Electrochemical Sensors for PEMFC Vehicles

L. Peter Martin and Robert S. Glass
Lawrence Livermore National Laboratory

presented to:

The DOE National Laboratory Fuel Cells for Transportation
Program Review
May 22, 2003

This work was performed under the auspices of the U.S. Department of Energy by University of California Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

There is an emerging need for hydrogen sensors for PEMFC vehicles*

- **Improvements are needed in:**
  - Size
  - Cost
  - Reliability, lifetime
- ***Safety sensor:* Monitors for leaks at strategic locations in FC vehicle**
  - Passenger compartment, wheel wells, hydrogen storage tanks
- ***Fuel sensor:* Monitors fuel gas quality at reformer output**
  - Most existing sensor technologies are not designed to operate in the fuel cell environment

*** From: *Sensor Needs and Requirements for Proton Exchange Membrane Fuel Cell Systems and Direct-Injection Engines*, U.S. DOE, Office of Transportation Technologies, UCRL-ID-137767, May, 2000.**

The objective is to develop solid-state electrochemical sensors for safety and fuel monitoring applications

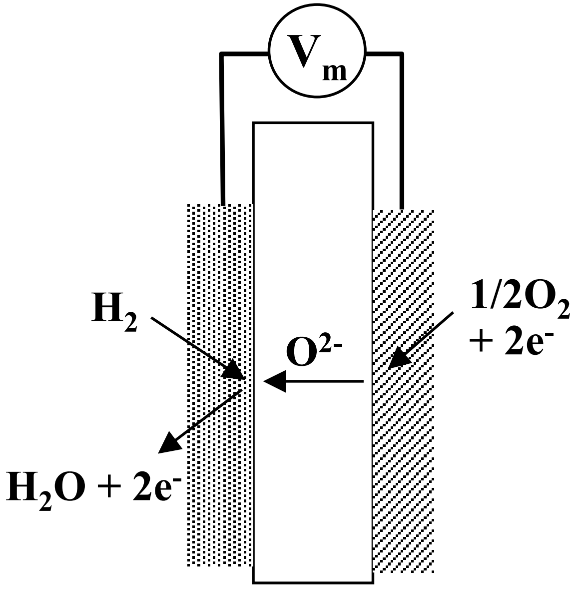
- ***Hydrogen Safety Sensor*** **performance targets*:**
  - **0.1 to 10% hydrogen in ambient air (10 – 98% relative humidity)**
  - **Response time under 1 second**
  - **Selectivity versus hydrocarbons, humidity**
  - **Operating temperature: - 30 to 80 ^{o}C**
- ***Hydrogen Fuel Sensor*** **performance targets*:**
  - **1 to 100% hydrogen concentration**
  - **10 - 30 mol% water, ~15% CO_2, <1% CO and CH_4**
  - **90% response time of 0.1 to 1 second**
  - **Operating Environment : 70-150 ^{o}C, 1-3 atm**

*** From:** ***Sensor Needs and Requirements for Proton Exchange Membrane Fuel Cell Systems and Direct-Injection Engines*****, U.S. DOE, Office of Transportation Technologies, UCRL-ID-137767, May, 2000.**

Safety Sensor: The approach is to apply new electrode materials to well-known oxygen conducting ceramics

- H_2 concentration is determined from the measured potential difference (V_m) between two electrodes
- The electrode potentials result from simultaneous, competing redox reactions
- Electrodes with different catalytic properties will have different steady-state potentials
- In principal, both reactions happen at both electrodes but…
- Electrode materials can be chosen so that:
  - Reaction I dominates @ reference electrode
  - Reaction II dominates @ sensing electrode

Potentiometric Safety Sensor



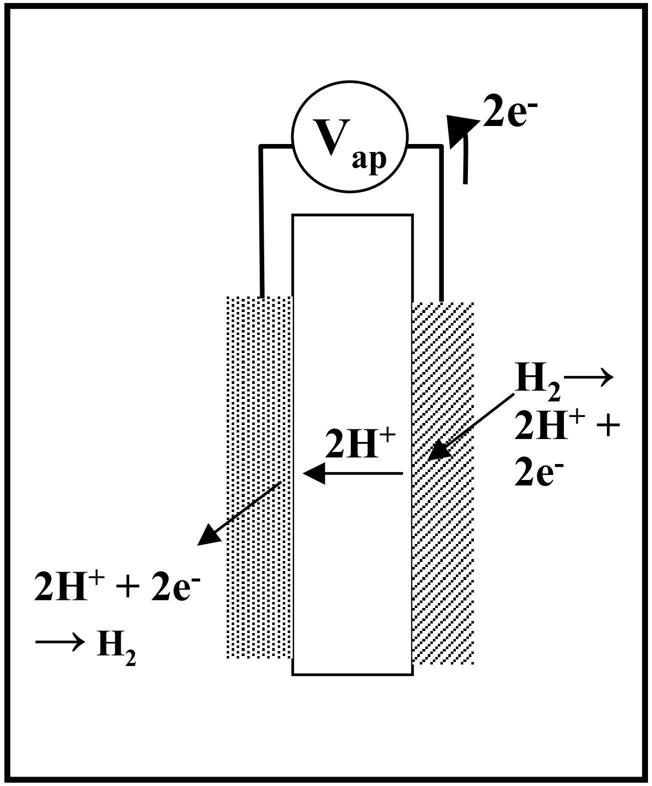
I: $1/2O_2 + 2e^- \longleftrightarrow O^{2-}$

II: $H_2 + O^{2-} \longleftrightarrow H_2O + 2e^-$

Fuel Sensor: The approach is to adapt novel proton conducting ceramics to a traditional sensor concept

- An applied potential (V_{ap}) ‘pumps’ H^+ ions through the electrolyte
- The resultant current is related to the H_2 concentration
- Most well known proton conducting ceramics either:
  - Are unstable at required H_2O/CO_2 levels
  - Do not have sufficient H^+ conductivity
  - Have unacceptable O^{2-} or e^- conductivity
- Initial efforts are to identify suitable electrolyte/electrode materials

Amperometric Fuel Sensor



A laboratory prototype for the *Safety Sensor* was reported last year

- **A non-integrated sensor**
  - **Tested in furnace hot-zone (not self-heated)**
- **2-3 second response time at 500 ^{o}C**
  - **Response benchmark is 0.2% H_2 in flowing air**
- **Selectivity to H_2 vs. CH_4 was 10x at 500 ^{o}C**
- **Sensor stability was excellent for 110 hours at 500 ^{o}C**
  - **Response to 0.2% H_2: 165±5 mV**
  - **Baseline in flowing air: 4±4 mV**
- **Lower temperature resulted in severe overshooting**

The 2003 milestones specify completion of the *Safety Sensor* and initiation of the *Fuel Sensor* development

- **Reduce *Safety Sensor* operating temperature below 500 ^oC (12/02)**
  - **Sensor operating temperature of 500 ^oC is compatible with requirements, but…**
  - **Lower operating temperature reduces power consumption**
- **Complete *Safety Sensor* development (5/03)**
  - **Develop self-heated safety sensor (6/02)**
  - **Characterize response and power consumption (5/03)**
  - **Package for sending out for independent testing (Ford) (5/03)**
- **Evaluate designs for the H_2 *Fuel Sensor* (7/03)**
- **Fabricate first prototype *Fuel Sensor* (9/03)**

Current status: The *Safety Sensor* is nearing completion and the *Fuel Sensor* has been started

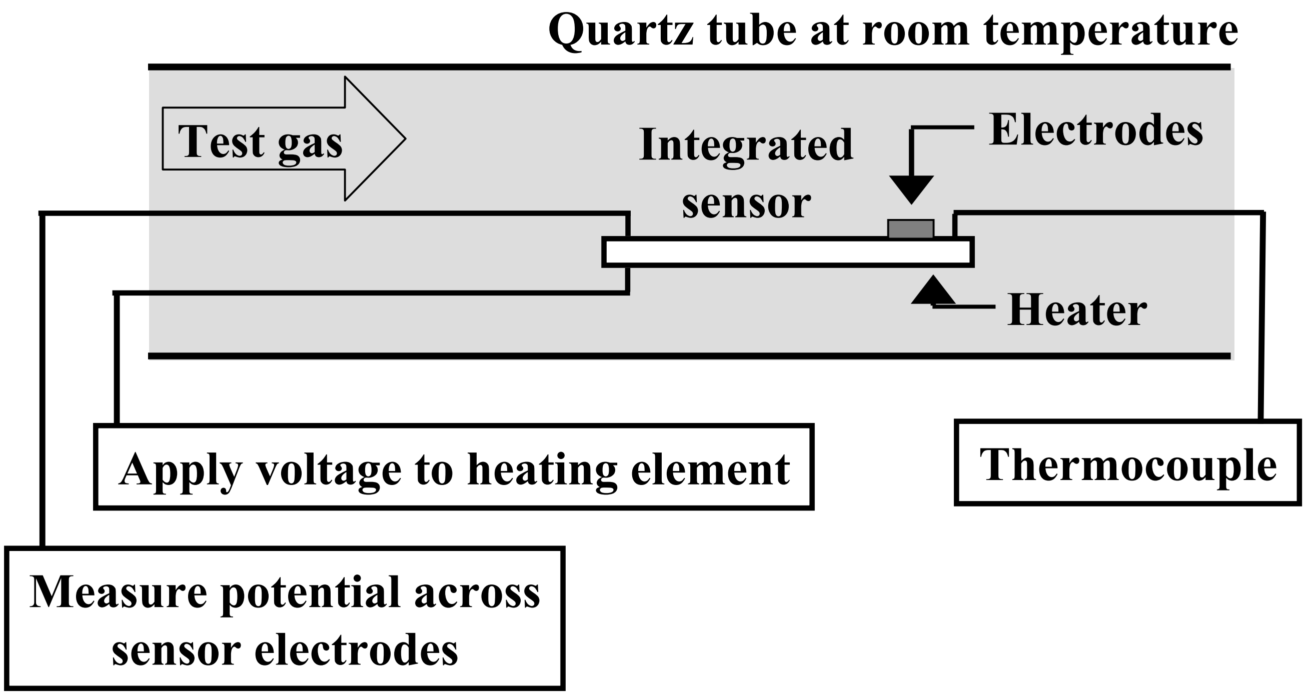
- ***Safety Sensor* development:**
  - **Electrode/electrolyte compositions have been finalized**
  - **Operating temperature has been reduced to 440 ^{o}C**
  - **An integrated, planar heater/sensor design has been established (heated substrates supplied by Ford)**
  - **A packaging concept has been implemented**
  - **External collaborators interested in testing/commercialization are being explored (Ford is currently testing)**

- ***Fuel Sensor* development:**
  - **A candidate electrolyte material has been selected**
  - **Processing techniques have been developed for the electrolyte**
  - **Preliminary laboratory prototypes have been fabricated and are being tested**

The project timeline indicates that we are on schedule…

Task	Year			
	FY 01	FY 02	FY 03	FY 04
H_2 Safety Sensor				
- Select approach/materials				
- Integrated (heated) sensor				
- Complete development				
H_2 Fuel Sensor				
- Select approach/materials				
- Fabricate 1st prototype				
- Complete development				

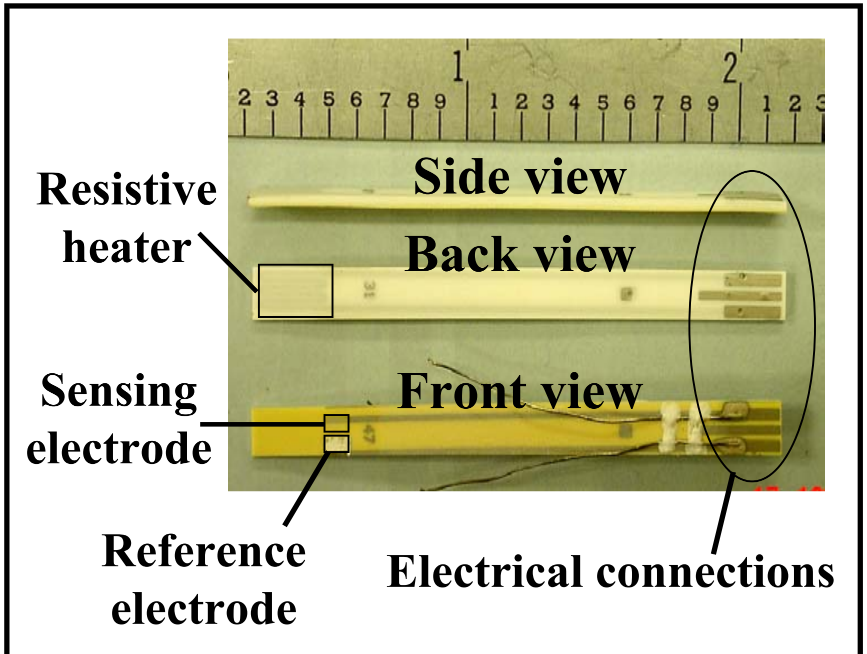
Integrated safety sensors are tested on the bench top by applying a voltage to the heating element



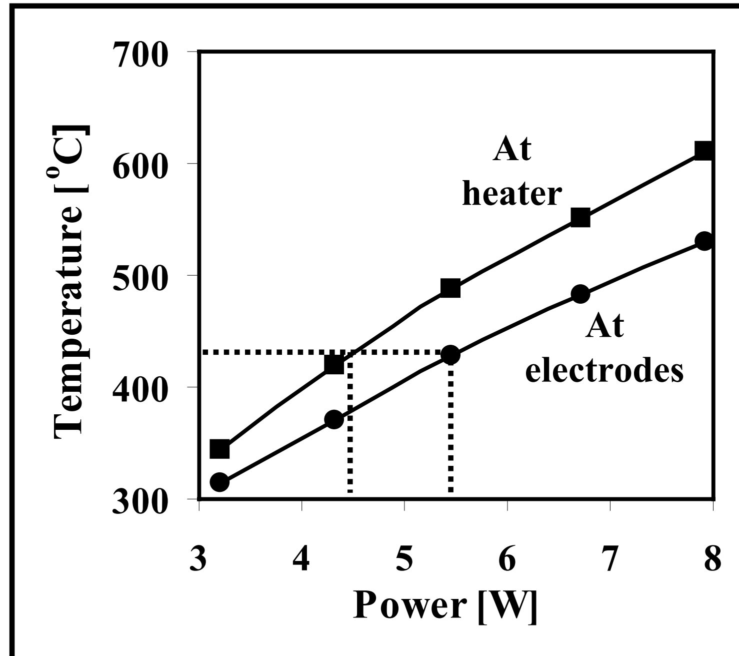
Heated substrates for the integrated sensors were supplied by Rick Soltis of the Ford Research Center

The integrated sensor consumes 5.5 W at the operating temperature of 440 ^oC…final design will reduce 10-20%

In the current design, the electrodes don’t align with the heater:

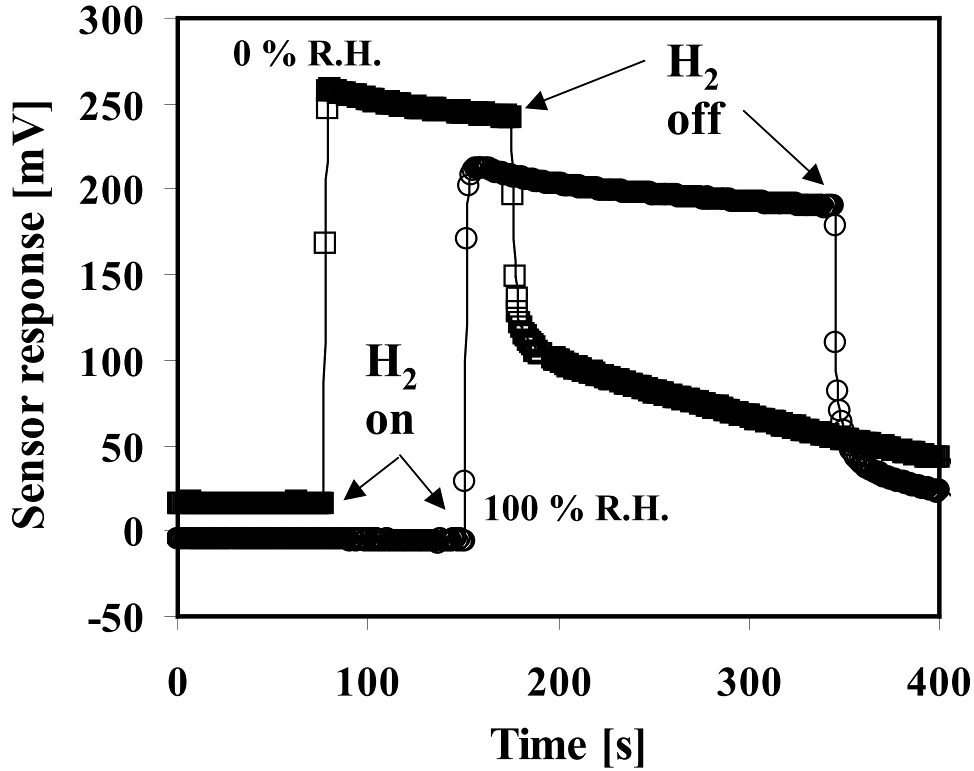


The misalignment requires higher power to heat electrodes:



The final design, currently being built, aligns the heater and electrodes

The integrated sensor responds in ≤ 2 seconds with a slight overshoot

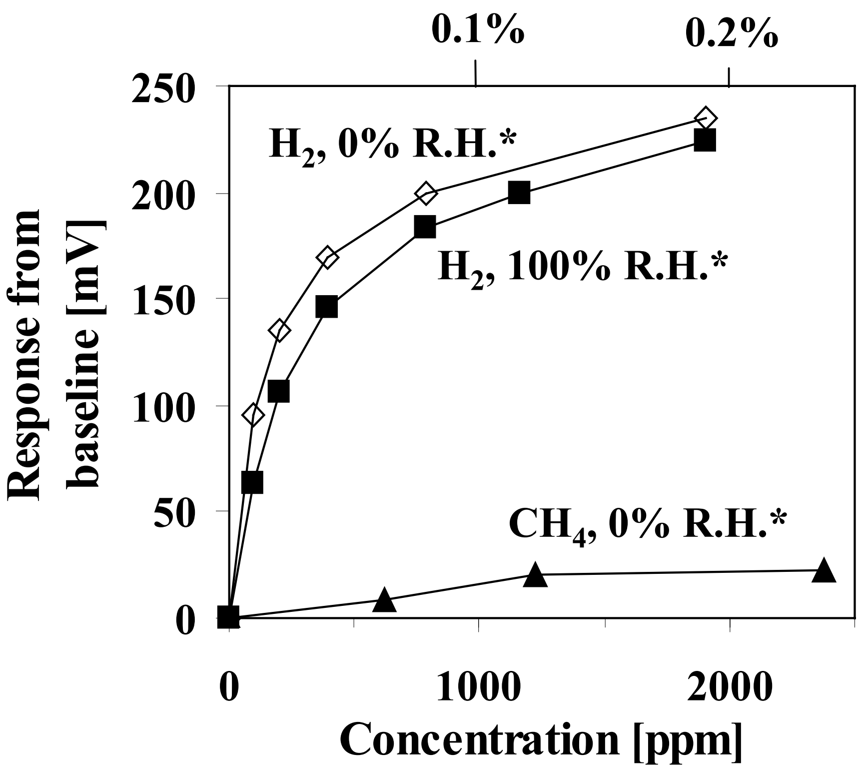


Test conditions:

- Operating temperature 440 ^{o}C
- Flowing air: 2 l/min
- 2000 ppm H_2 (0.2%)
- R.H. = Relative humidity
- 1 second between datum points

Electrode composition has been modified (from last year) to reduce selectivity versus humidity at the reduced operating temperature

The selectivity versus methane is high…The low operating temperature causes ~10% sensitivity to H_2O

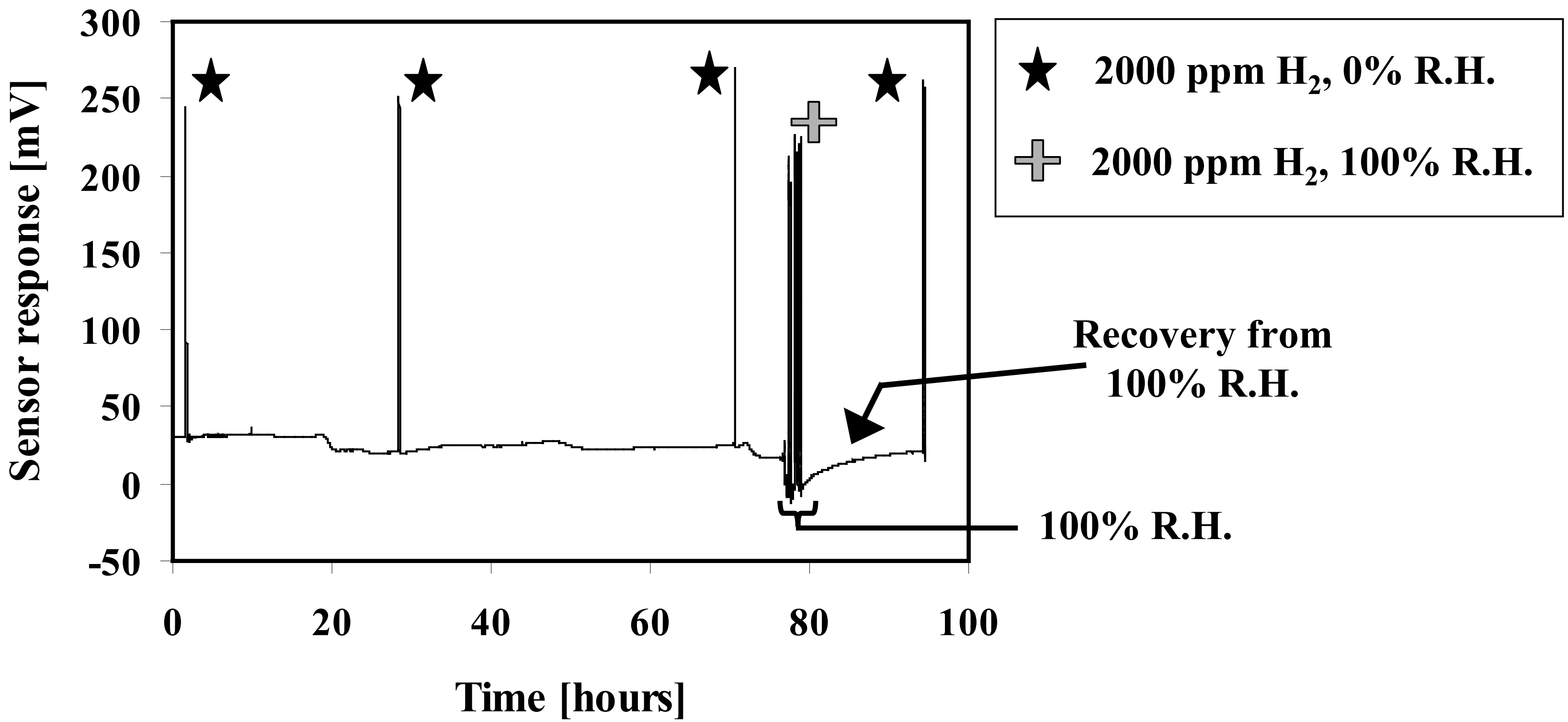


R.H. / 0.2% H_2	0% [mV]	100% [mV]
Baseline	20	-5
Absolute response	250	220
Response from baseline	230	215

*R.H = Relative humidity

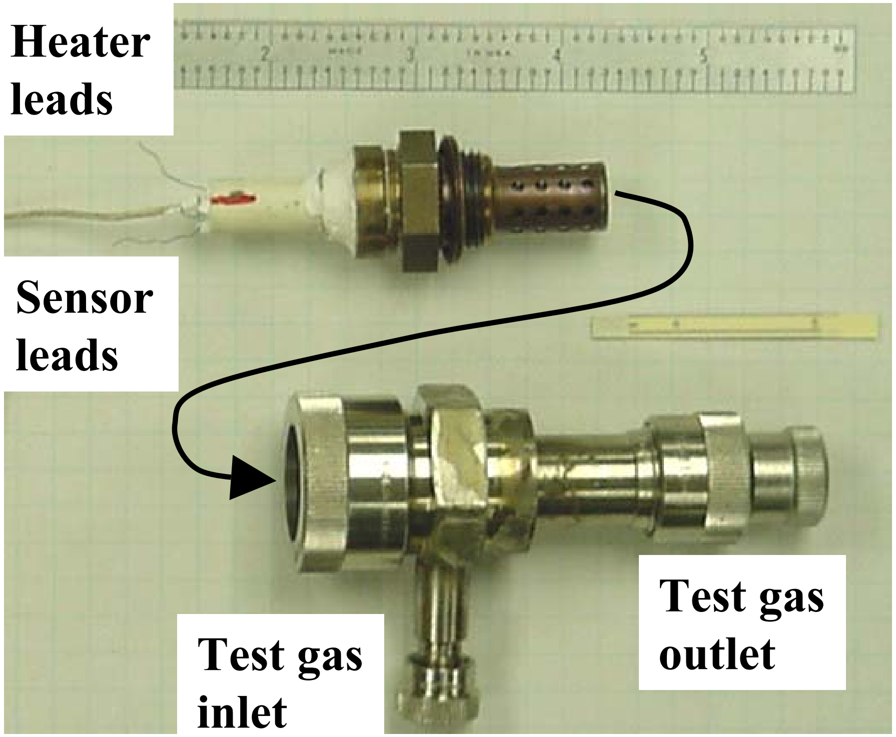
The sensor response saturates at ~300 mV when the H_2 concentration reaches ~2%

Long term testing indicates good baseline stability (no drift) and slow response to H_2O

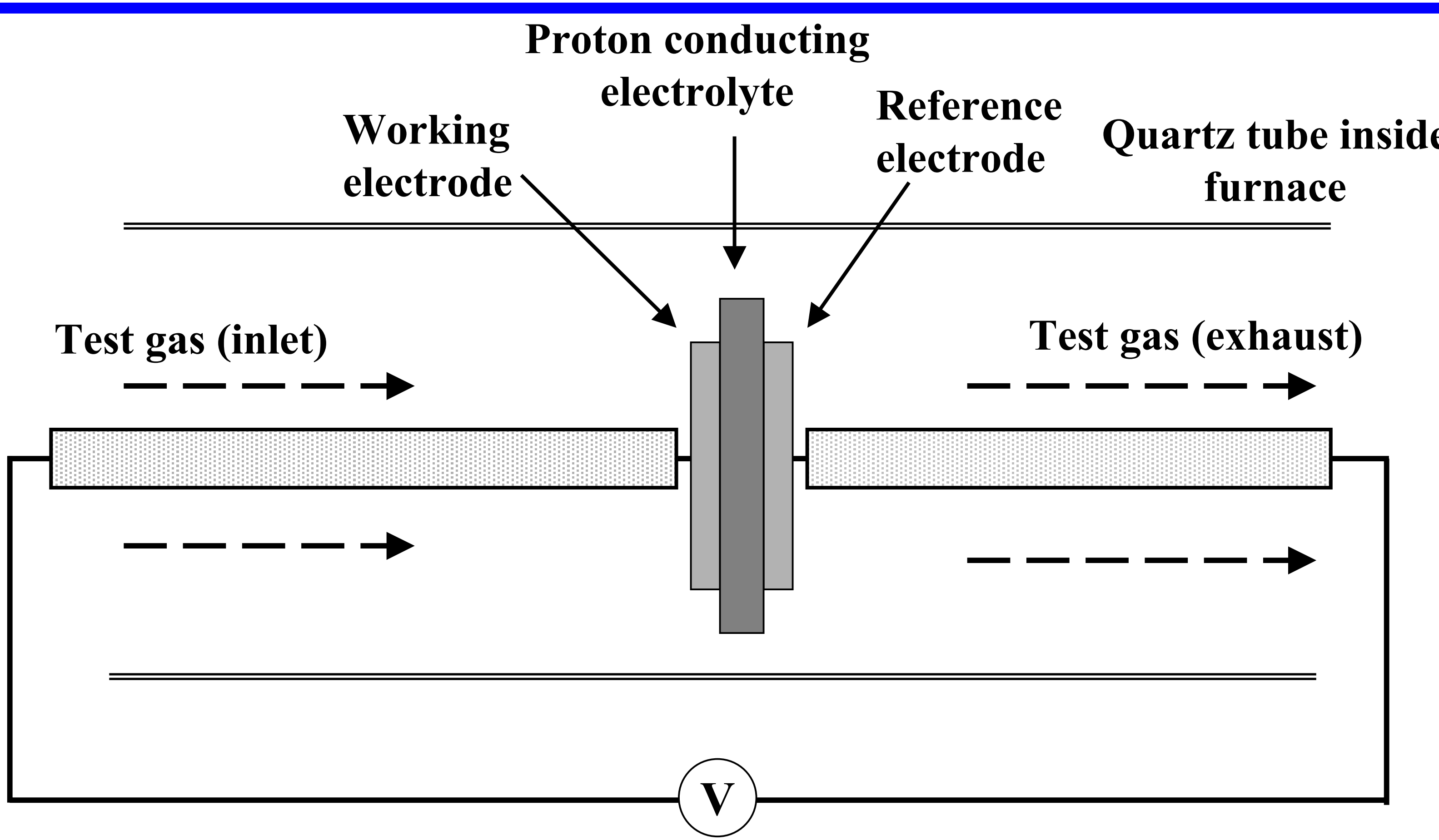


The difference in baseline between 0 and 100% R.H. is equivalent to ~25 ppm H_2 and can be corrected for in the sensor-control software

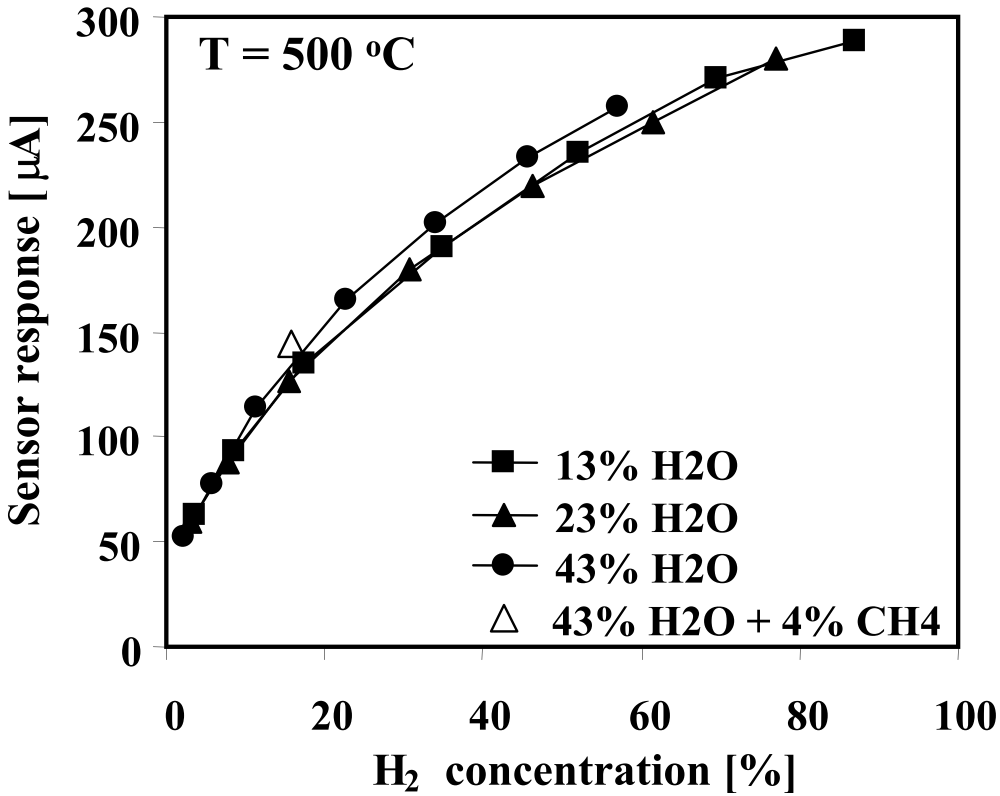
The integrated sensor can be easily packaged in a mountable, protective fixture



Fuel sensors are tested in a furnace by applying a voltage and measuring the current

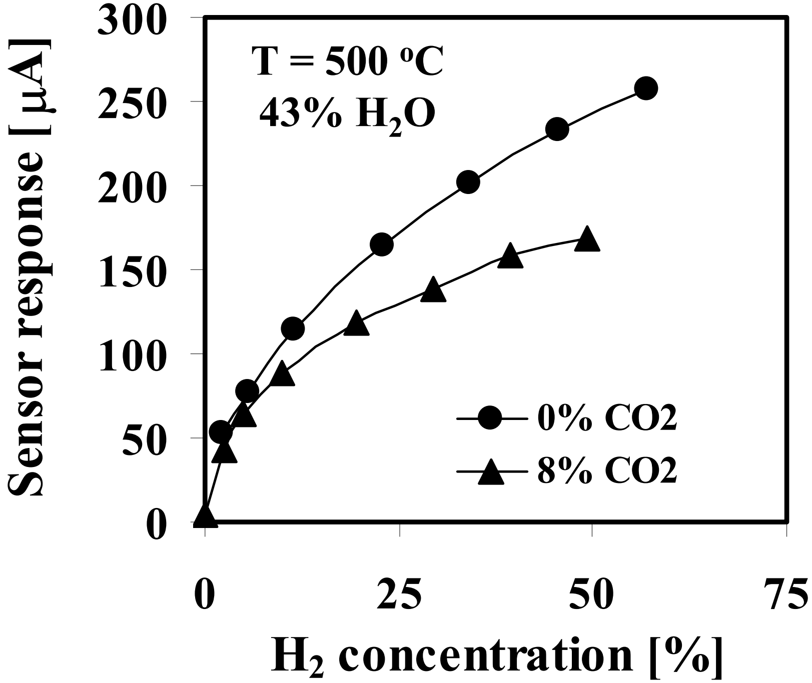


A first prototype of the proposed *Fuel Sensor* shows negligible CH_4 and H_2O cross-sensitivity



The data are promising, but the response is currently too slow (10's of seconds)

Presence of CO_2 causes a reversible signal reduction that may indicate an effect of O_2 partial pressure



- The signal is recovered on removal of the CO_2
- The effect is more severe at higher temperature
- O^{2-} and H^+ conductivities are closely related to oxygen deficiencies
- Oxygen pumps in the opposite direction as the hydrogen
- The mechanism can be clarified by isolating the reference electrode

Long term stability has not been established…

The approach to the Fuel Sensor development is to optimize the electrolyte stability/properties

- Catalytic experiments to elucidate sensing mechanisms
  - Isolated reference electrode
- Sensor stability:
  - The stability of the electrolyte needs further, and longer term, testing
  - Verify phase stability using TGA and XRD
  - Stability can be modified by changing stoichiometry, at the expense of conductivity (and vice versa)
- Response time (substantial improvement needed):
  - Slow response is partially related to experimental setup (gas handling)
  - Electrolyte conductivity can be improved with modified stoichiometry
  - Operating temperature may limit reaction kinetics (i.e. response time)
  - Alternate electrode materials may provide enhanced kinetics

Future milestones include completing the safety sensor and ramping up the fuel sensor development

- ***Safety Sensor:***
  - **Build final design (once heated substrates are delivered)**
  - **Locate external collaborator interested in testing / commercialization (Ford has agreed to test sensor)**
  - **Ford has expressed interest (supplied heated substrates gratis, currently testing prototype sensor)**

- ***Fuel Sensor (future milestones):***
  - **Evaluate various materials, processing, and designs (7/03)**
  - **Fabricate first prototype (9/03)**
  - **Seek industrial collaboration**
  - **Develop integrated fuel sensor**

Initial results are promising, but there's a long way to go…