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Hydrogen Sensors for On-Board Diagnostics

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Outline

- Automotive sensors
- Why Hydrogen sensors?
- Hydrogen detection techniques
- Detectors performances and limitations
- Conclusions
- References

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Automotive sensors

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Electronics ≅ 20% of value of a car in the 2000's

↕

Acceleration Sensors: airbags, vehicle dynamics control, antilock braking systems, anti-theft systems, active suspension control, headlight leveling

Pressure Sensors: air intake control, turbocharger pressure, oil pressure, atmospheric pressure, fuel-tank pressure, brake pressure, climate control, fuel pressure

Mass-flow Sensors: air intake control

Angular-rate Sensors: vehicle dynamics control, navigation and rollover systems.

Rotational-speed and Phase Sensors: wheel speed for ABS, engine speed, camshaft, and crankshaft phase for motor control, gear shaft speed for transmission control

Angle and Position Sensors: throttle valve angle, pedal angle or position, steering angle…..

Exhaust-gas Sensors

Sensing the Surroundings for Comfort and Safety: Radar and Video Sensors, Night-vision

New Sensors for Drivetrain and Motor Control: Engine Combustion Sensing

New Sensors for Chassis Systems: e.g Steering-torque sensors for electromechanical steering systems

Etc…..

Why Hydrogen sensors?

- **H_2 Properties**
  - lighter than air
  - fastest diffusing gas
  - molecular size, permeates easily through most materials
- **H_2 Limits in air**
  - Flammability: 4 – 75 %
  - Detonation: 18 – 59%
- **H_2 Ignition Energy in air**
  - 20 µJ (Gasoline/air 240 µJ)
- **H_2 Autoignition Temperature**
  - 585 ºC

Why on vehicles?

Driving forces for the use of a certain sensor may be market pull (consumer demand), technology push (OEM product differentiation by new feature), or legislation.

All three forces are likely to act in the case of H_2 sensors for H_2 powered vehicles

Possible locations on a vehicle:

- Passenger compartment
- Engine Compartment
- Tank
- Refueling system

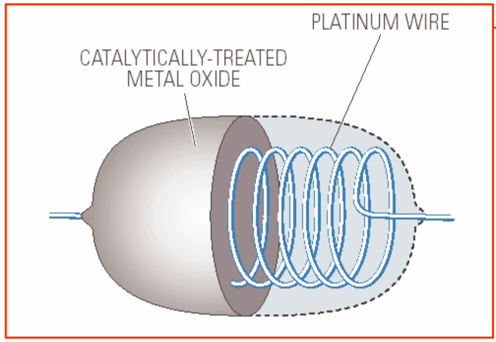
Which sensor is the best?

- Catalytic combustion
- Electrochemical
- Semiconductor
- Thermal conductivity
- ~~Flame Ionization~~
- ~~Infrared~~
- ~~Photo ionization~~
- Acoustic
- Field-effect
- Thermoelectric
- Optical
- Pd/Ni resistors
- Piezoelectric
- TiO_2 Nanotubes
- ……………………

DEPENDS ON

- ☞ **Gas & Concentration Range**
- ☞ **Fixed or portable, point or open path**
- ☞ **Environment (humidity, temperature, pressure, gas velocity, chemical poisons and/or interfering species)**
- ☞ **Power consumption, response time, maintenance interval**

Catalytic bead (pellistor)



Source: International Sensor technology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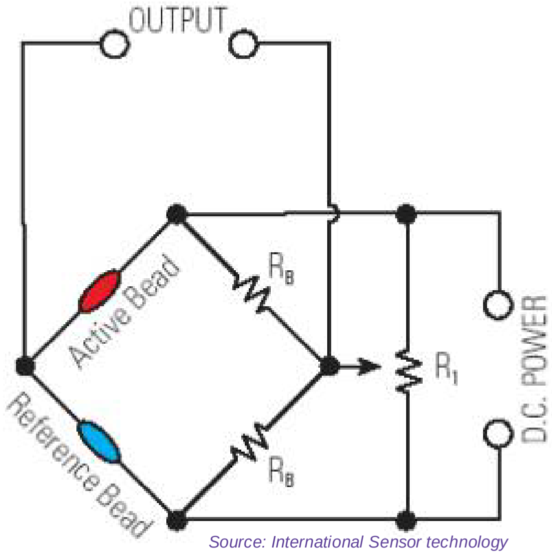


Source: International Sensor technology

H_2 ⇒ oxidation ⇒↑temp. ⇒ ↑resistance ⇒ alter bridge balance ⇒ signal

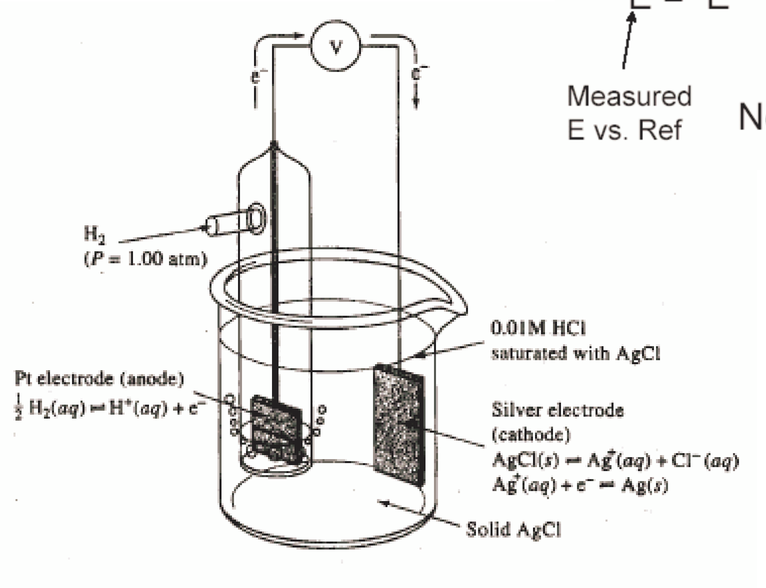
- **Issues:** Not selective; needs oxygen
- **Advantages:** Wide availability, reasonable price

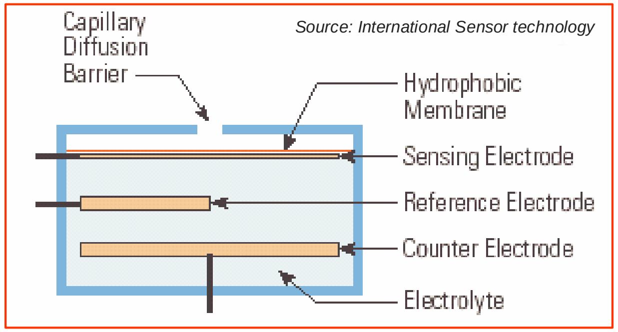
Electrochemical

$$E = E^{o\prime} + \frac{2.303\,RT}{nF} \log \frac{[Ox]}{[Red]}$$

Measured E vs. Ref

Nernst Equation





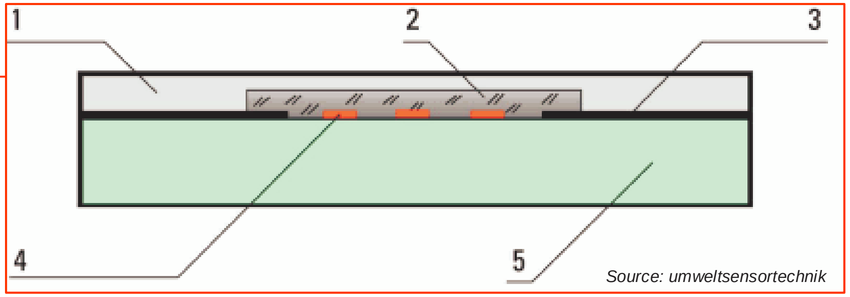
H_2 ⇒ oxidation at the WE ⇒ change of WE potential vs. RE

⇒ current between WE and CE ⇒ signal ⇓ (amperometric or potentiometric)

- **Issues:** Long response time
- **Advantages:** sensitive, selective, low power consumption

Semiconductor


Source: International Sensor technology



Source: umweltsensortechnik

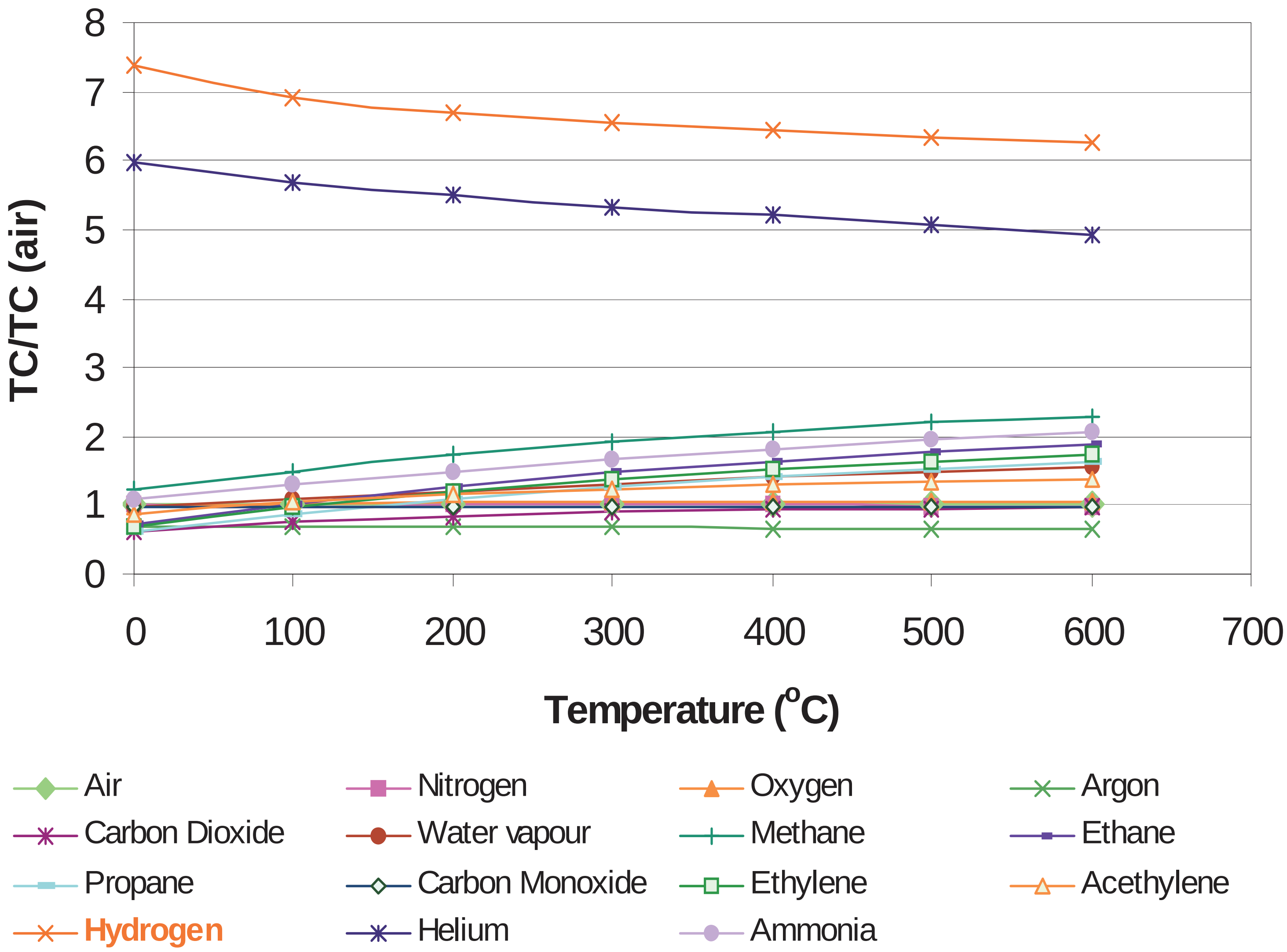
1 sensitive layer
2 insulating layer
3 Pt-contacts
4 Pt-heater
5 ceramics substrate

- Oxides from the transition metals (typically SnO_2) , are vacuum deposited onto a ceramic chip
- A heating element is used to regulate the sensor temperature

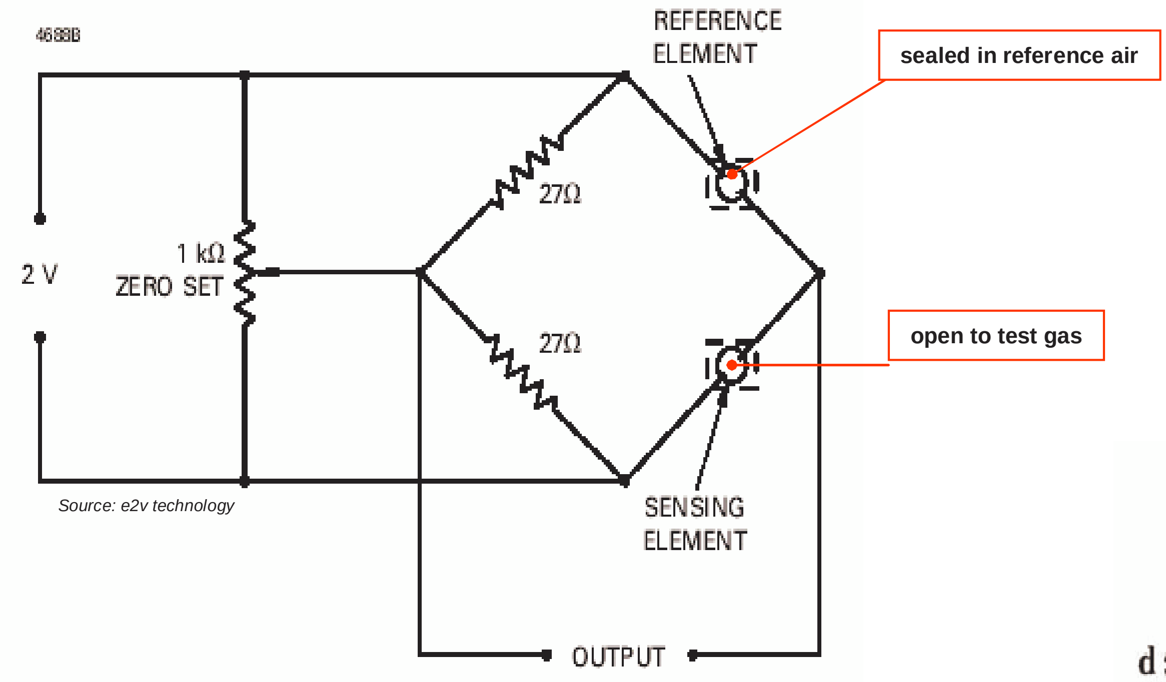
At at High T (~400ºC) in air:
Surface chemisorbed oxygen ⇒ e^- are removed from the conduction band.
Hydrogen chemisorption ⇒ oxidation ⇒ e^- are re-injected ⇒ resistance decreases ⇒ signal

- **Issues:** Suffers humidity, gets saturated easily
- **Advantages:** sensitive, selective, low price

Thermal conductivity

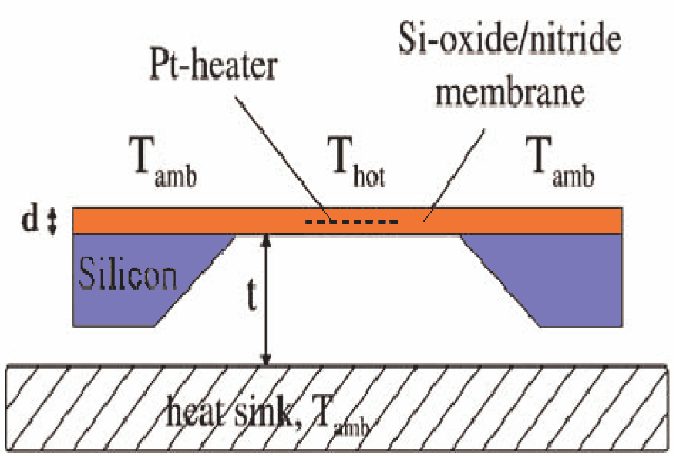


Thermal conductivity (cont)



TC (test gas) > TC (air) ⇒ SE loses more heat than RE ⇒ temp.↓ ⇒ resistance ↓ ⇒ bridge unbalances ⇒ signal

Known ΔT between a hot and cold element ⇒ Heat transfer via the test gas ⇒ Power supplied to maintain ΔT ⇒ signal



- **Issues:** may have low resolution
- **Advantages:** operating range up to 100% Vol., rapid response.

Field Effect Transistors (FET)

Based on the field effect generated by gases in metal oxide semiconductor field-effect transistor (MOSFET) devices with catalytic metals. The charging of the gate contact by the gas molecules results in a voltage change in the sensor signal (http://www.appliedsensor.com/)

H_2 adsorption on the catalytic metal gate ⇒ induces dipoles or charges ⇒ Alters gate contact voltage

- **Issues:**

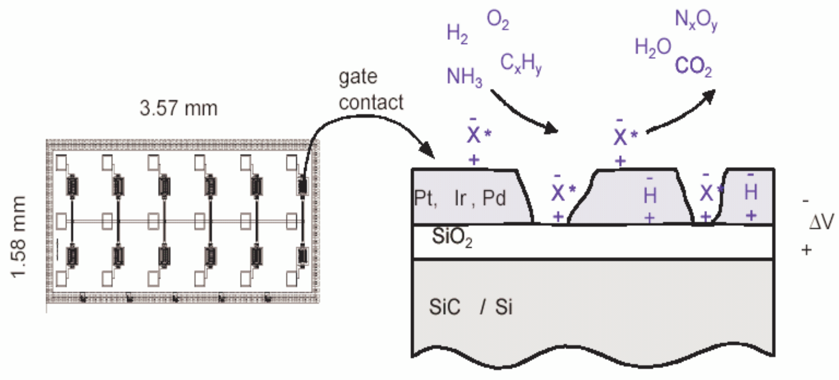
Saturates for high concentrations

- **Advantages:**

High sensitivity

Miniaturization

Source: AppliedSensors GmbH



Sketch of a MOSFET sensor illustrating the detection principle. The threshold voltage of the transistor changes due to the dipoles produced by the gas molecules.

Thermoelectric micro machined sensors

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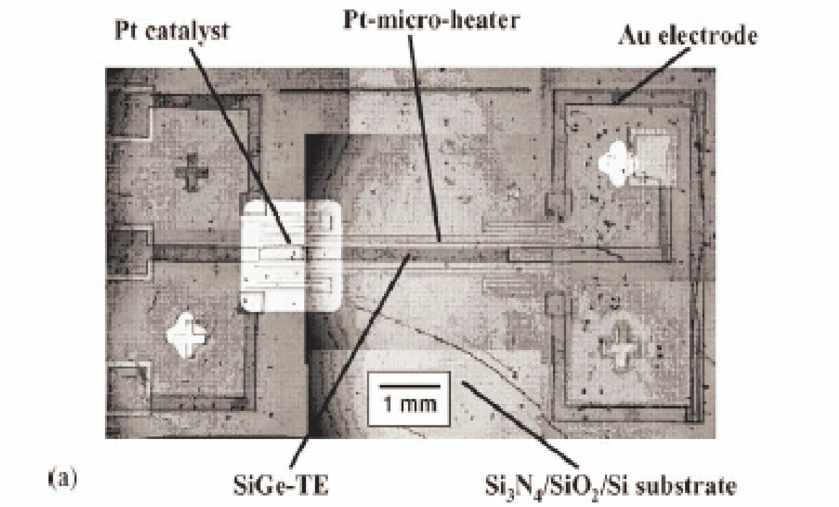
A platinum film is applied as a catalyst that oxidizes hydrogen selectively. The exothermal heat of the oxidation of hydrogen results in the temperature gradients across the sensor, and this gradient is converted into the voltage by the thermoelectric element.

(Kazuki Tajima, Sensors and Actuators B 108 (2005) 973–978; Naoya Sawaguchi et al., Sensors and Actuators B 108 (2005) 461–466)

- **Issues:** at room temperature, humidity decreases the signal/noise ratio.
- **Advantages:**
  High Hydrogen selectivity
  Miniaturization



Source: Elsevier

Micromachined resistors

It uses a Wheatstone bridge architecture, with two Pd/Ni sensor legs whose resistivity changes reversibly in the presence of H_2.

H_2 surface adsorbtion ⇒ Diffuses into bulk ⇒ Alters electrical properties

- **Issues:**

Affected by total gas pressure

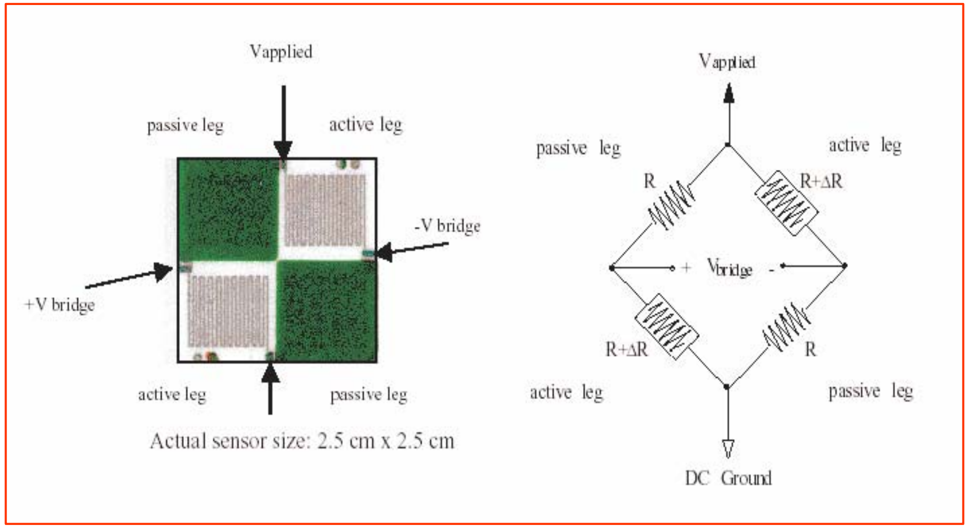
Poisoned by – CO, SO_2, H_2S

- **Advantages:**

Very wide detection range

Rapid response

Independent of environment



Source: B.S. Hoffheins, et al, Proceedings of the 1999 U.S DOE Hydrogen Program Review NREL/CP-570-26938

What to ask?

„The three S of gas detection“

- **high Sensitivity**
- **high Selectivity**
- **high Stability**

And…

- ☞ Simple System integration
- ☞ Low Energy consumption (10 mW)
- ☞ Low noise
- ☞ Long lifetime and calibration intervals
- ☞ Low cross sensitivity
- ☞ Fast response/recovery
- ☞ Inherent safety
- ☞ Low cost

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Indicative targets for H_2 vehicles

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• Measuring Range:	up to 100% LEL min.
• Accuracy of response:	± 5% of signal
• Sensitivity to H_2:	< 0.1 vol %
• Cross Sensitivity:	Deviation within ±10%LEL overall accuracy
• Response Time (t90):	Between 1 and 3 s
• Recovery Time (t90):	Between 1 and 30 s
• Ambient Temperature:	Tmin = -40ºC; Tmax between 85 and 120ºC
• Ambient Humidity:	0 to 95% R.H
• Ambient Pressure:	0.6 (or lower for refueling) to 1.3 bar absolute.
• Gas velocity:	0 to 50 m/s
• Long term stability:	± 3% of signal
• Operating Time:	6000 hours

- Low power consumption in operation & standby
- Electro-Magnetic Compatibility (EMC)
- Enclosed packaging/Intrinsecally safe

Plus and minus of most common detector types

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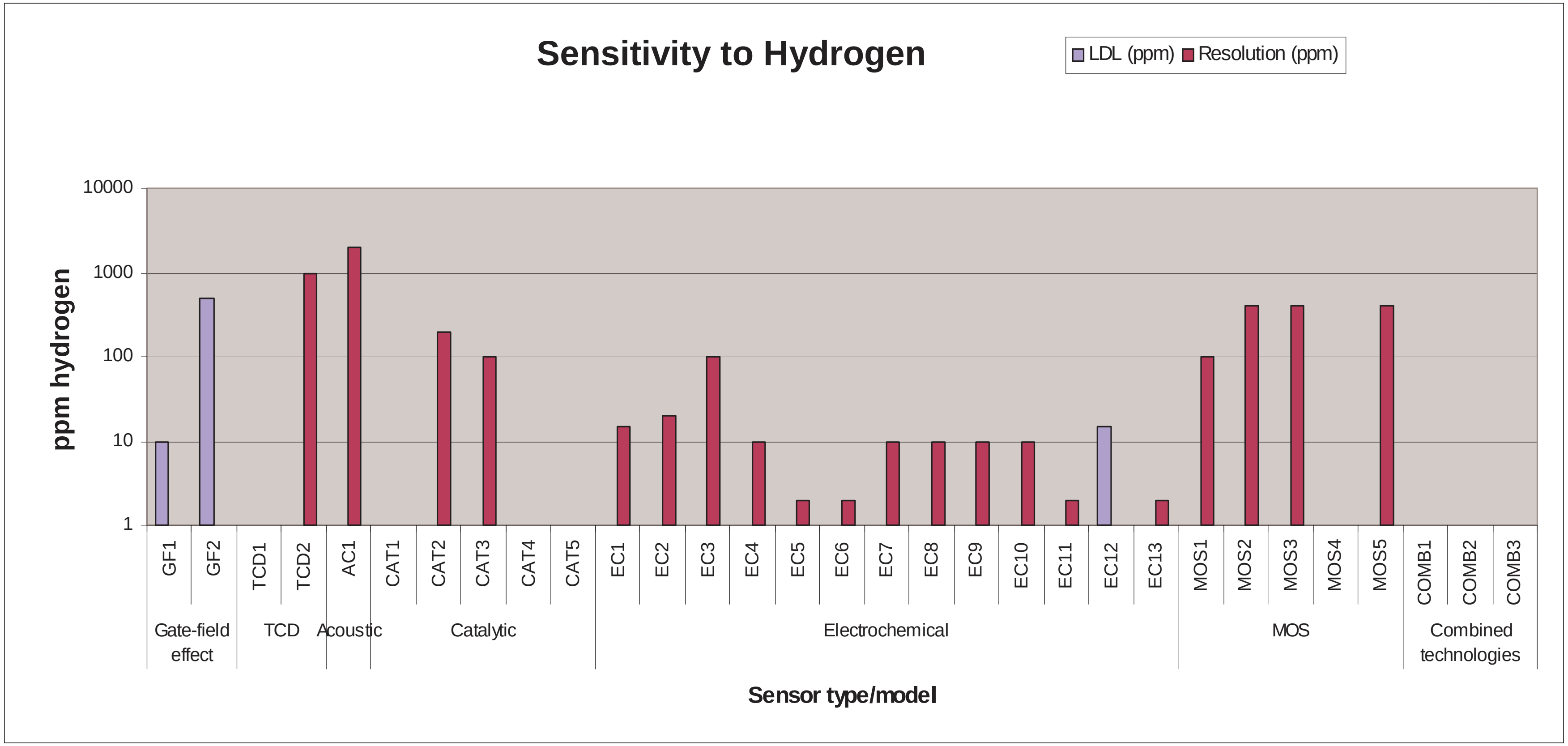
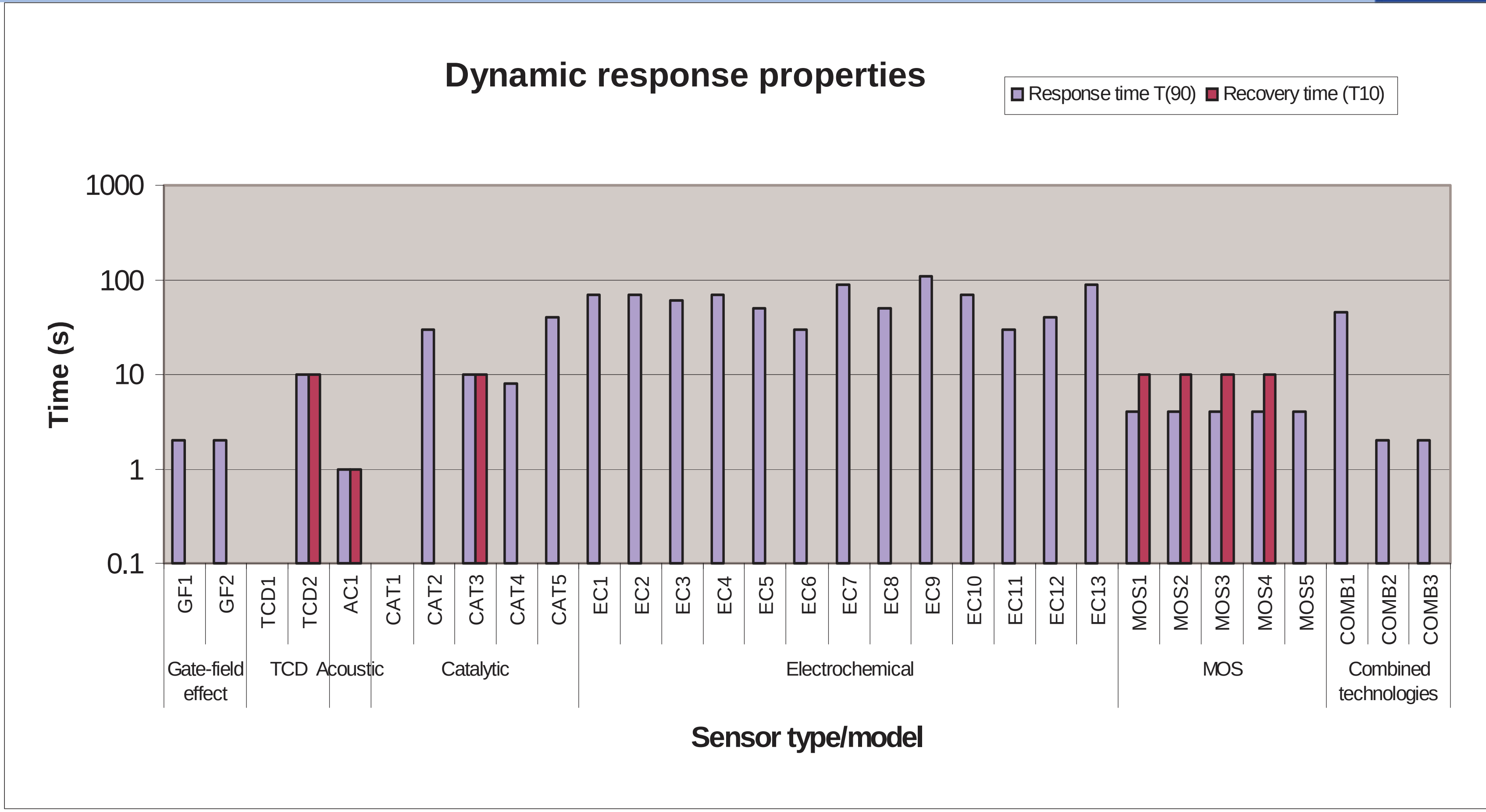
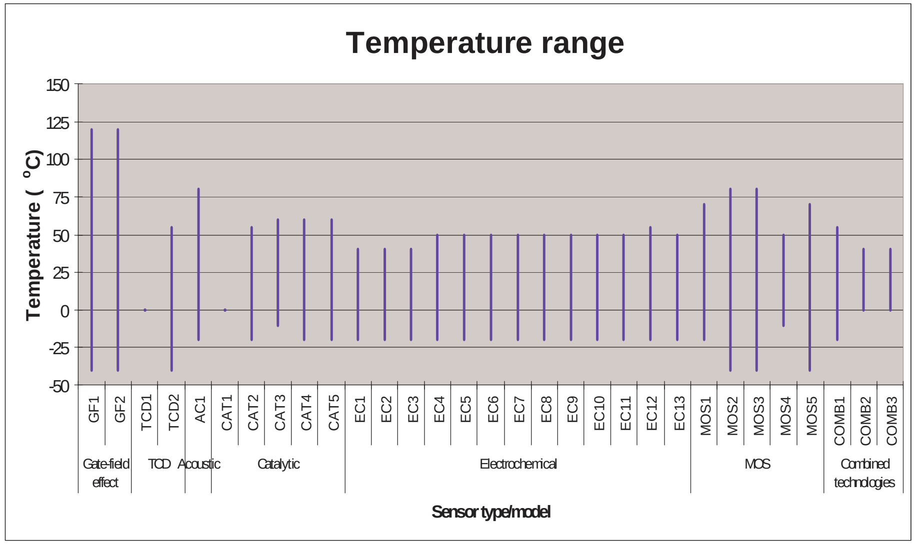
	≤LFL	Depends on species	No	Si, Alogenated compounds, H_2S, Pb	- Commercially available with acceptable lifetime - Wide temperature range	- Not H2 selective - High power consumption - Requires 5-10% O2 - Susceptible to poisoning by Pb, Si, P, S
	≤LFL	Medium	H_2S, SO_2, NO_x	no	- Selective to H2 - Sensitive down to 100ppm - Low power consumption - Resistant to poisoning	- Narrow temp range - Short expected lifetime - Needs regular calibration
	≤LFL	depends on species	SO_2, NO_x, H_2O	Si, Alogenated compounds SO_2	- Commercially available with acceptable lifetime - Wide temperature range	- Not H2 selective - High power consumption - Sensitive to humidity and temperature - Gets saturated easily
	(0)-100%	medium	CO_2, freons	no	- Wide range - No O2 to work - Long term stability - Resistant to poisoning	- Short expected lifetime - Not as sensitive as electrochemical/MO sensors - Sensitive to He

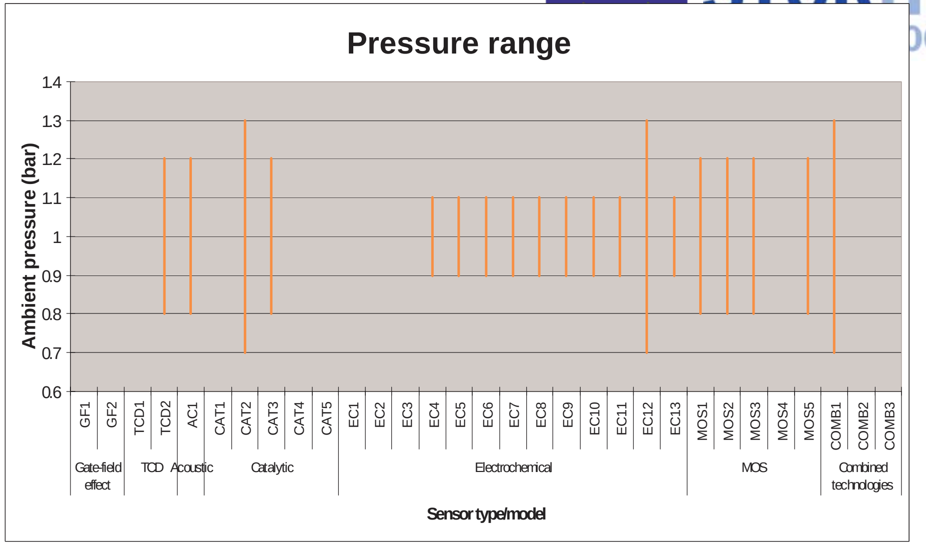


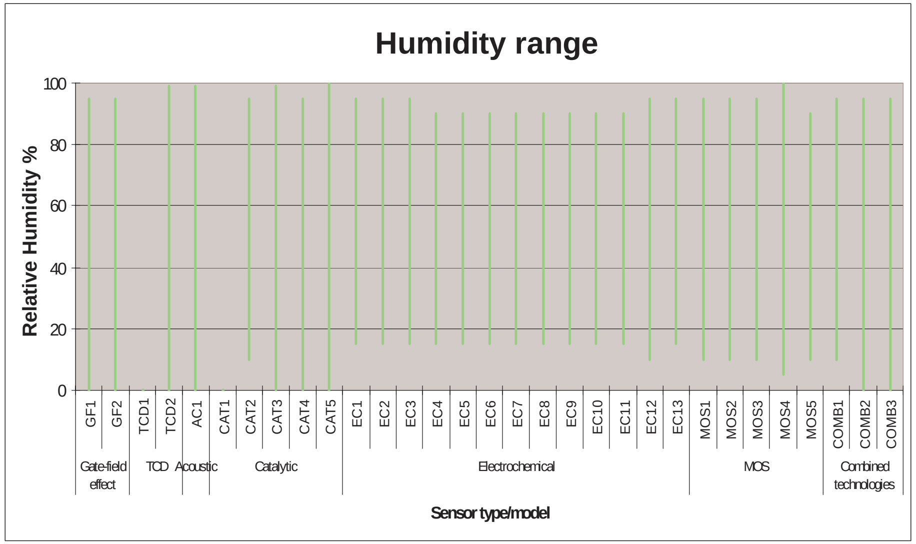
Sensitivity is rarely expressed as Limit of Detection. At least an indication can be drawn from resolution data. Electrochemical sensors couple a high resolution to good repeatability. Wide range systems have, rather logically, the lowest resolution.



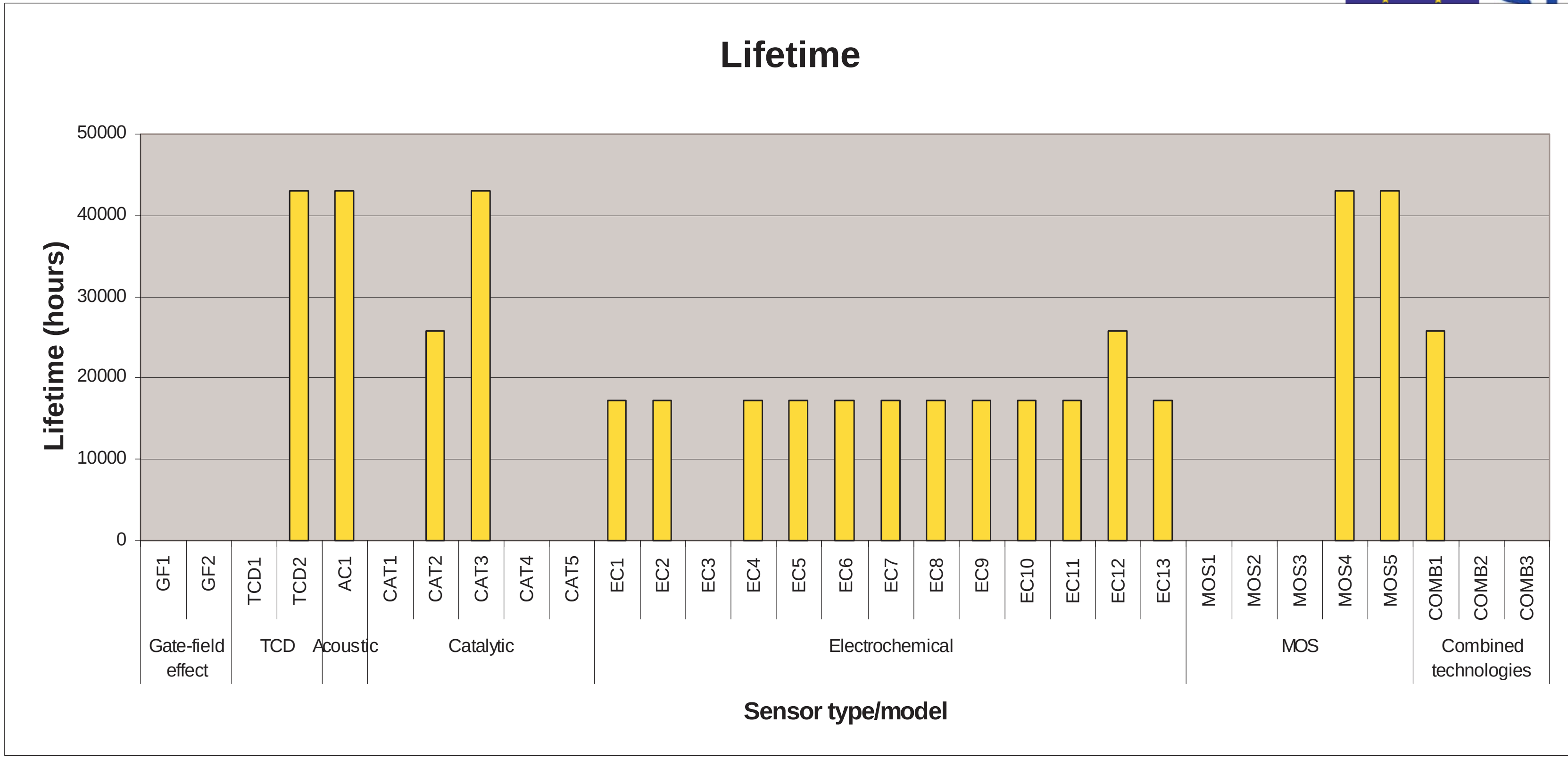
Gate-field, acoustic and combined (gate field + resistor) systems can be quite fast in their **response**, reaching 90% of the signal within 1 to 3 seconds after exposure. TCDs, MOS and some catalytic sensors are claimed to have a somewhat lower, but still rarther fast response (within 5 to 10-20 seconds). Electrochemical sensors have the slowest response, with a minimum of T(90) = 30 s, and a maximum of T(90) = 110 s.







Temperature, pressure and humidity ranges of commercial products are generally suitable for indoor applications where an acceptable degree of environmental control is in place. Mobile applications and/or sudden changes are a more delicate issue



A long **functional life** of a detector does not exempt from regular maintenance and calibration. Signal drift due to environmental conditions, degradation due to prolonged exposure to below-alarm level of reducing gas and/or sudden exposures to high concentrations are some factors to take into accont.

Conclusions

Hydrogen sensors are required:

- as an active safety measure in the operation of H_2 powered vehicles
- to promote acceptance of hydrogen from the public and authorities

Technologies presently used e.g at industrial premises do not match the combination of requirements for mass vehicle production (rapid response, wide detection range, low sensitivity to intefering gases, low price)

On-going research on miniaturised solutions (gate-field effect, semiconductor sensors, micromachined resistors, and/or combinations) is oriented in the right direction, but further development is needed to ensure reliability and low cost

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