Electrochemical Sensors for PEMFC Vehicles

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This presentation does not contain any proprietary or confidential information

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

Safety sensor: **Monitors for leaks at strategic locations in and around fuel cell vehicles or fuel cell stacks used in stationary applications**

- **Explore external collaboration to assist in commercialization (FY03, FY04)**
- **Perform long-term, multiple sensor testing and pursue commercialization (FY04)**

Fuel sensor: **Monitors fuel quality at reformer output, fuel cell intake, fuel cell exhaust**

- **Evaluate preliminary designs (FY03)**
- **Fabricate and test first prototype (FY03)**
- **Develop thin film design to reduce fuel sensor operating temperature (FY04)**

Discussions with various end users indicate a need for H_2 (fuel) sensors at stack input and outlet regardless of H_2 source (tanks or on-board reformer)

The project is in the 4th year and in the process of developing the 2nd of three sensors

	FY01	FY02	FY03	FY04	Total
Funding [$k]	200	200	200	115	715
Procurements and support [$k]	~20	~20	~20	~10	70
Travel [$k]	~10	~10	~10	~10	40
FTE [man-year]	0.47	0.47	0.47	0.26	1.67

Technical Barrier and Targets for the Hydrogen Safety and Fuel Sensors

Hydrogen Safety Sensor

- ***Technical Task Number 2:*** **Sensors Meeting 2010 Targets**

  "Verify low-cost sensors to monitor ambient concentrations of hydrogen for safety in the presence of other species found in the ambient air."
- ***Technical Barrier B:*** **Sensors**
- ***Technical Targets:***
  - **0.1 to 10% H_2 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

- ***Technical Task Number 1:*** **Chemical and Physical System Sensors**

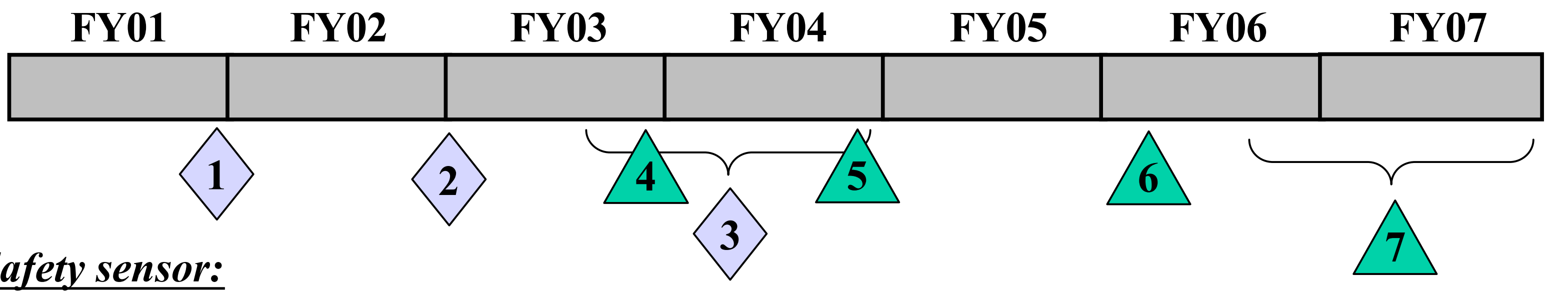
  "Determine hydrogen concentration at the fuel processor outlet over a wide range of concentrations and temperatures in the presence of other constituents in the reformate stream"
- ***Technical Barrier B:*** **Sensors**
- ***Technical Targets:***
  - **1 to 100% H_2 concentration**
  - **10 - 30 mol% 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**

Project safety… LLNL has implemented an Integrated Safety Management System

- *Pre-start review:* All activities are reviewed with safety and environmental teams
- *Hazard Assessment:* Safety personnel quantitatively evaluate specific hazards
- *Environment, Safety and Health* Manual: Provides extensive documentation of acceptable controls once hazards have been assessed
  - Fume hoods, flash suppressors, manned operation, limited flow rates, limited concentrations, limited quantities stored in the lab, interlocks, etc.
  - Safety and environmental personnel assist the PI to determine suitable safety controls
- Integration Work Sheet (IWS): Provides documentation of all procedures, hazards, controls, and personnel authorized to perform the work
  - The IWS clearly documents the chain of responsibility (PI, Facility, Directorate)
  - To perform work, an employee's name must be on the IWS
  - The hazards listed on the IWS 'trigger' required training for personnel named therein
  - The IWS must be authorized by PI, safety / facility personnel, and funding directorate
  - The PI is ultimately responsible to make sure all workers are aware of hazards and controls, and received proper training, and follow proper procedures

Handling potentially explosive gasses / gas mixtures in the lab requires safety precautions which can increase cost / duration of project

The project timeline and major milestones



Safety sensor:

1. **Select approach / materials: Potentiometric sensor with metal oxide sensing electrode**
2. **Demonstrate integrated sensor: Heated substrate demonstrated last year**
3. **Pursue commercialization: Currently in discussions with major auto and fuel cell developers**

Fuel sensor:

4. **Select approach / materials: Electrolyte stability is a key issue**
5. **Develop thin film design: Thin film electrolyte will decrease operating temperature**
6. **Second generation prototype / design: Optimize response time, sensitivity, stability**
7. **Pursue commercialization: Other applications besides on-board reformer**

The ultimate goal (i.e. project completion) is to commercialize the sensors

Safety Sensor: Numerous technologies have been reported, but response times are generally too long…

Technology	Reference	Temp. [°C]	Response time [s]
Micro-cantilever	*Sens. and Act.*, 2003	25	~90
Amperometric (nafion)	*J. ECS*, 2002	25	50 - 300
Surface acoustic wave	*Sens. and Act.*, 2002	30-70	100 - 1000
Thermoelectric	*Thin Solid Films*, 2002	25-100	50 - 100
Chemi-resistor	*J. ECS*, 2002 / Others	25-150	30 - 1000
Schottky diode	*IEEE Elect. Dev. Lett.*, 2002	80-380	2 - 70*
Varistor (ZnO-based)	*Sens. and Act.*, 1995	400-600	~120
Amperometric (ceramic)	*Sens. and Act.*, 2001	700	10 - 100
Various potentiometric	*Sens. and Act.*, 1996 / Others	25 - 900	5 - 7000

- The clear trend is decreasing response time with increasing temperature
- The most promising response times are from potentiometric sensors using ZnO sensing electrode and operating at T ≥ 600°C
- Our sensor is similar, but uses an electrode with higher electronic conductivity to get faster response at lower T

*The response of the schottky diode sensor saturates at ~1% H_2

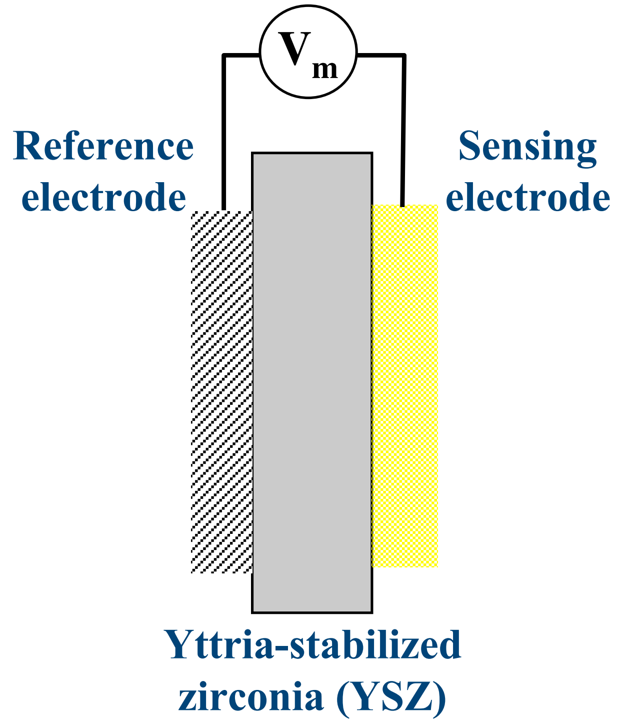
Safety Sensor: The approach is to apply new electrode materials to well-known oxygen conducting ceramics

- Two electrodes, Pt and tin-doped indium oxide, are placed on an oxide ion (O^{2-}) conducting electrolyte
- Preferred electrolyte is ceramic yttria-stabilized zirconia (YSZ) used in automotive O_2 sensors
- Each electrode acts as a local cell with both reactions:

  i. $1/2\ O_2 + 2e^- \leftrightarrow O^{2-}$

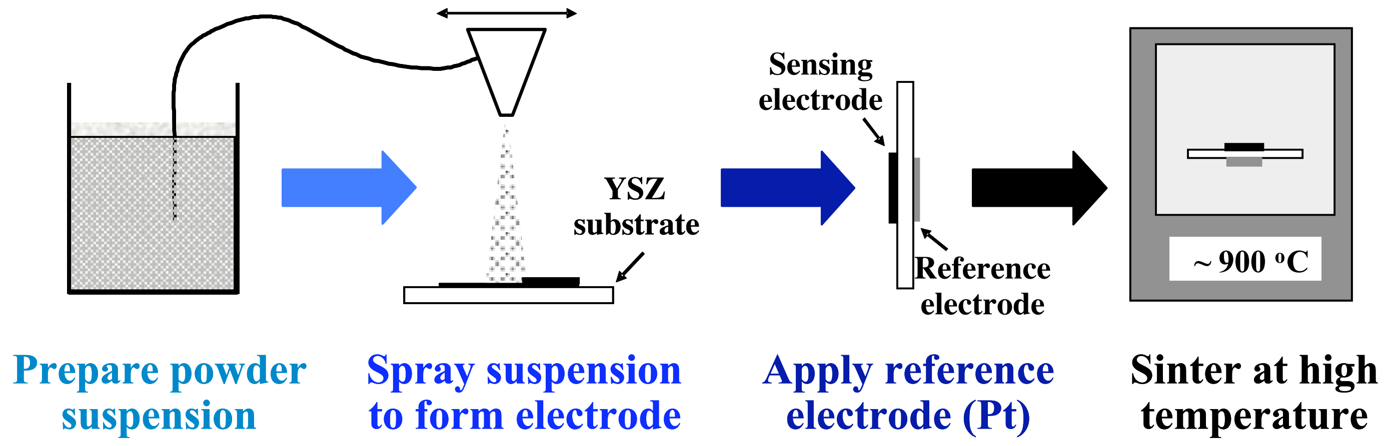
  ii. $H_2 + O^{2-} \leftrightarrow H_2O + 2e^-$

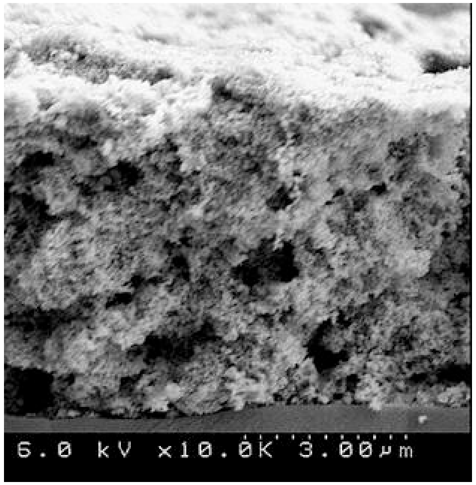
- The potential of each electrode will be determined by the balance of the currents from i. and ii.
- Electrode materials with different redox kinetics will have different potentials
- The measured difference in electrode potentials (V_m) can be correlated to the H_2 concentration



The electrolyte requires T > 400°C to have sufficient O^{2-} conductivity, but the high temperature speeds up the kinetics and gives fast response

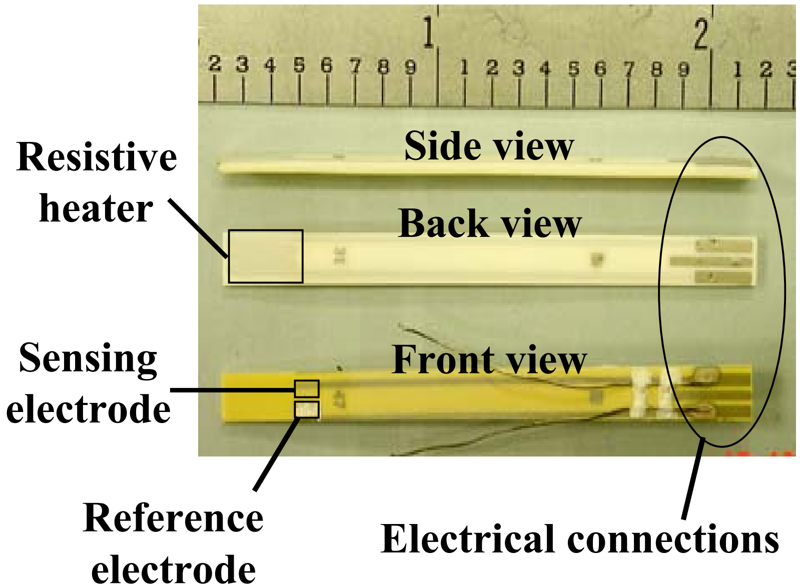
The sensor is fabricated by applying a nanocrystalline sensing electrode to a dense ceramic electrolyte

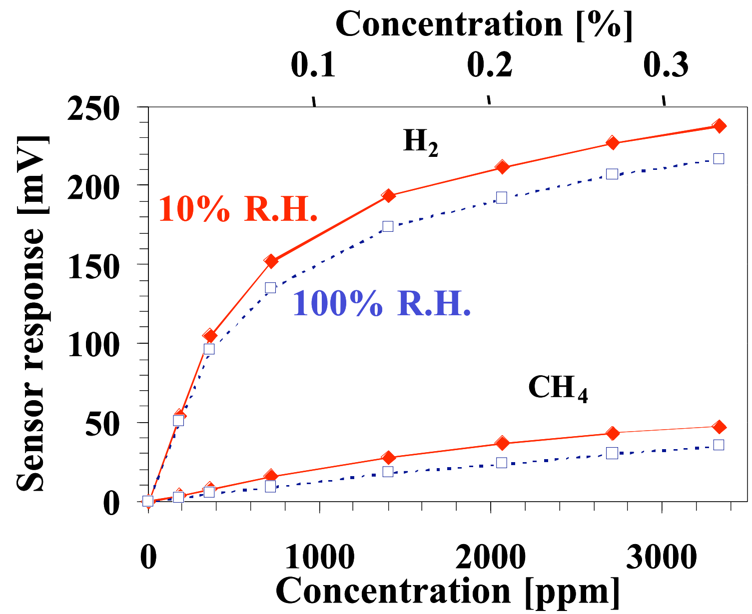




- The electrolyte is yttria-stabilized zirconia (YSZ)
- Sensing electrodes are 10% tin-doped indium oxide (ITO)
- Rh can be added to the sensing electrode as an organic precursor prior to sintering
- Typical electrode thickness is 3-15 µm
- Pt or AgPd reference electrodes are applied using screen printing ink

Last year we demonstrated a semi-integrated (self-heated) safety sensor with response time ~2 s or less





- Response was reported for up to ~3000 ppm H_2 in air
- Operating temperature as low as 440°C
- Power consumption was high, ~4.5 W, but miniaturization and packaging can make significantly lower
  - Consider micro-hotplate resistive sensors which can be used up to at least 600°C and draw <50 mW at 500°C

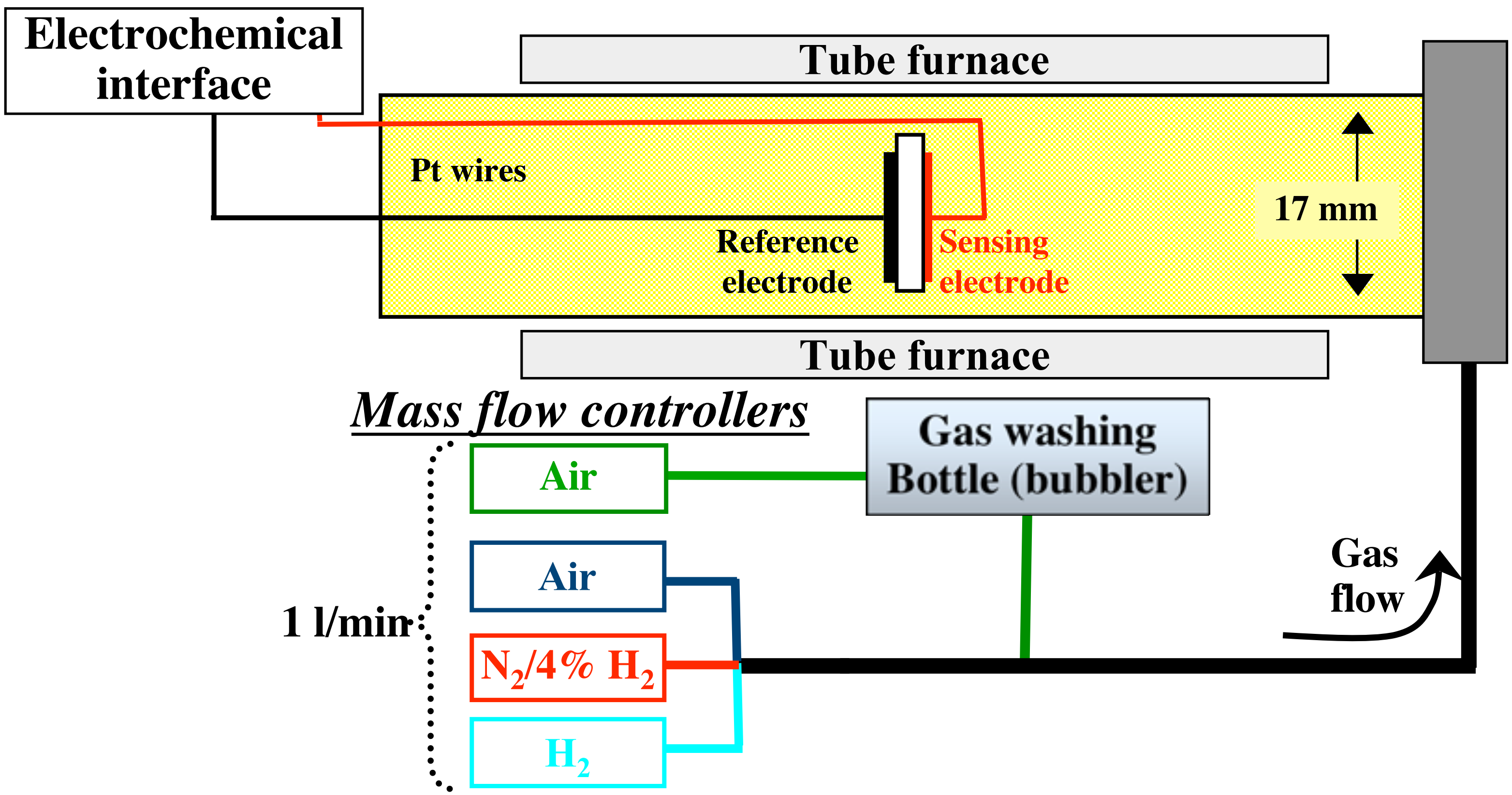
- Accepted for publication in *Solid State Ionics*

Last year we demonstrated the sensor approach, this year we focused on more fundamental characterization

- **Extensive testing of sensors with ITO and Rh:ITO sensing electrodes:**
  - **Extended range of H_2 concentration up to 10%**
  - **Performed more careful analysis of operating mechanism**
  - **Evaluated the effects of electrode thickness**
  - **Carefully documented sensor response times**
  - **Evaluated the effects on sensor performance associated with the addition of Rh to the sensing electrode**

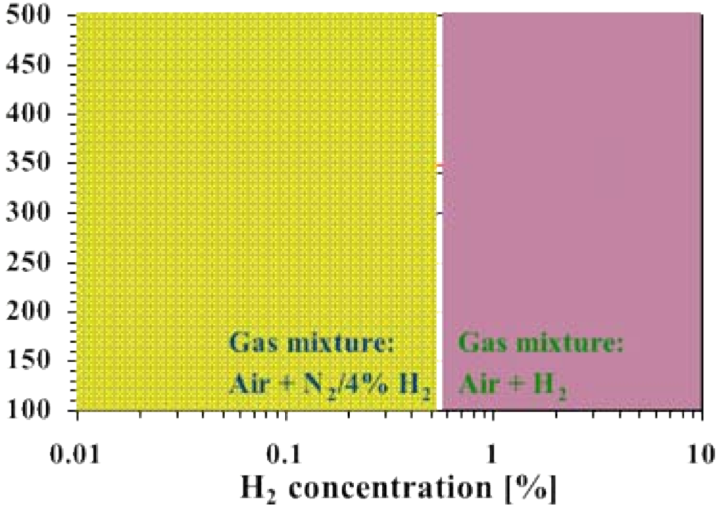
- **Commercialization efforts**
  - **Increase visibility: publications and presentations**
  - **Protect intellectual property: patent application in preparation**
  - **Initiate discussions with potential end user**

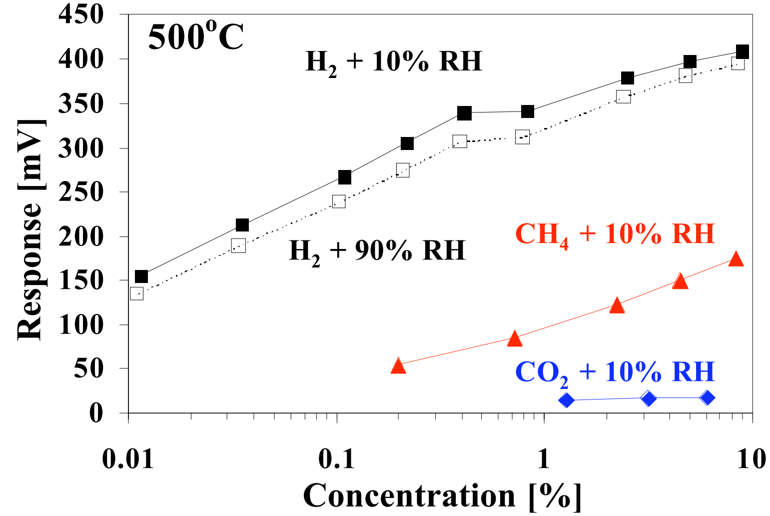
We performed sensor evaluation by furnace testing of laboratory prototypes to reduce cost / time

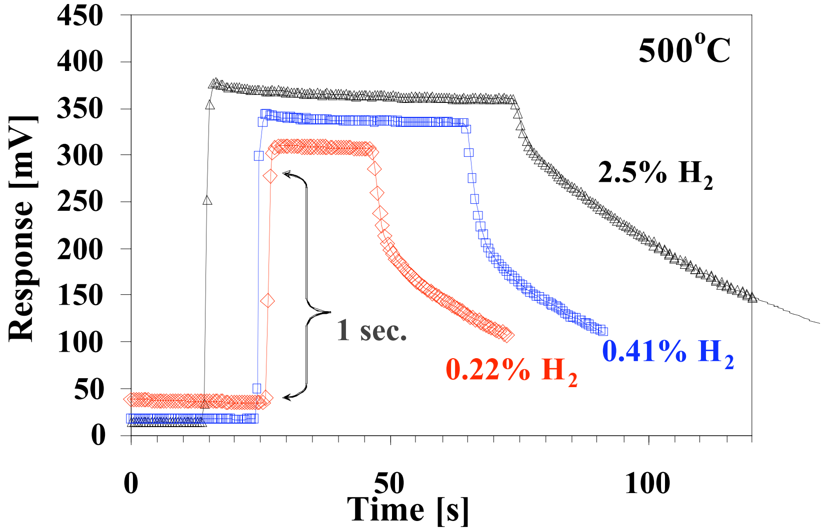


This testing method allows rapid testing of large numbers of sensors without consuming the expensive, high value-added heated substrates

Using the Rh:ITO sensing electrode, the sensor has good sensitivity, selectivity and response time



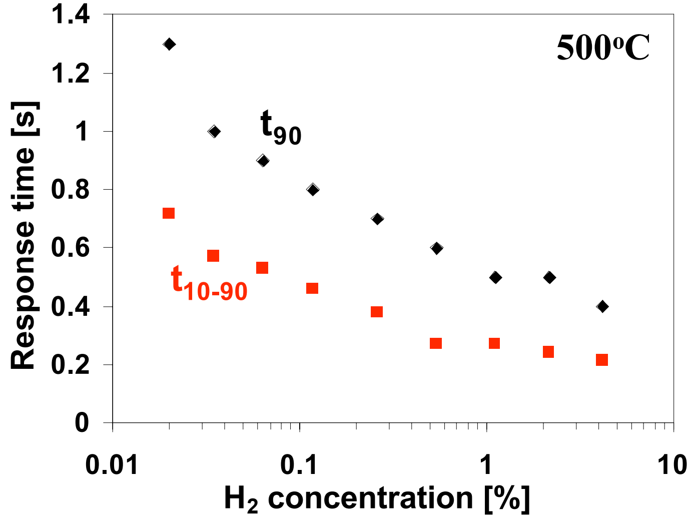


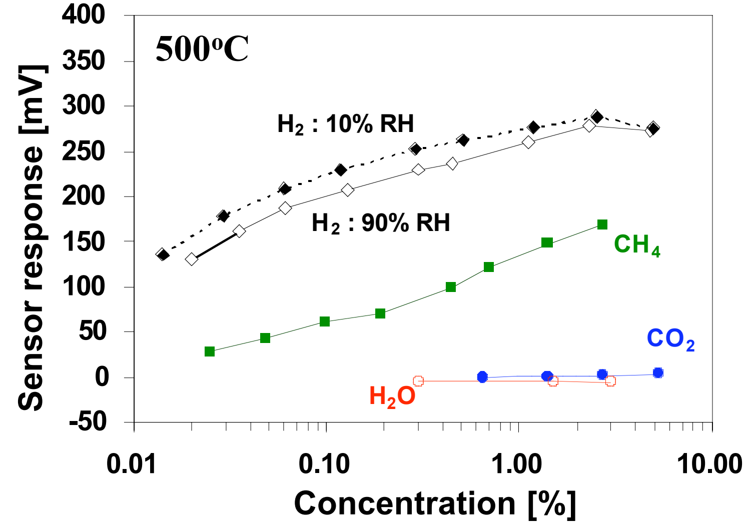


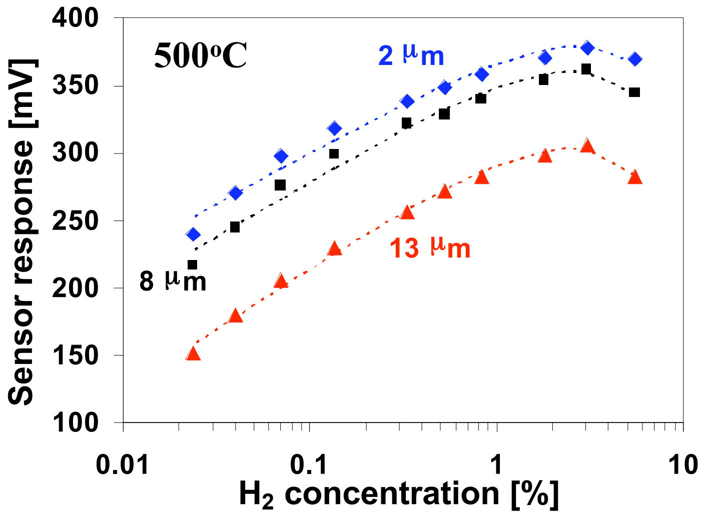
- **Response decays at the highest H_2 concentrations**
- **Selectivity versus CH_4 is consistent with last year**
- **Almost no sensitivity to CO_2**
- **Response time near 1 s at all concentrations**
- **What is the role of the Rh?**

- Presented at *204th Meeting of the ECS*, Oct. 2004

Sensors with ITO sensing electrodes are faster than Rh:ITO, but have slightly worse selectivity







- 90% response time, $t_{90} < 1$s for H_2 concentrations > 0.02% (200 ppm)
- Sensor has good selectivity and stability versus H_2O, CO_2, and CH_4
- Larger response for thinner electrodes indicates gas-phase reaction in electrode pores:

$$H_2 + \_\ O_2 = H_2O$$

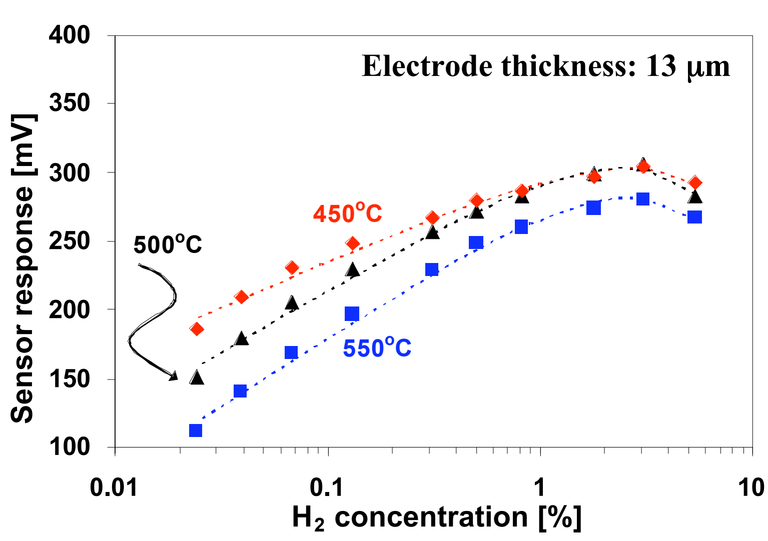
- Submitted for publication in *J. Electrochem. Soc.*

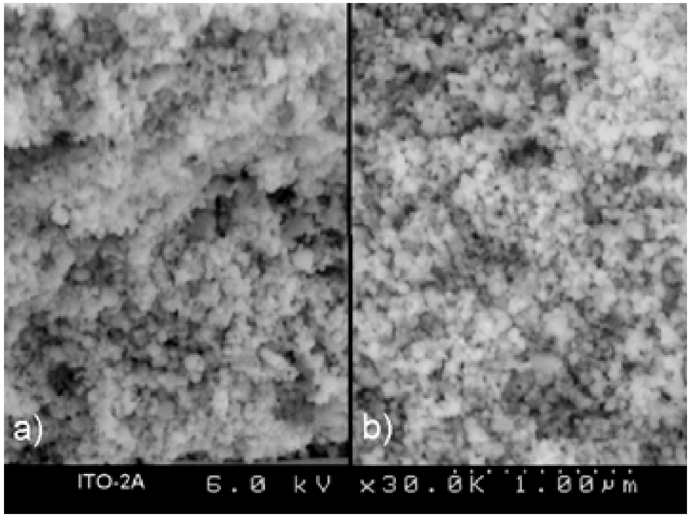
Extensive characterization of ITO electrodes (no Rh) indicates increased O_2 sensitivity versus Rh:ITO

- Sensor response is described by:

  $$E = C_1 + C_2 \ln[C(O_2)] - C_3 \ln[C(H_2)]$$

- Decay at high $C(H_2)$ results from dilution of O_2 by the added H_2
  - This corresponds to the 2nd term in the equation above
- Rh-addition appears to suppress this effect





SEM micrograph of the ITO electrode shows no significant aging effects:

a) prior to aging

b) after aging for 260 hours at 500°C

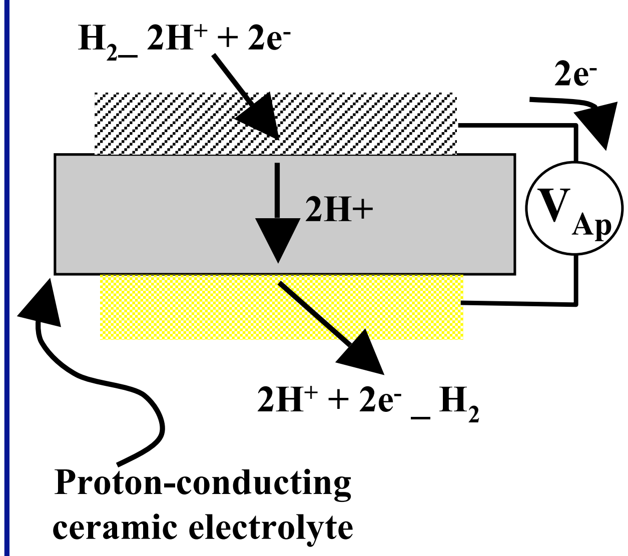
- Submitted for publication in *J. Electrochem. Soc.*

Commercialization efforts include increasing visibility and seeking industrial interest

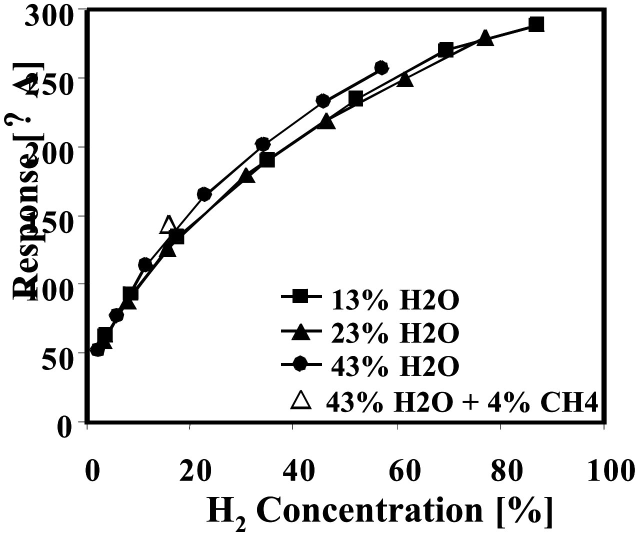
- **Presentations:**
  - **"Electrochemical Hydrogen Sensor for Safety Monitoring," poster presented at *The 14th International Meeting on Solid State Ionics* (June 22-27, 2003, Monterey, CA).**
  - **"Hydrogen Sensor Based on Yttria-Stabilized Zirconia Electrolyte and Rh-Promoted ITO Sensing Electrode," presented at *The 204th Meeting of The Electrochemical Society* (October 12-16, 2003, Orlando, FL).**
- **Publications:**
  - **"Electrochemical Hydrogen Sensor for Safety Monitoring," accepted for publication in a special issue of *Solid State Ionics* dedicated to the Proceedings of the 14th International Meeting on SSI (4/2003).**
  - **"Hydrogen Sensor Based on Yttria-Stabilized Zirconia Electrolyte and Tin-Doped Indium Oxide Sensing Electrode," submitted for publication to *The Journal of the Electrochemical Society*, April, 2004.**
- **Patent:**
  - **Provisional patent application made last year**
  - **Full patent application in progress**
- **Initiated discussions with a major fuel cell developer and an automotive company**
  - **The fuel cell developer is in process of discussing with a sensor manufacturer**

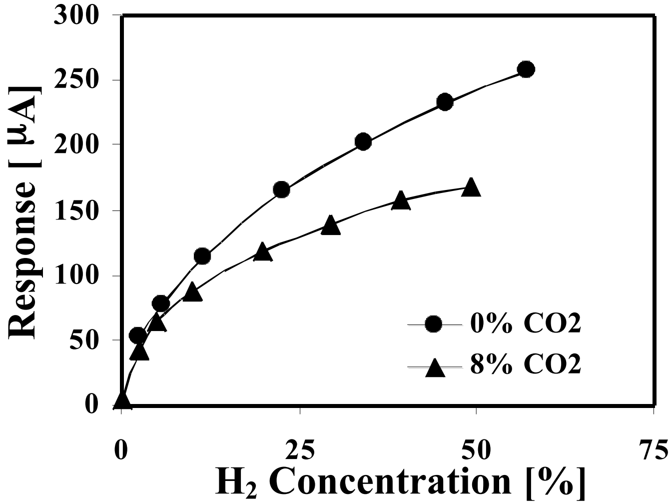
Fuel Sensor: The approach is to utilize proton conducting ceramics for an amperometric sensor

- 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 are believed to:
  - Be unstable at required H_2O/CO_2 levels (cerates)
  - Not have sufficient H^+ conductivity (zirconates)
- Initial efforts were to identify suitable electrolyte/electrode materials
  - Can a mixed cerate / zirconate give 'best of both worlds'
- The next task is to develop techniques to fabricate the thin film structure which will be necessary to reduce the operating temperature

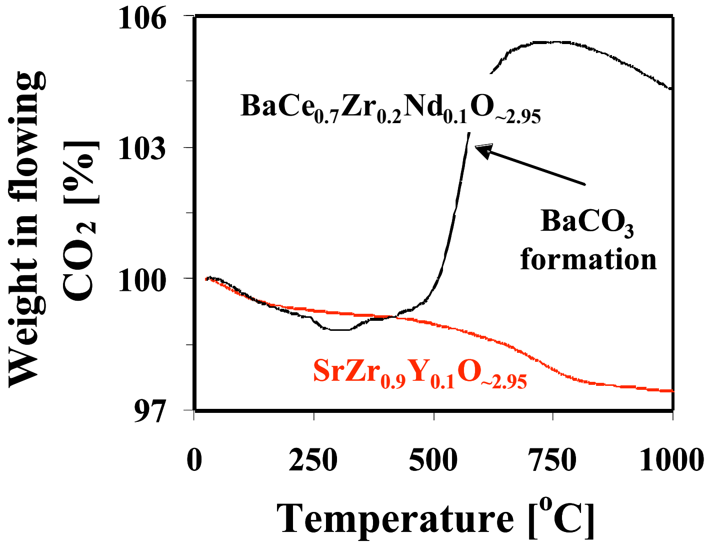


Last year we reported a *Fuel Sensor* with negligible CH_4 and H_2O cross-sensitivity, but poor stability

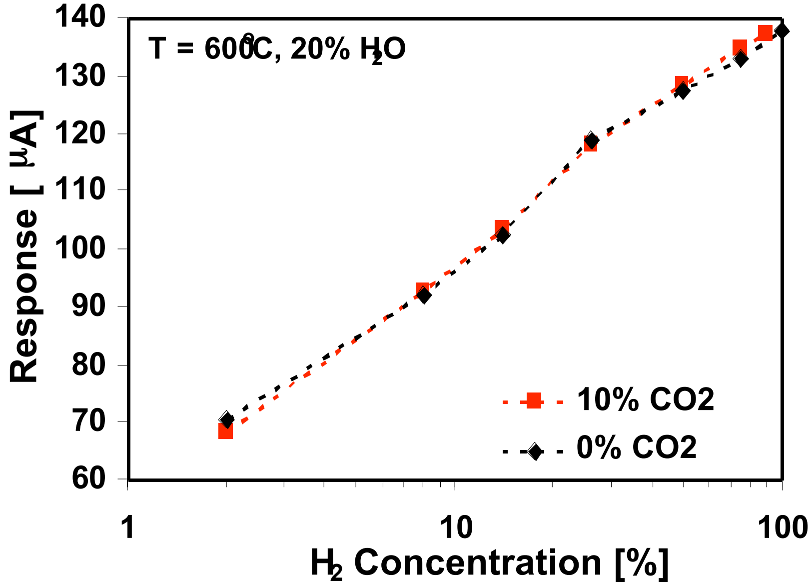


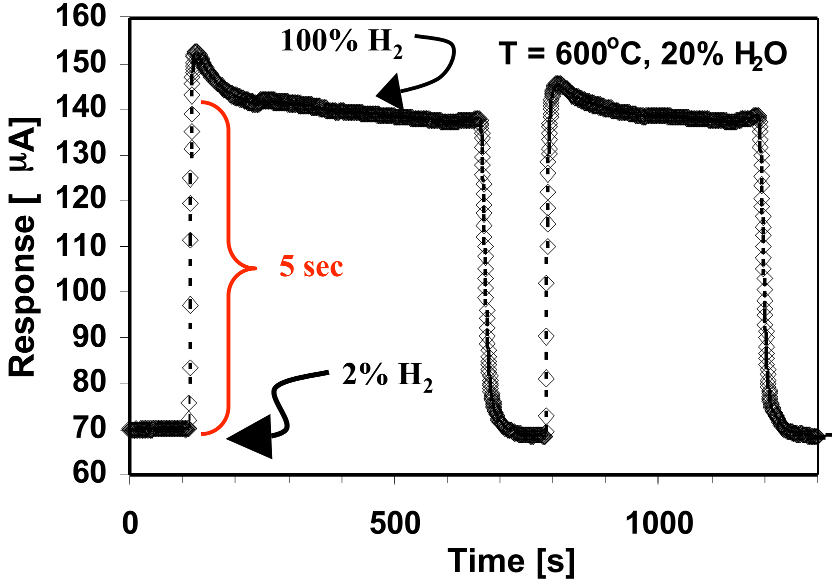


- Response to H_2, and CH_4 shown top-left
  - Mixed zirconate / cerate electrolyte
  - Operating temperature 600°C
- Interference from CO_2 shown top-right
  - Signal recovers slowly on removal of CO_2
- Weight gain in CO_2 shown at right indicates the formation of carbonate



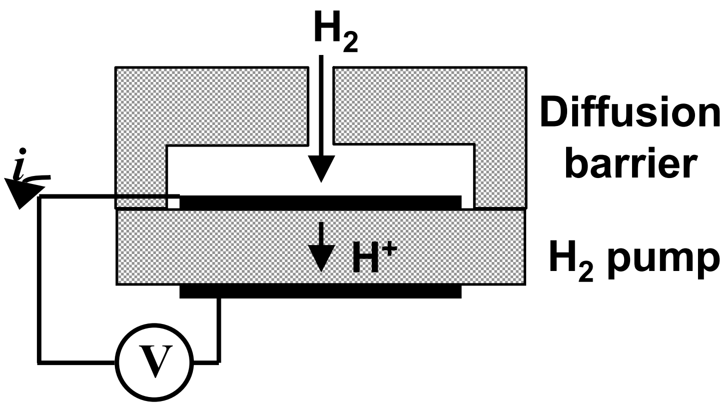
$SrZr_{0.9}Y_{0.1}O_{\sim 2.95}$ electrolyte was identified to provide sufficient sensitivity and to be stable in CO_2

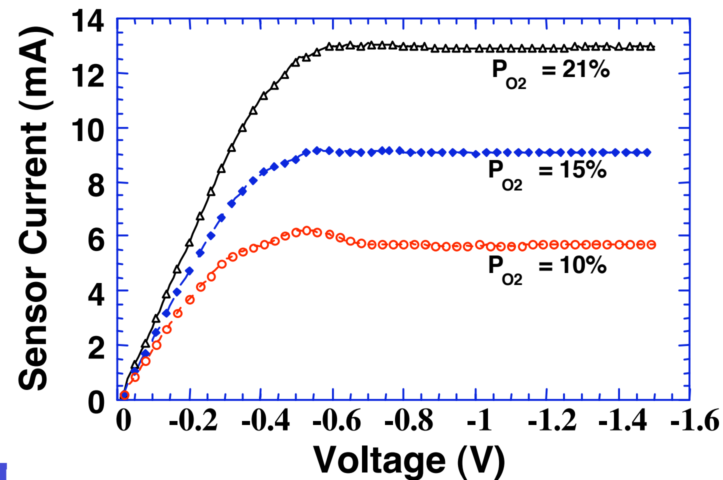




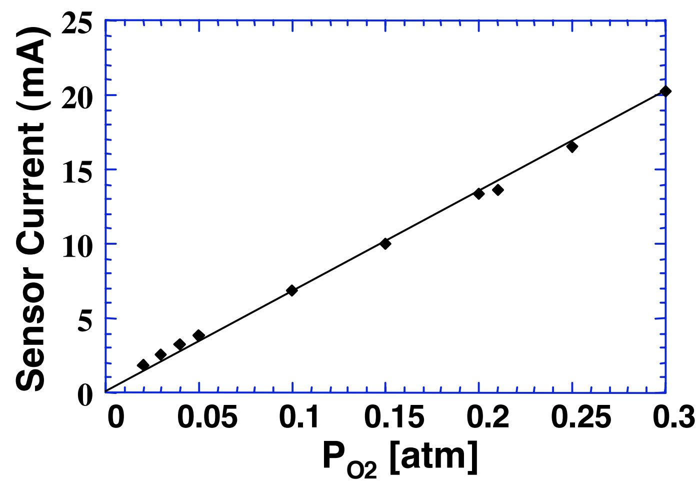
- The response is linear with the log of the H_2 concentration
  - Response can be 'forced' to be linear to H_2 concentration by the use of diffusion barrier
- Response time ~5 seconds from 2% to 100% H_2
  - Can improve response time by reducing thickness of the electrolyte (currently ~2 mm)
- Transient response on switching H_2 concentration corresponds to establishing H^+ non-equilibrium concentration gradient through the electrolyte thickness
  - Can reduce transient by reducing thickness of the electrolyte

When H_2 is removed from the cavity faster than it can diffuse in, the sensor is ‘diffusion limited’ and i α $[H_2]$





- **The diffusion barrier can be a dense layer with a single ‘hole’ or a porous layer**
- **When diffusion limited, the pumping current is proportional to the concentration**
- **This is an accepted and well-documented technique for linearizing amperometric sensors**
- **Data are shown for a previously developed O_2 sensor**



We are currently developing an organic precursor technique to fabricate thin electrolyte coatings

Current Fabrication Method

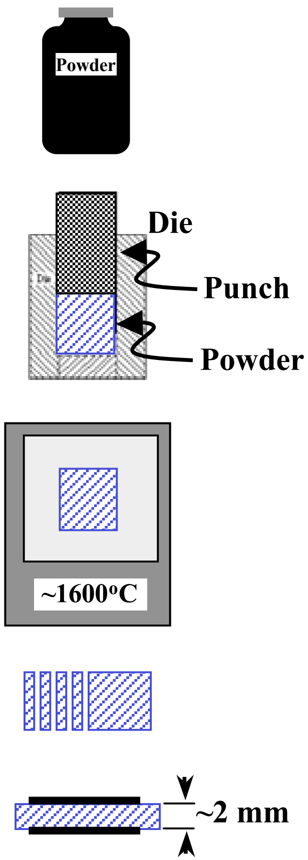
Start with micron-sized powder

Press into pre-form

Densify at high temperature

Cut sensor substrates

Add Pt electrodes



Proposed Fabrication Method

Prepare porous cermet substrate

Prepare organic precursor

Convert precursor to oxide powder

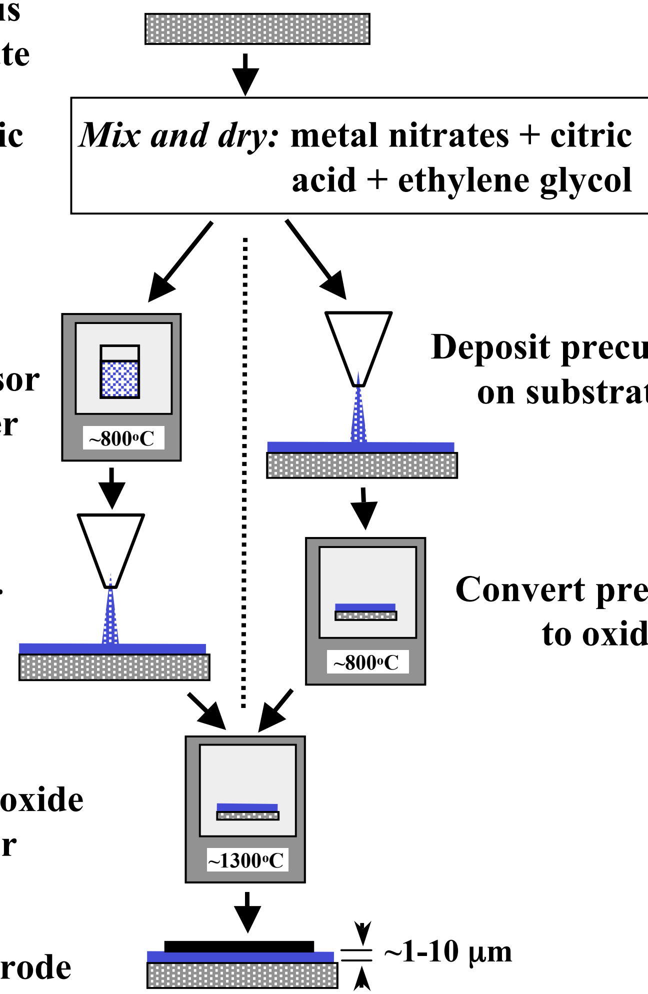
Spray powder on substrate

Deposit precursor on substrate

Convert precursor to oxide

Densify oxide layer

Add electrode



Address reviewer comments from last year for the Safety Sensor

- ***Reviewer:*** **"power consumption is critical…target should be identified."**
  - **Discussions with auto manufacturer: 1-1.5 W**
- ***Reviewer:*** **"Electrical power consumption reduction should be focus…"**
  - **Miniaturization can reduce operating power *significantly***
  - **Microhotplate resistive sensors have been reported which reach 400-500^{o}C at <50mW power consumption, so there is a precedent that the power constraints can be met**
- ***Reviewer:*** **"Focus on fundamental aspects of technology - let industry develop product"**
  - **We have considerably expanded the sensor characterization**
- ***Reviewer:*** **"CO_2 interferences could be significant"**
  - **Shown to be insignificant**
- ***Reviewer:*** **"Need to establish ties with fuel cell makers or auto companies"**
  - **Currently in discussions with a major FC developer, and an auto company**
  - **Economic factors become an issue with commercialization**
  - **Very difficult in a research lab setting to reach the point where a manufacturer is ready to pick up the technology**

Address reviewer comments from last year for the Fuel Sensor

- **"Currently, the H_2 fuel sensor is for on-board fuel processing only"**
  - **Even without on-board reforming, there is a strong need for H_2 fuel sensors both at intake and outlet**
  - **We've discussed this issue with FC developer and they have pointed out the need for this type of sensor in stationary and vehicular applications**
  - **We believe that this type of sensor will be required regardless of how the H_2 is delivered in the PEM FC-vehicle (tank or reformer)**