Hydrogen leak detection – low cost distributed gas sensors

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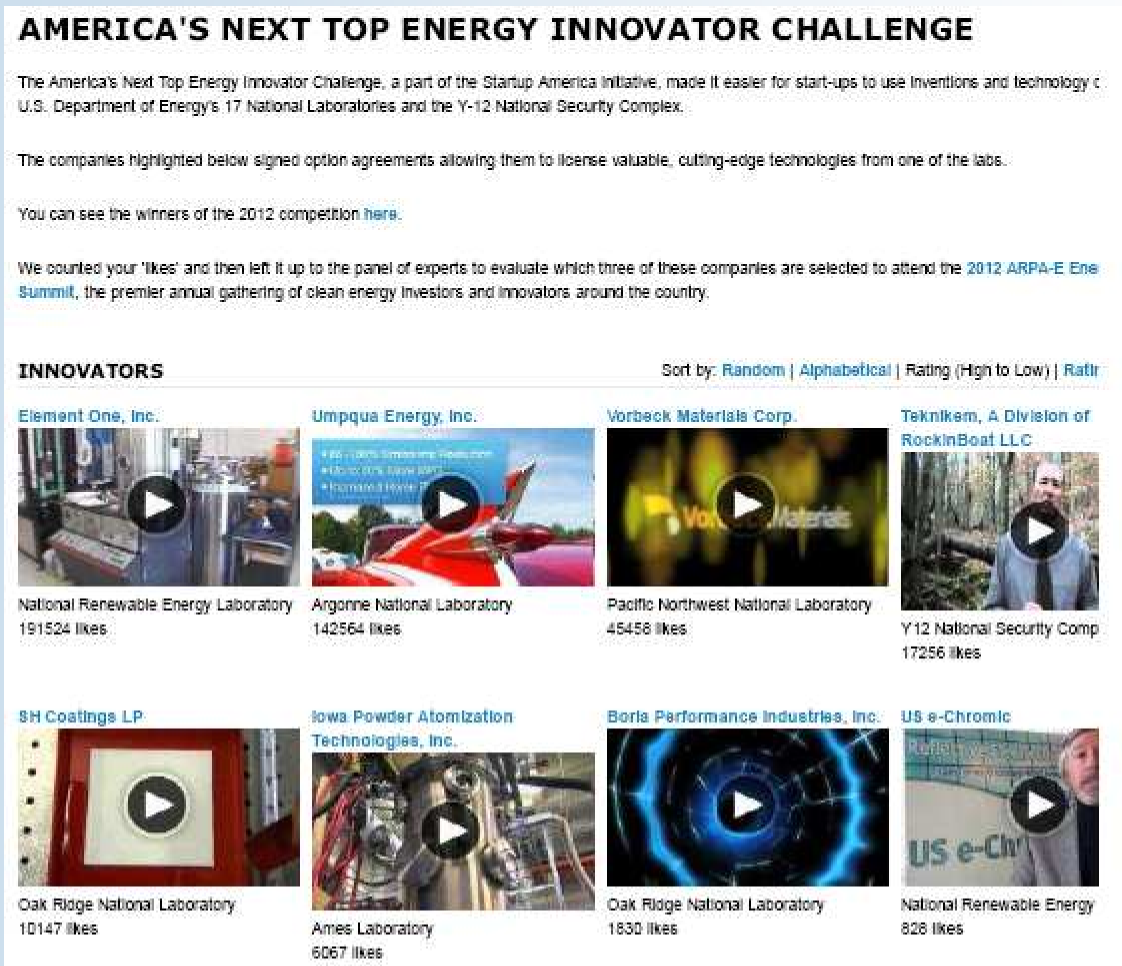
Summary

- Company/technology background
- Benefits of low-cost distributed sensors
- Technology, concepts and potential uses
- Technical challenges, status and plans

Company Background

- Incorporated in 2005, began R&D to begin development of low cost hydrogen indicators
- 2005 – Collaborative agreement with U.S. National Renewable Energy Laboratory (NREL) – Conducted early research efforts at NREL on thin film sensor research resulting in three additional patent applications
- 2007 – Successfully completed sensor durability tests at NASA/Kennedy Space Center
- 2011 – NREL vacuum deposition equipment put on long term loan to Element One.
- 2011 – Element One options to license three NREL patents
- 2012 – Named runner up in DOE's "America's Next Top Energy Innovator Challenge"

Element One named runner-up in DOE's "America's Next Top Energy Innovator" Challenge



AMERICA'S NEXT TOP ENERGY INNOVATOR CHALLENGE

The America's Next Top Energy Innovator Challenge, a part of the Startup America Initiative, made it easier for start-ups to use inventions and technology c
U.S. Department of Energy's 17 National Laboratories and the Y-12 National Security Complex.

The companies highlighted below signed option agreements allowing them to license valuable, cutting-edge technologies from one of the labs.

You can see the winners of the 2012 competition here.

We counted your 'likes' and then left it up to the panel of experts to evaluate which three of these companies are selected to attend the 2012 ARPA-E Ene
Summit, the premier annual gathering of clean energy investors and innovators around the country.

INNOVATORS

Sort by: Random | Alphabetical | Rating (High to Low) | Ratir

Element One, Inc.
National Renewable Energy Laboratory
191524 likes

Umpqua Energy, Inc.
Argonne National Laboratory
142564 likes

Vorbeck Materials Corp.
Pacific Northwest National Laboratory
45456 likes

Teknikem, A Division of RockinBoat LLC
Y12 National Security Comp
17256 likes

SH Coatings LP
Oak Ridge National Laboratory
10147 likes

Iowa Powder Atomization Technologies, Inc.
Ames Laboratory
6067 likes

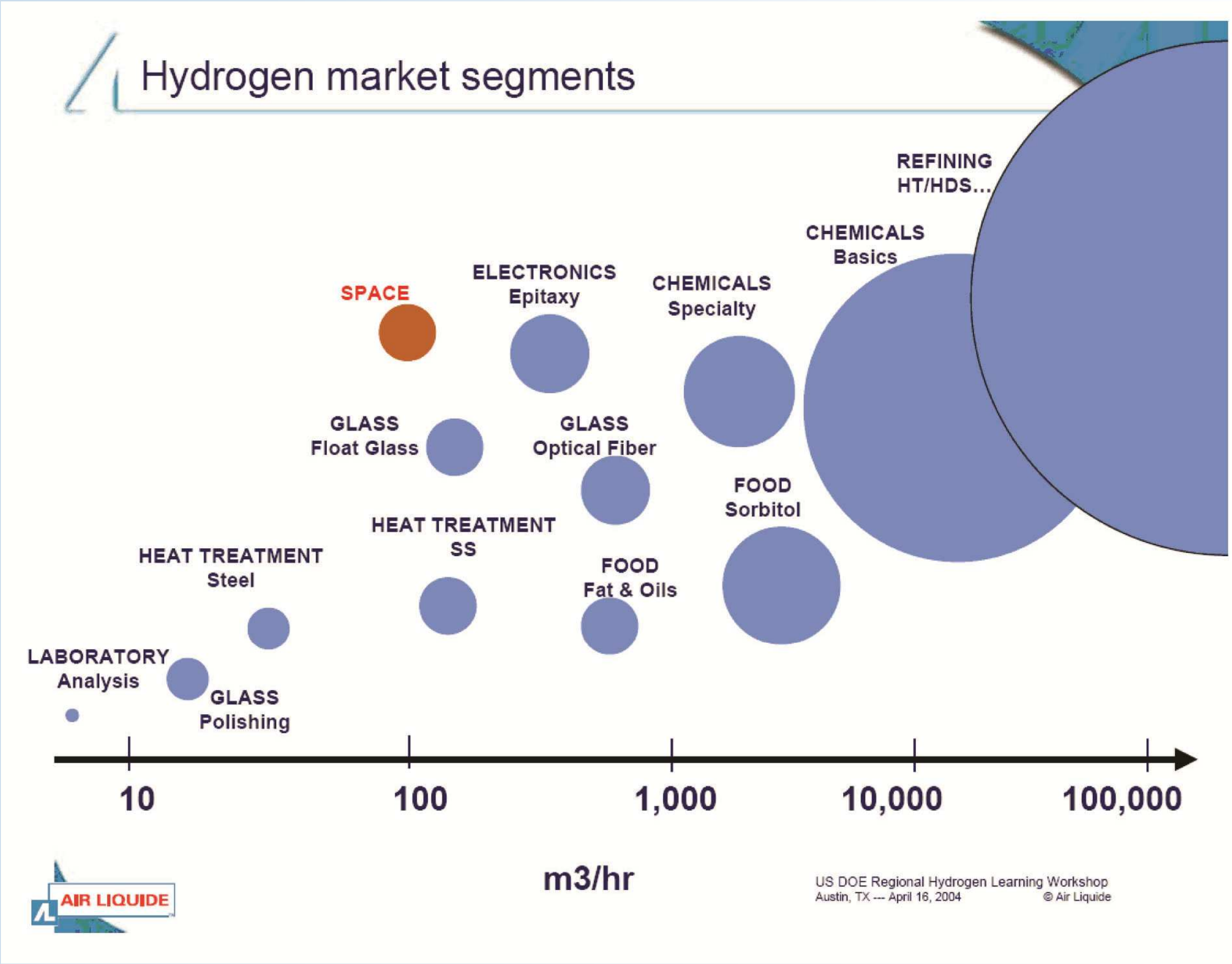
Borla Performance Industries, Inc.
Oak Ridge National Laboratory
1830 likes

US e-Chromic
National Renewable Energy
828 likes

Importance of gas leak detection today

- Gas detection is a **critical element** of the safe manufacture, handling and use of many industrial gases.
- The **$700+ million gas detection market**, served by more than twenty-five OEMs and hundreds of maintenance contractors, is mature and stable with a projected annual **growth in the 3 to 6% range**.
- The **global hydrogen market** in 2010 was estimated at **53 million metric tons** with 12% in the merchant hydrogen market and a **growth rate of 5-6% per year.**
- There is a **growing requirement** due to increasing regulations, codes and standards for gas leak detection that can be economically satisfied using our technology.
- Due to **limited refinery capacity**, downtime in the oil and gas refining industry has become of critical importance as most refineries are operating at peak capacity.
- Current electronic gas detectors, once installed, require regularly scheduled **calibration and maintenance**. Low cost leak detectors can be easily and cheaply replaced on a regular schedule at the same time by the same people who perform the calibration.
- The market for fuel cells is growing, and hydrogen's potential use as a **fuel** could quadruple the current hydrogen market.

The current markets are diverse and growing; the potential future markets are huge



A number of methods have been used in the past to detect hydrogen leaks:

- ***Bubble testing*** – simplest method, no continuous monitoring, inert gases, low pressures;
- ***Catalytic combustion*** - detects heat of combustion, works well for low concentrations, not for inert environments or pure hydrogen, not hydrogen specific;
- ***Thermal conductivity* -** works well in stable environments with minimal temperature change, background gas must have conductivity very different from hydrogen;
- ***Electrochemical* -** sensors use a liquid electrolyte and require a gas permeable membrane for the hydrogen to reach the electrolyte, but varying temperature affects gas diffusion making the sensor unreliable.
- ***Mass Spectrometers* -** extremely sensitive, expensive, require skilled operators and may have long response times.
- ***Gas Chromatographs*** - similar to mass spectrometers and have the same disadvantages.
- ***Ultrasonic*** leak detection – technology improving, but cannot determine exact location or whether combustible mixture is present.
- ***Glow plugs*** and heat sensors - less common, glow plug ignites any combustible mixture and a heat sensor detects the fire.
- ***Semi-conducting Oxide*** sensors rely on surface effects with a minimum oxygen concentration. This technique is relatively new, but they do not work in inert atmospheres and performance degrades at lower temperatures.

Many classes and Types of H_2 Sensors

- ***Electrochemical Sensors***
  - *Amperometric, potentiometric [low T and high T]; solid/liquid electrolyte*
- ***Pd-film and Pd-alloy films***
  - ***Electronic - resistor, capacitor, transistor***
  - ***Thermoelectric***
  - ***Optical evanescent wave***
  - ***Mechanical [SAW, cantilever]***
- ***Metal Oxide Sensors (MOX sensors)***
  - ***Heated metal oxides***
- ***"Pellistor"-type combustible gas sensors***
  - ***Hot Pt or Pd catalyst with Pt resistance thermometer***
- ***Thermal conductivity – non selective; semi-selective***
- ***Optical Devices***
  - ***colorimetric and indicator dyes***
  - ***Evanescent wave – with film of Pd or other material***

The reason for heightened interest in H_2 Safety

Very large quantities of hydrogen are safely used in industry today, but it’s **hard to contain** and **difficult to detect leaks**.

Hydrogen is a **very large industrial commodity** with a growing market; its anticipated use as fuel could quadruple the market to more than 2 trillion cubic meters per year, and

The introduction of hydrogen as a consumer fuel has caused heightened concern over its **safety** with a corresponding increased interest in hydrogen sensors and leak detection.

Hydrogen Characteristics

- Odorless, colorless
- High propensity to leak
- Low ignition energy
- Invisible flame
- High energy content
- Difficult to detect, lighter than air, diffuses rapidly

NASA/Kennedy Space Center - H_2 storage and supply pipeline

- ~ 800,000 gallon liquid hydrogen tank
- ¼-mile supply vacuum jacketed
- pipeline
- Area evacuated during refueling
- Numerous electronic sensors
- Line purged with helium after fueling space shuttle
- Leak detection difficult after the fact

NASA/KSC Hydrogen Detectors

Due to rapid dispersion, wind direction and direction of leaks, electronic hydrogen detectors have difficulty detecting leaks as little as a few inches away from the leak source.

Even when a leak is detected by an electronic sensor, it does not tell you where the leak source is. It can be quite labor intensive and time consuming to locate the leaking fitting.

Desirable characteristics of sensors for leak detection

In evaluating concepts for an ideal hydrogen sensor, it is apparent that no single sensor type can have all of the below characteristics, and the relative importance of each criterion varies with each application.

In general, the ideal sensor would:

- be **very inexpensive**, so that it could be **used prolifically** wherever the potential for a flammable mixture of hydrogen exists;
- Positive indication of **both** the absence of hydrogen, as well as the presence of hydrogen;
- be **simple, reliable, easily incorporated** into the system it is monitoring, and not require an external power source;
- be **hydrogen specific and sensitive** enough to detect concentrations well below the LFL;
- have a **rapid response time** as well as provide **historical information** of leaks; and
- have a **long useful life** operating over a wide range of conditions and environments.
- Hydrogen leaking from a system should be **detectable by one or more of the human senses** (sight, smell, hearing, taste, and touch). A typical electronic detection system is comprised of a sensor, transducer, and a device such as a bell, buzzer or light. A simpler system would be one in which the sensor itself is detectable by one or more of the human senses (e.g. color change, odorant).

The need for very low-cost, distributed visual leak detectors have been recognized by the U.S. DOE

U.S. DOE Multi-year plan 2003-2010:
"Although safety-by-design and passive mitigation systems are preferred, it will still be necessary to develop technologies to detect hydrogen releases or other system failures. ***For example, coatings that change color upon exposure to hydrogen can provide immediate visual evidence of a leak***, while other coatings can be used to rapidly catalyze any small amounts of hydrogen that do escape."

Critical Research Topic:
"The overall goal is to develop low-cost sensor technologies that are not based on conventional practices, that can be directly integrated with hydrogen systems, and that are resistant to contamination."

…Goal #3: Develop a sensing technology for a wide-area determination of hydrogen presence prior to any combustion or local temperature rise."

Precedents: visual detection of gases and liquids

Decals for carbon monoxide detection in aircraft cabins; visual indicators to complement electronic sensors.

Acid/base pH Detecting Paint provides instant visual indication of pipe and joint failures. Once the leak is repaired, a neutralizing solution is used to return the paint to it’s original color.

Element One's Technology

Element One has created revolutionary "smart" coatings for the detection of hydrogen that change color, either reversibly or non-reversibly, to provide both current and historical information about hydrogen leaks.

This makes it possible to produce a wide array of very low-cost, reliable sensors which can be economically deployed at all potential leak sites.

We have extended this technology to several additional hazardous gases:

- Hydrogen Sulfide
- Ammonia
- Chlorine

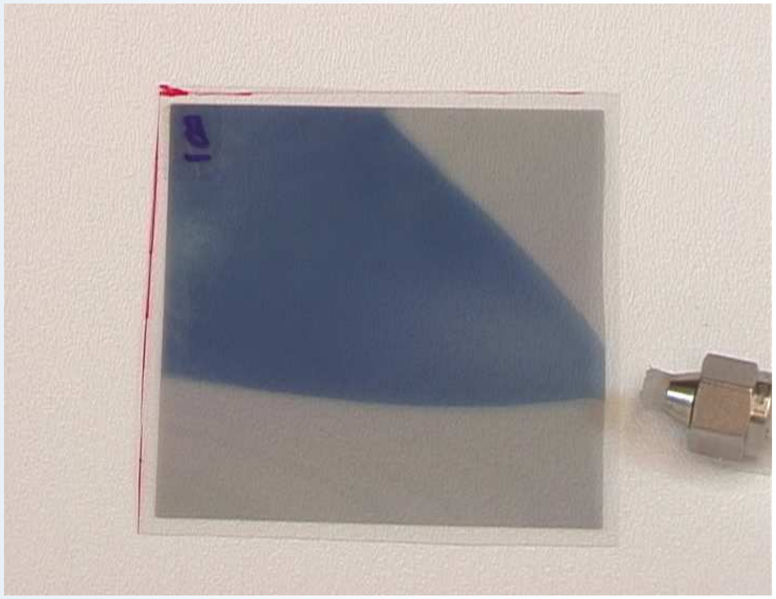
Element One, Inc. has developed and patented the technology for a wide array of very low cost hydrogen gas sensors.

These chemically active, or chemochromic, materials form the basis novel thin films or “smart coatings” that change the hazardous gas safety paradigm by warning of an incipient leak while it is still small enough to be treated as a routine maintenance issue, rather than a safety problem requiring a system shutdown or other emergency measures.

When used to supplement electronic sensors, these new products can dramatically provide new levels of safety and economy in any industrial operation that uses hydrogen.

“Smart” Coatings Benefits

- ✓ Positively indicates both the presence and absence of H_2
- ✓ Reversible or non-reversible
- ✓ Sensitive (.04% - 1/100 LFL)
- ✓ Inherently safe
- ✓ Convenient/very low cost
- ✓ No instrumentation needed
- ✓ Many possible new applications
- ✓ May be used in wireless sensor networks



A mixture of 10% H_2 in nitrogen passing over Element One’s reversible thin film sensor

Chemochromic reactions

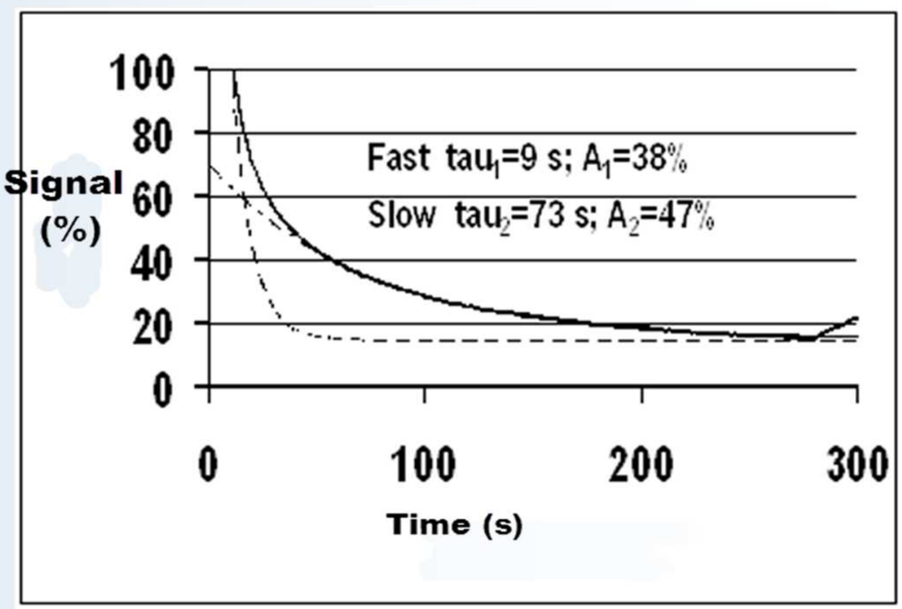
The hydrogen sensor is based on the catalyzed reversible partial reduction of a transition metal oxide with a resulting dramatic color change from light gray to black.

For example, tungsten trioxide:

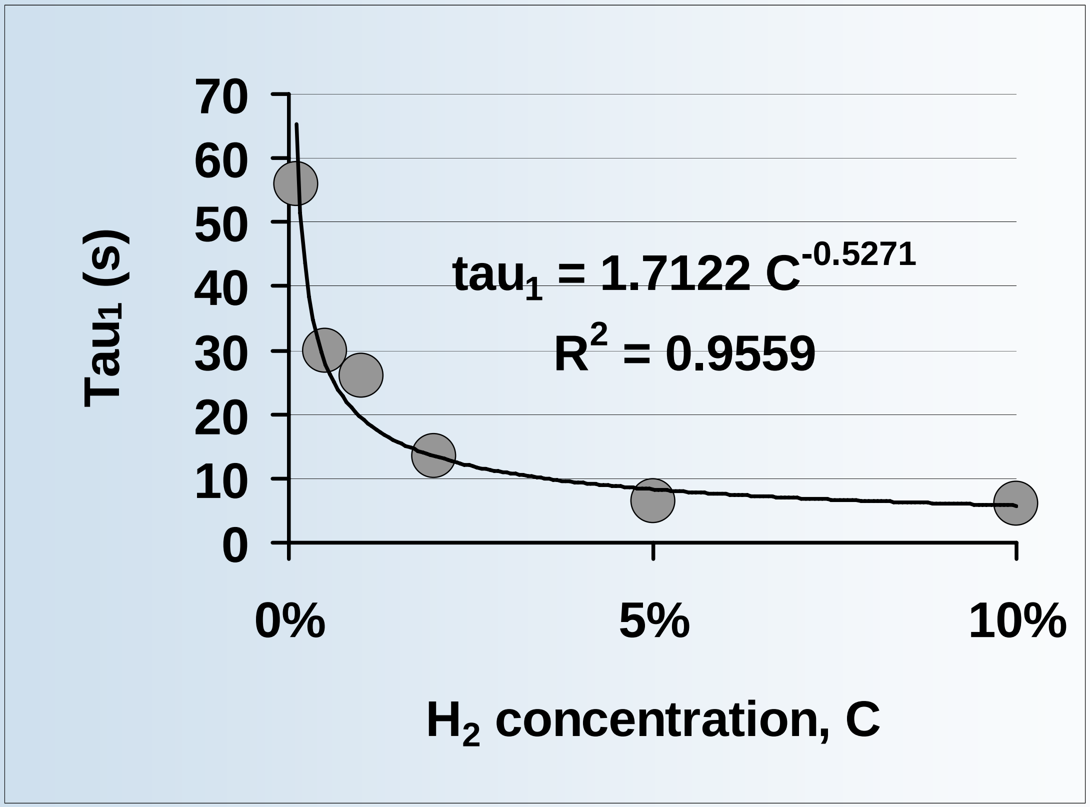
$$Pd + xH_2 + x/4O_2 + WO_3 \quad \leftrightarrow \quad H_xWO_3 + x/2H_2O + Pd$$

The chemical reaction the rate is expected to be first-order and the response is expected to exhibit an exponential shape

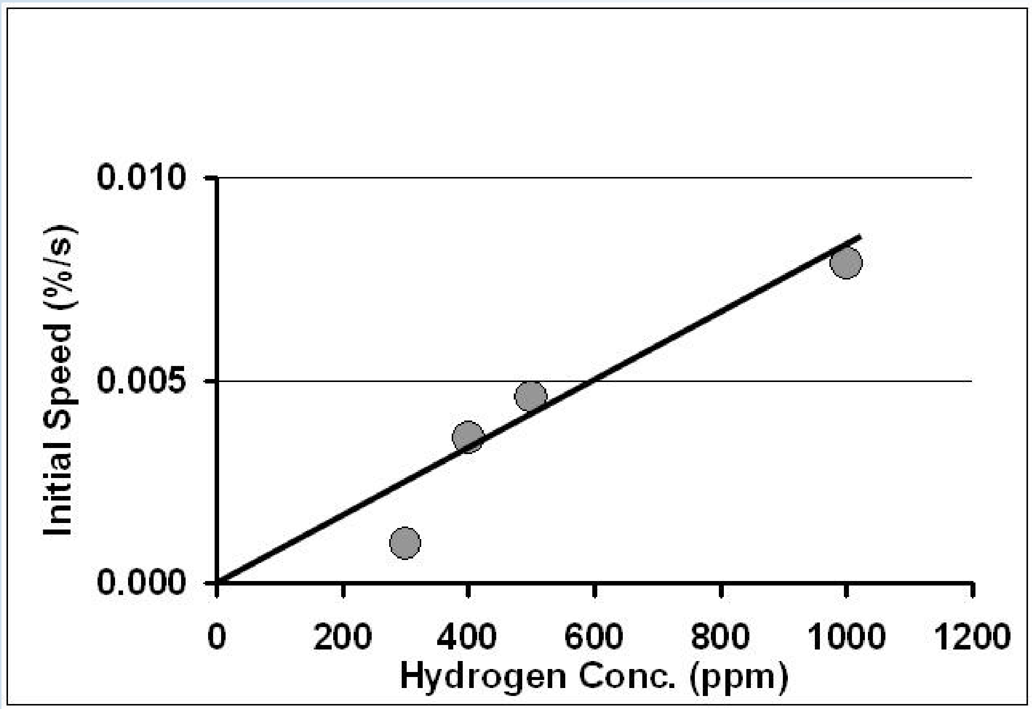
The response function is characteristic of two parallel first-order reactions – a faster reaction and a slower reaction. We speculate that the two different reaction rates occur because there are two different kinds of sites where the hydrogen actually reacts with the WO_3.



The speed of response is proportional to the square root of hydrogen concentration.

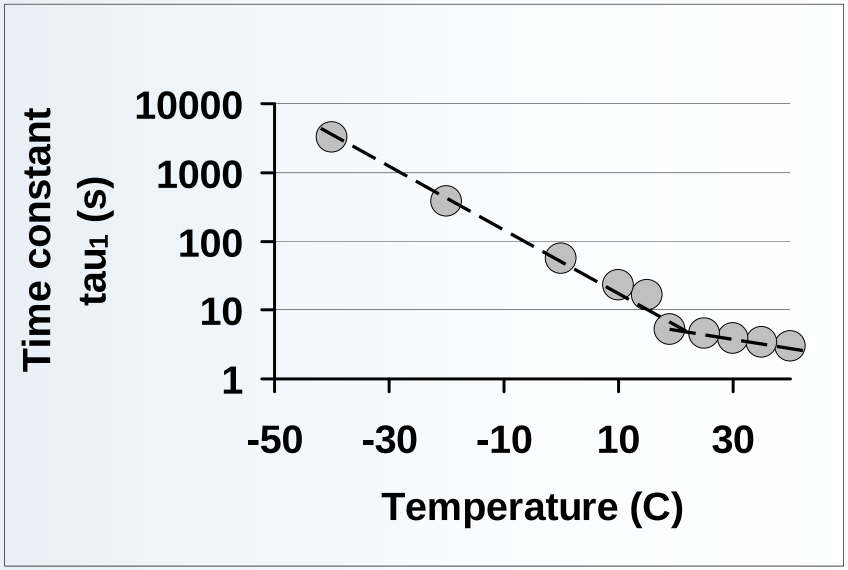


The response becomes slower and slower as the hydrogen concentration is decreased and exhibits a lower response limit of about 300 ppm H_2 in air

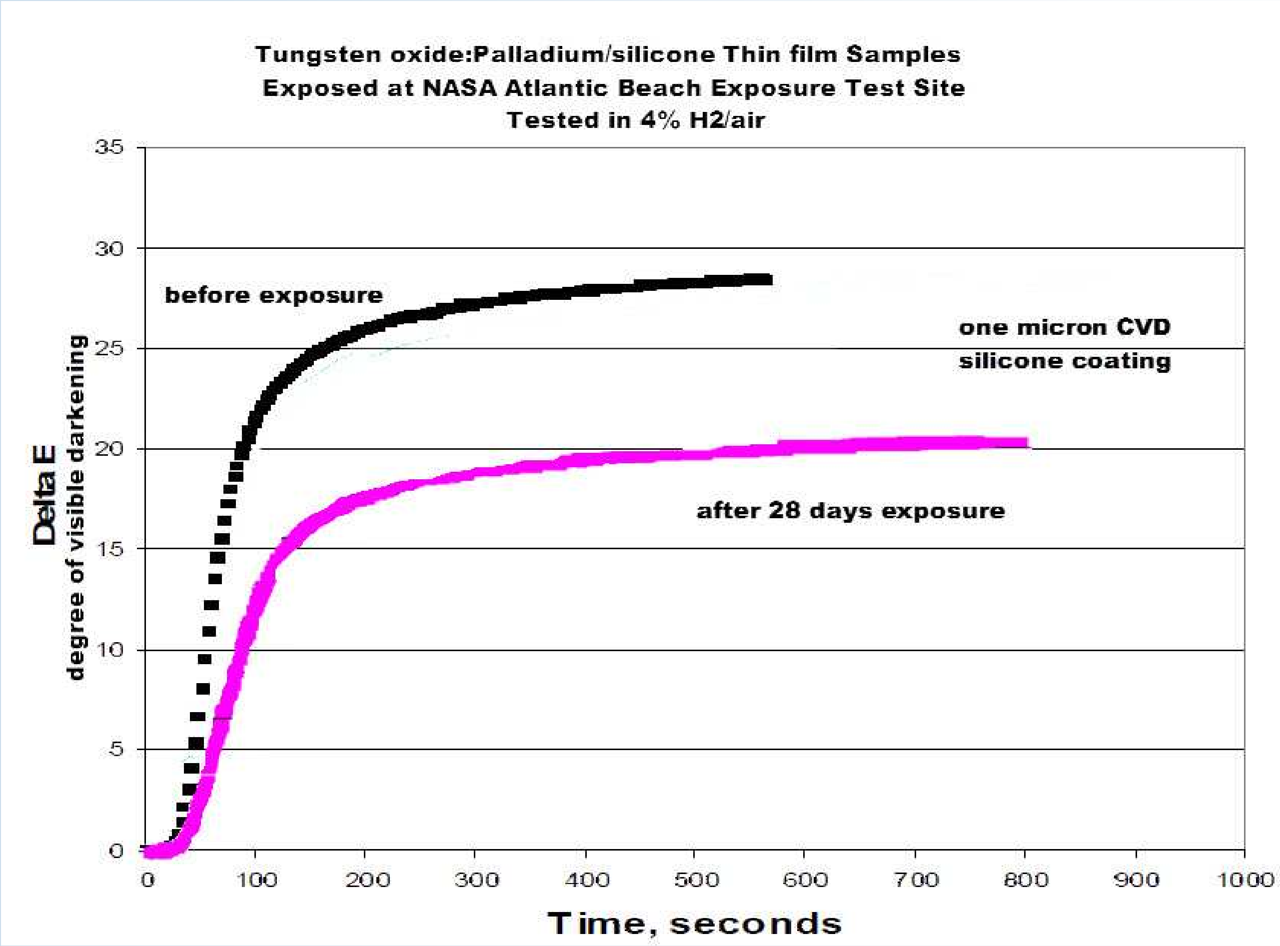


Temperature dependence of response speed

- The two segments of temperature dependence show two different thermal activation energies – a higher energy barrier for the reaction at temperatures below 15 C and a lower barrier above 15 C.

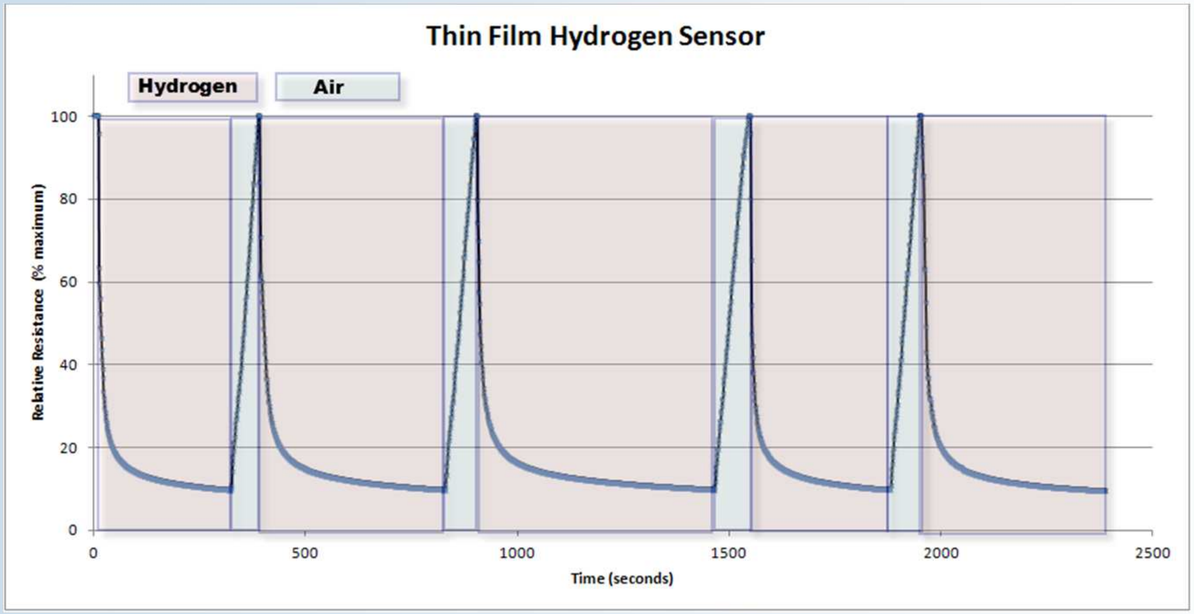


The effectiveness of a thin silicone protective coating on durability of a thin film hydrogen sensor



RFID Sensor prototype cycling tests

The sensor is repeatable and does not appear to suffer from exposure to the high hydrogen concentration as do many thin film sensors.

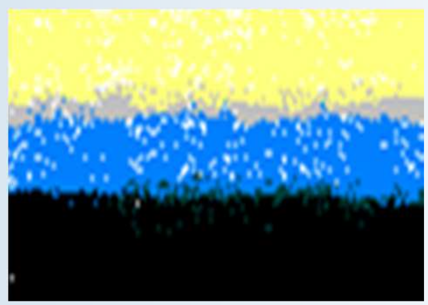


Technical Approach

To meet the varying requirements of different applications, Element One’s research has taken two directions:

1. **Thin films** that both change color and resistance for use in low cost wireless sensors.
2. **Color changing pigments** for coatings for visual indication

Vacuum deposited
Multi-layer
Thin film



Hydrogen selective membrane ~100 nm

Catalyst 3 nm

Transition metal oxide 500 nm

Substrate

Synthesized
Nano-particles

Nano-powder transition
Metal oxide (~50 nm)

Catalytically
activated (~5%)

Comparison of Pigments v. Thin Films

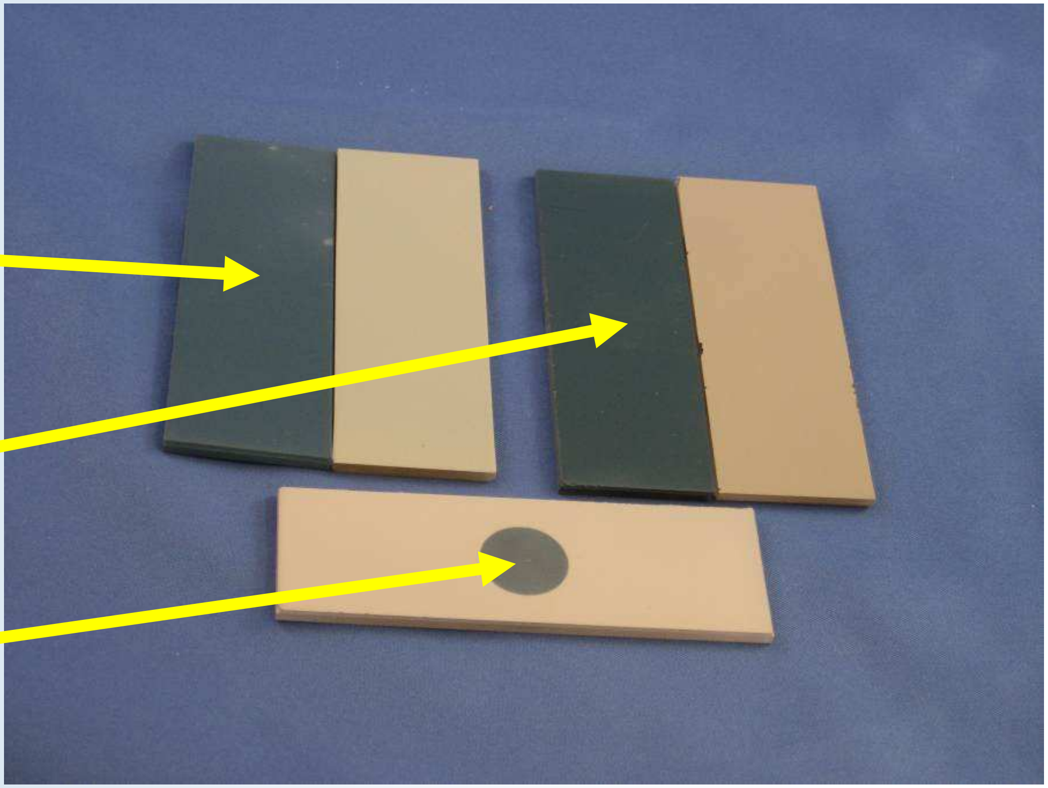
Pigments	Thin Films
Slower response	Faster Response
Easier to produce	Vacuum deposition process
Visual indication only	Both visual and resistance change
Incorporated into paints or inks	Multi-layer deposition process
More oxide material/catalyst per unit area	Less oxide material/catalyst per unit area
Generally more durable	Requires protective coating

DeteCoat™ Smart Coatings

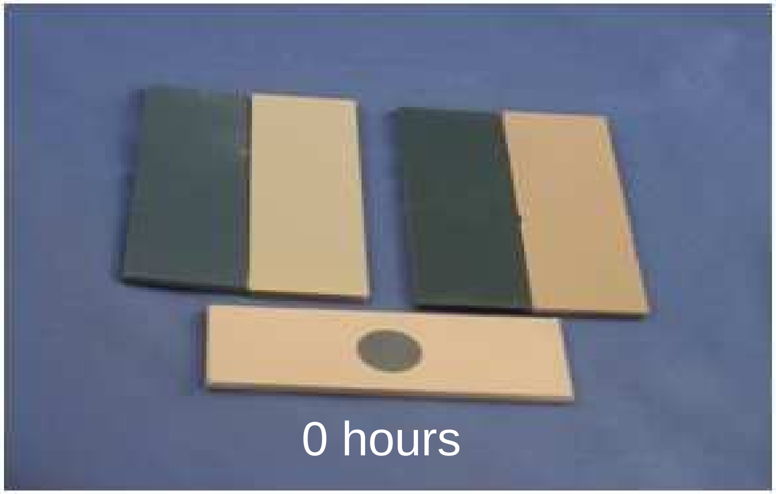
Pigments for “smart paints” or inks

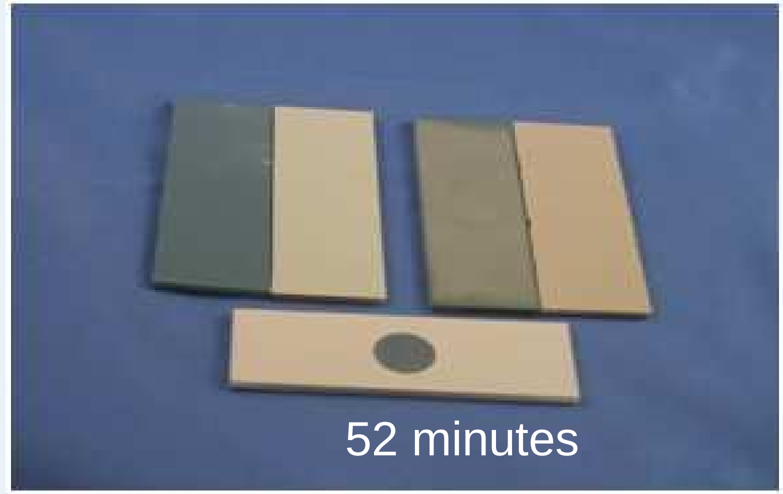
Paint formulations may be customized for desired performance:

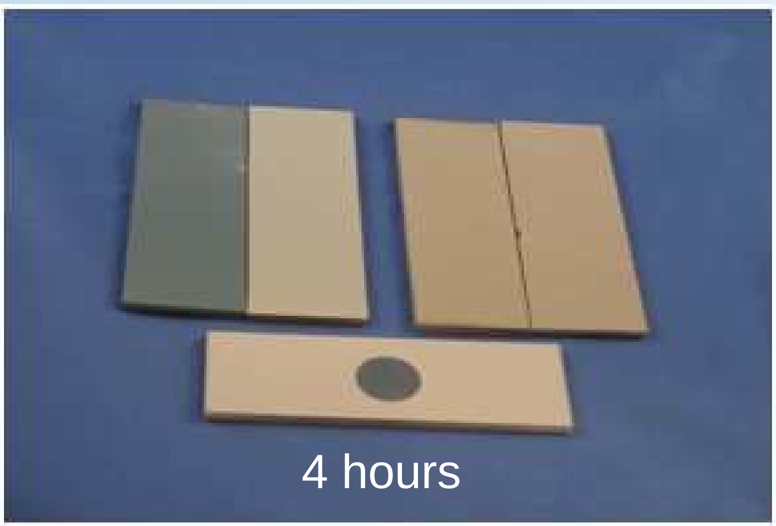
- **Reversible Coating 5804 (~24 hour bleach time)**
- **Reversible Coating 5811 (~1 to 2 hour bleach time)**
- **Non Reversible Coating**

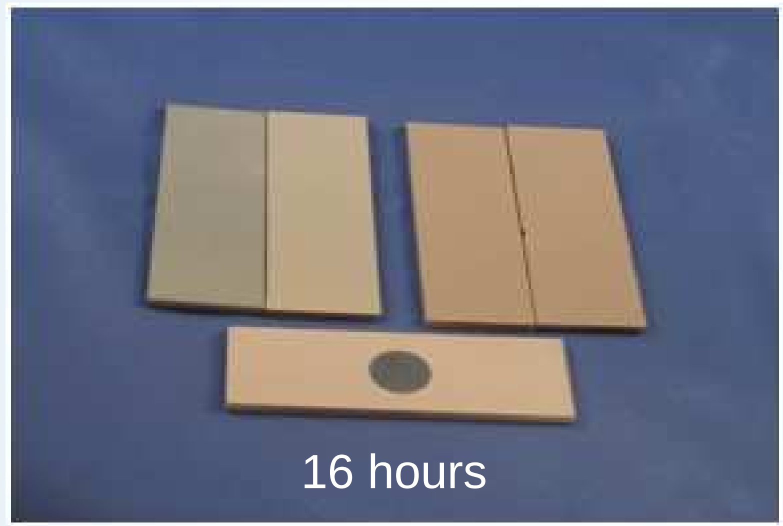


Reversibility can be varied



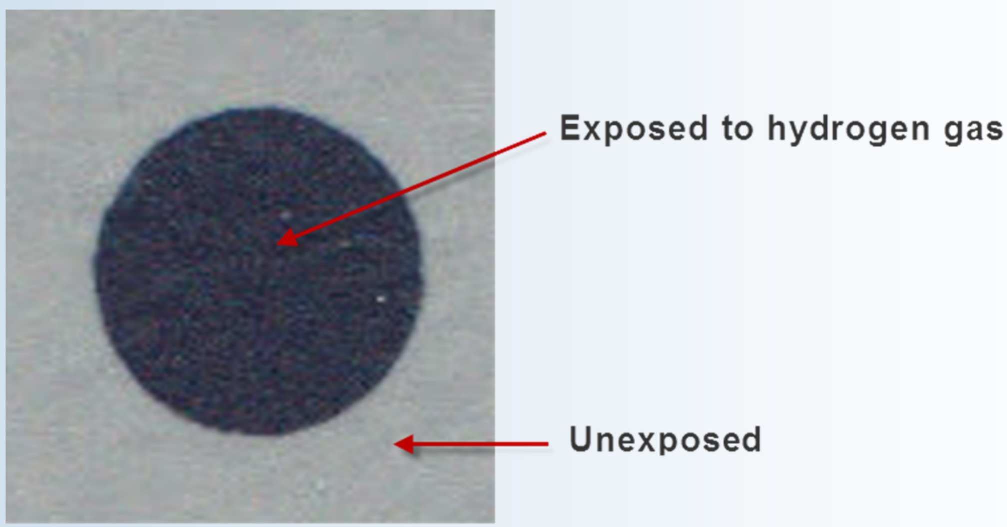






DeteCoat Mechanisms

- A polymer coating with a reactive pigment
  - Transition metal micro-particles plus mixed precious metal catalysts
- Hydrogen gas diffuses through the polymer and is dissociated on the catalyst
- Dissociated hydrogen reacts with the metal oxide
- The colorless oxide is partially reduced and becomes intensely colored



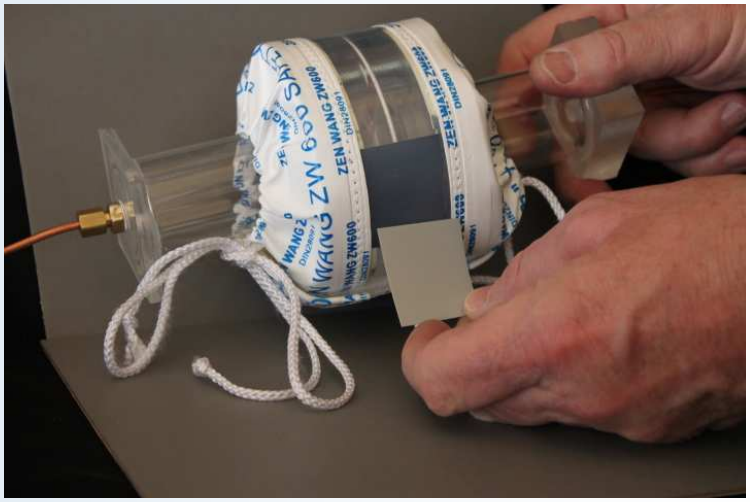
Early Applications

- **Hydrogen gas leak indicator**
  - ✓ In flange shields
  - ✓ In safety badges and warning signs
- **Coatings**
  - ✓ On pipeline fittings - flanges, couplings, valves, etc.
  - ✓ On pressure/reaction vessels and storage containers

DeteCoat™ in a Flange Safety Shield

Coloration of Hydrogen Leak indicator. Flange shield applied to a mock-up of a steel flange with a very small intentional hydrogen gas leak of 0.004 moles per second for 20 minutes.

Time = 0 (start)



Time = 20 (end)

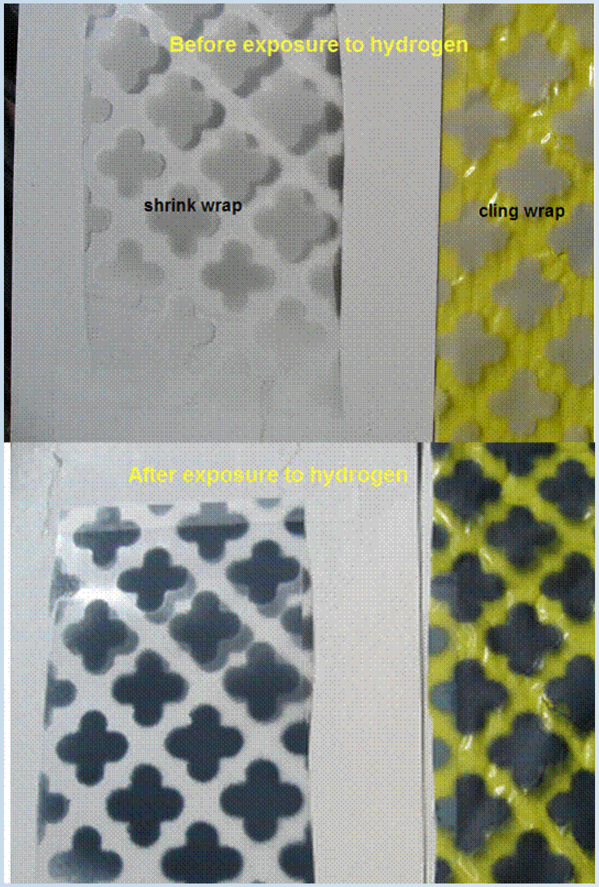
Visual Leak Detection Small Fittings

DeteCoat™ applied to a fitting visually shows the existence and location of a leaking joint.

This method will indicate leaks that are smaller than can be detected with bubble tests.

Conformable wraps - indicating tapes with coating on the inside

Conformable wraps – heat shrink



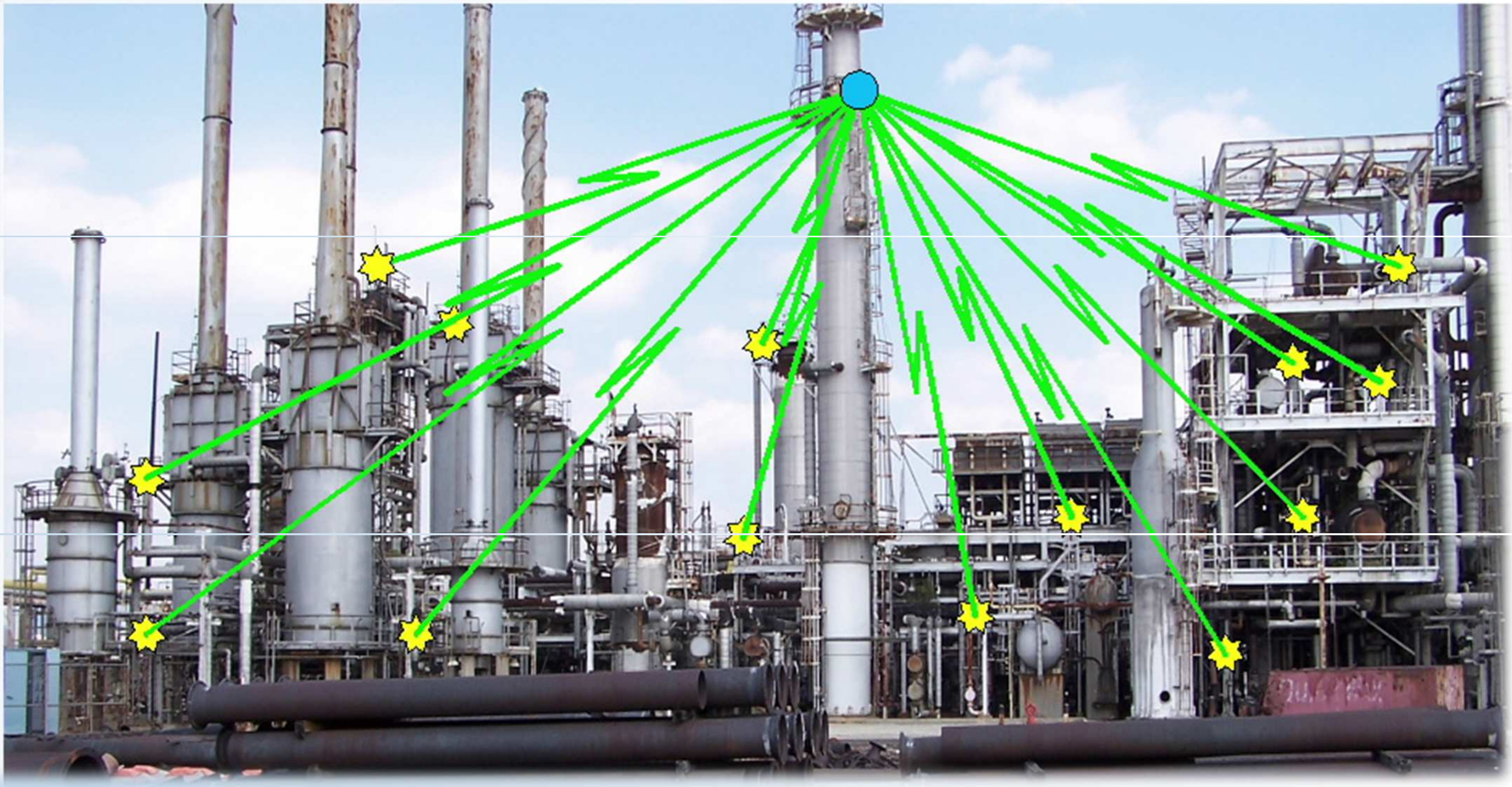
- Thin films withstand heat shrinking process
- Equipment or tanks may be encapsulated with a protective leak detecting conformable wrap

Conformable Wraps - Tanks

A common failure mode of high pressure composite tanks is increased permeation/seepage

Decals, paint pens, markers, applicators

Low-cost Wireless Sensor Networks



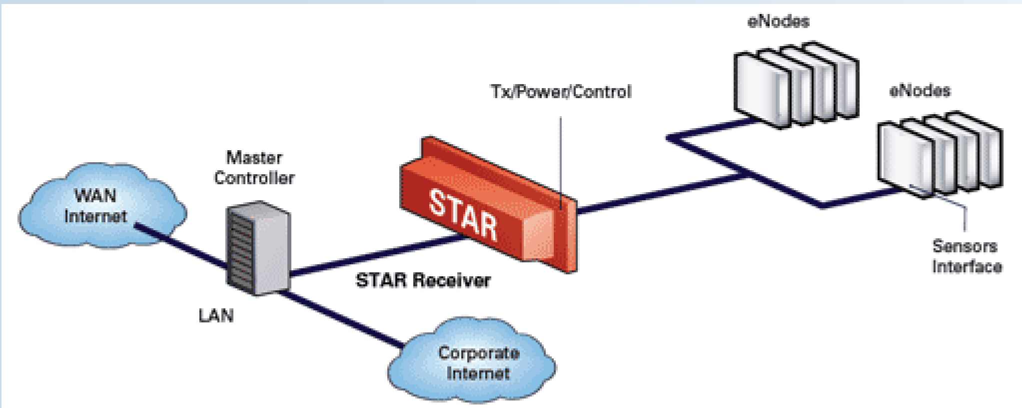
Passive RFID wireless sensors

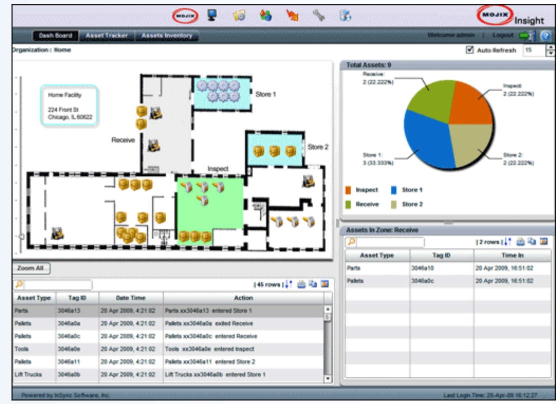
"Passive Wireless Sensors may save BP more than $50 million a year." - *Dave Lafferty of the BP Chief Technology Office, World's first Passive Wireless Sensor Tag (PWST) workshop, Houston, TX July 2011 in Houston, Texas*

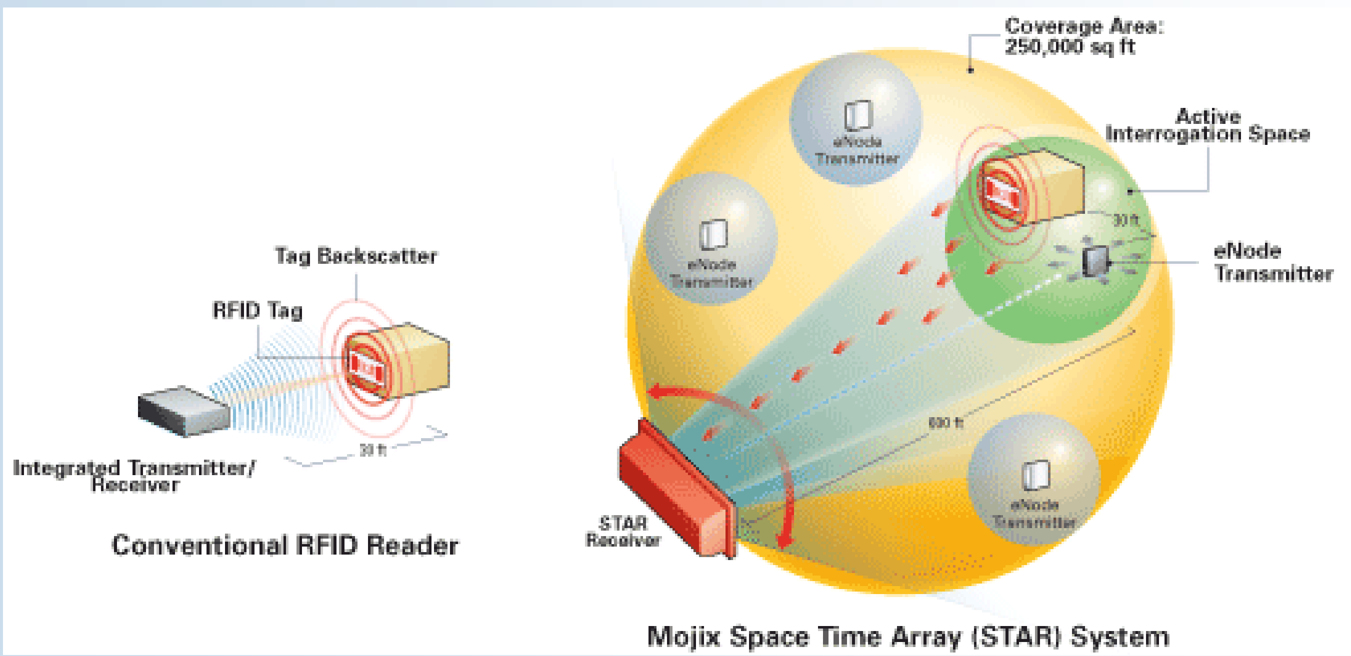
“The potential applications of PWST are numerous. Wired sensors, or generation 1 sensors as BP calls them, cost BP an average of $10,000 a piece to install. That may seem extraordinary, but not when you consider the cost of wiring *safely*. What BP really likes is Passive Wireless sensors (generation 4) at a cost of $10.00 per sensor.

– *Louis Sirico, http://rfid.net/applications/energy/289-passive-wireless-sensor-tags-benefit-energy-aerospace-transportation-a-industry*

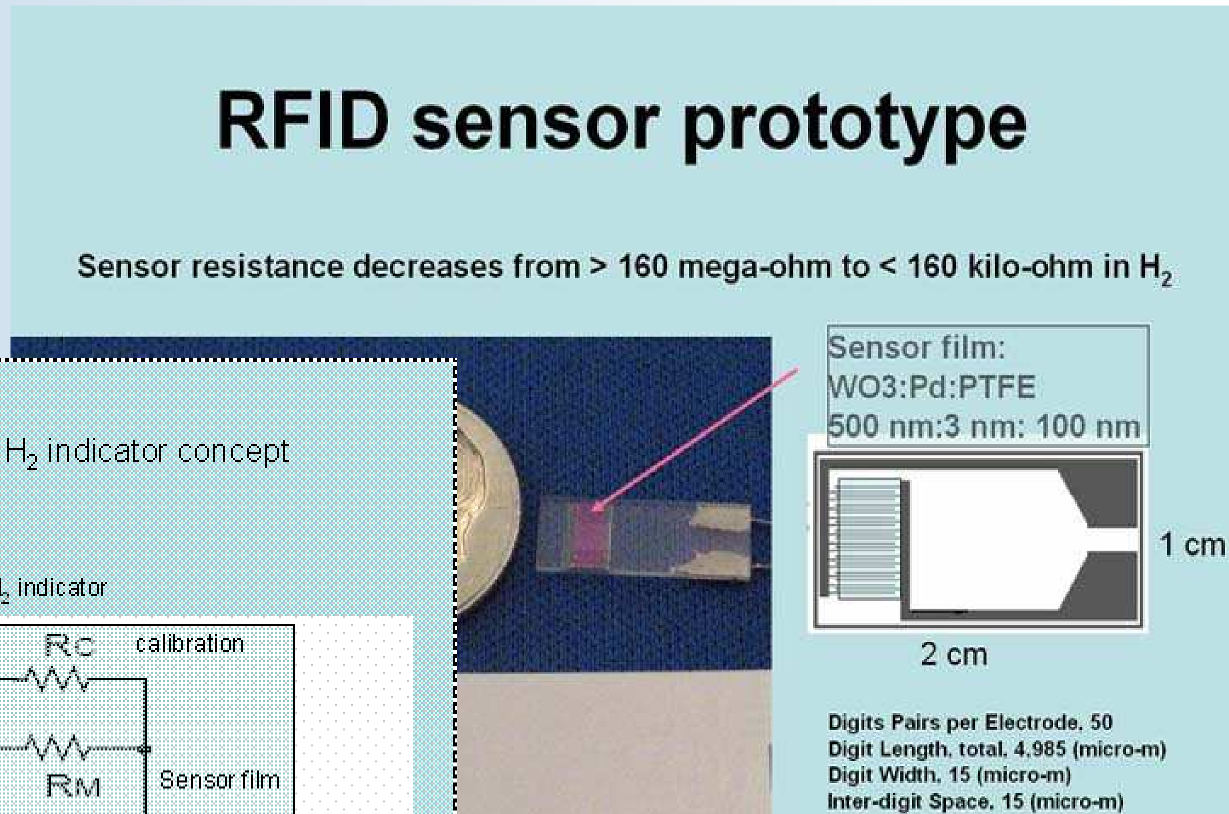
Mogix/Insync Long Range Passive RFID Architecture

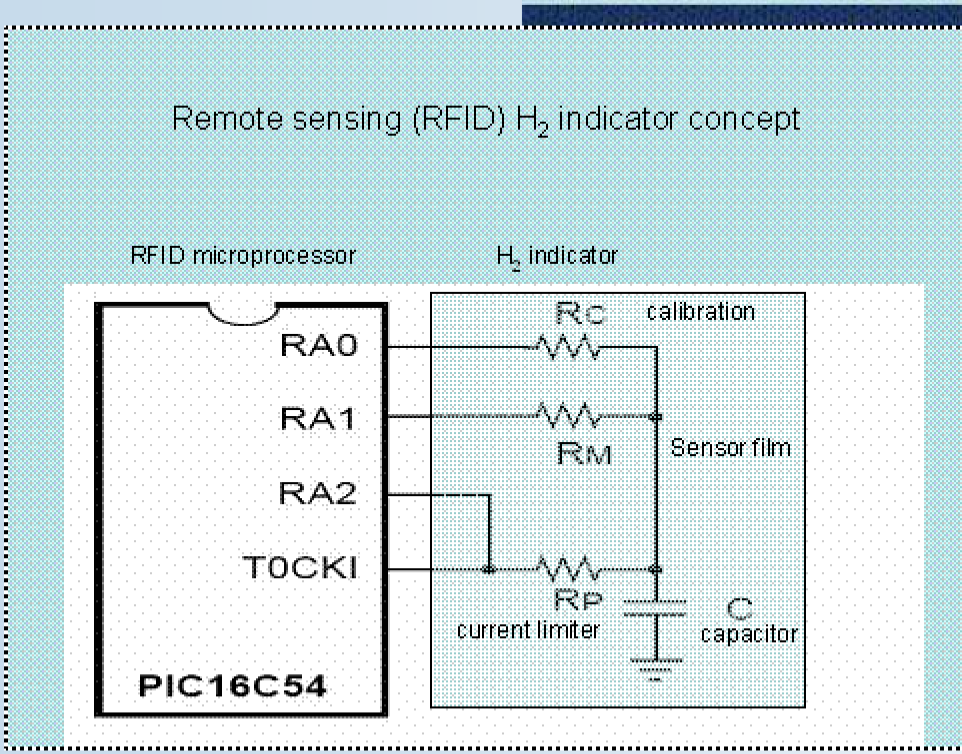




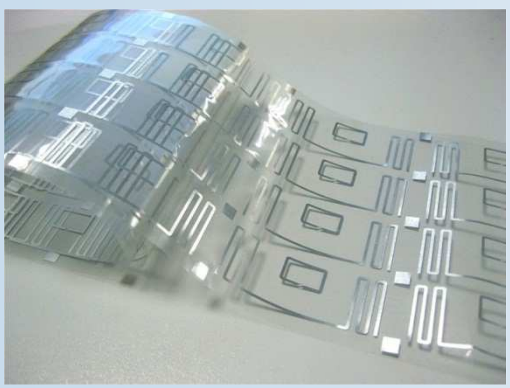


Thin film hydrogen resistance sensor





Smart pipe covers may be visual only or wireless



Gas
Sensor
+
RFID
Tag
+
Long
range
antenna

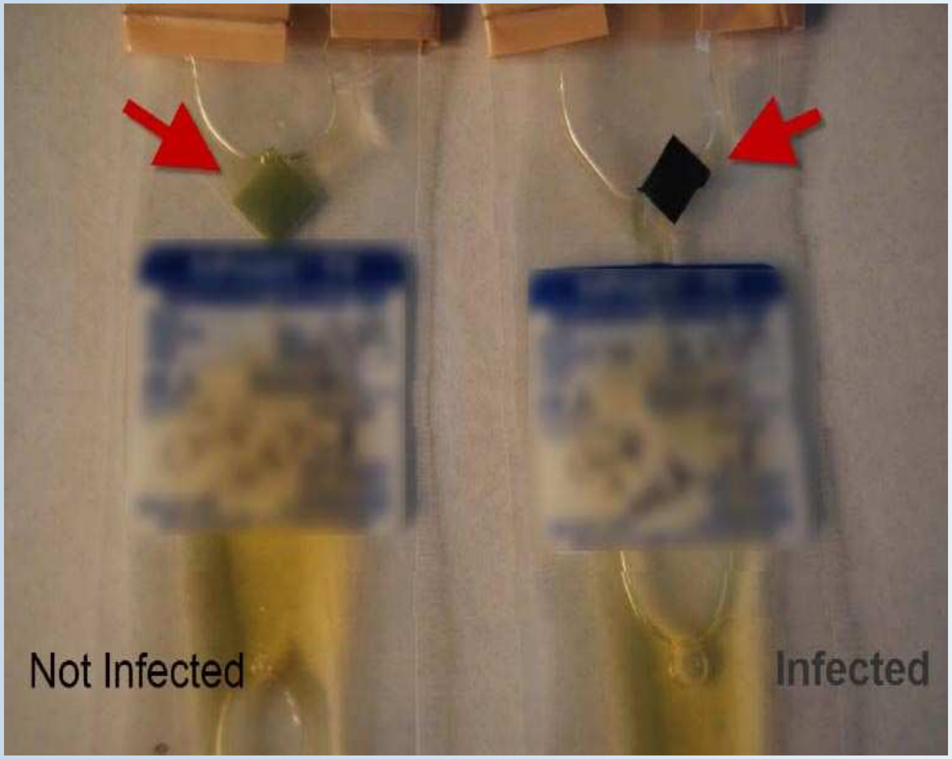
RFID sensors for inventory and leak detection

Smart leak checking during refueling

Leak Checking for First Responders

RFID sensors could be used to check for hydrogen system integrity at accident scenes involving hydrogen vehicles.

Medical Diagnostic Testing



- Used in low cost test kit to detect **most common STD** infection of humans in industrialized countries.
- Estimated **180 million** new cases annually worldwide.
- North America – **7.4 million** new infections each year
- Rate of **asymptomatic** cases as high as 50%.

Hydrogen sulfide sensor for low-cost screening test for contaminated drywall

"Radon Test" analogue for screening existing homes and suppliers

Serendipity!
Solar water purification in less developed countries

Element One responded to a solicitation to adapt our technology to indicate sufficient solar irradiation in bottled water to make it safe to drink.

More potential applications

- Protective, leak detecting coating for fuel cells, electrolyzers, related equipment and piping
- Zinc Air Batteries
- Nuclear Waste Monitoring
- Solar Energy Systems (wind/PV hydrogen)
- Testing of electrical transformer oil
- Portable Power Units
- Hydrogen mine introduction initiative
- Packaging for food products
- Medical Testing
- Environment testing – e.g H_2S in ground water

Technical Challenges - Coatings

- Improved UV/chemical resistance of pigments
- Optimization of pigment/catalyst loading
- Improved understanding of factors affecting speed of response, reversibility, sensitivity
- High temperature coatings
- Fast drying formulations
- Low VOC carriers for pigments
- Incorporation of indicating pigments into inks

Technical Challenges – Thin Films

- Optimization of catalyst and oxide loading
- Improved protective coatings for better durability and selectivity
- Development of thin film sensor for integration into RFID tags
- Develop algorithms for quantitative interpretation of wireless signals
- Long term laboratory and field testing of most promising sensor designs

Current R&D Priorities

- Complete R&D activities to address technical challenges mentioned
- Field testing to better understand markets and products
- Occupy new lab facilities and resume fabricating thin films.
- Maintain current IP position and secure additional IP.

Summary

- Because of their extremely low-cost, hydrogen these new visual and thin film sensors can be abundantly deployed to provide a previously unattained levels of confidence that hydrogen leaks will not go undetected greatly reducing the potential for loss of hydrogen and the formation of dangerous flammable clouds.
- These sensors can be an invaluable tool for leak checking during construction, maintenance repairs, and normal operational safety checks.
- The transition metal oxide thin film sensor when integrated into the new generation of passive RFID networks can reduce the cost of each additional sensor to under $10. Extending their applicability to new markets and uses.

Thank you!

Element One, Inc.

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Table 3.8.2. Targets for Hydrogen Safety Sensor R&D

- Measurement Range: 0.1%-10%
- Operating Temperature: -30 to 80°C
- Response Time: under one second
- Accuracy: 5% of full scale
- Gas environment: ambient air, 10%-98% relative humidity range
- Lifetime: 10 years
- Interference resistant (e.g., hydrocarbons)