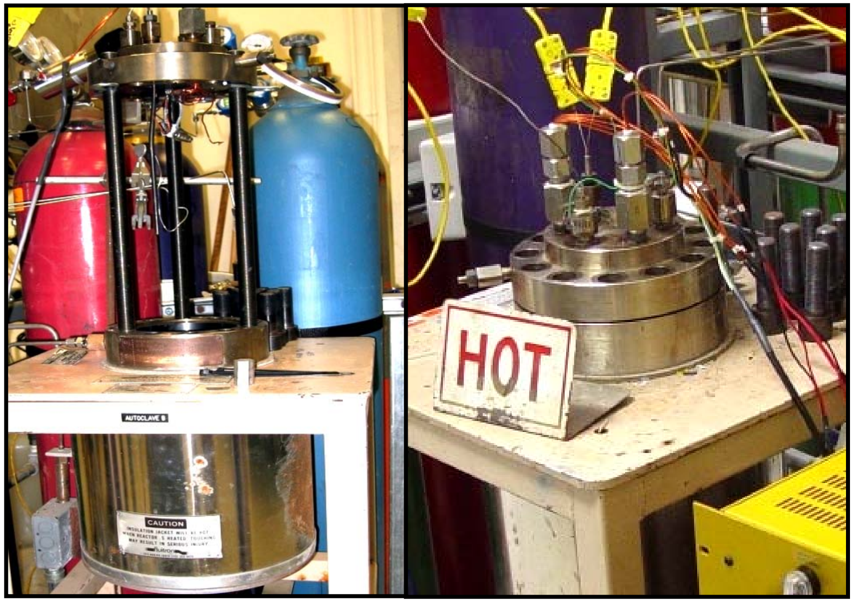
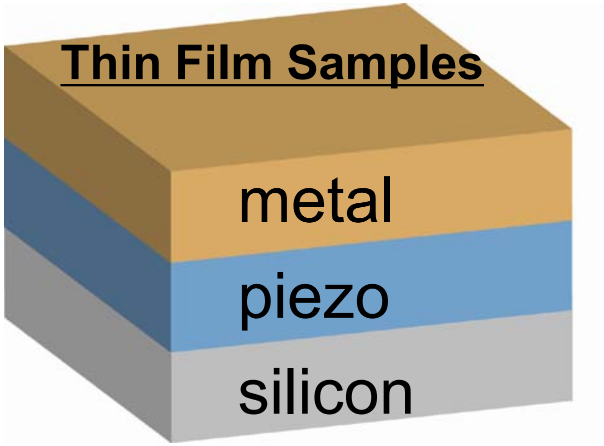
Approach:
Piezoelectric Degradation (Hydrogen Charging)

- Samples charged in High Pressure Autoclave
- 100% H_2 or D_2
- Up to 5,000 psi (345 bar)
- Temperatures up to 300 C
- Designed to simulate real injector conditions
- Large samples possible





- Thin film piezoelectric samples made via sputter coating
- $PbZr_{0.5}Ti_{0.5}O_3$ (PZT) and $BaTiO_3$ materials used
- Metal electrodes

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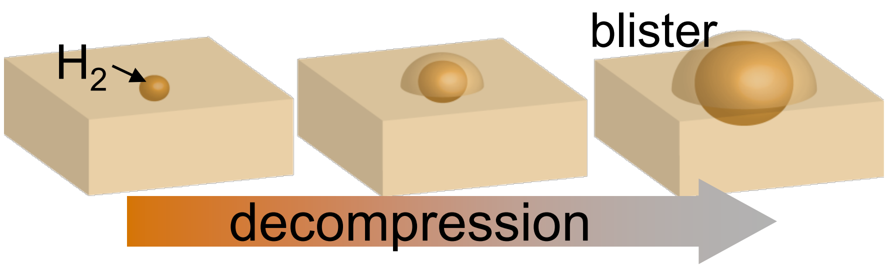
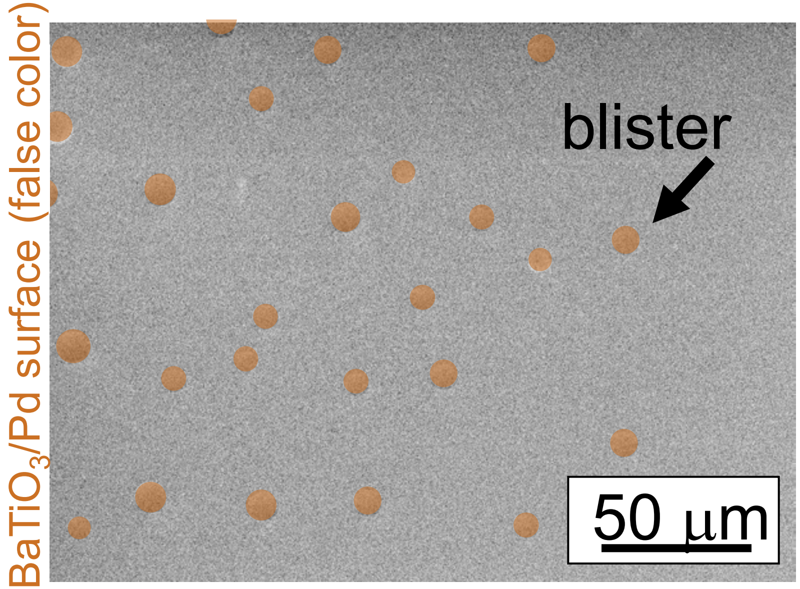
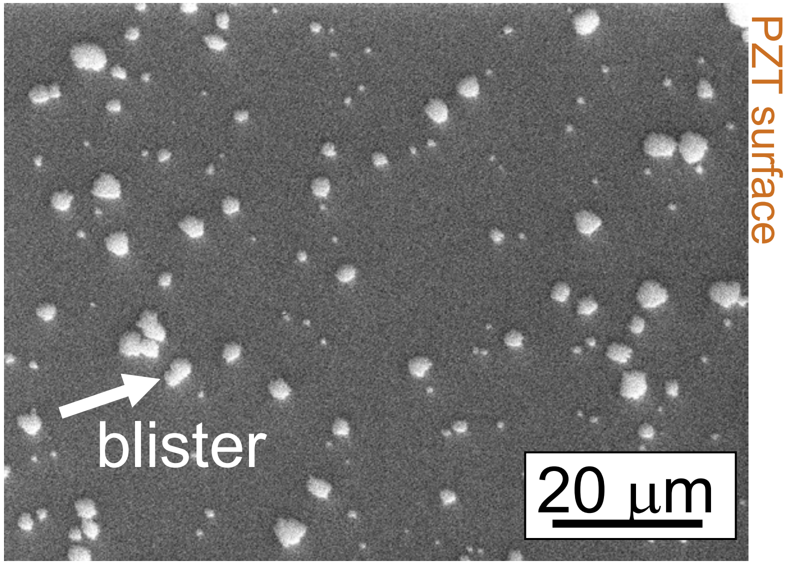
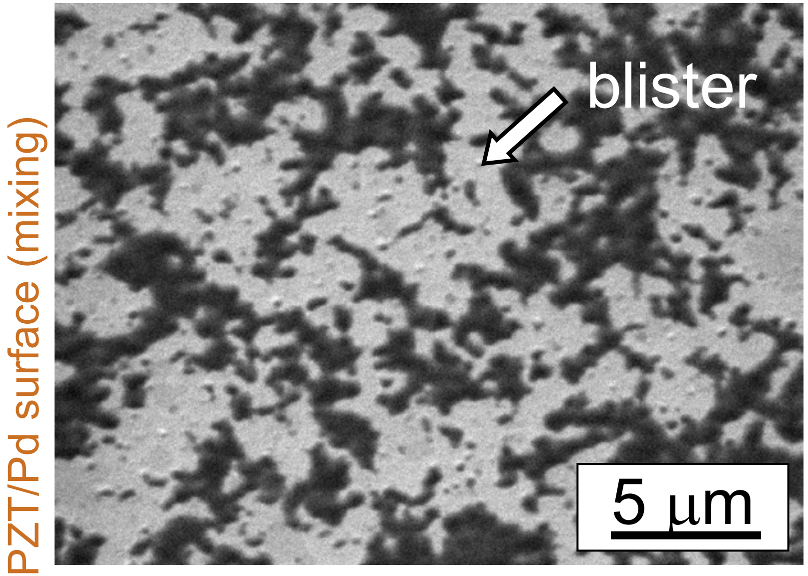
Technical Progress:
Piezoelectric Surface Degradation

- H_2 charged samples show surface blistering except $BaTiO_3$
- PZT/Pd H_2 charged surface shows Pd/Pb mixing (confirmed with RBS)

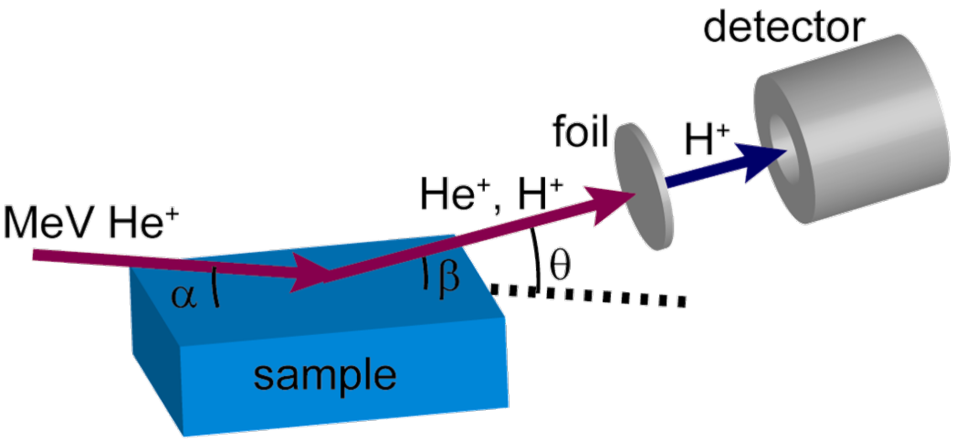




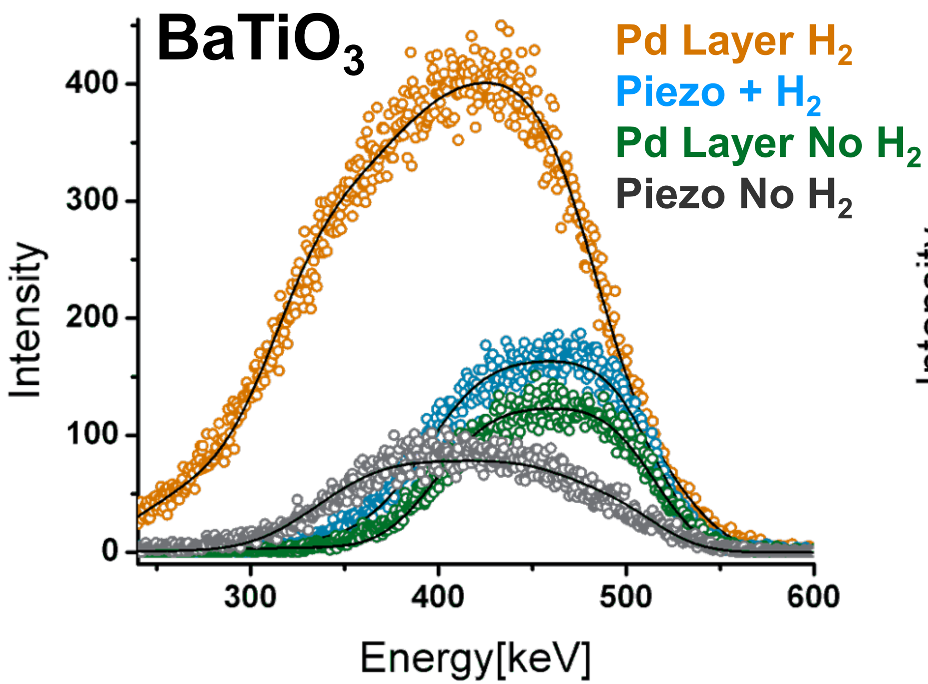


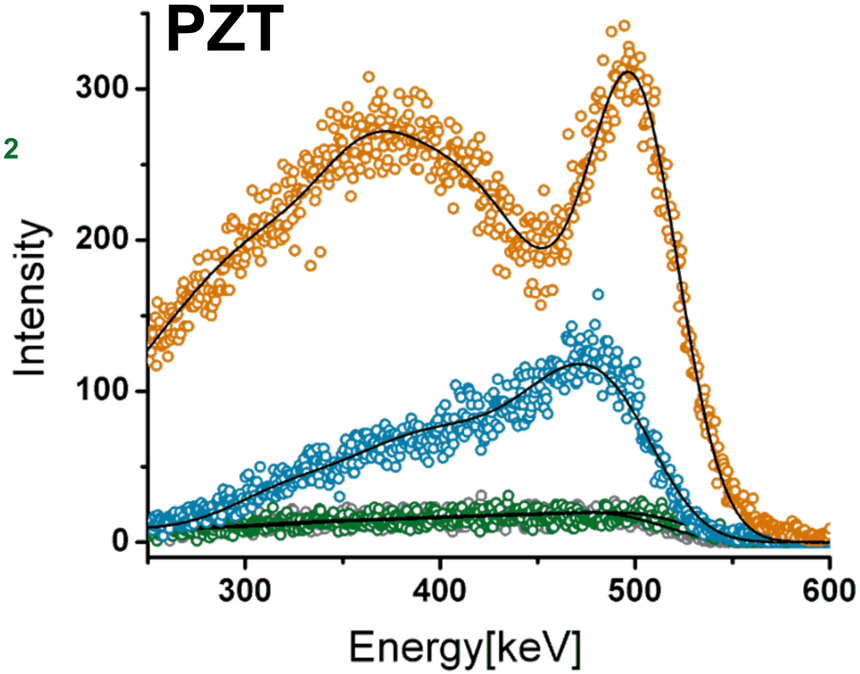


Approach:
Piezoelectric Hydrogen Absorption (Ion Scattering)



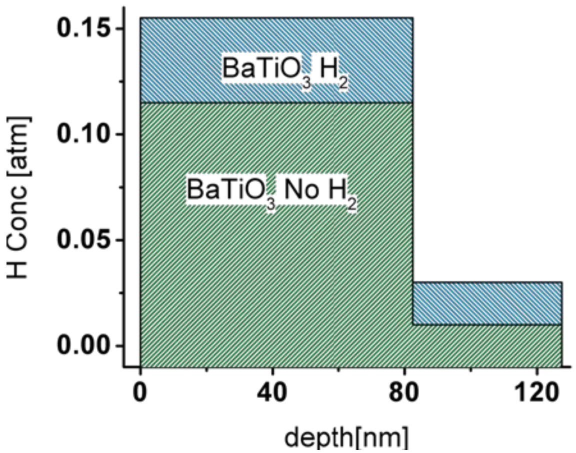
- Elastic Recoil Detection Analysis (ERDA) ion scattering is sensitive to hydrogen
- Hydrogen depth profiling of charged and control samples

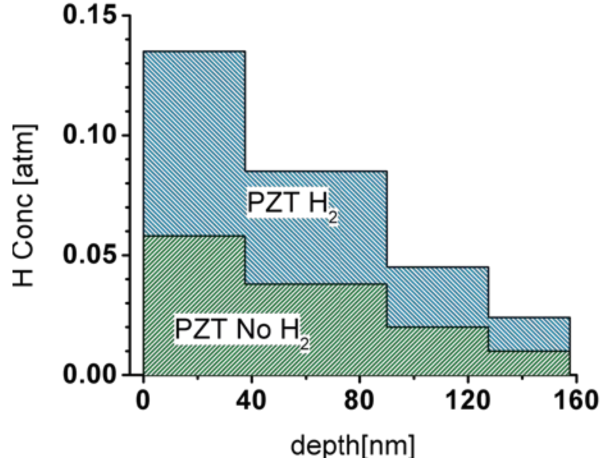




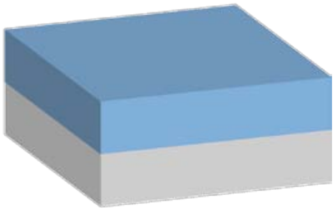
Technical Progress:
Piezoelectric Hydrogen Depth Profiles

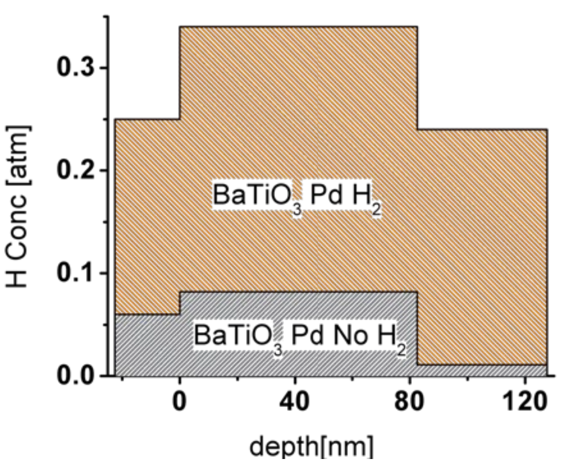
- Fits of ERDA spectra give hydrogen depth profiling
- Compared with control (uncharged sample) for residual hydrogen

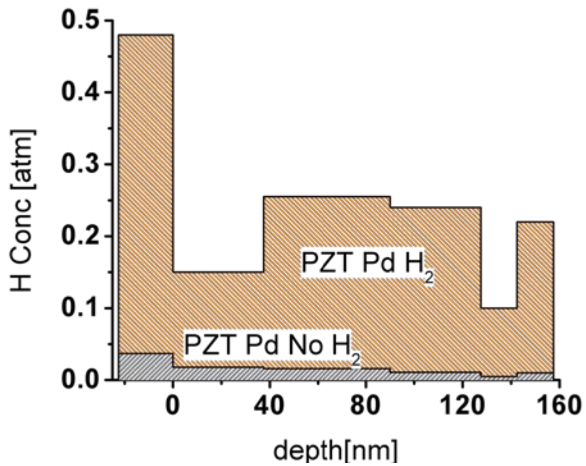




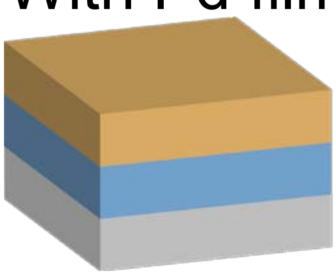
Piezo film only







With Pd film



Approach:
Neutron Scattering Studies of H_2 in Piezoelectrics

Why Neutrons?

- Scattering Cross-Section varies greatly among the elements/isotopes!
- Hydrogen strongly scatters neutrons (invisible to X-rays)
- Neutron techniques can measure dynamics as well.

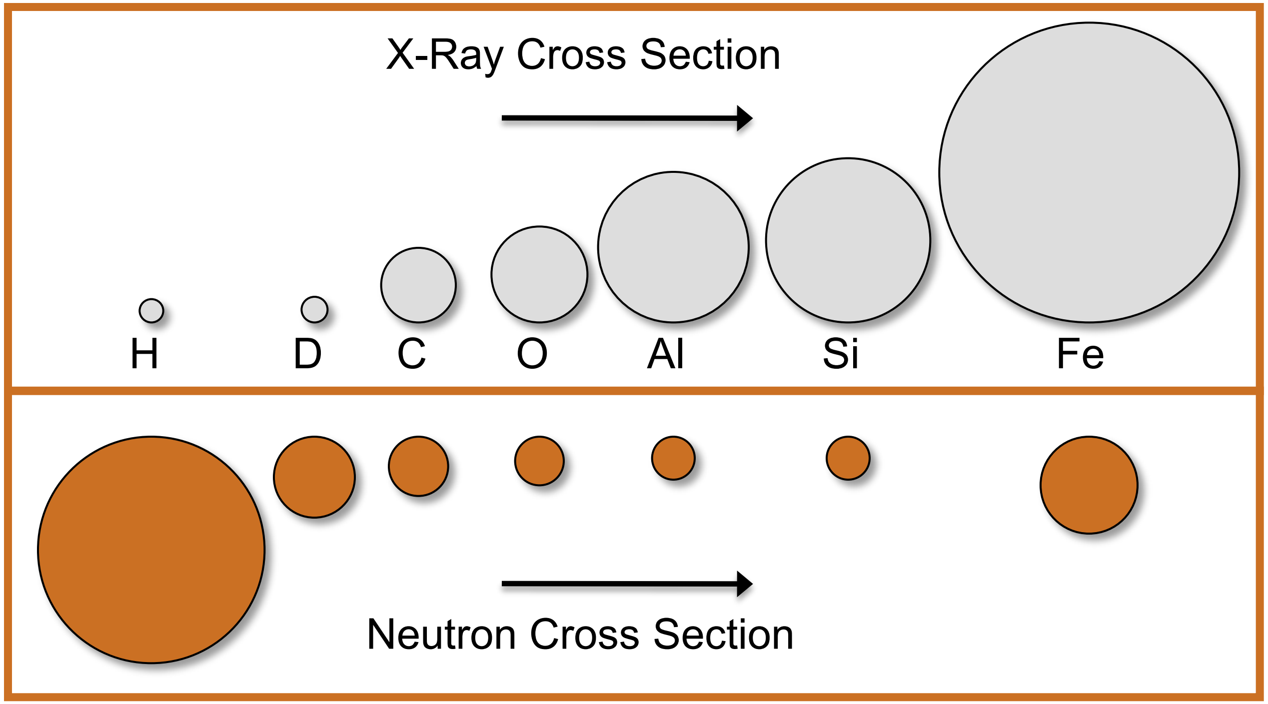
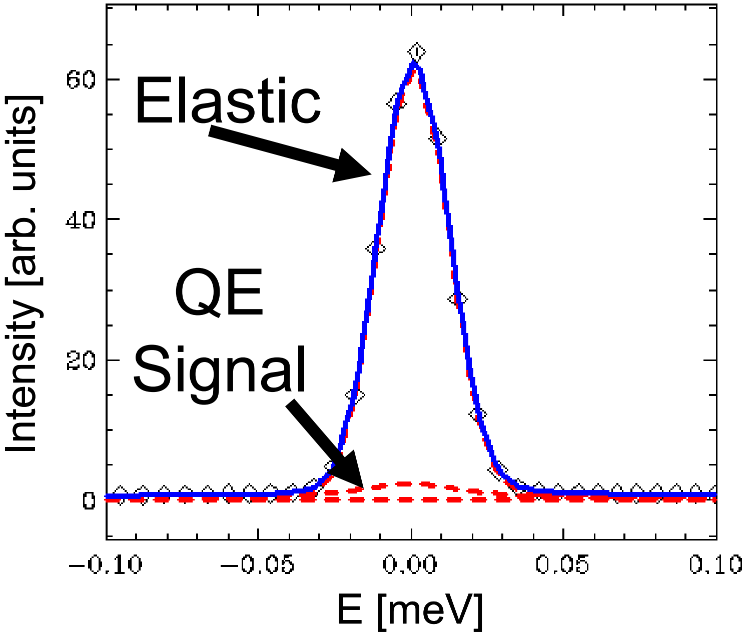


*Figure adapted from NIST NCNR website

Technical Progress:
Piezo Hydrogen Diffusion (QENS)

- Dearth of information about diffusion within piezoelectrics
- Quasi-Elastic Neutron Scattering (QENS) directly measures hydrogen diffusion within materials
- Neutrons very sensitive to hydrogen
- Measured diffusion process for PZT and $BaTiO_3$ at different temperatures
- May be other diffusion processes for these materials



PZT

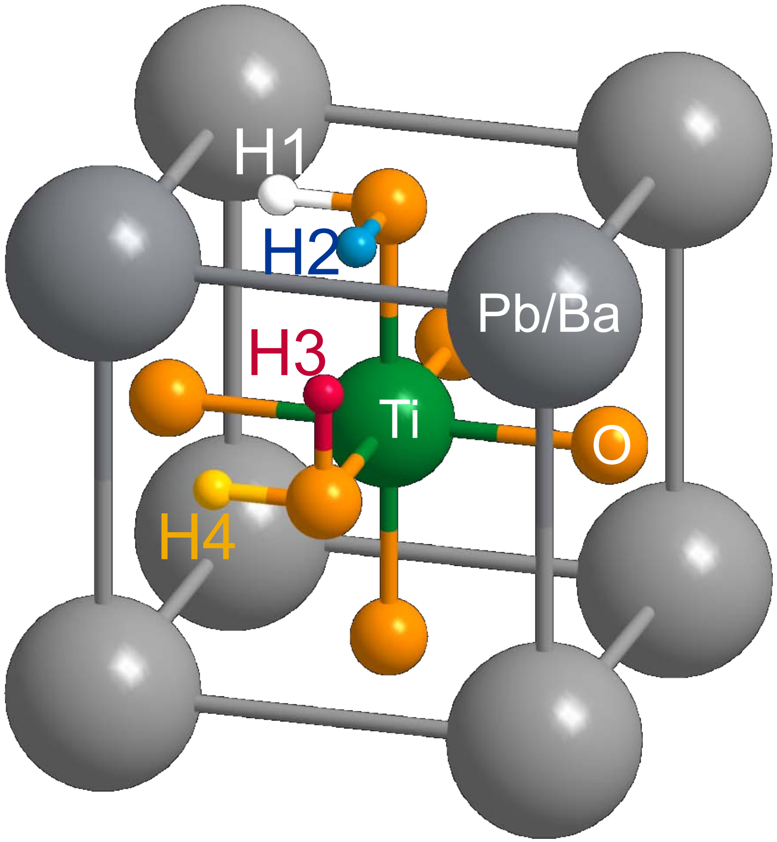
T [K]	D [10^{-9} m^2/s]
250	0.49 ± 0.01
300	0.52 ± 0.08
350	0.78 ± 0.42
380	1.11 ± 0.58

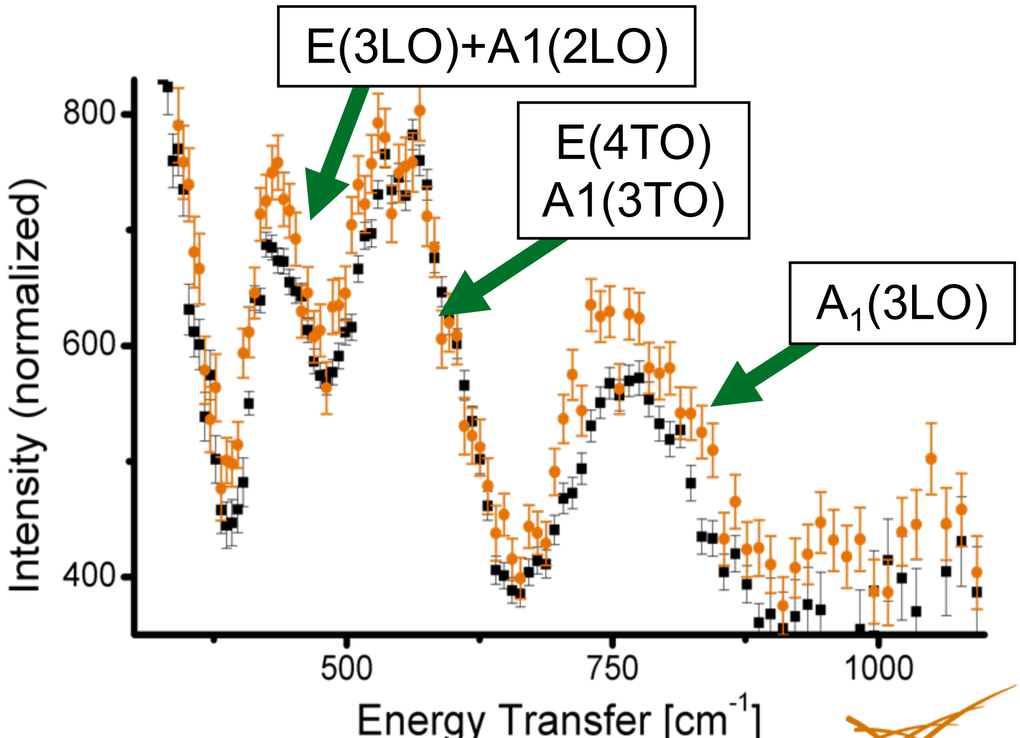
$BaTiO_3$

T [K]	D [10^{-9} m^2/s]	τ [10^{-9} s]	L[Å]
250	0.14 ± 0.04	0.12± 0.02	3.2
300	0.47 ± 0.13	0.11± 0.01	5.6

Technical Progress:
Piezoelectric Local Hydrogen Environment

- Hydrogen is theorized to adsorb in the OH form
- OH bond expected to be in the Pb or Ba plane
- Filter Analyzed Neutron Spectroscopy (FANS) shows enhancement of Ti-O or Zr-O vibrations indicating H bound to oxygen as expected





Summary:
Piezoelectric Hydrogen Compatibility

- High pressure hydrogen is readily absorbed into piezoelectrics in the range of 4% concentration at 2,400 psi and 100 C
- The presence of metal over-layers (Pd) greatly enhances hydrogen absorption to 10 to 20% concentration at 2,400 psi and 100C
- Qualitative difference in absorption between PZT and $BaTiO_3$
- Surface degradation, including blistering and Pb diffusion is observed with blistering being stronger in the case of PZT
- FANS measurements corroborate theory that hydrogen resides on oxygen within the lattice via increased vibrational signal
- QENS measurements indicate rapid diffusion with a jump length of approximately 3 Å. Other diffusion processes may also exist
- Future work will explore adsorption/desorption (P,T) and other diffusion processes

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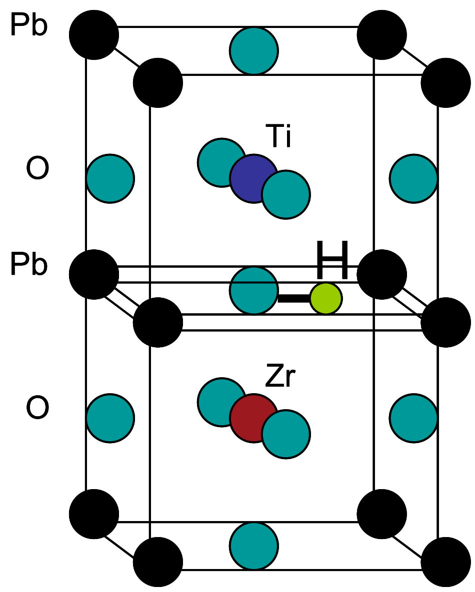
Approach:
Numerical Modeling of H_2 Piezoelectric Behavior

- Use Density Functional Theory to predict H absorption/diffusion
- Goal to develop further understanding of H absorption diffusion and means to mitigate or reverse degradation
- Complements Experimental Efforts



Preliminary Results:

- H prefers Zr-rich environment
- H acts as a donor (spontaneously ionizes) implies Proton Diffusion
- Activation Barrier Calculations in progress

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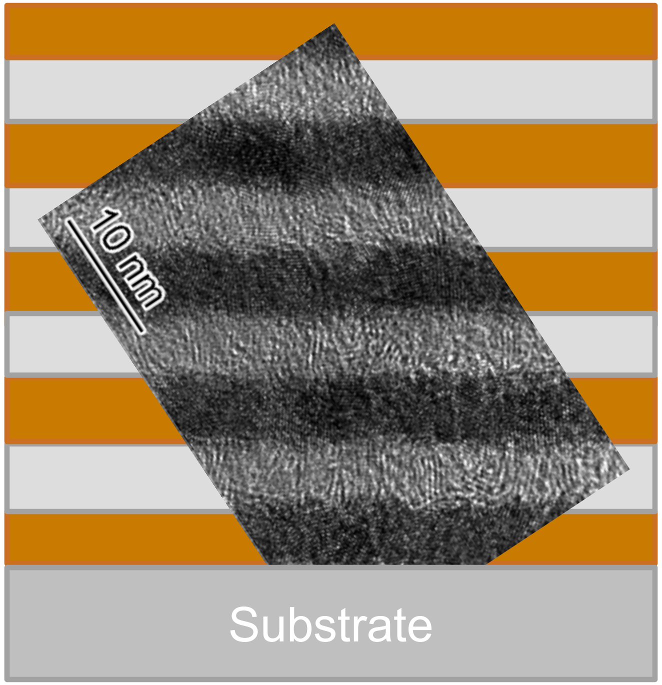
Approach:
Nanolaminates for Improved Wear Resistance

- 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 a “best-of-both-worlds” scenario
- Mature technique for producing nano-structured materials
- Tasks:

  1. Design and fabricate nanolaminate coating materials applicable to H_2-ICE systems.
  2. Measure the friction / wear characteristics of injector materials in hydrogen environments (*in-situ* and *ex-situ*).



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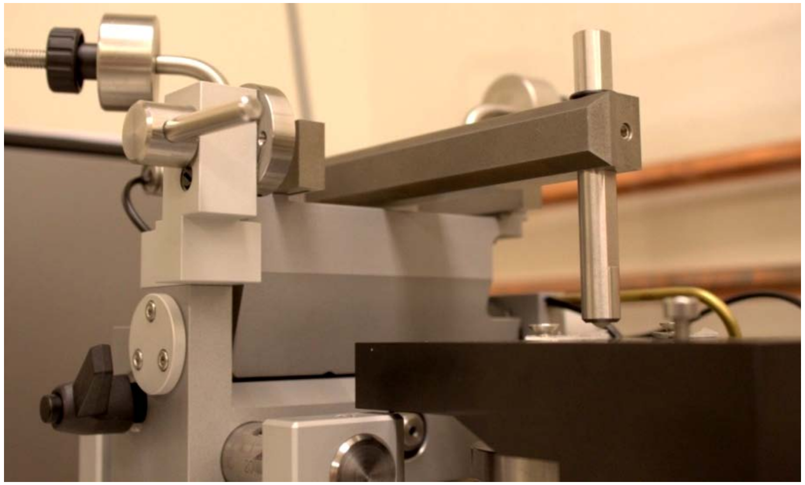
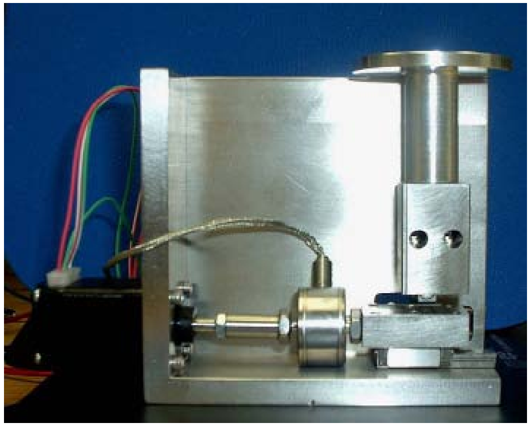
Approach:
Tribological Measurements on Nanolaminates

- Two tribometers are being used to evaluate lubricity and wear characteristics of Cr/N and B/N nanolaminates.
- A total of 93 tests were conducted in argon, hydrogen, and air. Due to a relatively high variability, refinements have been made to the test fixture.
- Coatings were tested using similar loadings in reciprocating tribometer, and testing is now focusing on an argon environment so that tribological characteristics can be optimized.





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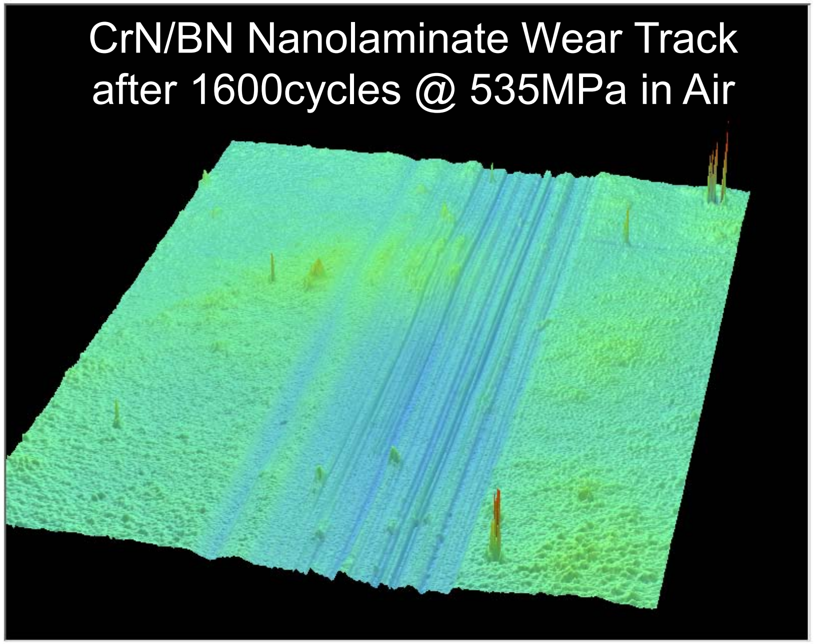
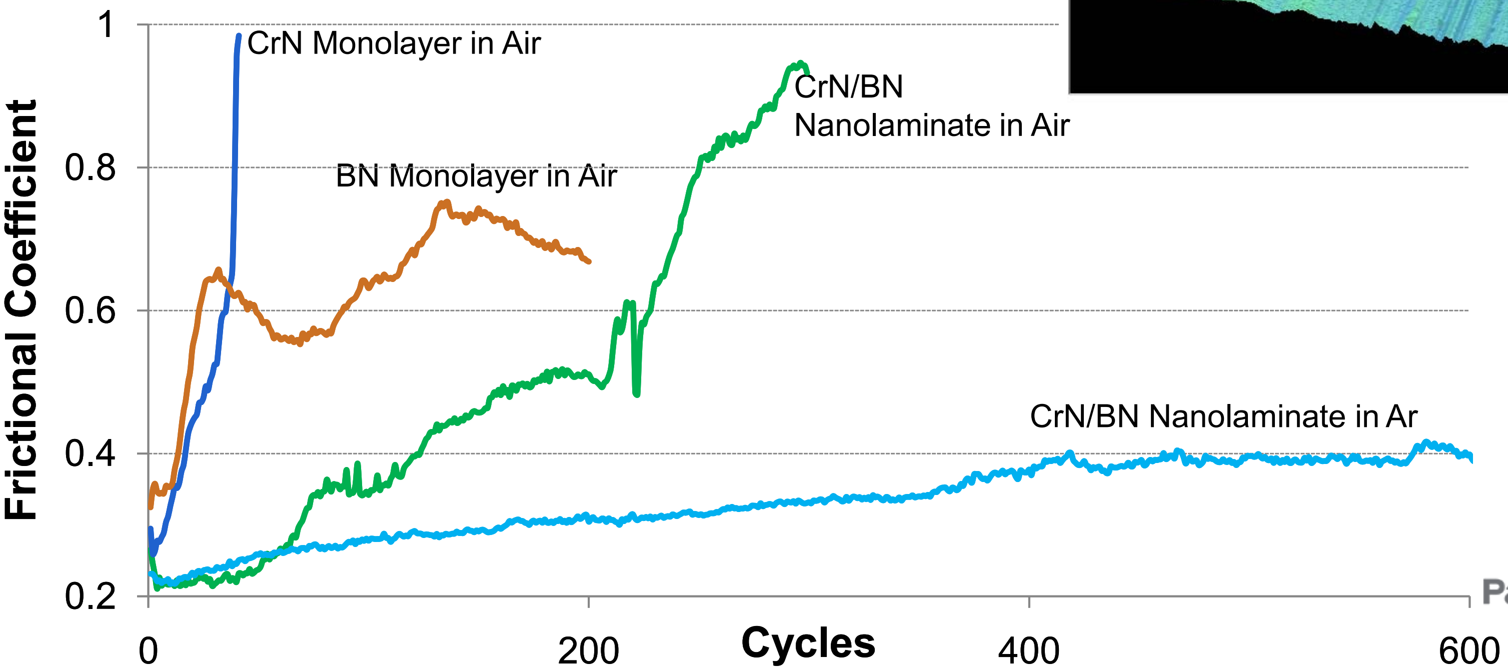
Technical Progress:
Nanolaminate Tribology

- Nanolaminates had superior tribological properties relative to the individual monolayers
- Nanolaminate characteristics are modified for improved triboligical properties before final evaluation in hydrogen gas.





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Collaborations

- **Pacific Northwest National Laboratory**
  - Prime contractor within the DOE VT program
  - FFRDC, National Laboratory
  - Hydrogen Piezoelectric degradation testing
  - Nanolaminate advance wear and sliding friction studies
- **Westport Innovations**
  - Industrial partner
  - Work on improved barrier coatings for actuators
  - Supply actuators for Ford Motor Co. test cells
  - Providing industrial perspective and consultation

Proposed Future Work (FY10 & FY11)

- Complete model of hydrogen absorption in piezoelectrics as a function of temperature, pressure, and electrode material based on ion scattering experiments
- Investigate means and extent of piezo degradation reversal by performing hydrogen desorption studies with ion scattering
- Investigate means and extent of mitigation of H_2 damage by investigating potential improve H_2 barrier materials over the current epoxy.
- A statistically-designed experiment is underway (FY 10) to optimize coating deposition parameters and to evaluate the effects of hydrogen charging on the wear characteristics. The following variables are being evaluated in CrN/BN Nanolaminates:

Item	High	Low
Deposition Environment	5:1	2:1
Ion Assisted Deposition	Yes	No
Charged (Hours)	300	0
Machine	CSM	Home
Test Environment	Argon	H2 or Air
Contact Stress	600MPa	300MPa
Speed (cm/S)	0.5	2.0

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Project Summary

- Relevance: Improved performance and reliability of fuel injectors for Hydrogen Internal Combustion Engines.
- Approach: Evaluate kinetics and mechanism for deterioration of piezoelectric materials by hydrogen and examine potential remedies: Develop and evaluate novel coating methods for improved actuator reliability.
- Technical Progress: Used experimental and modeling methods to evaluate hydrogen damage in lead zirconium titanate (PZT), and developed improved nanolaminate coatings for application in high-wear areas of actuators.
- Collaborations: Partnered with Westport International and Ford Motor Co.
- Future work:
  - Complete evaluation of hydrogen damage in PZT, and recommend potential remediation methods.
  - Complete statistically-designed experiments of Cr/N and B/N coatings in argon and in hydrogen.

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