

2011 DOE Vehicle Technologies Program Review Hydrogen Materials Compatibility for the H-ICE

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5/10/2011

Project ID #
PM019

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Overview

Timeline

- ▶ Project start date: FY 06
- ▶ Project end date: end FY11
- ▶ % complete: 50% (this FY)

Budget

- ▶ Funding received in FY10: \$300K
- ▶ Funding for FY11: \$100K

Partners

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

Barriers

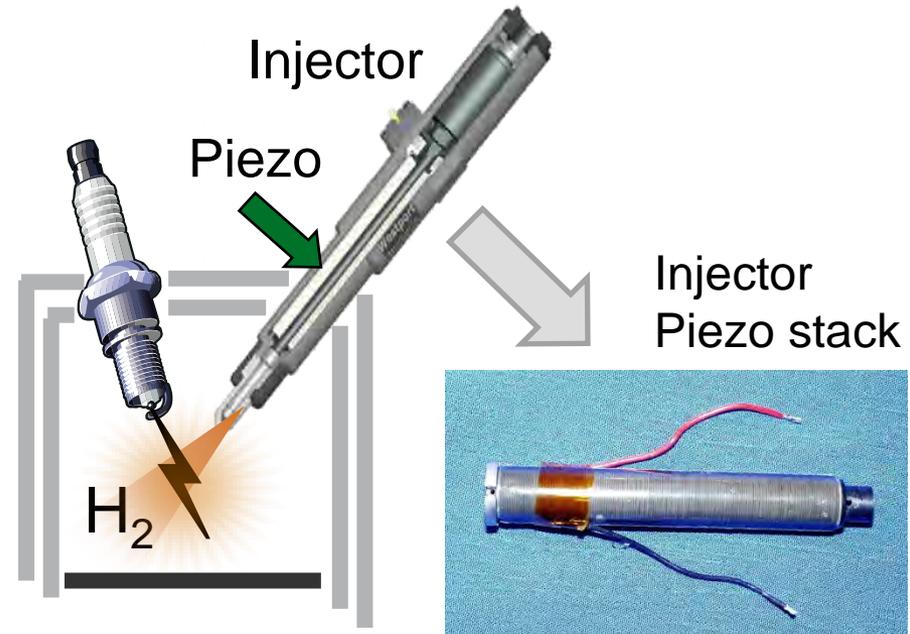
- ▶ Hydrogen materials compatibility for injector components of H2 internal combustion engine (H-ICE)
 - Piezoelectrics fail in high pressure hydrogen environment

Objectives & Relevance:

H2 Materials Compatibility Piezo Fuel Injectors

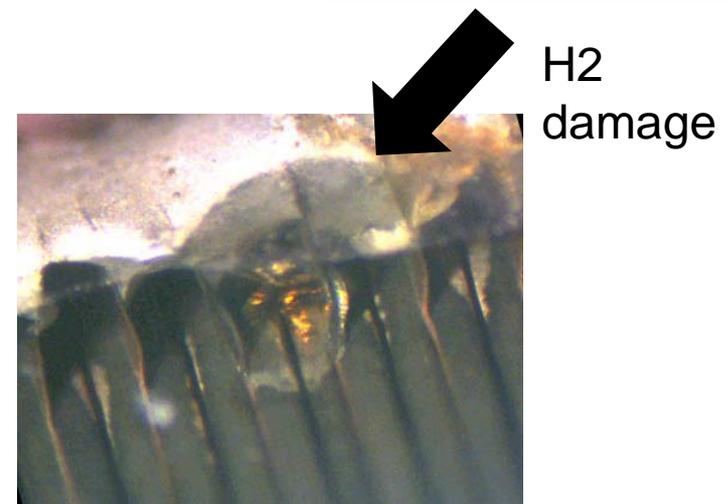
Challenges

- ▶ Non-petroleum based ICE's with higher thermal efficiency are sought
 - ▶ Direct injection hydrogen ICE (H-ICE) have demonstrated 45% brake thermal efficiency (Ford 09)
- ▶ Gaseous fuels such as H₂ can seriously damage or degrade ICE components



Objectives

- ▶ To determine H₂ materials compatibility of piezoelectric injectors
 - ▶ H₂ absorption
 - ▶ Degradation/damage
- ▶ Evaluate improved materials compatibility through materials selection

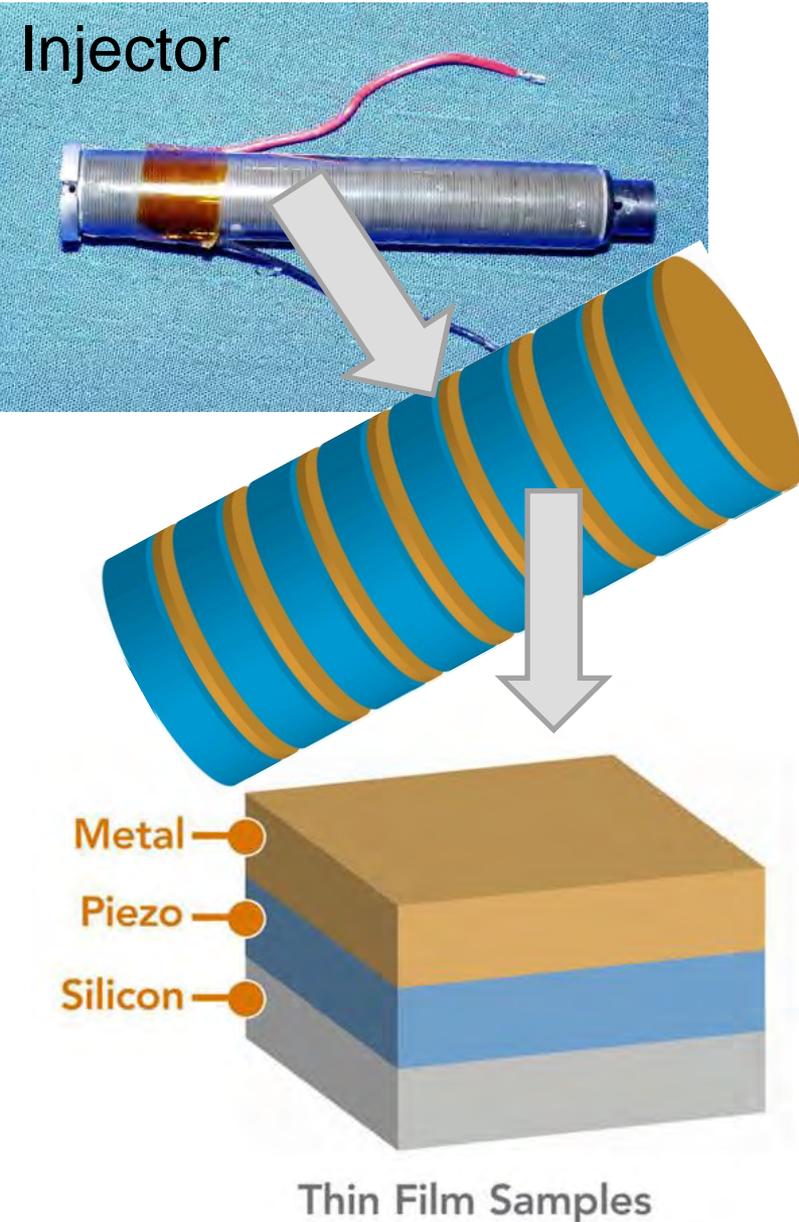


Milestones FY11

- ▶ **M1** - Evaluate effects of electrode metal selection on high pressure H₂ induced piezoelectric damage with Elastic Recoil Detection Analysis (ERDA) ion scattering technique.
- ▶ **M2** – Evaluate hydrogen damage to piezo/metal stack with SEM including surface diffusion of Pb or other elements.
- ▶ **M3** – Evaluate H diffusion in lead zirconate titanate (PZT) and barium titanate (BTO) with nuclear magnetic resonance (NMR) measurements to act as a check for previous neutron results.
- ▶ **M4** – Present results and findings at AMR meeting.

Approach:

Hydrogen Induced Injector Piezo Damage



H2/Piezo Compatibility

- ▶ Evaluate H2/Piezo compatibility
 - ▶ Thin films made to simplify system
 - ▶ High Pressure H2 charging
 - ▶ Surface Damage
 - ▶ Blistering, Pb diffusion
 - ▶ H2 absorption/diffusion
 - ▶ Evaluate different electrode materials



Approach:

Materials Evaluation: Piezo & Electrode tests

Samples

- ▶ Evaluating different piezoelectrics and electrodes
 - ▶ Goal to mitigate H₂ induced damage
- ▶ Piezoelectrics
 - ▶ PZT (PbTi_{0.5}Zr_{0.5}O₃)
 - ▶ BTO (BTiO₃)
- ▶ Metal Electrodes: Chosen to span the range of H₂ activity.
 - ▶ Copper (currently used in injectors)
 - ▶ Palladium
 - ▶ Tungsten
 - ▶ Titanium
 - ▶ Aluminum
- ▶ Samples charged 1 week, 4,700psi H₂

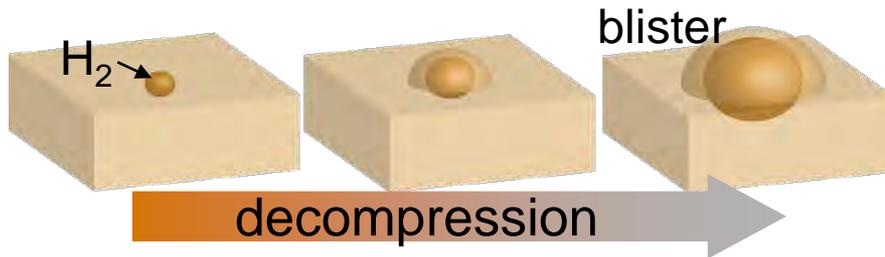
Metal	ΔH	$\Delta S/k$	$C^* \sim \text{Exp}(\Delta S/k - \Delta H/kT)$
Al	0.7	-6	4.1×10^{-15}
Ti (hcp/bcc avg.)	-0.6	-6.5	3.4×10^7
Zr (hcp/bcc avg.)	-0.7	-6	4.0×10^8
W	1.1	-5	4.1×10^{-21}
Pd	0.1	-7	1.9×10^{-5}
Cu	0.4	-6	9.7×10^{-11}
Pb values not found, solubility thought to be negligible.			*Note: C is proportional to the H concentration

Data from Y. Fukai, "The Metal-Hydrogen System", 2nd ed, Springer (2005)

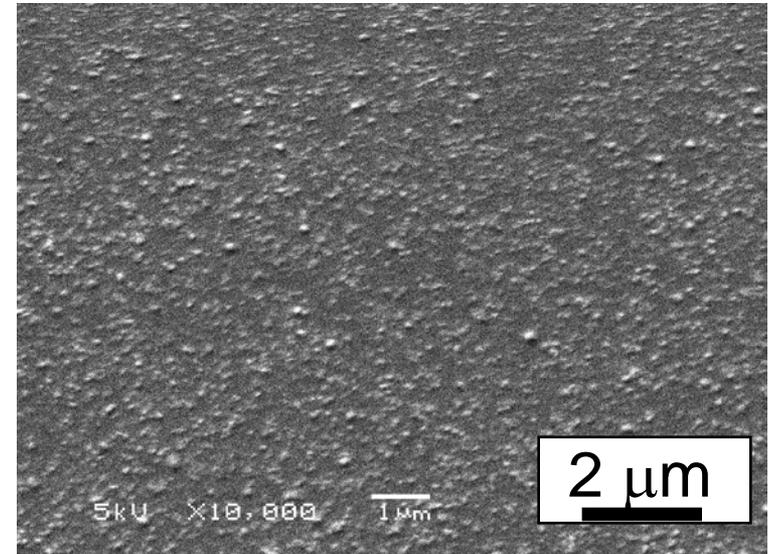
Technical Progress:

Piezoelectric Surface blistering

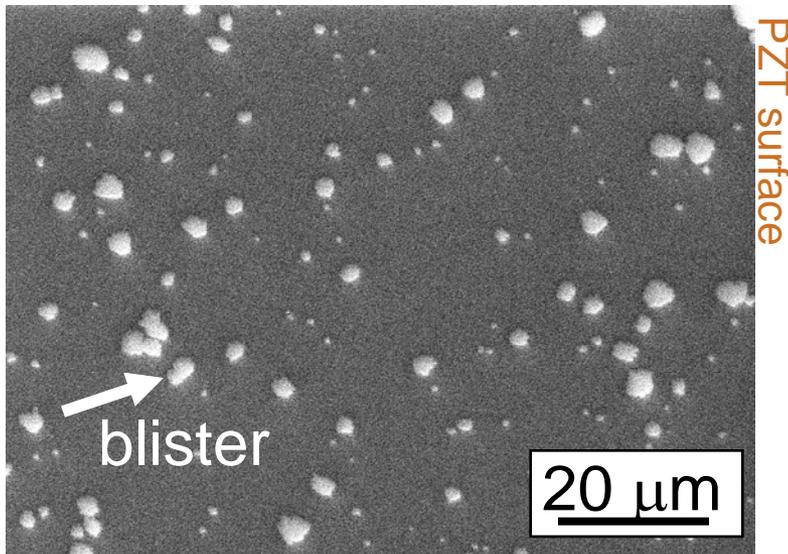
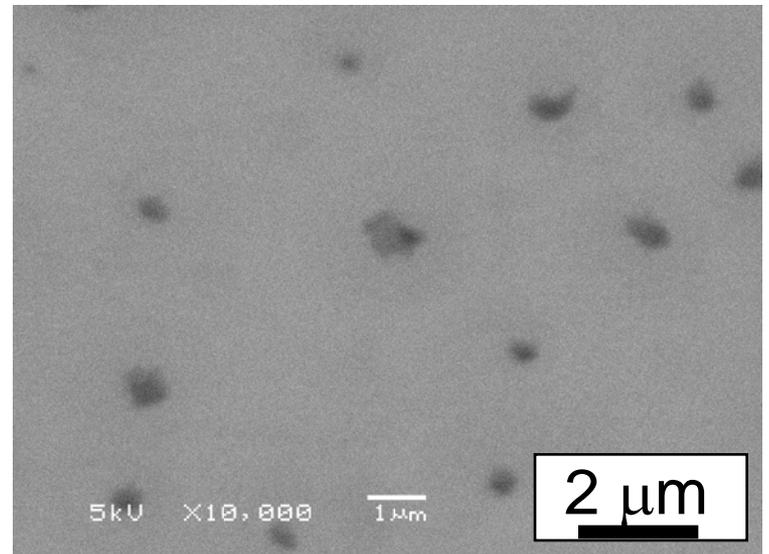
- ▶ H₂ charged samples are prone to blistering
- ▶ Materials Dependent
- ▶ Pb surface diffusion also evident



Cu/PZT surface



W/PZT surface



Technical Progress:

Piezoelectric Surface blistering Preliminary Results

- ▶ Blistering caused by absorption of H into metal or piezo
 - ▶ Ruptures surface during decompression
- ▶ Materials dependent
 - ▶ Cu, Al, W, Pd on PZT all exhibit varying degrees
 - ▶ Cu, Pd, W on BTO also exhibit blistering (Al, Ti on BTO not tested yet)
- ▶ Pb migration from PZT may increase blistering
- ▶ Calculations indicate that most metals mix with Pb

$$\Delta H \sim -P \left(\Delta W_f \right)^2 + Q \left(\Delta n_{ws} \right)^2$$

W_f = work function

N_{ws} = Wigner-Seitz electron density

	W_f	ΔW_f	N_{ws} $\times 10^2$	ΔN_{ws} $\times 10^2$	ΔH [arb.]
Al	4.3	0.1	2.2	0.9	8e-5
Pb	4.2	0	1.3	0	0
Cu	4.7	0.45	3.6	2.3	4e-4
Ti	4.3	0.2	2.7	1.4	2e-4
Pd	5.1	0.9	3.7	2.4	2e-4
W	4.6	0.4	4.8	3.5	1e-3

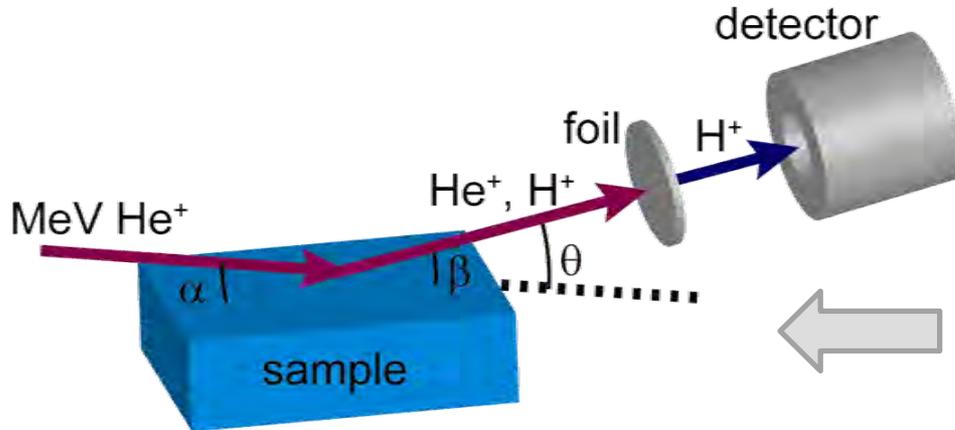
$$P/Q = 4.4 \times 10^{-4} \text{ (electron/(au)}^3\text{)}^2/V^2$$

• ΔH overall scale is arbitrary here

Miedema, J. Phys. F: Metal Phys., 1973

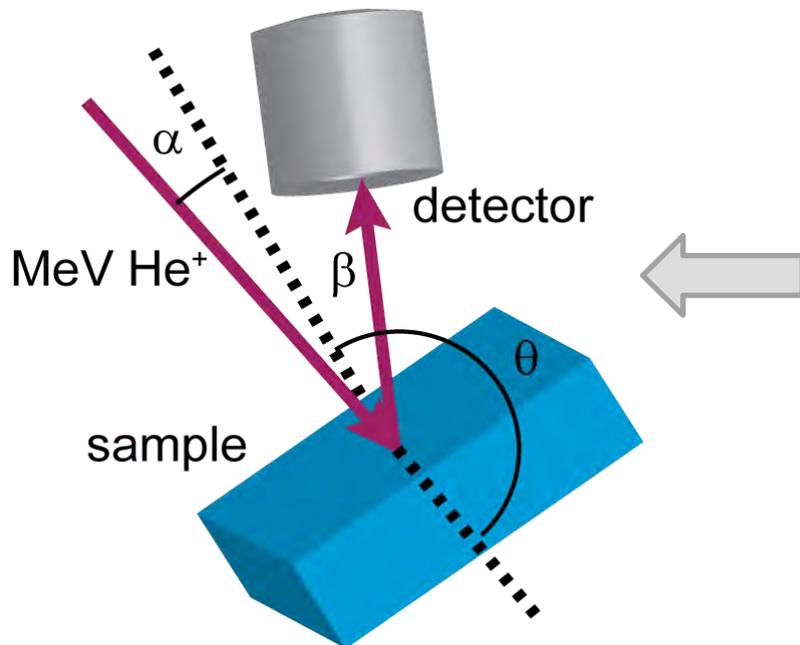
Approach:

PZT Hydrogen Absorption (Ion Scattering-ERDA/RBS)



ERDA

- ▶ Very few techniques can measure hydrogen content
- ▶ Elastic Recoil Detection Analysis (ERDA) ion scattering is very sensitive to hydrogen
- ▶ Hydrogen depth profiling of charged and control samples



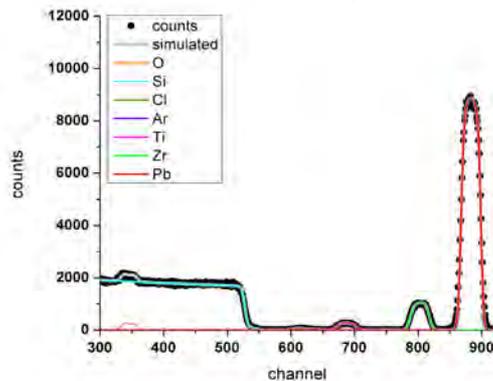
RBS

- ▶ Rutherford Backscatter Spectrometry (RBS) used to probe heavy element diffusion
- ▶ Diffusion of heavy elements can damage piezo or cause shorts

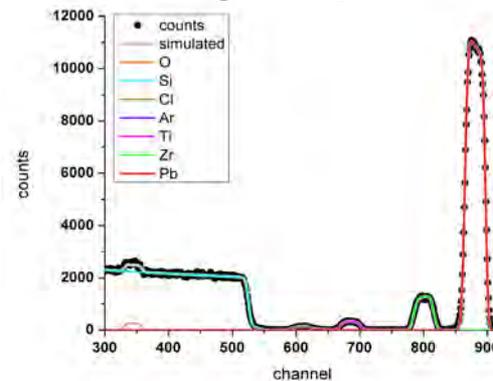
Technical Progress: RBS/ERDA results – Bare PZT

- ▶ RBS gives heavy element depth profile
- ▶ ERDA yields hydrogen depth profile

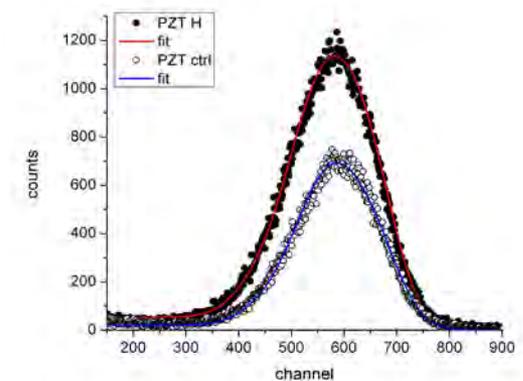
RBS – control spectra



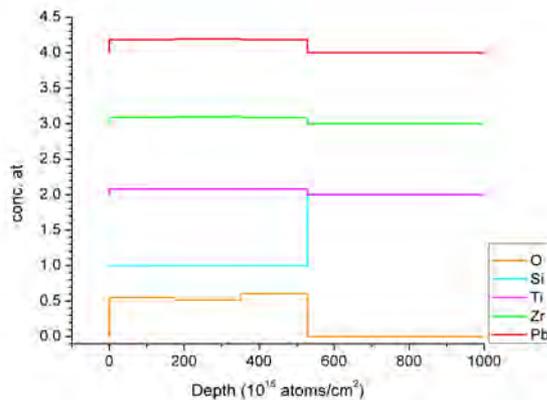
H2 charged spectra



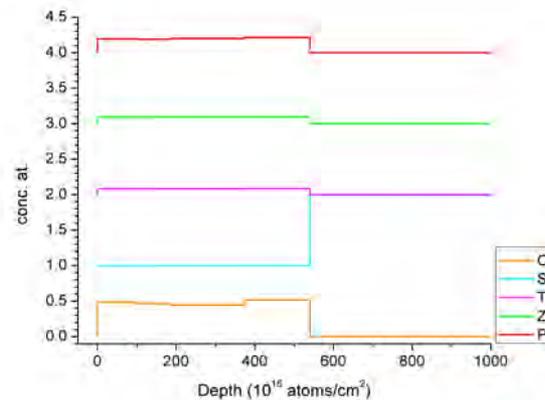
ERDA spectra



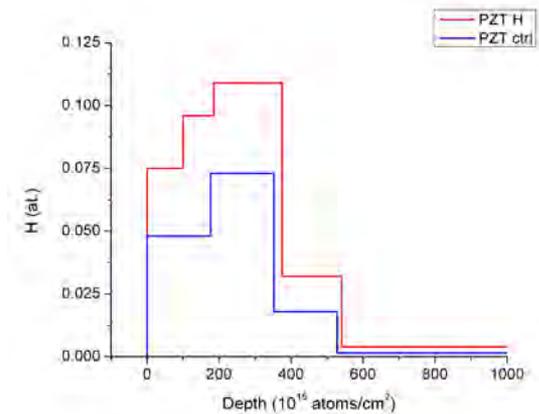
RBS – control profile



H2 charged profile



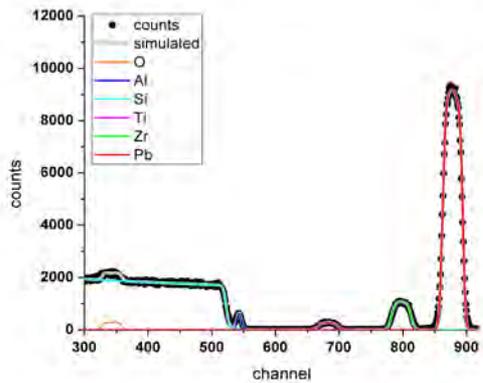
ERDA – H depth profile



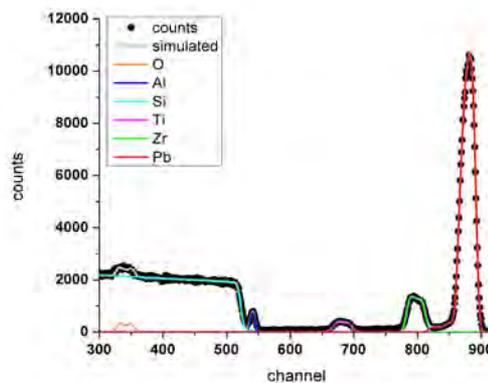
Technical Progress: RBS/ERDA results – PZT/Al

- ▶ PZT/Al shows high amounts of absorbed H₂
- ▶ Pb/Al surface mixing is inconclusive with RBS

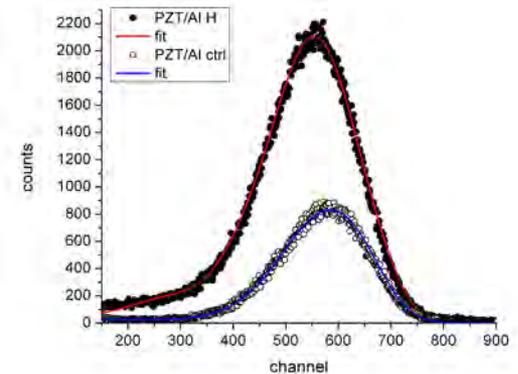
RBS – control spectra



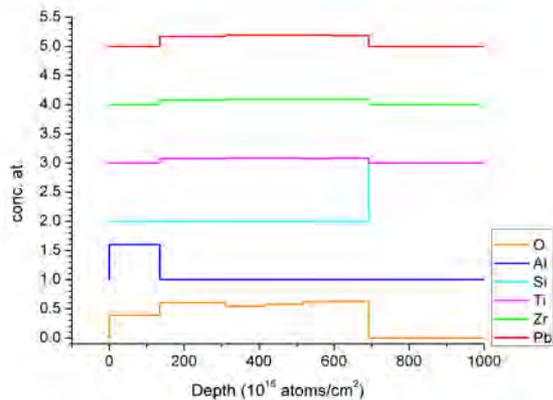
H₂ charged spectra



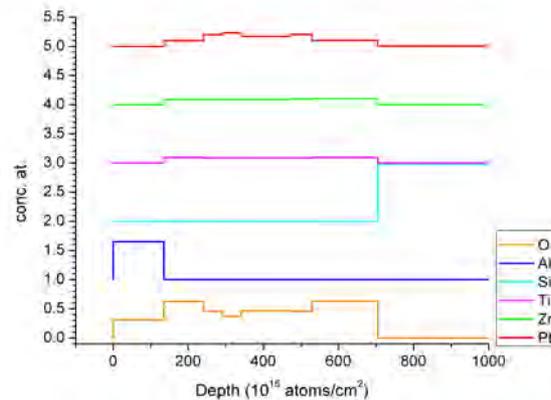
ERDA spectra



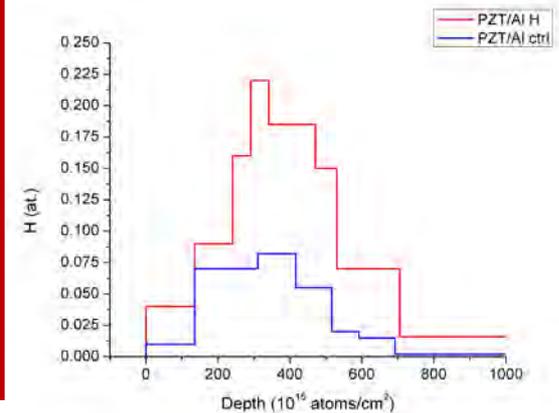
RBS – control profile



H₂ charged profile



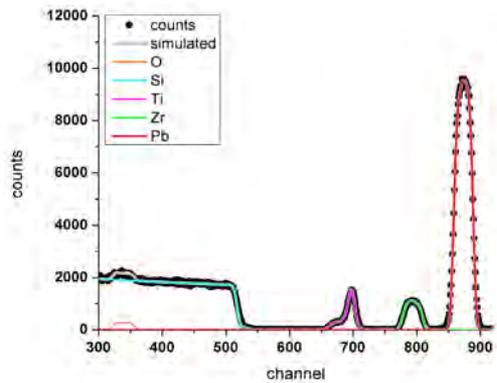
ERDA – H depth profile



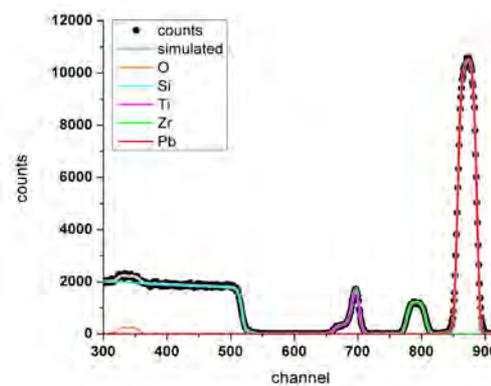
Technical Progress: RBS/ERDA results – PZT/Ti

- ▶ Little difference in H₂ absorption between control and charged
- ▶ Pb/Ti surface mixing is inconclusive with RBS

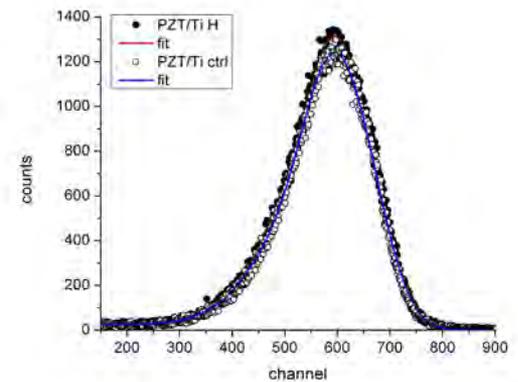
RBS – control spectra



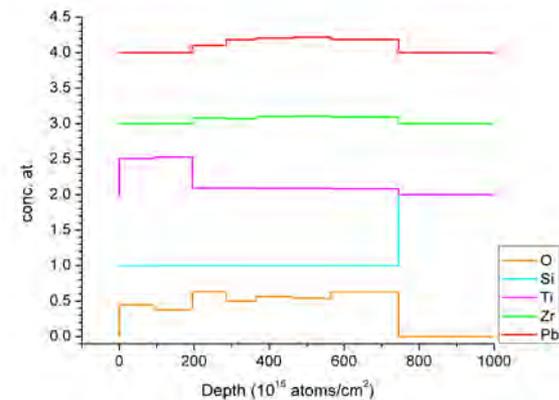
H₂ charged spectra



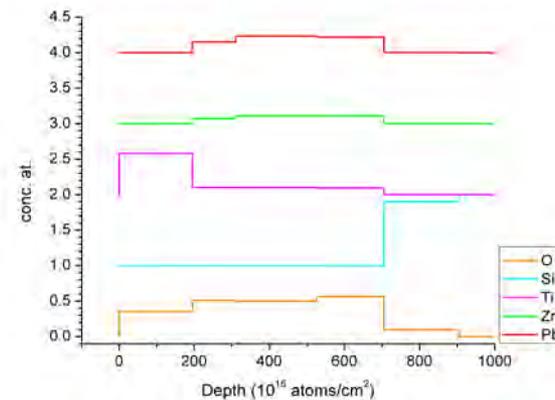
ERDA spectra



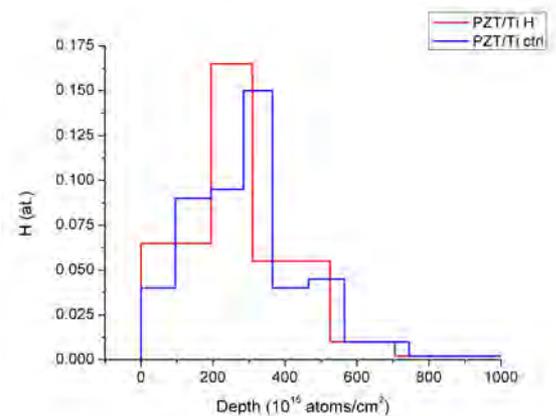
RBS – control profile



H₂ charged profile



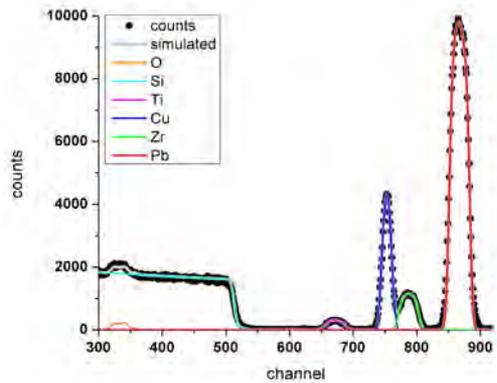
ERDA – H depth profile



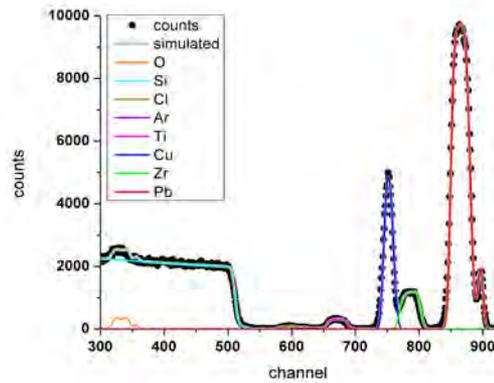
Technical Progress: RBS/ERDA results – PZT/Cu

- ▶ Slight increase in H2 after charging
- ▶ Pb/Cu mixing is evident

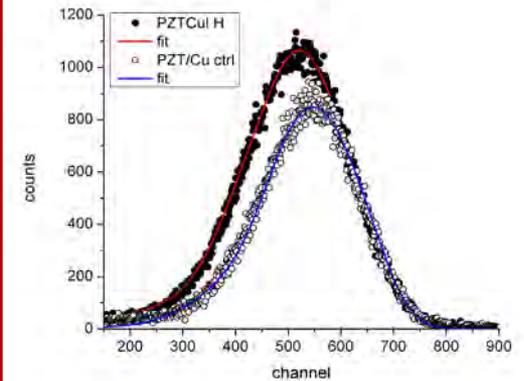
RBS – control spectra



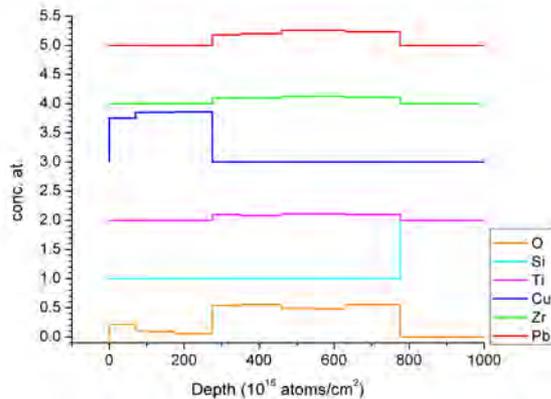
H2 charged spectra



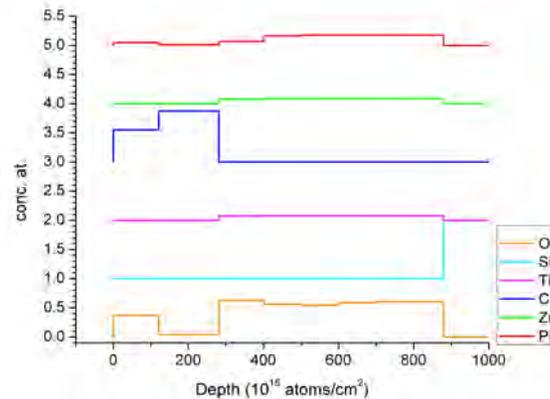
ERDA spectra



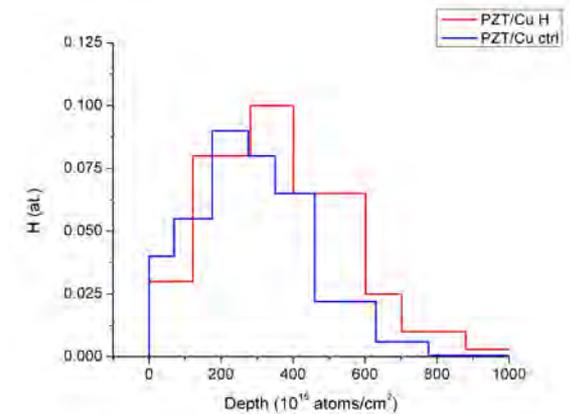
RBS – control profile



H2 charged profile



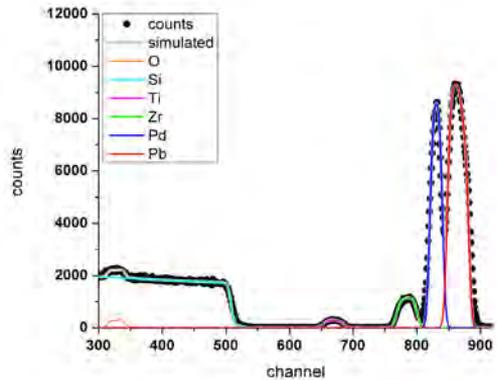
ERDA – H depth profile



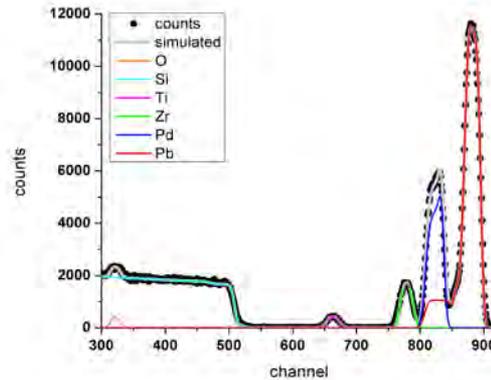
Technical Progress: RBS/ERDA results – PZT/Pd

- ▶ Large increase in H2 absorption
- ▶ Pb/Pd mixing occurs

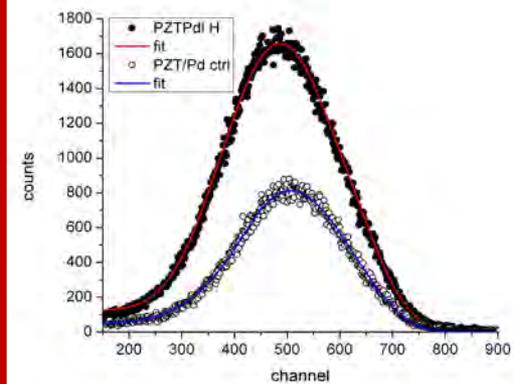
RBS – control spectra



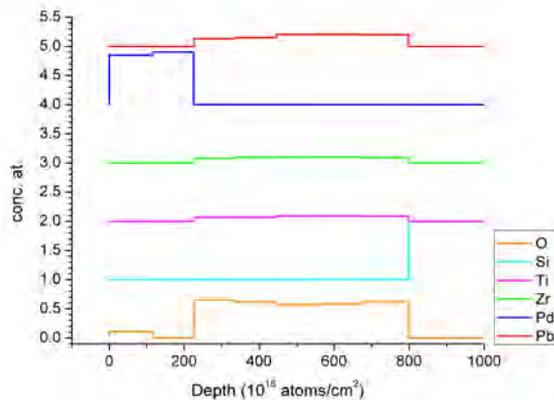
H2 charged spectra



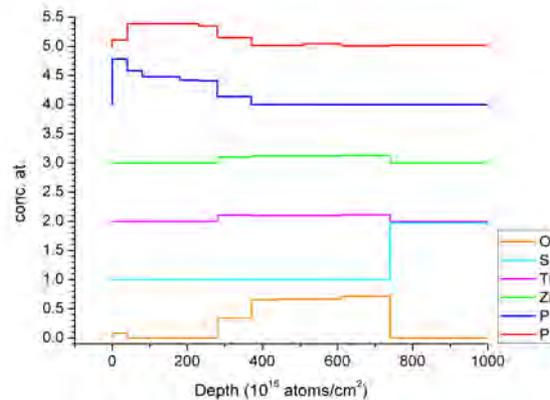
ERDA spectra



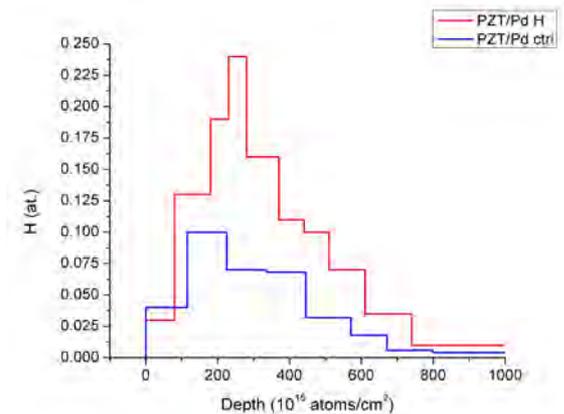
RBS – control profile



H2 charged profile



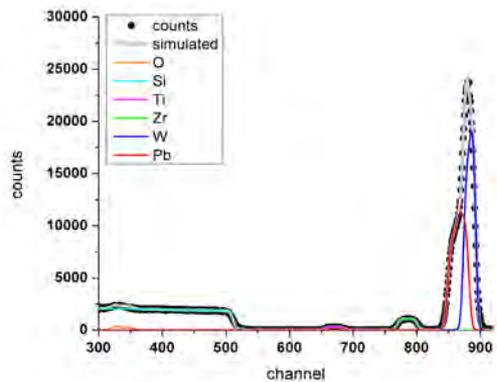
ERDA – H depth profile



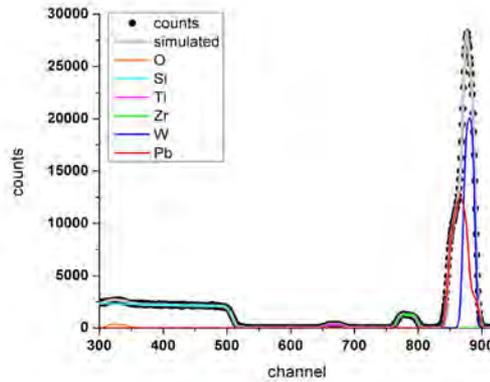
Technical Progress: RBS/ERDA results – PZT/W

- ▶ Small increase in H2 absorbed
- ▶ Some Pb/W mixing occurs

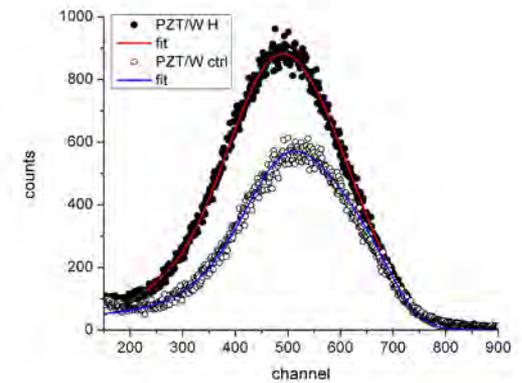
RBS – control spectra



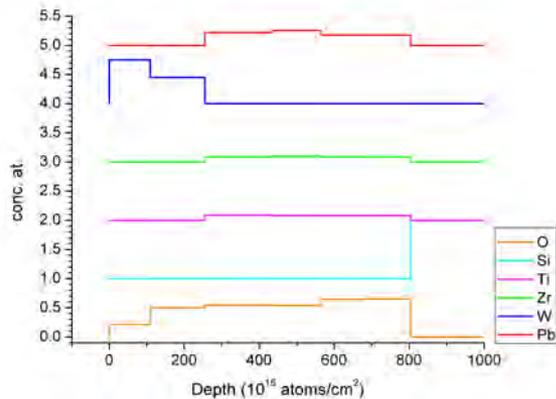
H2 charged spectra



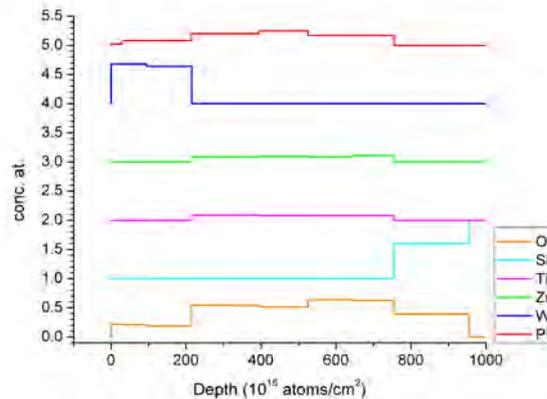
ERDA spectra



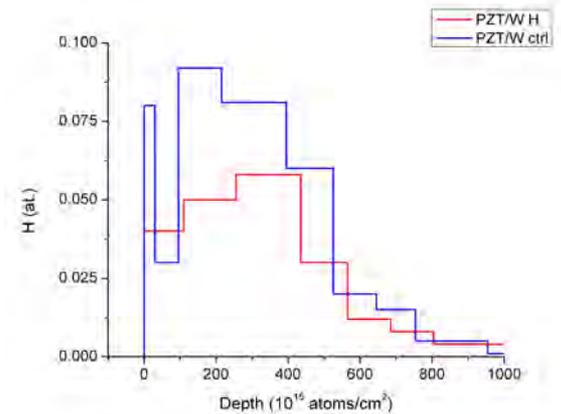
RBS – control profile



H2 charged profile



ERDA – H depth profile



Technical Progress:

Discussion of RBS/ERDA results

- ▶ RBS data indicates that Pb/metal mixing occurs in the PZT/W, PZT/Cu, PZT/Pd systems. Data for PZT/Al and PZT/Ti are inconclusive. RBS for BTO samples is planned.
- ▶ Preliminary SEM/EDX supports the RBS data showing that Pb does come to the surface in the PZT/W, PZT/Cu to form a segregated surface phase. The same is true for PZT/Al. SEM/EDX is planned for the remainder of the samples, including BTO/metal samples.

Sample	Control H	Charged H	Difference	Pb mix
PZT	8 at. %	11 at. %	3 at. %	NA
PZT/Al	8 at. %	20 at. %	12 at. %	Yes
PZT/Cu	9 at. %	10 at. %	1 at. %	Yes
PZT/Ti	14 at. %	16 at. %	2 at. %	No?
PZT/W	6at. %	9 at. %	3 at. %	Yes
PZT/Pd	9 at. %	24 at. %	15 at. %	Yes

Technical Progress:

Piezoelectric Hydrogen Compatibility

- ▶ Piezo injectors are subject to hydrogen poisoning and damage due to high pressure hydrogen uptake.
- ▶ We have evaluated high pressure hydrogen uptake as a function of electrode material and find that for PZT that the largest uptake (vs. control) was in the order of Pd > Al > W > Ti > Cu. The highest overall H concentration was as follows: Pd > Al > Ti > Cu > W.
- ▶ Nearly all metal layers showed blistering or surface diffusion of Pb into the electrode with the possible exception of Ti, though Ti has high levels of absorbed H. This Pb surface diffusion was especially noticeable for Cu, Pd, and W. Similar measurements on BTO/metal stacks are planned.
- ▶ Additional work is planned to determine the best materials choice for high pressure hydrogen based on Pb migration, blistering damage, and hydrogen absorption.

Collaborations

- ▶ **Pacific Northwest National Laboratory**
 - Project funded by DOE Vehicle Technology Program
 - PNNL is a multi-program DOE National Laboratory
 - Hydrogen Piezoelectric degradation testing

- ▶ **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

- ▶ Remaining FY11
 - ▶ Complete evaluation of remaining piezo metal stacks to evaluate H uptake and damage
 - ▶ Evaluate H diffusion in PZT and BTO powders with NMR
- ▶ Proposed Future Work
 - ▶ Evaluate potential polymer hydrogen barrier coatings such as parylene and organosilicate (clay) impregnated epoxies to mitigate H₂ absorption and damage
 - ▶ Evaluate temperature dependent H₂ desorption in piezoelectrics to evaluate H₂ damage recovery

Project Summary

- ▶ Relevance: Improved performance and reliability of fuel injectors for Hydrogen Internal Combustion Engines – non petroleum fueled.
- ▶ Approach: Evaluate piezo damage based on materials selection of piezo and electrode material with ion scattering (ERDA/RBS) and SEM.
- ▶ Technical Progress: Evaluated Pb diffusion in 5 different PZT/metal systems with RBS. Evaluated H uptake with ERDA in 5 different PZT/metal systems. Looked at surface blistering and Pb surface migration with SEM/EDX.
- ▶ Collaborations: Partnered with Westport International and Ford Motor Co. (past years)
- ▶ Future work (remaining FY11):
 - Complete ERDA/RBS and SEM damage studies on remaining BTO/metal (5 types) systems
 - H diffusion studies in PZT and BTO with NMR to complement earlier neutron work.
 - Compile report evaluating H₂ materials compatibility.