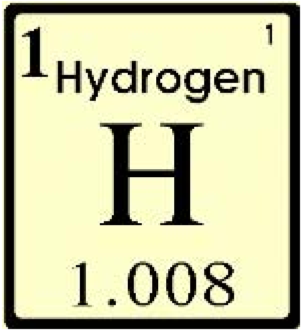



# “Nanotechnology and the Emerging Hydrogen Economy”

Scott Fischler, President/CEO Netozoic, Inc.

Nanotechnology Colloquium
Nanomaterials Application Center
Texas State University

September 25, 2006
Austin, TX

# “Nanotechnology and the Emerging Hydrogen Economy”

## Netozoic, Inc.

Consulting organization specializing in alternative energy technology commercialization.

In collaboration with a diverse network of strategic partners, Netozoic is active in a broad range of projects including:

- National and regional petroleum reduction initiatives
- Alternative energy technology commercialization and export
- Novel hydrogen production methods
- Biomass and waste-to-methane/waste-to-hydrogen production
- (anaerobic digestion and ultra-high temperature gasification)
- Development and delivery of hydrogen public education programs
- Advanced solar, wind, water and green building technologies
- Nanotechnology R&D and commercialization

## Why Hydrogen?

- The emerging Hydrogen Economy holds great potential for a more diverse, flexible global energy supply.
- Hydrogen holds great potential to transform humanity’s relationship with energy.
- There is significant investment (totaling in the billions of dollars) by the energy and automotive industries, public and private laboratories, as well as our federal government to spur the development of the Hydrogen Economy.
- The U.S. and other nations are actively developing hydrogen-based technologies and infrastructure to reduce dependency on fossil fuels.




1 Hydrogen 1
H
1.008

## Challenges and Obstacles

- The wide-scale availability of hydrogen fuel cell vehicles, a transportation revolution in the making, remains several years from commercial viability due to a range of issues including cost and durability.
- The technologies for producing, storing and delivering hydrogen cost-competitively with the entrenched oil and gas infrastructure is still developing.
- Uniform codes and standards for the safe handling of hydrogen have not yet been established.
- Public policy and tax incentives for hydrogen are lagging other renewable energy technologies.
- Hydrogen infrastructure in the U.S. is in the early development stages, with a few noteworthy exceptions.

**Hydrogen Fuel Cell Vehicles on Display**

# Nanotechnology's Role in the Hydrogen Economy

- Nanotechnology holds enormous potential as an enabler of many core and critical technological advancements that will propel hydrogen into the mainstream.
- Nanotechnology will foster significant reductions in the cost of components, and provide substantial gains in production and operational efficiencies, creating a wide range of commercial opportunities.
- Nanotechnology is revolutionizing hydrogen sensing and safety technology, utilizing palladium nanoparticles to detect trace quantities of hydrogen.
- Significant advancements have already been made in utilizing carbon nanotubes for the safe and efficient storage of hydrogen.
- Recent developments in Hydrogen Internal Combustion Engine (HICE) vehicle technology and stationary hydrogen utilization for distributed energy generation suggests that the Hydrogen Economy, and wide-scale adoption of hydrogen technologies, is imminent.
- Nanotechnology will be a key enabler of the emerging Hydrogen Economy, presenting significant opportunities to accelerate the technology curve.

# The Falling Cost of Technology Over Time

- Introduced in 1972, the Texas Instruments TI-2500 “Datamath” was one of the first battery-operated hand-held calculators sold. It had only four basic functions: addition, subtraction, multiplication and division. It cost $149.99 ($660.00 in 2005 dollars).
- Today a Texas Instruments TI-108 solar-powered hand-held calculator sells for $4.49 and has much more advanced functionality than the TI-2500.
- The cost of this technology has fallen by a multiple of 146.

TI-2500


TI-108

# Researchers Brief U.S. Senate on Future of Hydrogen Economy

- On Jan. 11, 2005 in Washington, D.C. members of UC Davis' Hydrogen Pathways Research Program in the Institute of Transportation Studies briefed U.S. senators and staffers on the future of fuel cell vehicles. The Hydrogen Pathways Research Program is the leading program worldwide for the study of issues related to a transition to hydrogen as a transportation fuel.
- The briefing, presented to the Senate caucus on Hydrogen and Fuel Cells, co-chaired by Senator Byron Dorgan (D-N.D.) and Senator Lindsey Graham (R-S.C.), discussed the latest findings from the hydrogen and fuel cell research at UCD and the current activity at the California Fuel Cell Partnership.
- The group stated that “hydrogen is one of the only long-term fuels that allows for radical combined reductions in greenhouse gases, air pollutants and oil use in the transportation sector. Early on during the transfer to fuel cell vehicles, hydrogen would probably be obtained from hydrocarbons such as natural gas. The process would later transition toward zero-carbon sources, which could be renewable energy like solar and wind, or hydrocarbons with the carbon sequestered."
- Over time, “a substantial increase in the use of renewable resources such as wind, solar, and biomass, hydrogen could be produced with domestically available resources.”

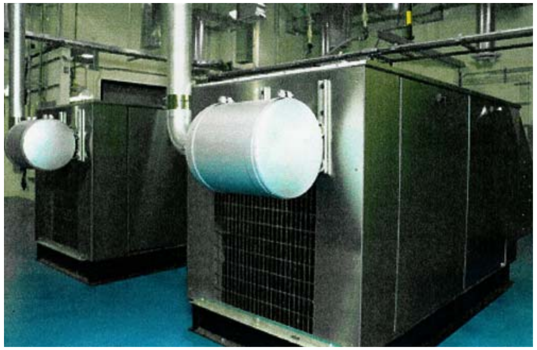
Source: UCD Aggie 01/19/05

# Hydrogen Safety

- The perception of hydrogen, specifically regarding its safety, remains burdened by misconceptions and controversies surrounding the Hindenburg disaster of decades past.
- Iconic images and accounts of the Hindenburg disaster are indelibly etched in our collective memory.
- Developments in nanotechnology, especially in the realm of leak detection using nanosensors, will help alleviate negative perceptions surrounding hydrogen.

# “Nanotechnology and the Emerging Hydrogen Economy”

## Hydrogen Overview





- Hydrogen is an energy carrier, NOT an energy source.
- When hydrogen combines with oxygen in a fuel cell it produces electricity to power a vehicle or a building. The by-product is water.
- When hydrogen burns in an internal combustion engine the exhaust is clean water vapor.

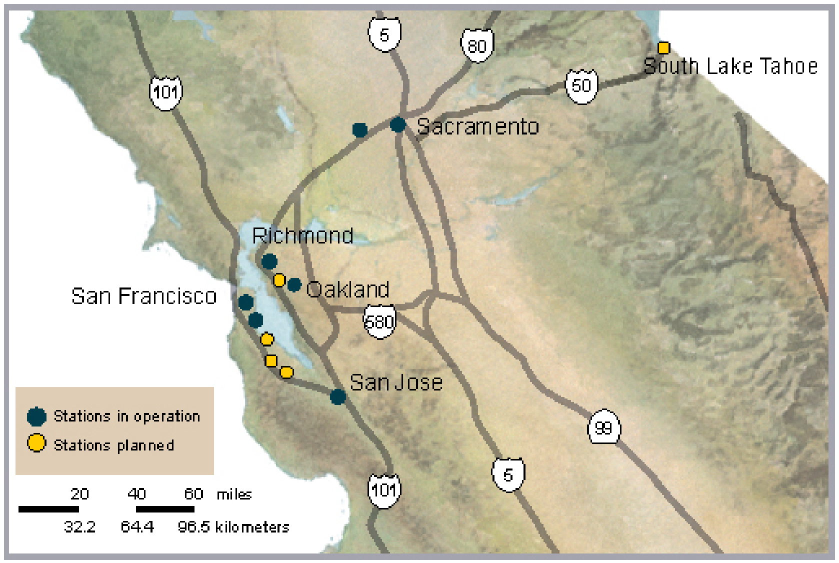
1 Hydrogen 1
H
1.008

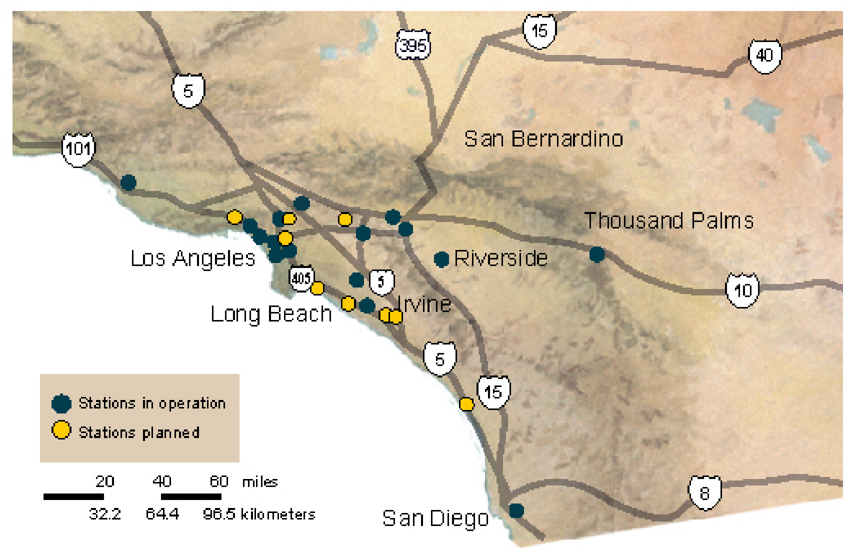
# California Hydrogen Highway Network
# Executive Order on Hydrogen

"The goal of the California Hydrogen Highway Network initiative is to support and catalyze a rapid transition to a clean, hydrogen transportation economy in California, thereby reducing our dependence on foreign oil, and protecting our citizens from health harms related to vehicle emissions. We have an opportunity to deal with these problems by investing in California's ability to innovate our way to a clean hydrogen future, thus bringing jobs, investment, and continued economic prosperity to California. We have an opportunity to prove to the world that a thriving environment and economy can co-exist.” -- Governor Schwarzenegger April 20,2004



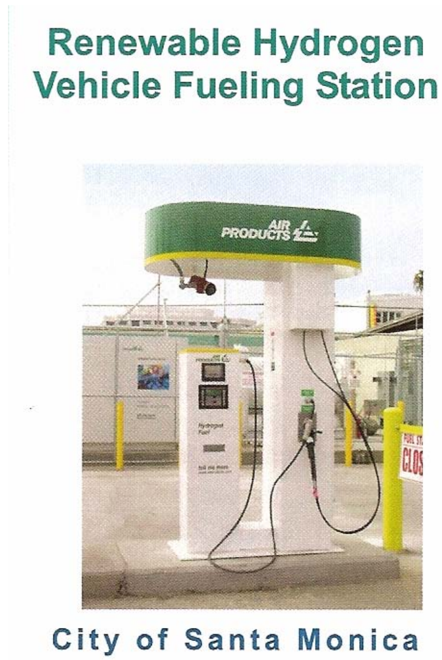
# California Hydrogen Fueling Station Map



# “Nanotechnology and the Emerging Hydrogen Economy”

## Hydrogen Fueling Stations

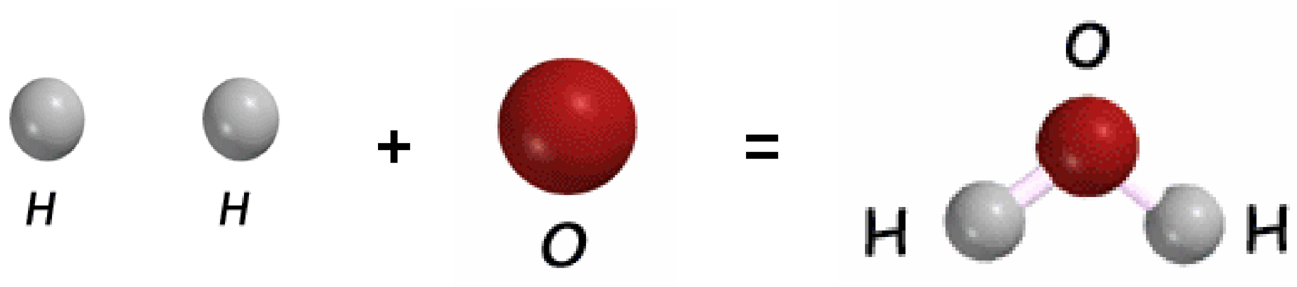






1 Hydrogen 1
H
1.008

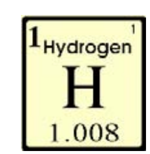
# Chemistry 101 Revisited

## Two Hydrogen Atoms + One Oxygen Atom = $H_2O$

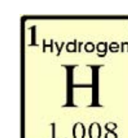



Electrolysis: The process of using an electrical current to split water into hydrogen and oxygen

September 20, 2006 - QuantumSphere Files Patent on Catalyst Device for Low-Cost, High-Efficiency Hydrogen Electrolysis -- QuantumSphere (QSI), a manufacturer of nano metals and alloys for applications in renewable energy and other markets demanding advanced materials, has announced the recent filing of another patent relating to the production of hydrogen by electrolysis using its proprietary nano electrodes. Using electrodes composed of QSI nanometals, QuantumSphere has achieved up to 80% efficiency at lower current flow rates (100 mA/cm2) and approximately 60% efficiency at higher rates (1,000 mA/cm2). Over the next year, QSI believes it will achieve or exceed the DOE 2010 target of 75% efficiency at rates beyond 1,000 mA/cm2 through further optimization. As a result, the company believes it has enabled electrolysis to more easily compete with hydrogen generation by steam reformation.



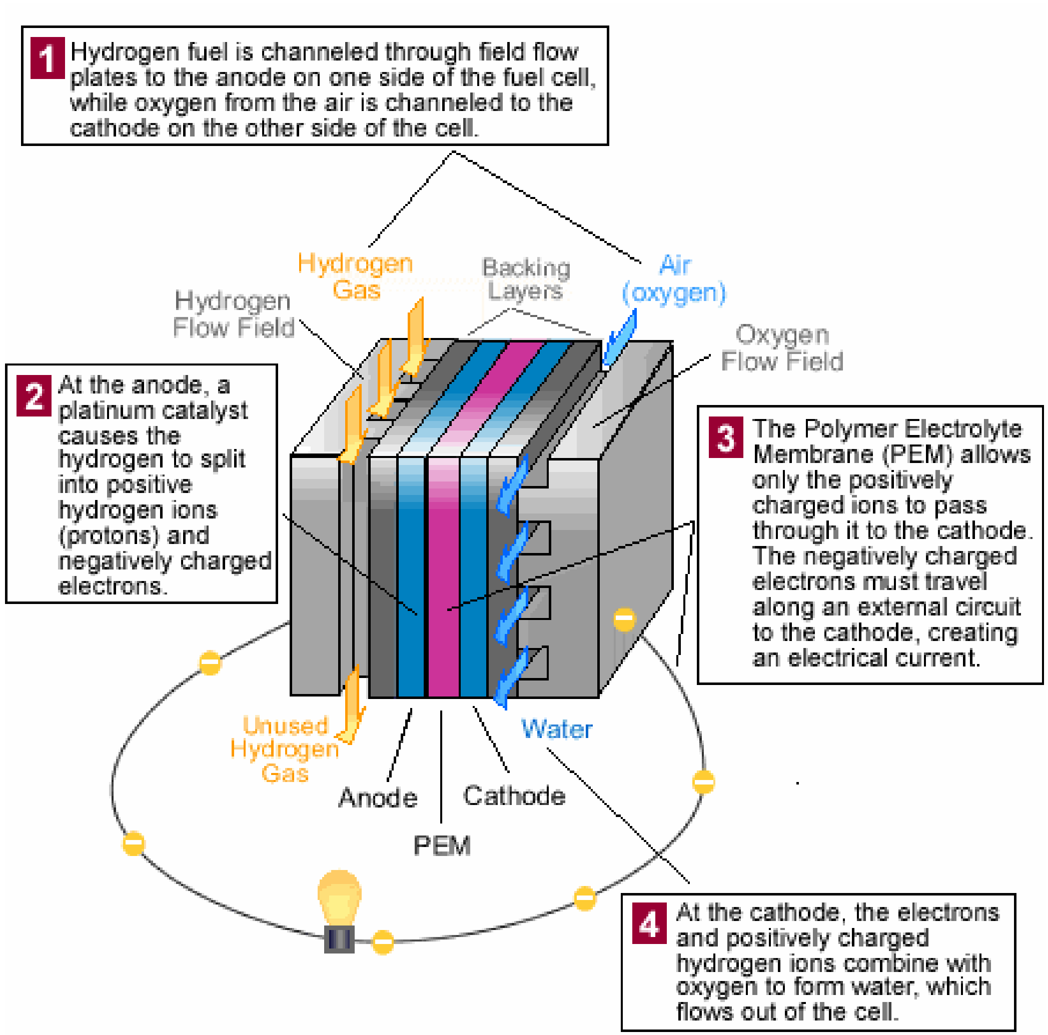
# Sampling of International Hydrogen R&D Activity

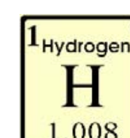



# Sampling of International Hydrogen R&D Activity

- U.S./France
  - "HyRadix and France's IFP (Institut Français du Pétrole) announced a joint multi-year development program to extend the capability of HyRadix' Autothermal Reforming (ATR) technology to process liquid hydrocarbon feed stocks. Initial work will focus on the production of hydrogen from ethanol." – Source: Green Car Congress
- Iceland
  - "Iceland is in the early stages of a decades-long experiment in which the whole country will, in effect, serve as a laboratory. If the experiment is successful, Iceland will become the world's first hydrogen economy by the year 2050." – Source: Foreign Service Journal
- Argentina
  - "Wind energy is the most widespread renewable energy source in Argentina - and Patagonia in particular has extraordinary potential due to its strong and constant winds." – Source: BBC
  - "A laboratory situated in the southern Patagonia region of Argentina is producing hydrogen from wind energy to supply power to a village -- and prove that it is possible to replace the polluting fuels derived from petroleum. The Patagonian energy project is a candidate for inclusion on the list of what are known as Clean Development Mechanisms under the Kyoto Protocol on climate change -- energy technologies that do not emit so-called greenhouse gases that contribute to global warming. The "Wind-Hydrogen" project is the South American chapter of a broader programme of the International Centre for Hydrogen Energy Technology of the United Nations Industrial Development Organisation (UNIDO)." – Source: Tierramérica

# Hydrogen Fuel Cells Demystified



# “Nanotechnology and the Emerging Hydrogen Economy”

## Hydrogen Fuel Cell Vehicles

**TOYOTA FCHV**

**VOLKSWAGEN TOURAN HYMOTION**


**NISSAN FCV**

**DAIMLERCHRYSLER "F-CELL" FCV**

**GM HYDROGEN 3**


**THE FORD FOCUS FCV**


**HONDA FCX**

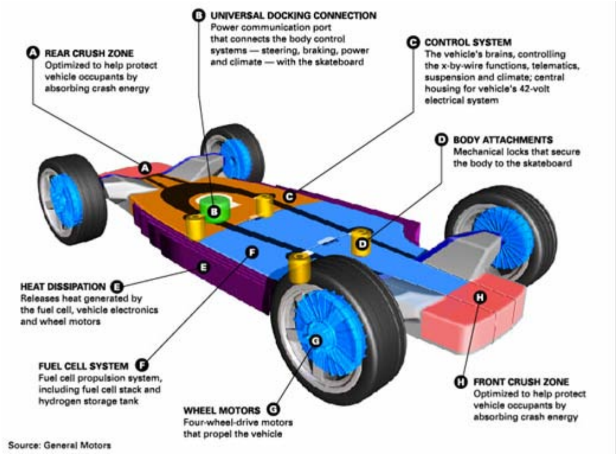

**HYUNDAI TUCSON FCEV**


1 Hydrogen 1
H
1.008

# Honda FCX Fuel Cell Vehicle



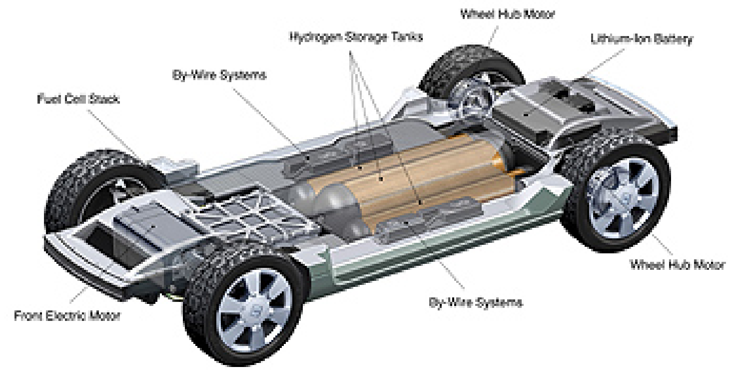
# GM Autonomy - Hydrogen FC Concept Vehicle

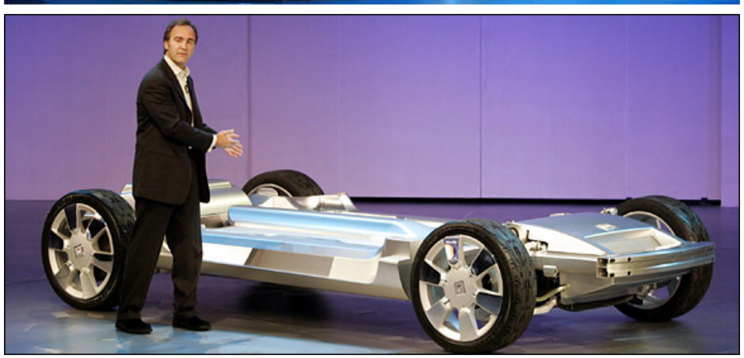



1 Hydrogen 1
H
1.008

# "Nanotechnology and the Emerging Hydrogen Economy"

## GM Sequel Hydrogen FC Concept Vehicle

1 Hydrogen 1
H
1.008

## Nanotechnology and Hydrogen Fuel Cells

- Stanford University, 2005 -- Micro and Nano Scale Electrochemistry Applied to Hydrogen Fuel Cells
- Investigate the conductivity of assemblies consisting of micron and submicron catalyst particles on polymeric electrolyte membranes. Platinum catalyst particles are deposited with the help of a Focused Ion Beam (FIB) system. The FIB allows fabrication of prescribed patterns of platinum particles, which in turn enables systematic studies of particle geometry and its effect on fuel cell behavior. The smallest catalyst particles created by FIB are of the order of hundreds of nanometers.
- To study fuel cell behavior with catalyst particles of less than 10 nanometer diameter, nano-indentation of platinum coated AFM (Atomic Force Microscopy) tips onto a Nafion electrolyte surface is employed. The platinum tips are connected to an impedance spectrum analyzer to measure fuel cell performance.
- Fuel cells offer the promise of cleaner electricity with less environmental impact than traditional energy conversion technologies. However, today fuel cell technology is not economically competitive with traditional energy conversion technologies. Recently, fuel cell costs have declined due to technological successes wrought by the incorporation of nano-structured materials. In spite of this success, greater cost reductions and other significant challenges remain.



1 Hydrogen 1
H
1.008

# Fuel Cells Provide Uninterruptible Power Supply

Two fuel cells provide supplemental power at 4 Times Square in New York City (Conde Nast Building).

The two fuel cells, which together generate 400 kilowatts of electricity, normally will provide a portion of the building's general power requirements.

If there is a utility blackout the systems are capable of operating independent of the utility grid to maintain power to critical mechanical components and external landmark signage on the facade of the building.

# Hydrogen Powered Energy Appliances


# Nano-Scale Electrocatalysts

- University of Wisconsin, 2006 – Three-Dimensional Nano-Scale Catalytic Surface Area
- A polymer-electrolyte membrane (PEM) fuel cell generates current by stripping hydrogen atoms from a chemical source, breaking them apart on a catalyst (such as platinum), and harvesting the electrons. The hydrogen ions (protons) left over from this process are separated from the fuel by an electrolyte, and when brought into contact with the atmosphere they bind to oxygen molecules and produce water. The more fuel you can bring into contact with the catalyst, the more current can be drawn from the cell. A high catalytic surface area is the key to efficiency.
- To compress more power into smaller volumes, researchers have begun to build fuel cells on the fuzzy frontier of nanotechnology. Silicon etching, evaporation, and other processes borrowed from chip manufacturers have been used to create tightly packed channel arrays to guide the flow of fuel through the cell. The point is to pack a large catalytic surface area into a wafer-thin volume. This approach is not only expensive, but inherently limited by its two-dimensional nature.
- This new method not only improves the performance of nano-scale fuel cells, but completely sidesteps the need for industrial-strength technology. “Even the best electrocatalysts, on a flat surface, give only hundreds of microamps per square centimeter. What you really want is … to increase the surface area by orders of magnitude.” Lux explains to PhysOrg.com, “To do this you need a three-dimensional structure.”

## Nano-Scale Electrocatalysts

- Lux and Rodriguez found their fuel channels ready-made in a commonly available, porous alumina filter costing only about $1. The filter is riddled with neat, cylindrical holes only 200 nanometers in diameter, and was already being used at their lab as a template for the growth of nanowires. Lux hit on the idea of creating nanowires in a platinum-copper alloy, then dissolving the copper by soaking the filter in nitric acid. In place of a solid nanowire, each hole was left with a porous platinum electrode. The partially dissolved wires are structurally complex, as befits their random nature, and have an enormous surface area for their size.
- To build a fuel cell, they fill the pores with acid. A sheet of electrolyte-loaded filter paper (or polymer-electrolyte) is placed between two of the nano-electrode arrays to carry off the hydrogen ions. Electrodes can then be placed anywhere on the outer surface of the sandwich, allowing the electrical connections to be easily configured. Stacks of these fuel cell arrays can be connected in series or parallel, to provide higher voltage or current respectively.

http://www.physorg.com/news11654.html

# “Nanotechnology and the Emerging Hydrogen Economy”

## Hydrogen Internal Combustion Engine (HICE)

Shelby Cobra Hydrogen ICE


Ford Hydrogen ICE Shuttle Bus

Quantum Prius Hydrogen ICE

SunLine Transit Hydrogen ICE


*World's first Hydrogen Hybrid Internal Combustion Engine (HHICE)*

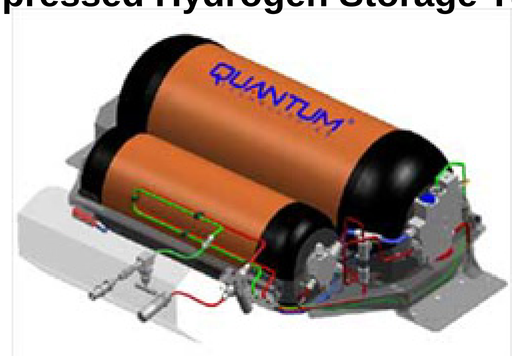
Chevrolet SSR Hydrogen ICE

1 Hydrogen 1
H
1.008

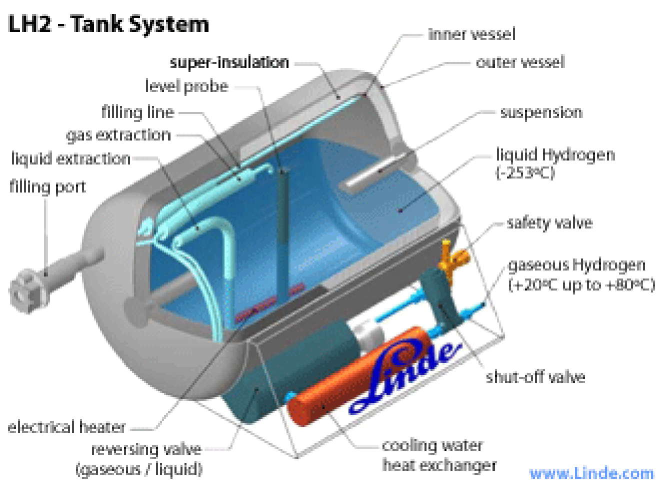
Netozoic, Inc.

# Hydrogen Storage Systems

**Compressed Hydrogen Storage Tank 5000 psi**




**Liquid Hydrogen Storage Tank**




**Metal Hydride Hydrogen Storage Containers**

# Carbon-Based Materials for Hydrogen Storage

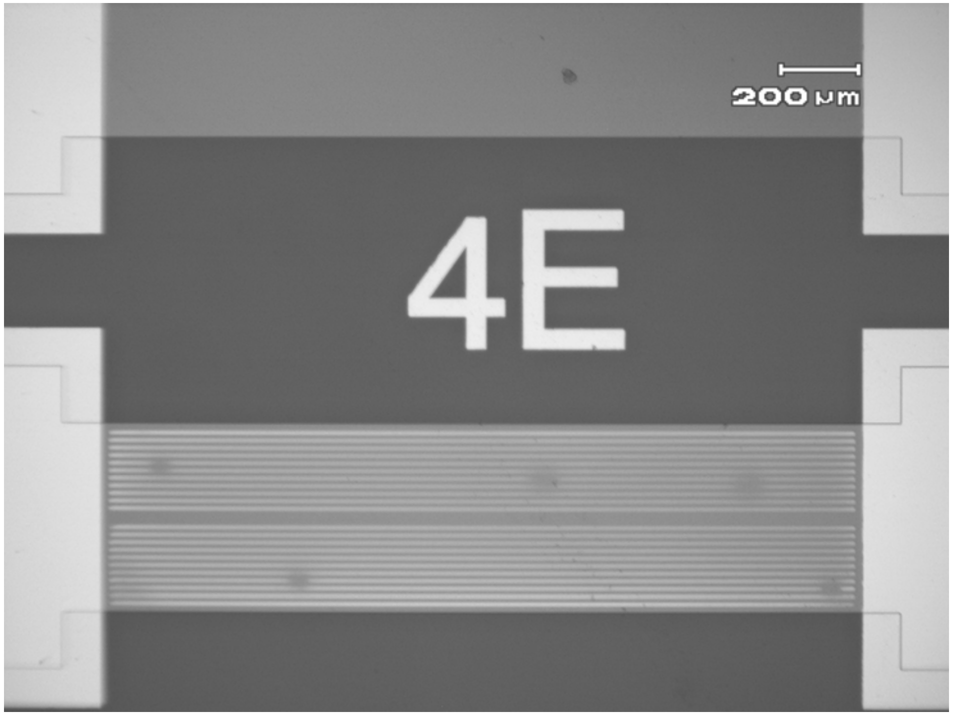
- This category of materials-based storage technologies includes a range of carbon-based materials such as carbon nanotubes, aerogels, nanofibers (including metal doped hybrids), as well as metal-organic frameworks, conducting polymers and clathrates. If structures can be tailored at the nano-scale, hydrogen storage could be enhanced.
- Single-walled carbon nanotubes are being studied as hydrogen storage materials because of published hydrogen gravimetric capacities in the range of 3-10 wt.% at room temperature. However, there has been controversy due to difficulty in reproducing these results. Hence, the current R&D focus for carbon nanotubes has been on establishing reproducibility. Recent results at NREL show that while no hydrogen storage was observed in pure single-walled carbon nanotubes, roughly 3 wt.% was measured in metal-doped nanotubes at room temperature.
- The room temperature gravimetric capacity measured in carbon nanotubes is below the 2010 system target of 6.0 wt.% and further improvements must be made. In addition, low-cost, high-volume manufacture processes must be developed for single-walled carbon nanotubes in order for them to be economically viable in vehicular applications. The DOE Hydrogen Program has a go/no-go decision point planned on carbon nanotubes at the end of FY2006 based on a reproducibly demonstrated material hydrogen storage gravimetric capacity of 6 wt.% at room temperature.

www.eere.energy.gov/hydrogenandfuelcells/storage/carbon_materials.html

# Carbon Nanotubes for On-Board Hydrogen Storage

- U.S. DOE Go/No-Go Decision -- August 28, 2006
- A Federal Register Notice has been issued to solicit input related to DOE's upcoming go/no-go decision on pure carbon nanotubes for on-board vehicular hydrogen storage.
- DOE's Office of Hydrogen, Fuel Cells, and Infrastructure Technologies will review the current status of hydrogen storage in carbon nanotubes against specific technical criteria and compile all input during September 2006 for consideration in the decision planned in October 2006. Relevant technical documents or position papers are due by September 15, 2006.

# Palladium Nanoparticle Hydrogen Sensor Dual Sensors Layout




Reference Element

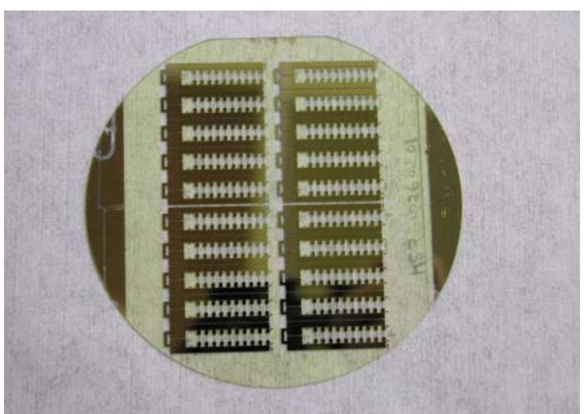
Working Element

Source: Applied Nanotech, Inc.

# Hydrogen Sensor Process

1. Glass substrate cleaning
2. Metal film deposition
3. Sensor Patterning
4. Contact pads deposition
5. Wafer dicing
6. Electro-plating
7. Chip dicing
8. Packaging
9. Conditioning
10. Testing
11. Quality Control

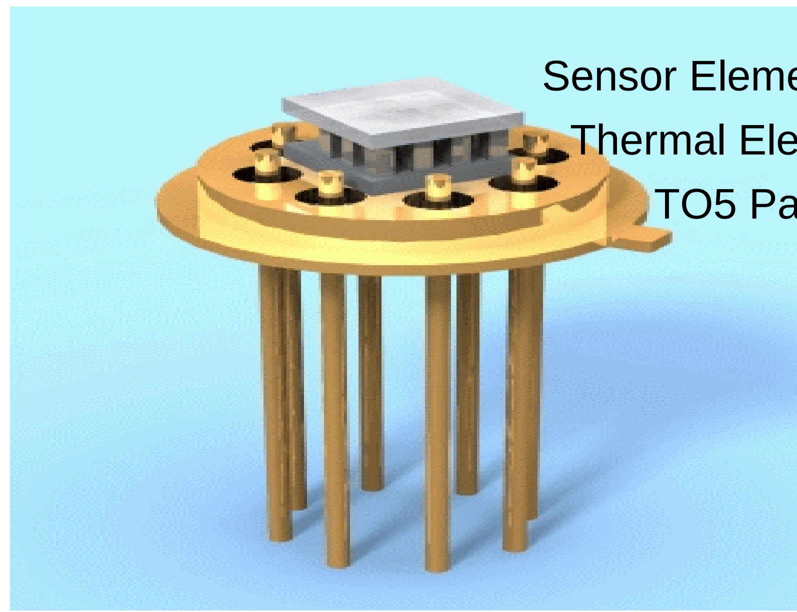
Photograph of a 100-sensor patterned glass wafer



Source: Applied Nanotech, Inc.

# Palladium Nanoparticle Hydrogen Sensor Mounted on an Embedded Heater Package

- Pd nanoparticles
- Dual sensors circuit
- Embedded heater package
- Robust package housing design
- Easy to manufacture
- Wide sensitivity range
- Very low power
- Low cost
- Large working temperatures range (from -10 to 100$^{o}$C)
- No interference with $N_2$, $NH_3$, $O_2$, and $CO_2$




Source: Applied Nanotech, Inc.

# Palladium Nanoparticle Hydrogen Sensor - Vehicle Testing


Source: Applied Nanotech, Inc.

# “Nanotechnology and the Emerging Hydrogen Economy”


## Applied Nanotech, Inc.
*A subsidiary of* NANO-PROPRIETARY, INC.

3006 LONGHORN BLVD., SUITE 107 AUSTIN, TX 78758
PHONE (512) 339-5020 ♦ FAX (512) 339-5021 ♦ WEBSITE: WWW.NANO-PROPRIETARY.COM

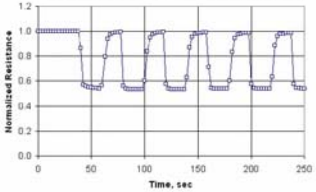

### Hydrogen Sensor

**Specifications**

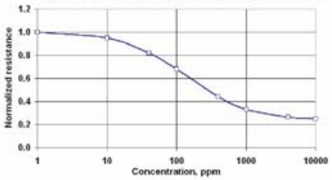
- Sensitive Material: Pd nanoparticles
- Substrate material: Glass
- Operating Temperature*: -30°C to 120°C
- Storage Temperature: -60 °C to 80°C
- Sensor Dimensions: 4 X 4 $mm^2$
- Package: TO-5/TO-8
- Typical Resistance: 2.2 kΩ
- Sensor Power: 2mW
- System Power (w/TEC): ~ 1 W
- Operation Range: 10 – 40,000 ppm
- Response Time: 1sec at 1% $H_2$
- Accuracy: ±20%
- Repeatability: ±10%
- Part # ($H_2$ in gas): NPHS-TO5
- Part # ($H_2$ in gas): NPHS-TO5
- Part # ($H_2$ in liquid): MNPHS-TO5
- Part # ($H_2$ in liquid): MNPHS-TO8
- Controller is available on request

*Using an integrated thermo electric cooler (TEC)

**Response of ANI sensor to 1% $H_2$ at 80°C**




**Typical calibration plot for hydrogen sensor**




**Operating Principle**

- Pd based nanoparticles undergo phase transition and expand in presence of hydrogen.
- The resistivity of the sensor decreases with exposure to hydrogen.
- Temperature of the sensor is kept constant by an integrated TEC.

**Features**

- Nanosized palladium particles allow measurements in wide range of $H_2$ concentrations
- Low cost in volume
- Stable operation
- Convenient electronic packages
- No false alarms

**Applications**

- Fuel Cells
- Automotive
- Back-up power systems
- Portable gas detectors and monitors
- Power transformers
- Other applications where hydrogen measurements or detection required

**TO-8 (left) and TO-5 (right) packages**


IN USA AND EUROPE +1 (512) 339-5020 EXT. 130 PHONE
+1 (512) 339-5021 FAX
SALES@APPLIEDNANOTECH.NET
IN ASIA +81-3-5214-6144 PHONE
+81-3-5214-6148 FAX
MMATT@NIFTY.COM

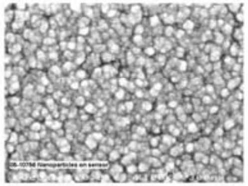


## Applied Nanotech, Inc.
*A subsidiary of* NANO-PROPRIETARY, INC.

3006 LONGHORN BLVD., SUITE 107 AUSTIN, TX 78758
PHONE (512) 339-5020 ♦ FAX (512) 339-5021 ♦ WEBSITE: WWW.NANO-PROPRIETARY.COM

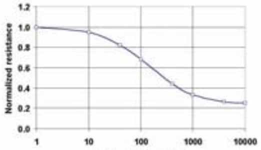

### ANI’s Metal Nanoparticle Sensor Platform

ANI’s metal nanoparticle sensor platform is best represented by ANI’s $H_2$ sensor that employs the property of palladium particles to dissociate and dissolve hydrogen.



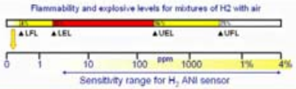
*SEM image of Pd nanoparticles deposited on sensor substrate*

Nanosized Pd clusters can dissolve more hydrogen than bulk palladium at low $H_2$ pressures due to the surface effect. This results in a wider operation range of the $H_2$ sensor that spans from 10 *ppm* to 4%.

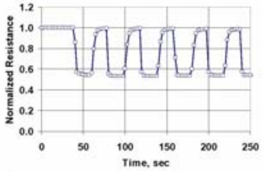



*Response of ANI hydrogen sensor in a range from 1 ppm to 1% $H_2$ at 80°C*

This operation range is critical for the most of safety or leak detection applications since the lower flammability level of hydrogen is only 4%.

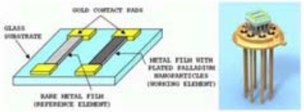



Response time to hydrogen is the other key sensor parameter. A typical on-off plot for the ANI hydrogen sensor shows very fast operation at 1% $H_2$.




*Response time of ANI $H_2$ sensor is around 2 sec. and recovery time less*

Stable performance of the device is ensured by the design approach where sensor uses a reference element and a built-in thermoelectric cooler (TEC). The temperature of the sensor is kept constant at 80°C.



*ANI sensor architecture and package*

The sensors use convenient TO-5 or TO-8 packages with openings protected by a metal mesh or polymer membrane. An available sensor controller supports TEC temperature control, drift compensation, resistance and concentration data readout. The controller has RS-232 port for communication with a computer, as well as an analog signal output.

**Applications:**

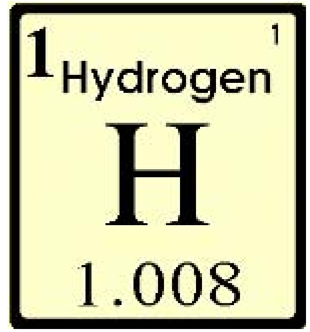
| | |
|---|---|
| Automotive | Power transformers |
| Reformers | Leak detection |
| Hydrogen storage | Fuel cells |


IN USA AND EUROPE +1 (512) 339-5020 EXT. 114 PHONE
+1 (512) 339-5021 FAX
SALES@APPLIEDNANOTECH.NET
IN ASIA +81-3-5214-6144 PHONE
+81-3-5214-6148 FAX
MMATT@NIFTY.COM


Source: Applied Nanotech, Inc.

# Conclusions

- Nanotechnology holds enormous potential as an enabler of many core and critical technological advancements that will propel hydrogen into the mainstream.
- Nanotechnology will foster significant reductions in the cost of components, particularly in the areas of hydrogen production, storage, leak detection and materials.
- Nanotechnology is revolutionizing hydrogen sensing and safety technology, utilizing palladium nanoparticles to detect trace quantities of hydrogen.
- Nanotechnology will be a key enabler of the emerging Hydrogen Economy, transforming humanity’s relationship with energy.




# “Nanotechnology and the Emerging Hydrogen Economy”

Scott Fischler, President/CEO Netozoic, Inc.

scott@netozoic.com
www.netozoic.com
505-473-1517