Gas Phase Sensor Development at LLNL

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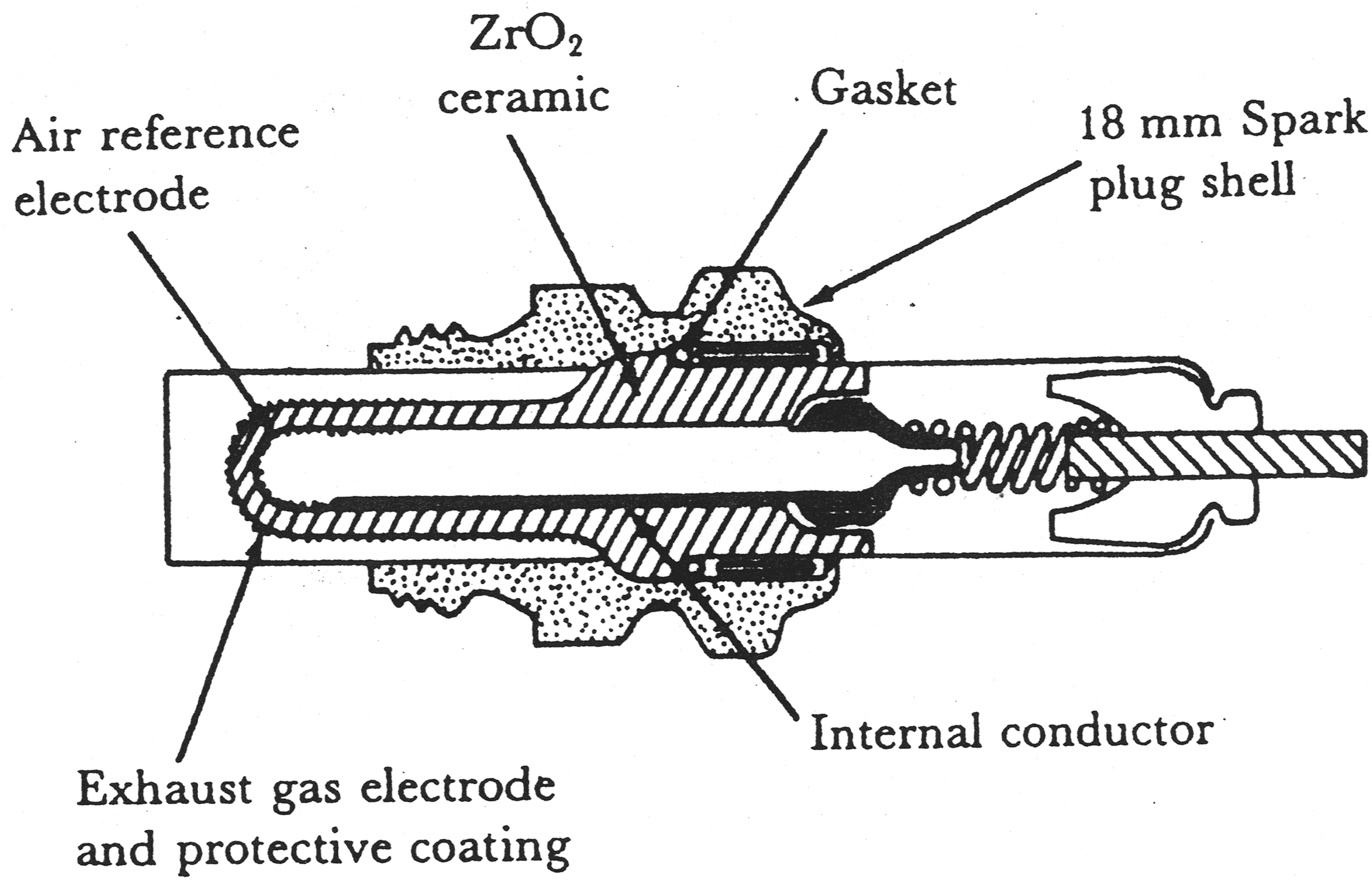
A variety of sensor technologies can be considered for gas phase sensing

- **Electrochemical**
- **Optical**
- **Thermal**
- **Mass**

Solid state electrochemical sensors have a proven history in high temperature, chemically harsh environments - the EGO sensor is simple and rugged



(From E.M. Logothetis in Chemical Sensor Technology, 3, Kodansha Ltd.: 1991, p. 89)

Automotive industry and fuel cell criteria for sensors are similar

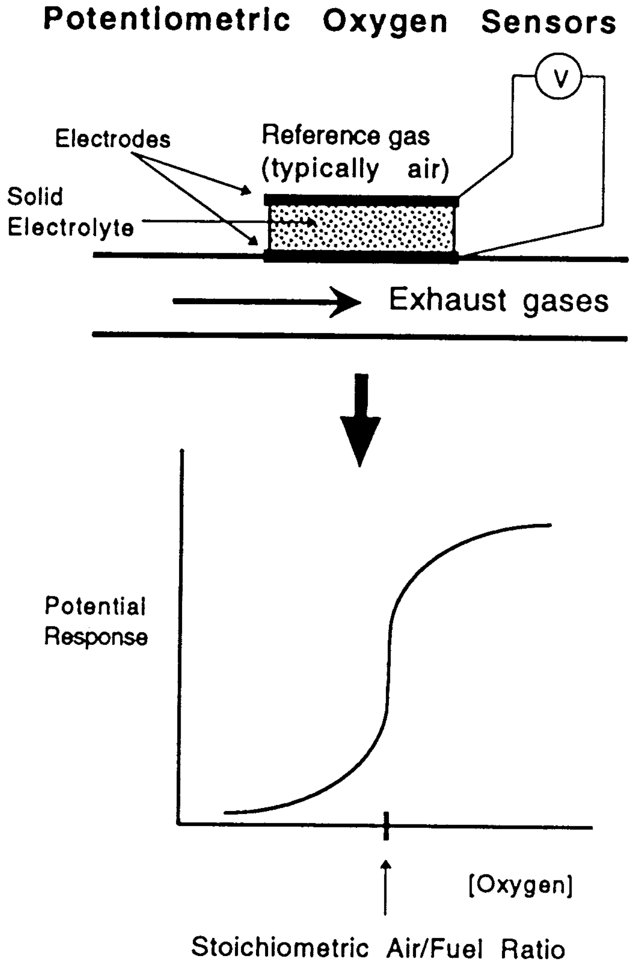
- Reliability
- Sensitivity
- Selectivity
- Durability
- Manufacturability
- Integration
- Low cost

→ **Need materials which can provide adequate response while surviving prolonged operation in a high temperature, high stress, corrosive environment**

Additional exhaust emission sensor requirements

Exposure to a variety of gases, with approximate composition out of the engine:	Nitrogen 77.4% Hydrogen 0.3% Carbon dioxide 10% Hydrocarbons 0.1% Water 10% Nitrogen oxides 0.1% Oxygen 1% Sulfur dioxide 0.1% Carbon monoxide 1% P, Si, Zn, Mn Trace
Temperature:	-40 to 800°C, with spikes to 950°C possible
Flow rates:	10-30 g/s normal; maximum of 150 g/s
Pressure:	30 inches of mercury
Shock:	Mechanical shock of 50 G with vibration levels to 15 G
Electronic:	Radio frequency compatibility to meet corporate/government standards. No EMI interference
Lifetime:	10 years or 100,000 miles without intervention
Calibration:	Self-calibrationg; short- and long-term drifts not permitted
Response time:	1 second or less preferred. Need not monitor individual cylinder events
Size:	Packaging must fit under vehicle body
Power:	Compatible with 12 V DC
Other:	Must be totally interchangeable (10 million devices/year)
Measurement strategy:	If relationship is inferred (e.g. measure hydrogen and infer HC), it must be robust, well-established, and documented

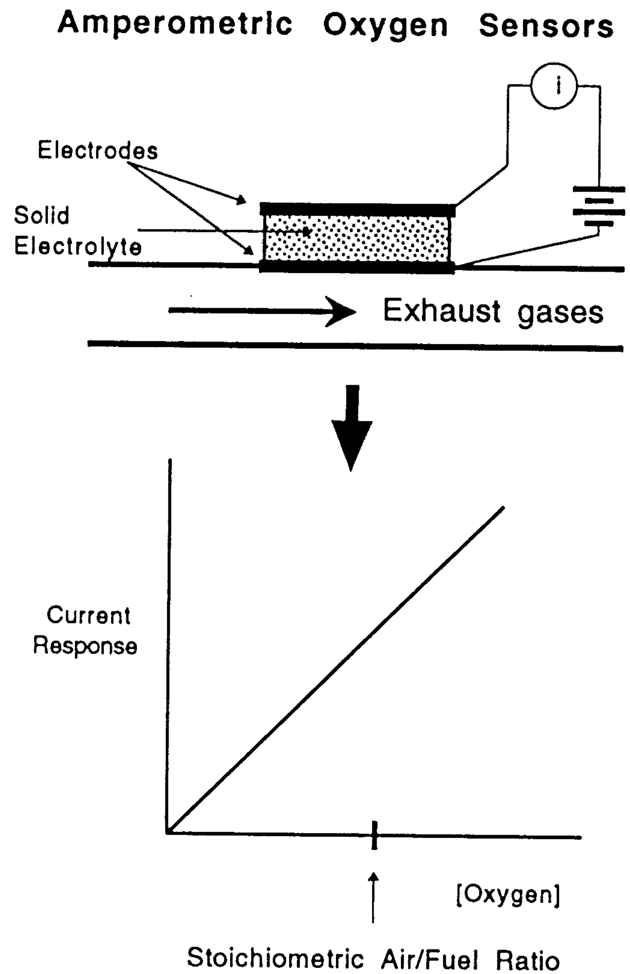
There are two operational modes for electrochemical sensors



(a) Potentiometric (O_2 sensor example)

$$E = \frac{RT}{nF}\ln\left(\frac{P_1}{P_2}\right)$$

– Insensitive over much of oxygen range



(b) Amperometric (O_2 sensor example)

$$i_l \propto C_x$$

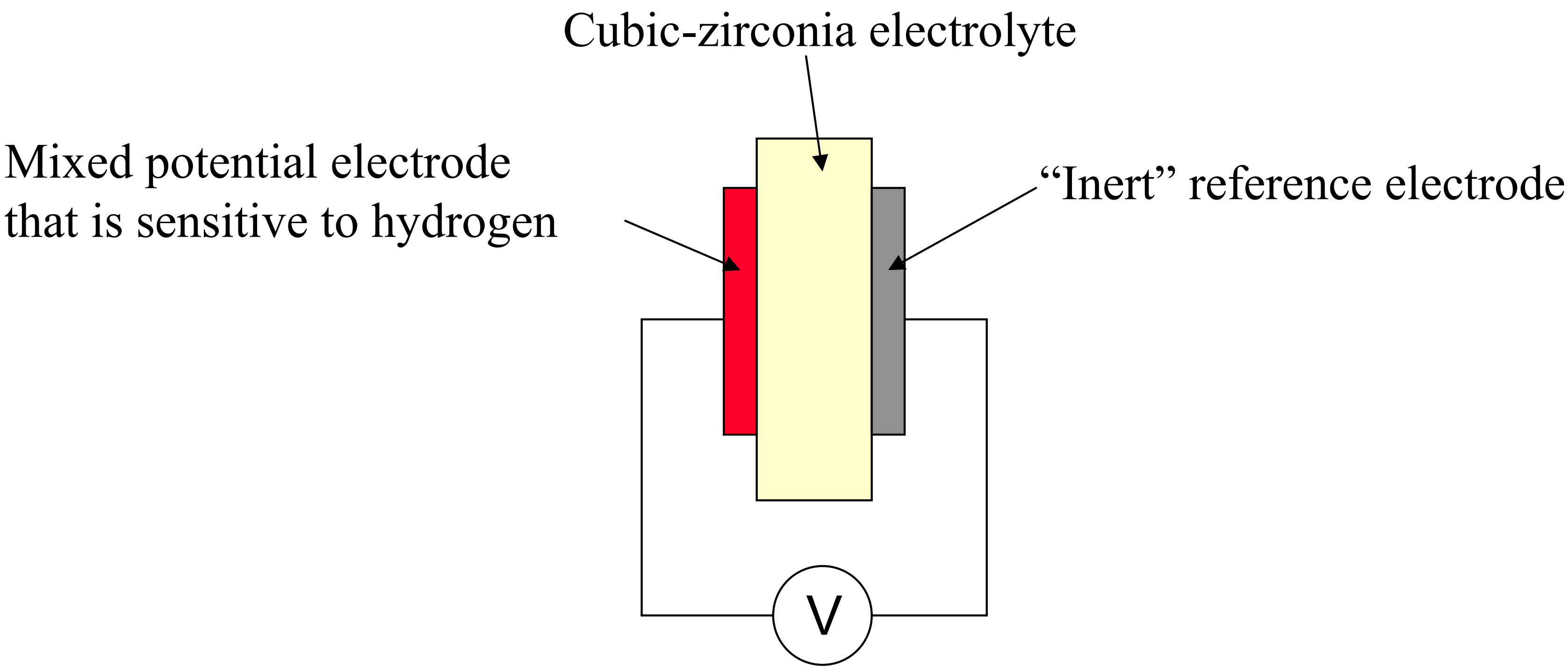
– Linear over much of oxygen range

Electrochemical sensors for PEMFC vehicles - technical targets

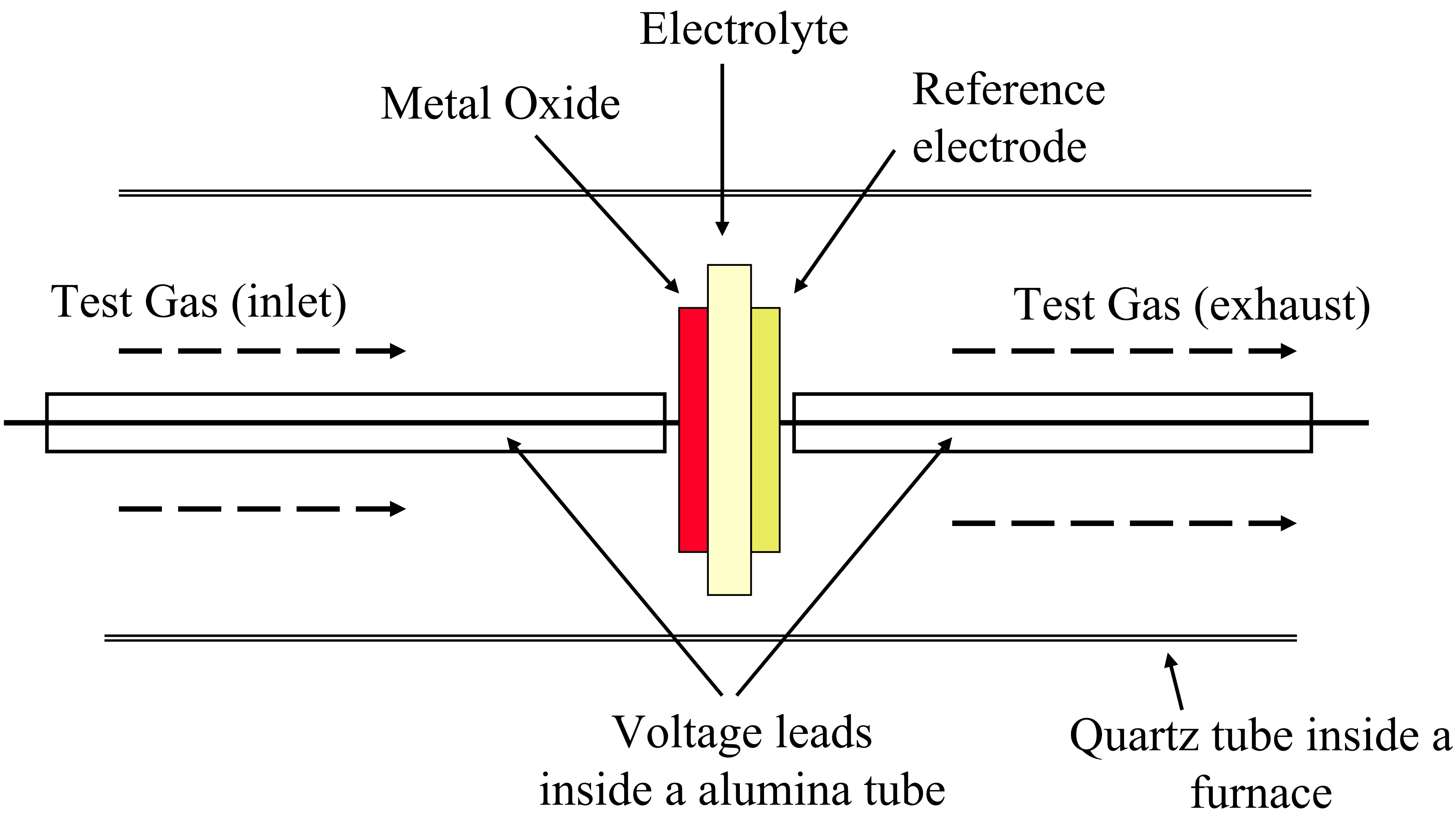
- **Hydrogen "safety" sensor**
  - 0.1 to 10% hydrogen in ambient air
  - Response time under 1 second
- **Hydrogen sensor**
  - 1 to 100% hydrogen concentration in fuel gas
  - Response time of 0.1 to 1 second for 90% response
- **CO sensor**
  - 1 to 1000 ppm CO in fuel gas
  - Response time of 0.1 to 1 second

Approach

- **Use proven technology: zirconia-based oxygen sensor**
- **Develop mixed potential electrodes that are sensitive to hydrogen for use without the need of a reference gas**

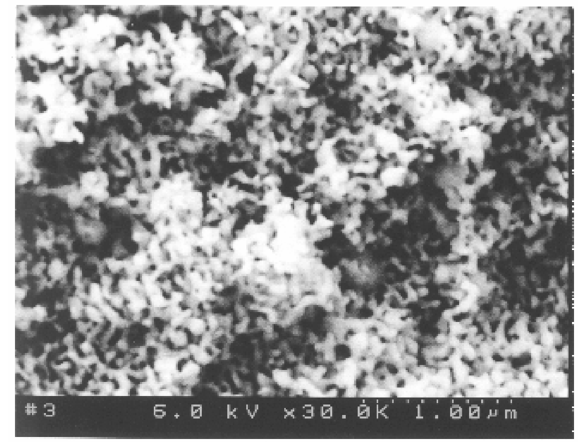


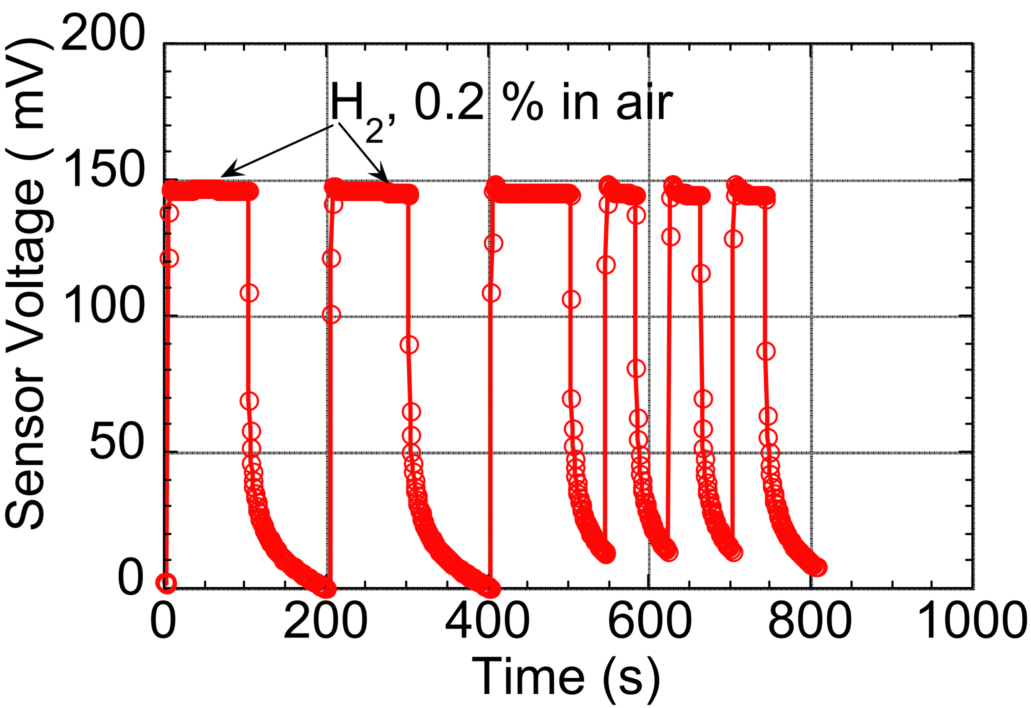
Experimental set up



With nanocrystalline electrode, sensor response time is reduced to 2-3 s

We use the Colloidal Spray Deposition technique to deposit the nanocrystalline metal oxide electrode.



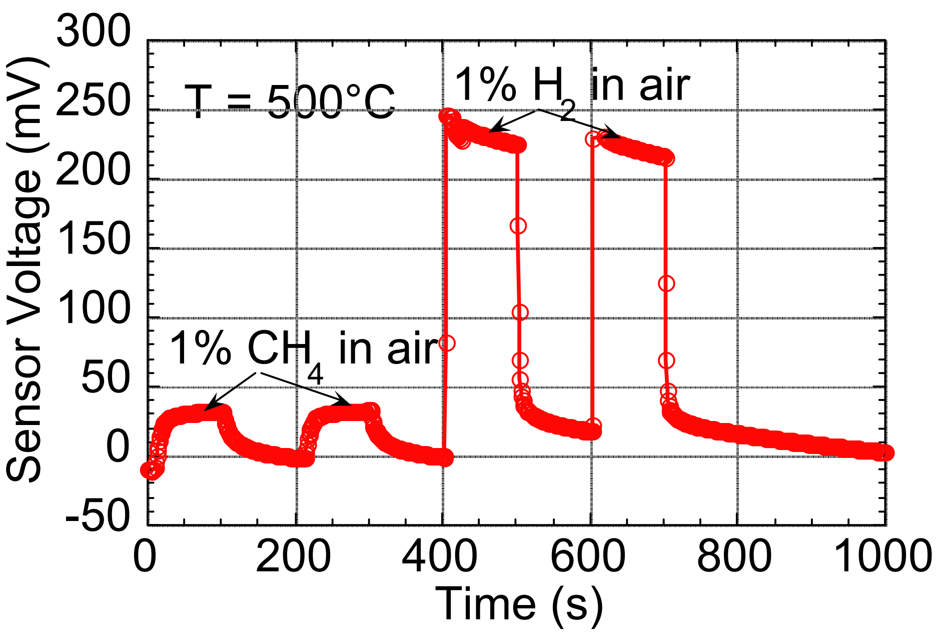


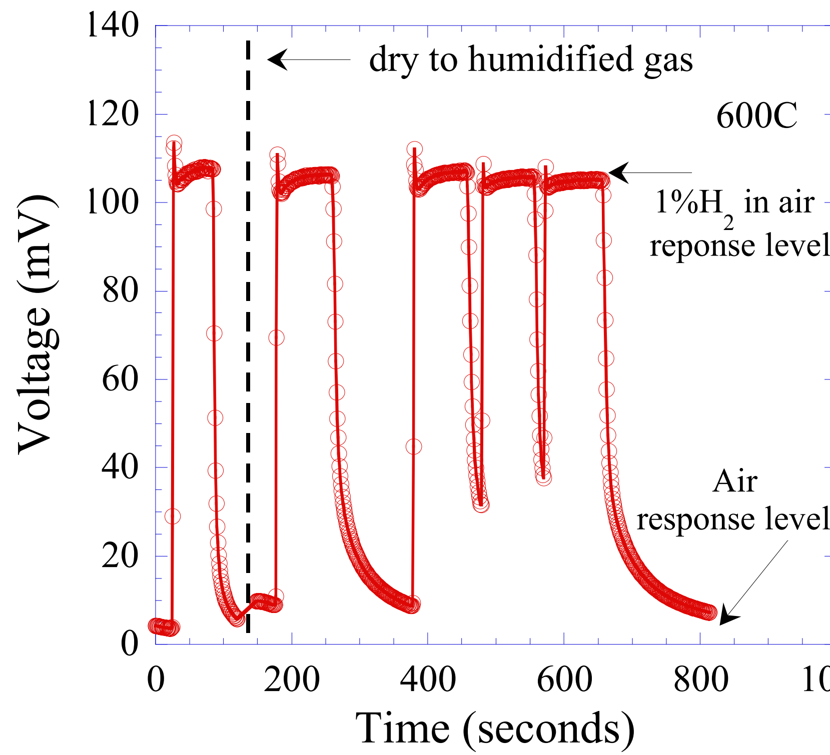
Time between 2 data points: 1 s

Sensor response to hydrogen in air at 500°C.

The response time is 2-3 s. However, the recovery time is much longer

Sensor has good selectivity

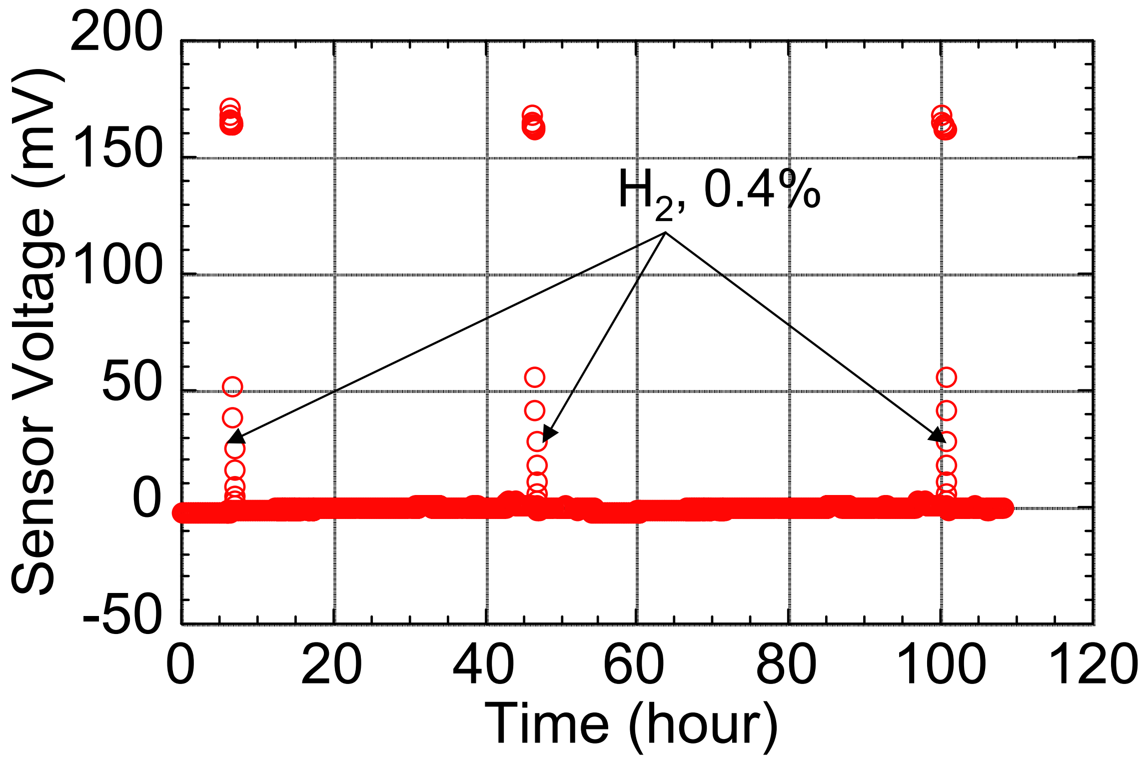




- Sensor is one order of magnitude more sensitive to hydrogen than to methane

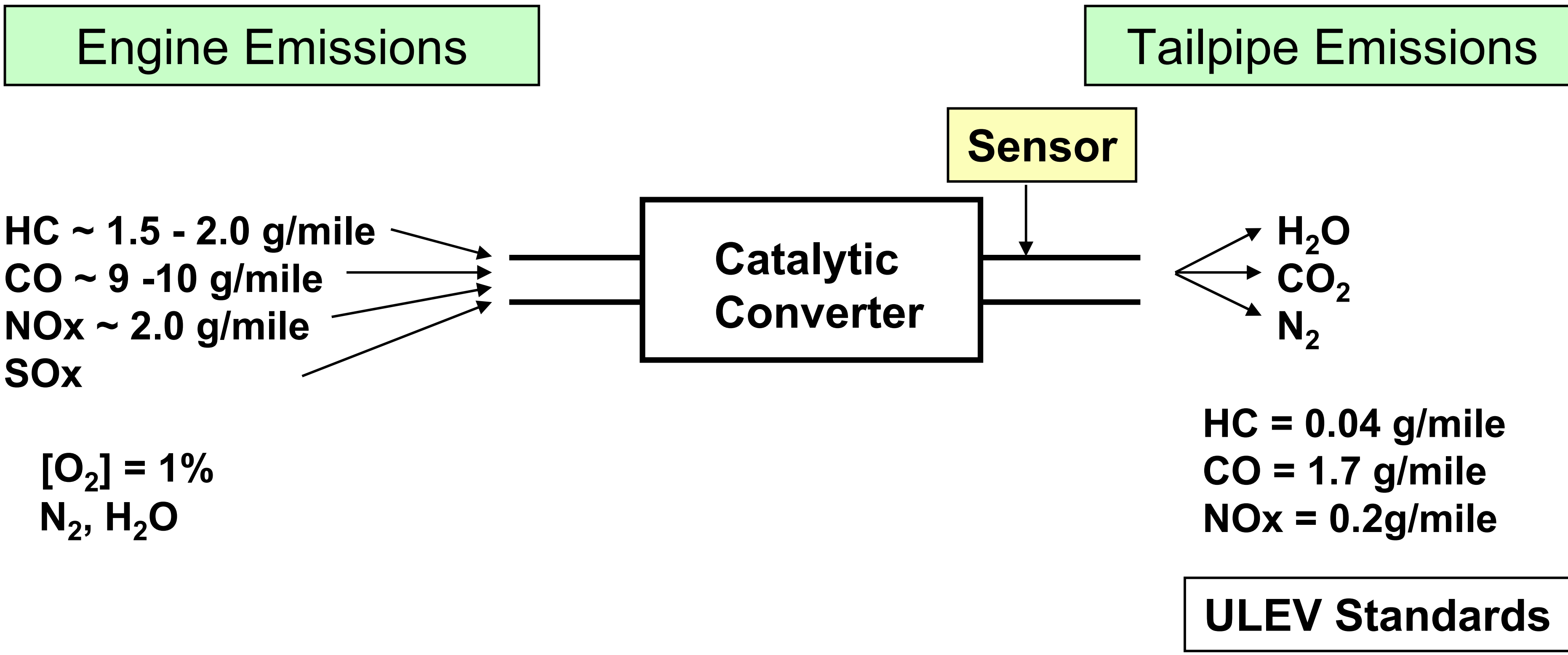
- Sensor response level identical when switche from dry to humid atmosphere (100% RH)
- Response time is < 3 sec
- Recovery time is < 200 sec

No drifting has been observed



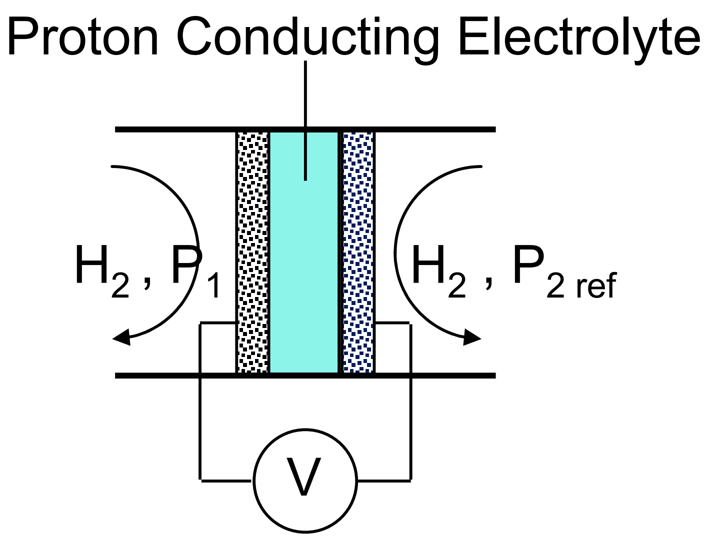
- **Baseline drifting is a major issue with conventional resistive sensors**
- **No baseline drifting nor signal amplitude change were observed with the mixed potential sensor**

Hydrocarbon sensor development for on-board monitoring of catalytic converter performance



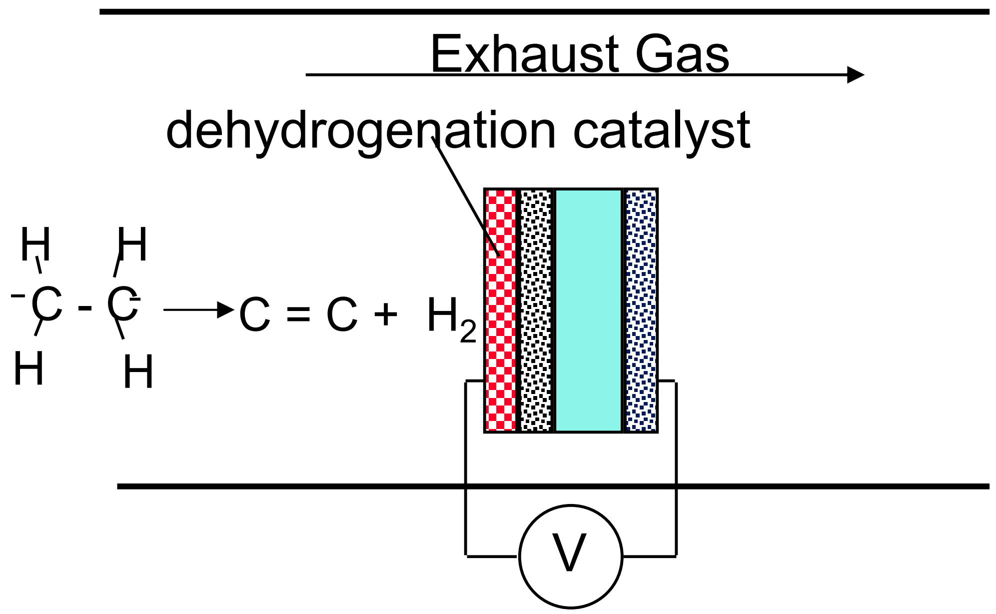
Principle of LLNL hydrocarbon sensor

Hydrogen Sensor



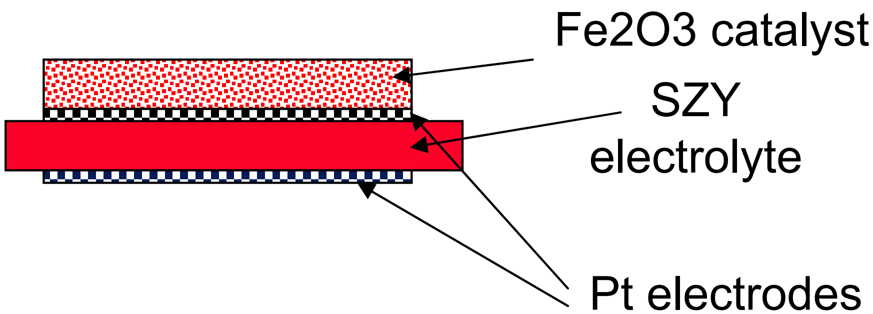
$$E = RT/nF \ln (P_1/P_2)$$

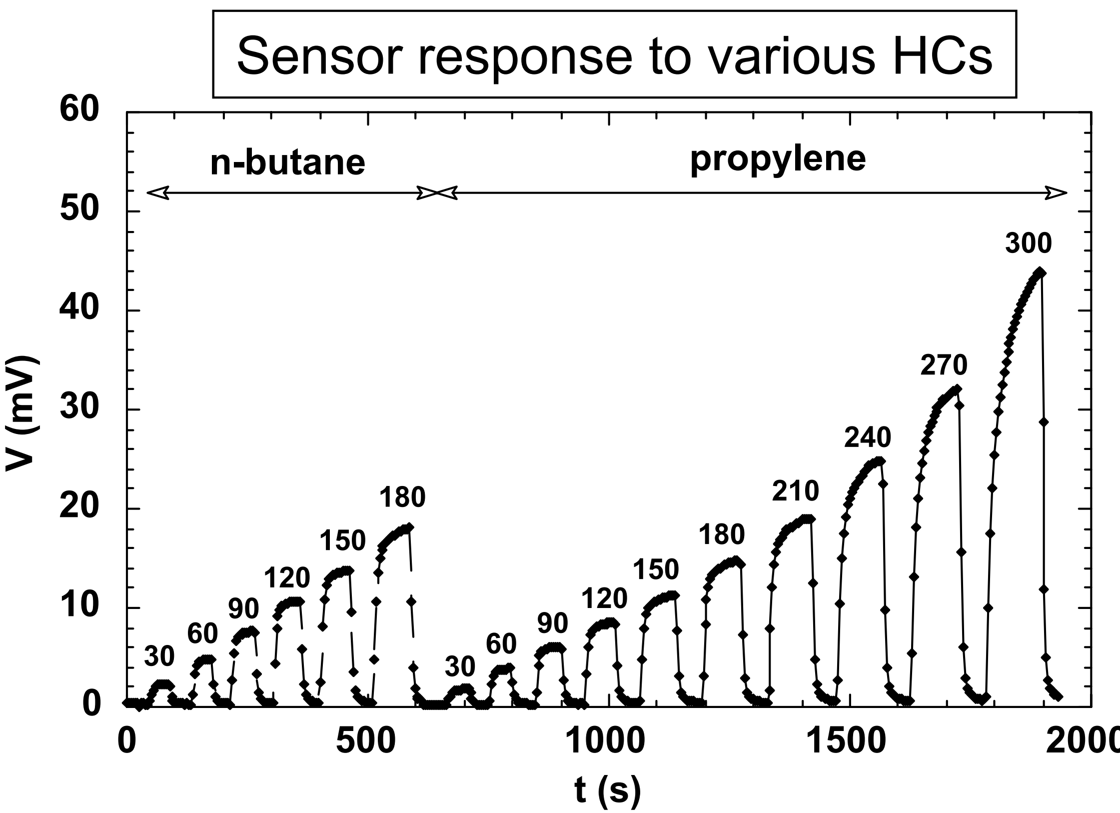
LLNL Hydrocarbon Sensor



Possible Catalytic Reactions:
- dehydrogenation
- steam reforming
- cracking

First generation HC sensor

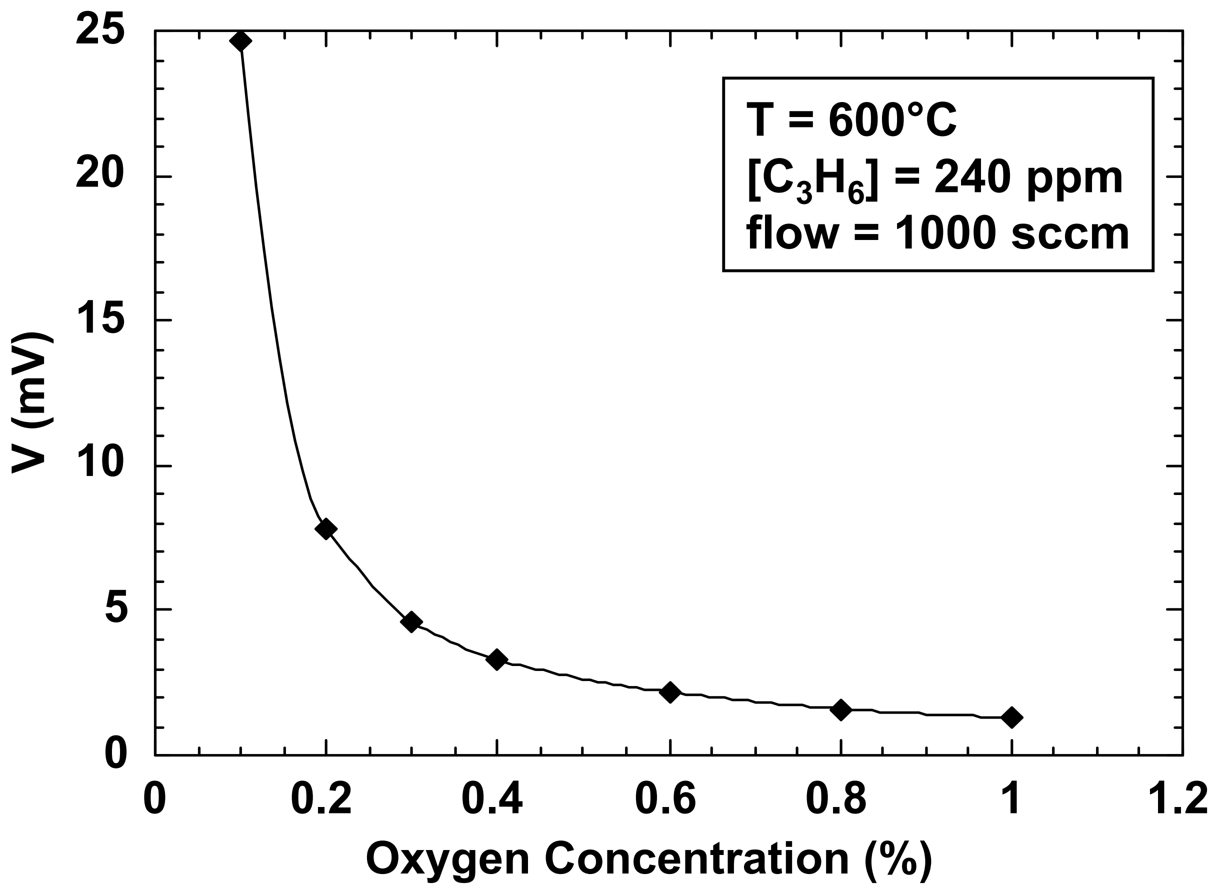




T = 600°C
$[O_2]$ = 0.1%
$[H_2O]$ = 5%
[HC] in ppm
N_2 balance
flow = 1000sccm

SZY: $SrZr_{0.9}Y_{0.1}O_3$

The problem was a strong effect of oxygen on sensor signal

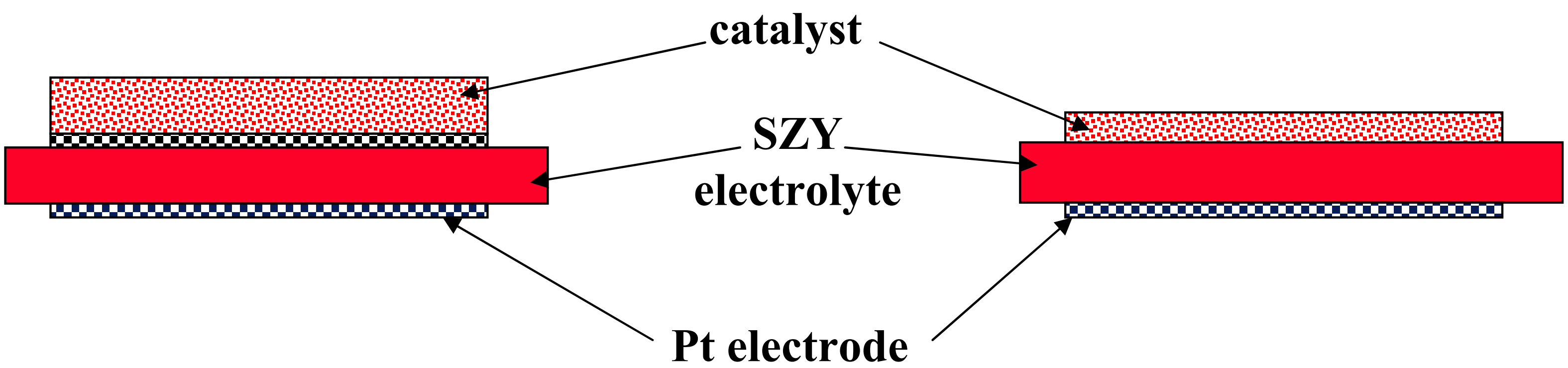


The effect of oxygen may come from the reaction between hydrogen and oxygen

Second generation sensor design

Old design: two Pt electrodes with the HC decomposition catalyst covering one electrode

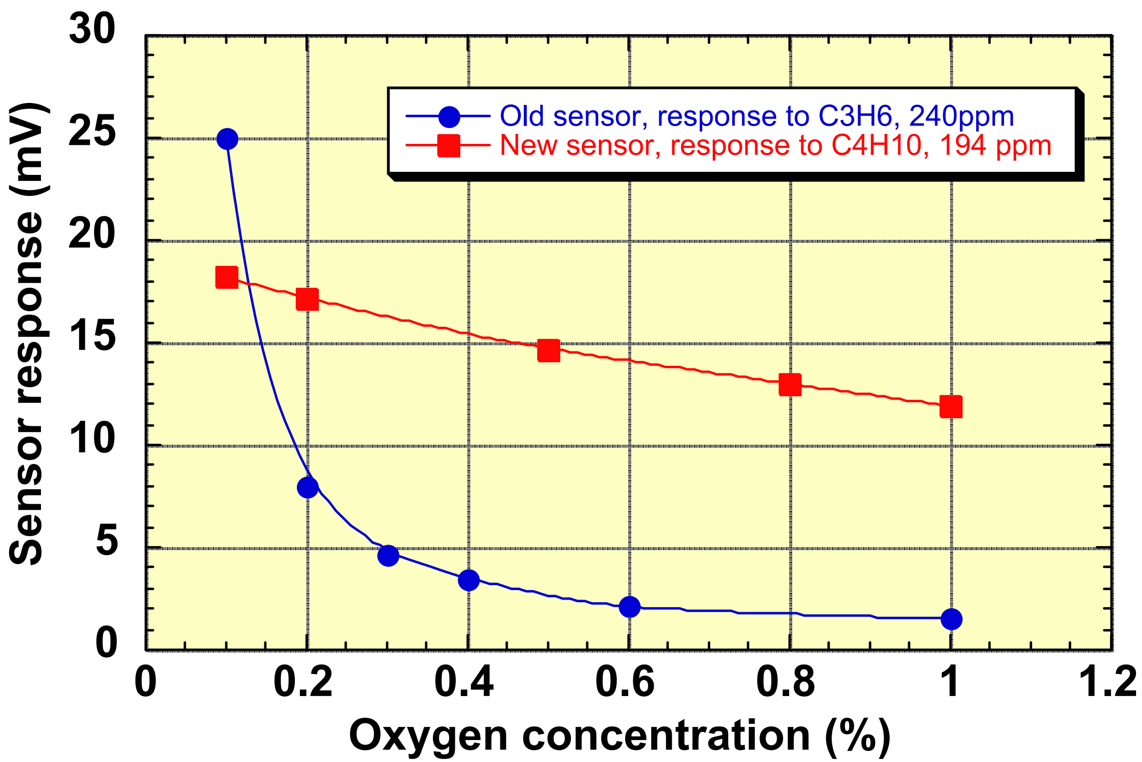
New design: the catalyst is also one of the 2 electrodes



Problem: Pt catalyses the hydrogen oxidation, causing strong influence of the oxygen concentration on sensor signal

The correct selection of the catalyst can minimize the hydrogen oxidation, thus reducing the oxygen effect

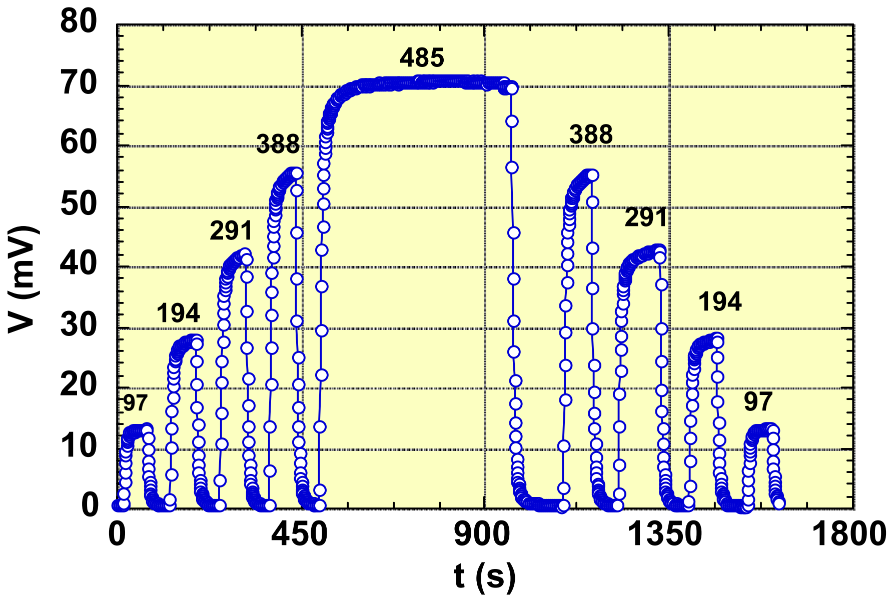
Effect of oxygen concentration on sensor response

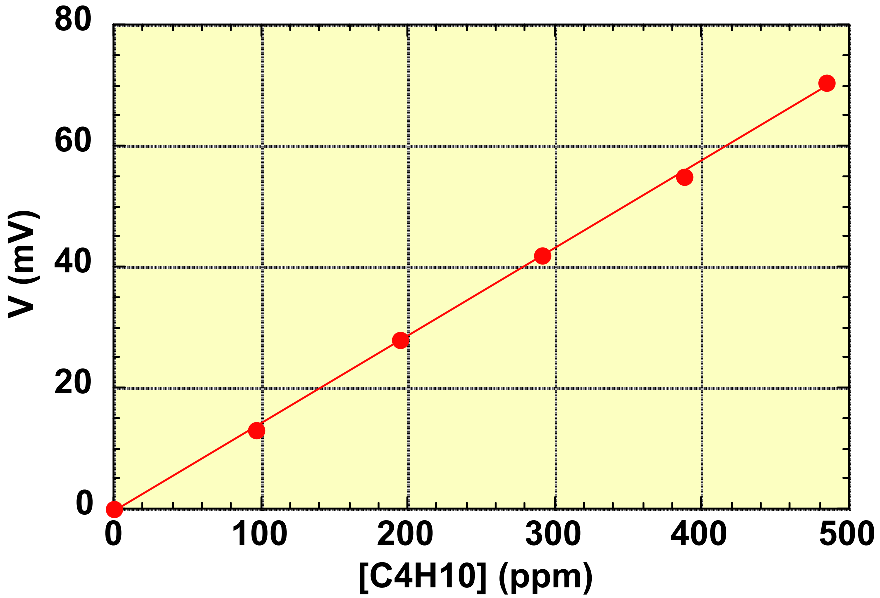


The new sensor is significantly less sensitive to oxygen concentration in exhaust gas

Sensor response to hydrocarbons

Response to n-butane

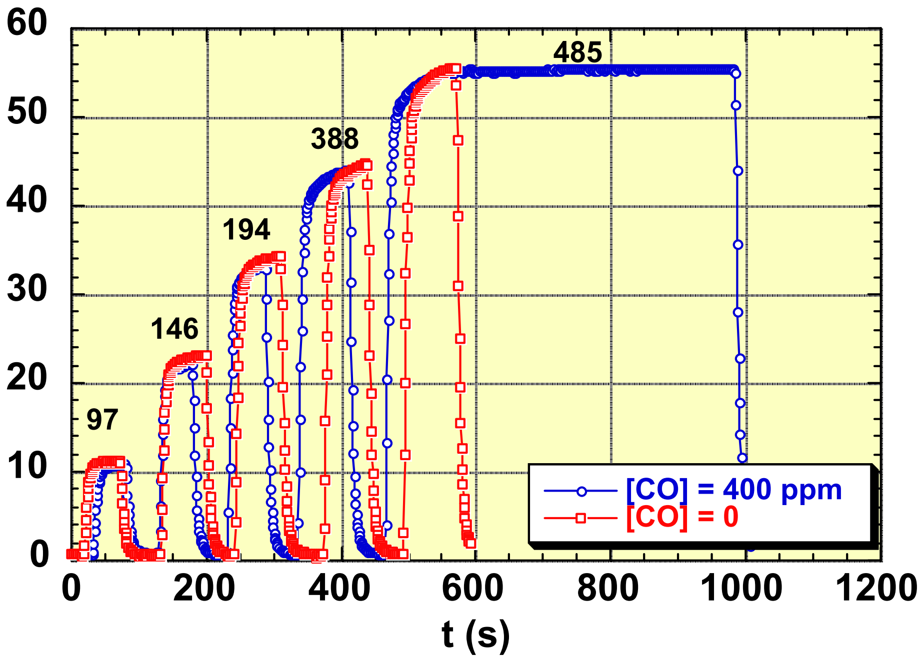




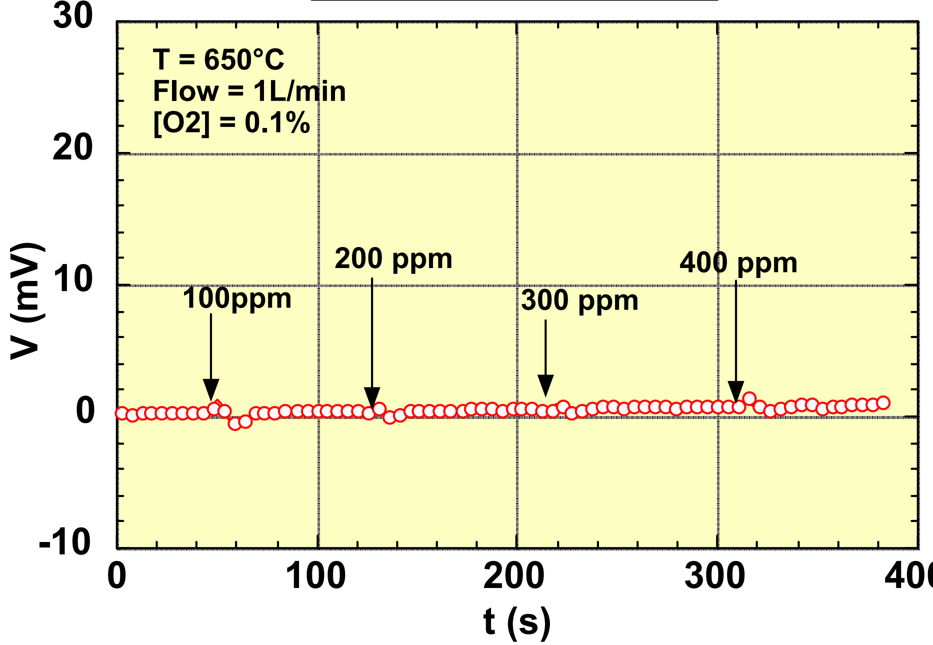
Flow = 1L/min
$[O_2] = 0.1\%$
$[C4H10]_{stoich.} = 154$ ppm

The sensor can be used in both lean-burn and fuel rich conditions

Sensor response in the presence of CO and HC

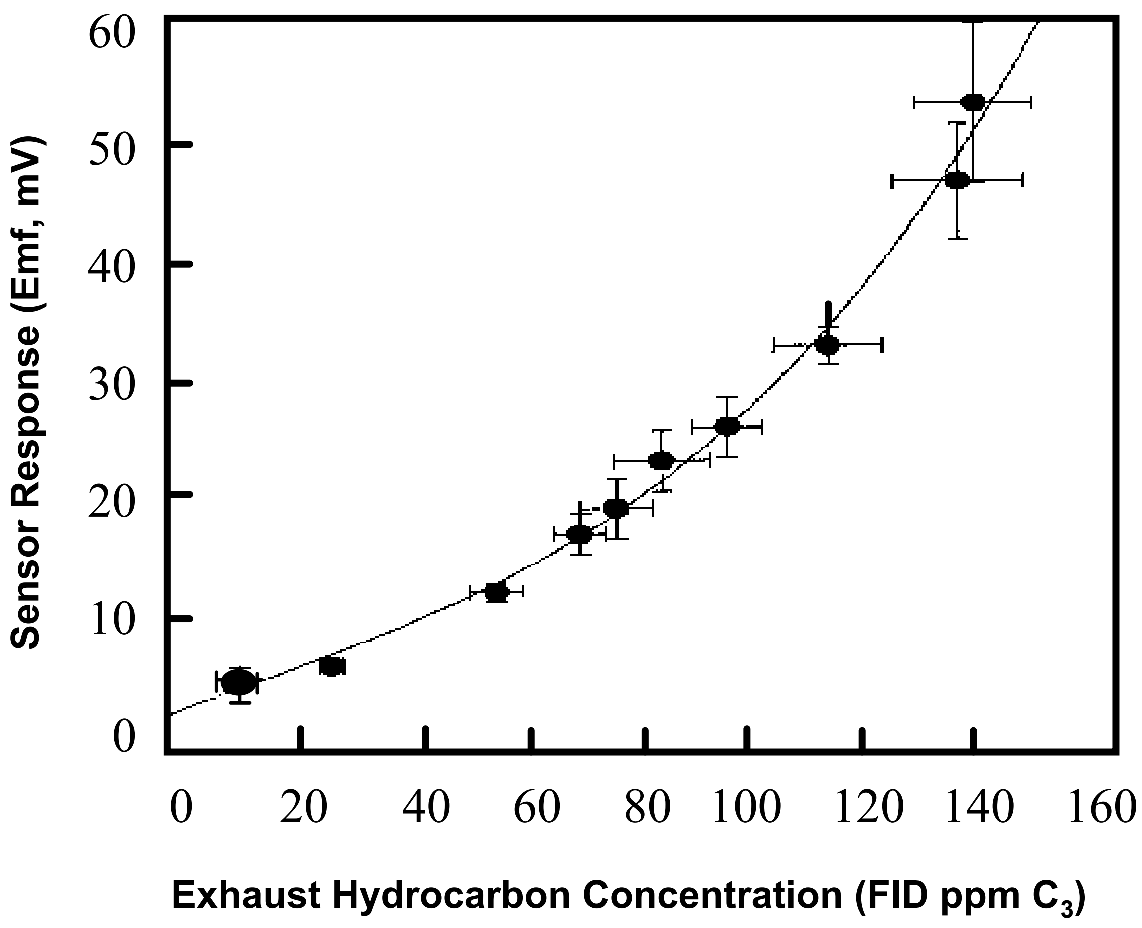


Response to CO



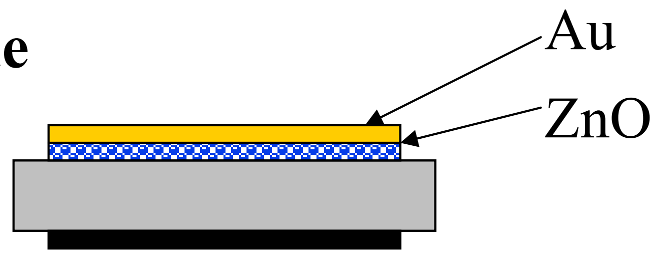
Unlike the older generation sensors, the new sensor is virtually insensitive to the presence of CO, even when both CO and HC are present in the exhaust gas

Results of the Dynamometer testing of LLNL NMHC sensor at Ford Laboratories

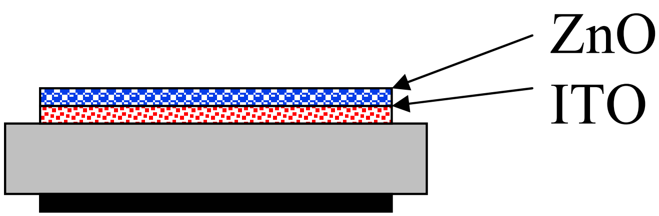


Approaches to increase the electronic conduction in the catalyst layer

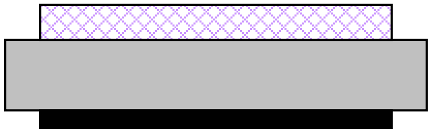
- **Indium doped zinc oxide**



- **Bi-layer ZnO/Au**



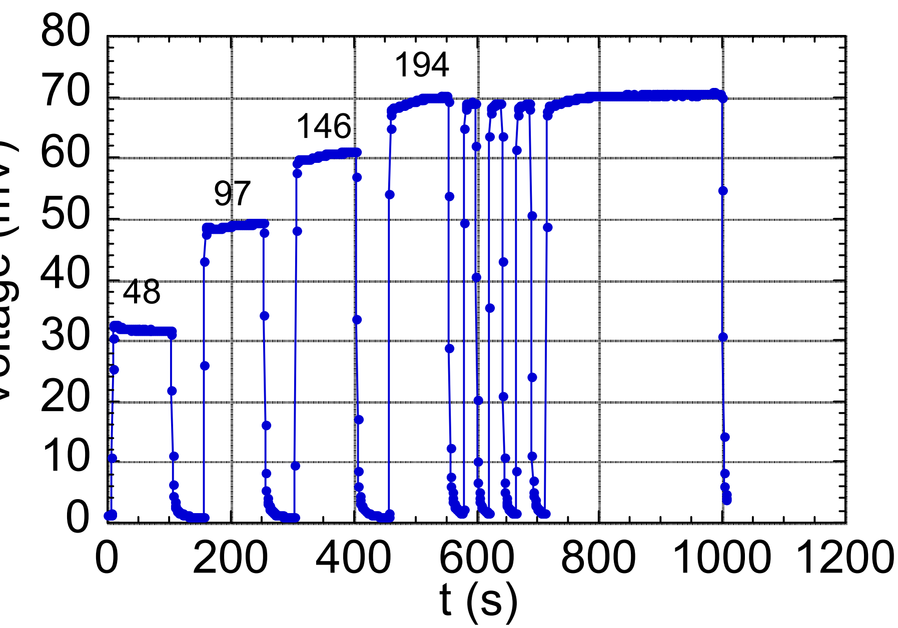
- **Bi-layer ITO/ZnO**



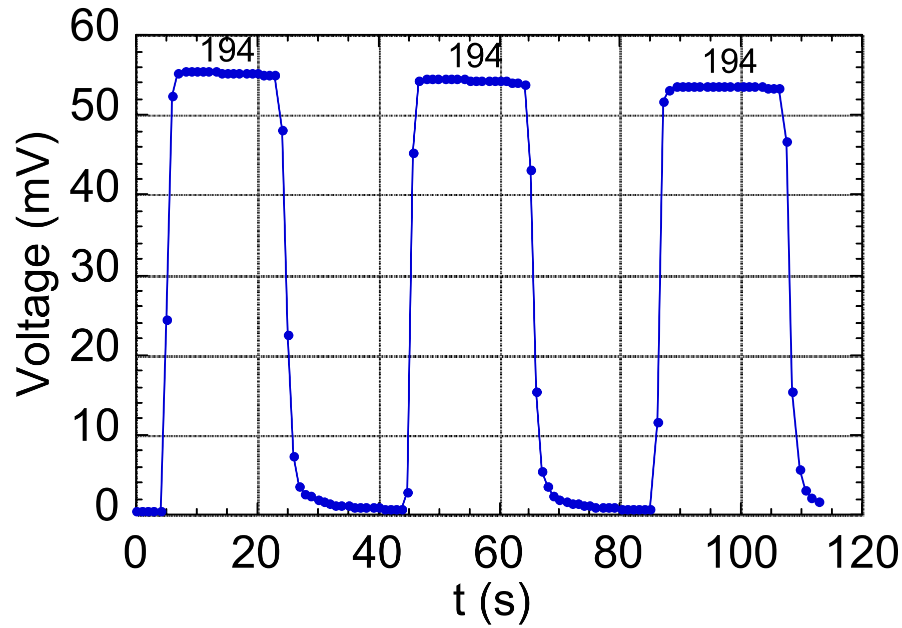
- **Composite catalyst**

Composite ZnO + ITO catalyst

Sensor response to C4H10 at 700°C

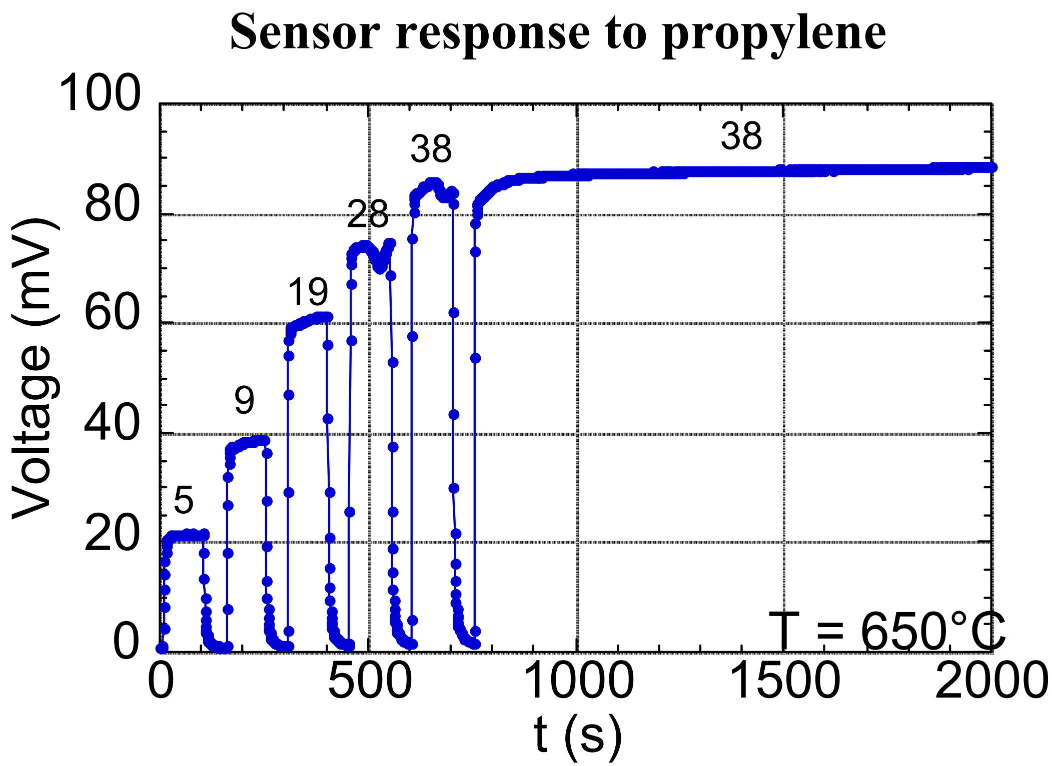


Sensor response to C4H10 at 750°C



- **Catalyst composition is 60/40 mole % of ZnO/ITO. There is a continuous conduction path in the catalyst**
- **Response time is about 2 s. This is the limit of the gas phase exchange in the test chamber!**

Sensor sensitivity

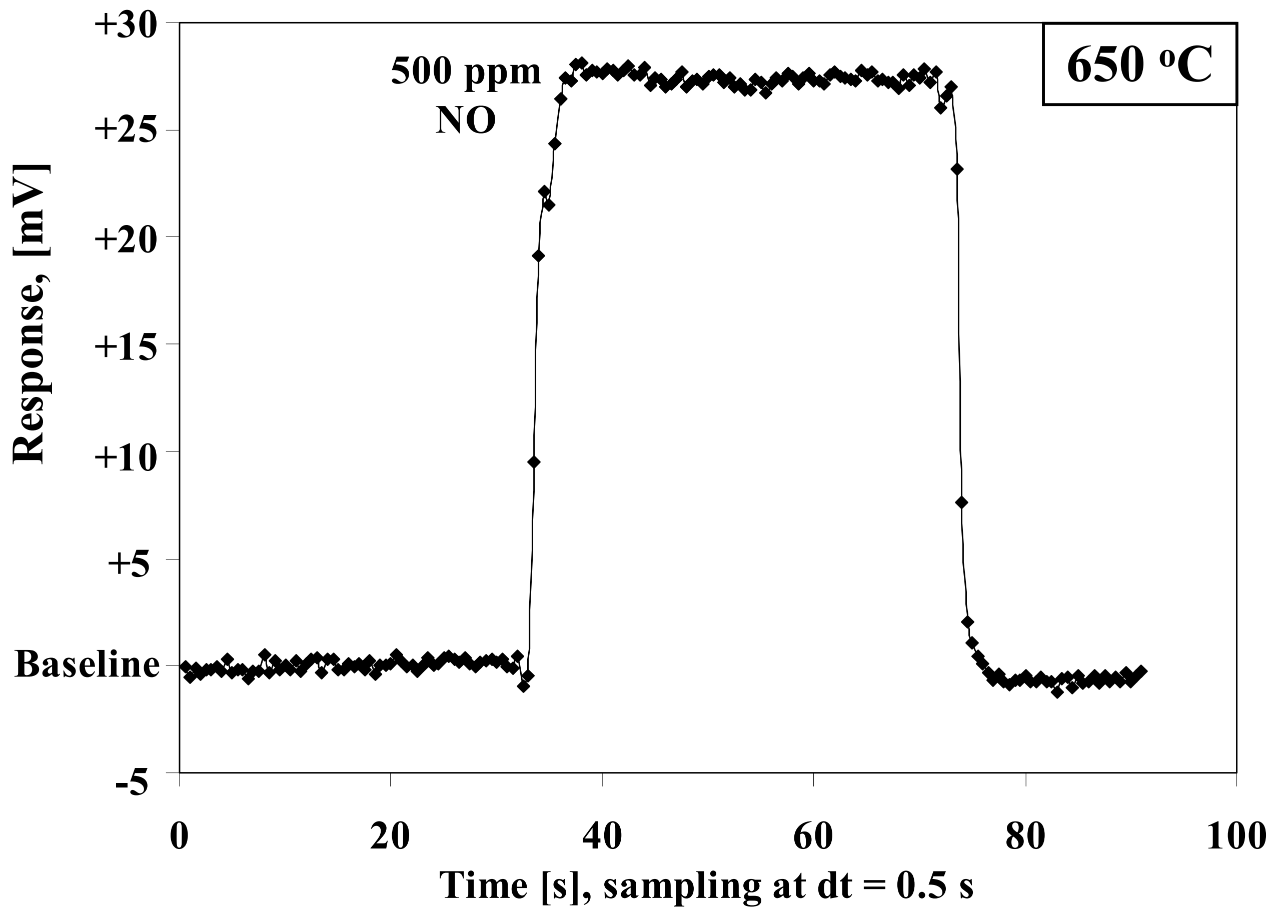


- The sensitivity to propylene is unusually high
- Detection limit could be below 1 ppm propylene
- The detection mechanism is unclear
- R.t at 650°C is 4 to 8 s

Improved NO_x sensing technology is needed for new vehicle emissions monitoring requirements

- **Most advanced current design (electrochemical) is complex, expensive to fabricate, and suffers from poor stability and selectivity**
- **We are developing a solid state electrochemical NO_x sensor for compression ignition direct injection (CIDI) engines that has high selectivity and low fabrication cost**
- **Target performance:**
  - Sensitivity to NO_x: 1 - 1,000 ppm at operating T > 400° C
  - Response time: 1 second or less
  - Minimized (or no) cross-sensitivity to O_2, SO_x, NH_3, urea, HCs, etc.
  - Long term stability
  - Packagable/Integratable

$NiCr_2O_4$ sensor with a current bias gives increased NO sensitivity and 90% recovery time of ~1.5 seconds



NO_2 sensitivity is high: > +90 mV (500 ppm) with 90% recovery in ~ 4 seconds

Comparison of fuel cell feed gas and engine exhaust

Engine exhaust (vol. %)

Nitrogen	77.4
Nitrogen oxides	0.1
Hydrogen	0.3
Oxygen	1
Carbon dioxide	10
Sulfur dioxide	0.1
Hydrocarbons	0.1
Carbon Monoxide	1
Water	10
P, Si, Zn, Mn	Trace

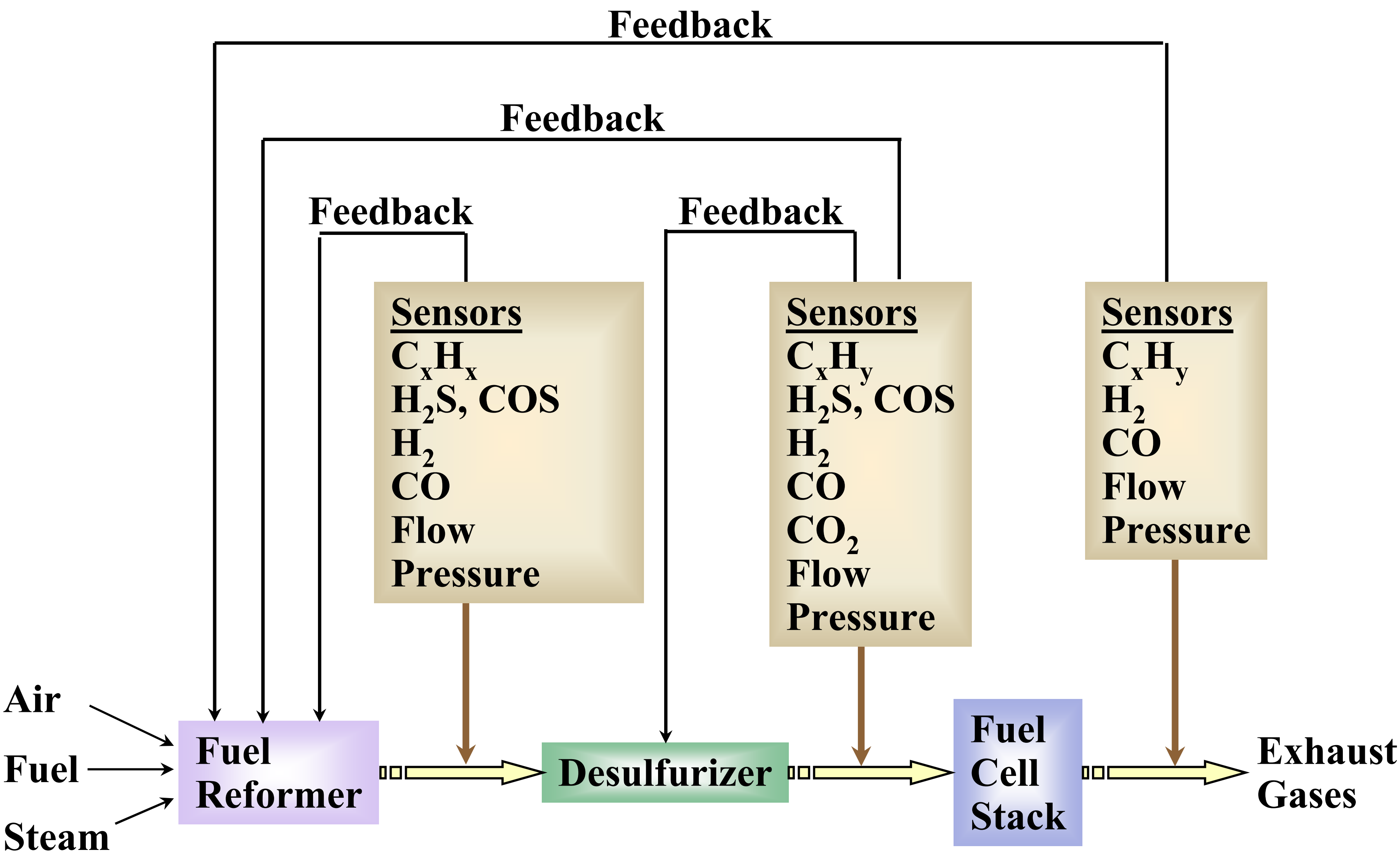
Reformed gasoline composition (vol. %)

Component	Before SOX (PROX)	After SOX (PROX)
H_2	34.8	32.1
H_2O	28.6	29.1
CH_4	0.4	0.4
CO	0.7	<10 ppm
CO_2	14.8	14.9
N_2	20.4	23.2
Ag	0.3	0.3

Gas composition from a pressurized, fluidized-bed coal gasifier (vol. %)

	H_2	CO	CH_4	H_2O	CO_2	N_2	H_2S	COS	NH_3
Air mode	16.8	27.9	1.8	3.8	2.8	46.0	0.68	0.02	0.16
Oxygen mode	29.4	38.0	4.0	17.3	9.5	0.54	1.07	0.02	0.24

Sensors for diagnostics and feedback control for fuel cell systems



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Sensor Needs and Requirements for
Proton-Exchange Membrane Fuel Cell Systems and Direct-Injection Engines

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UCRL-ID-137767

Summary

- **Solid state electrochemical sensors can meet the demands of operation in harsh environments**
- **Fuel cell performance can be optimized with embedded sensors**
- **Chemical sensors take a long time to develop - don't wait!**
- **Nothing is perfect**