2005 DOE Hydrogen Program

Development of Sensors for Automotive PEM-based Fuel Cells

DOE Agreement DE-FC04-02AL67616

Donna Ho - DOE

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UTC FC/UTRC

May 26, 2005

Project ID #
FC30

Overview

Timeline

- Start: April 2002
- End: September 2005
- 90 Percent complete

Budget

- Total project funding
  - DOE share: $2.9 MM
  - Contractor share: $720 M
- Funding received in FY04: $1076 M
- Funding for FY05: $540 M

Barriers

- Barriers addressed
  - Cost and Durability
  - Reliability
  - Size
  - Manufacturability

Partners

- UTC Fuel Cells/UTRC
- ATMI
- Illinois Institute of Technology (IIT)
- NexTech Materials

Objectives

- Develop suite of sensors for CO, H_2, O_2, H_2S,, flow, temperature, pressure, and relative humidity that meets performance requirements
- Demonstration of new H_2 safety sensor
- Develop new measurement principles to meet sensitivity requirements
- Improve reliability in harsh fuel cell system environments
- Path to low cost (<$20 / sensor) at 200k qty

Approach

- **Sensor development program utilizes a team approach**
  - UTRC for program coordination and physical and chemical sensor evaluation
  - Illinois Institute of Technology (IIT) for chemical sensor evaluation
  - Advanced Technical Materials (ATMI) for MEMS sensor development
  - NexTech Materials for electrochemical and solid state sensor development

Team Member	**T**	**ΔP**	**RH**	**flow**	**O_2**	**CO**	**H_2**	**SO_2**	**H_2S**	**NH_3**	**Technological Expertise / Responsibility**
UTC FC	X	X	X	X	X	X	X	X	X		Testing on S300 Breadboard
UTRC	X	X	X	X	X	X	X	X	X		Testing in reformate simulator
ATMI							X	X	X		Develop Using MEMS Silicon Microhotplate
IIT	X		X		X	X	X	X	X		Testing in Benchmark Facility
NexTech						X		X	X		Develop Using Solid State Electrochemical

Summary of IIT Accomplishments

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- **Market Survey**
  - Initial survey and report (completed)
  - updates and additions (on-going, but essentially completed)

- **Benchmark Sensors**
  - First round testing (completed)
  - Performance Reports (completed)

  (safety application, concentration, interference, analytic performance)
  - Second round testing (on-going)
    - safety and feed stock
    - Humidity effects on new sensors being tested
    - Effect of H_2S and CO on ATMI H_2 sensor being tested
  - broader concentration range, temperature range, pressure dependence, interference (CO and H_2S), moisture effects on performance

IIT Benchmark Testing of Viable Sensor Technologies

- IIT evaluated over 70 H_2 sensing technologies
- Tiered approach used to evaluate sensor technologies
  - Gas concentration, operating temperature, water vapor pressure
  - Effect of pressure, other background gases
  - Long-term testing
- Hydrogen Sensors (Reformer)

  -H2 Scan, Makel Engineering, ATMI, KSC NASA
- Hydrogen Sensors (Safety Application)

  -H2 Scan, Applied Sensors, Makel Engineering, ATMI, Figaro, Transducer Technology, Inc., Argus Group, Nemoto Environmental Technology, Applied Nanotech
- Carbon Monoxide Sensor

  -NexTech Materials

(Sensors currently available are listed in blue)

Summary of ATMI Accomplishments

- **LEL**
  - Developed and tested rare earth hydride based MEMS sensors
  - Demonstrated performance against program targets
  - Delivered alpha prototypes for IIT& UTRC for evaluation
- **Stack**
  - Developed and tested Pd, Ir, and Rh quad-layer sensors
  - Demonstrated performance against targets
  - Delivered prototypes to IIT for evaluation
- **H_2S**
  - Developed noble metal thin film sensors
  - Demonstrated detection of 10 ppb H_2S

NEXTECH MATERIALS

Summary of NexTech Accomplishments

- **Sulfur Sensors**
  - Delivered alpha prototype to UTRC for evaluation
    - Obtained 400 hours of lifetime data
  - Exhibited sensitivity at the **100 ppb** level
  - Cross-sensitivity to CO tested; not an issue
  - Smaller substrate with integrated heaters are being tested for beta prototype calibration
  - Automated stand for long-term testing has been constructed
  - Established sensitivity of H_2S sensor in methane background

- **Carbon Monoxide Sensors**
  - Demonstrated sensitivity at the **5ppm** level
  - Addressing baseline drift issues
  - Delivered alpha-prototypes to IIT and UTC
  - Testing and verification of Los Alamos prototypes have begun

Sensor Evaluation Status

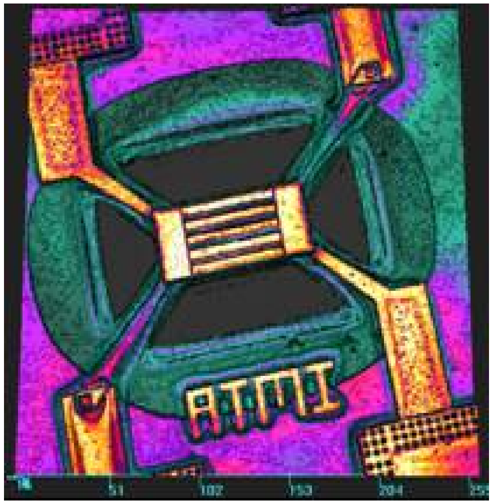
- Physical Sensors
  - Sensors for T, P, DP, Relative Humidity (RH), and Flow evaluated in PEM fuel cell simulator in near-condensing flow regime
  - State-of-the-art physical sensors meeting program needs selected
- Chemical Sensors
  - First round of sensor testing and qualification completed
  - Multiple H_2 sensors evaluated for sensitivity, selectivity, and performance
  - α prototype CO sensor received from NexTech Materials
  - Evaluating next generation of sensors from ATMI and NexTech to address cross-sensitivity and drift issues

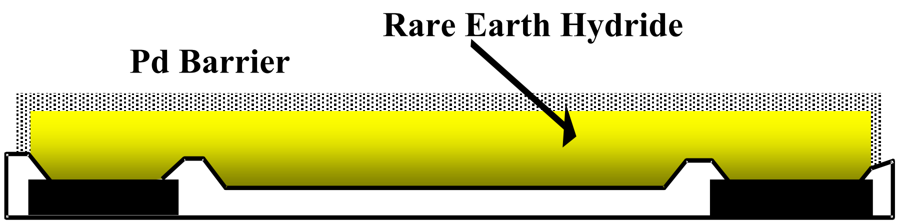
Physical Sensor Evaluation Status

Sensor	Operating Principle	Positive Attributes	Comments
Temperature	Thermistor	0 to 250 °C, -40 to 750 °C	Response time slow but within program needs
Pressure	Strain gauge (Druck)	Silicon based IC compatible fabrication.	May be mass produced and miniaturized
RH	Polymer capacitive (Panametrics)	0 to 180 °C, 0-100% RH	Recovery from condensing flow regime
Flow	Thermal dissipation	Most cost effective	Response fluctuation due to condensation

ATMI Sensors - Goals and Approach

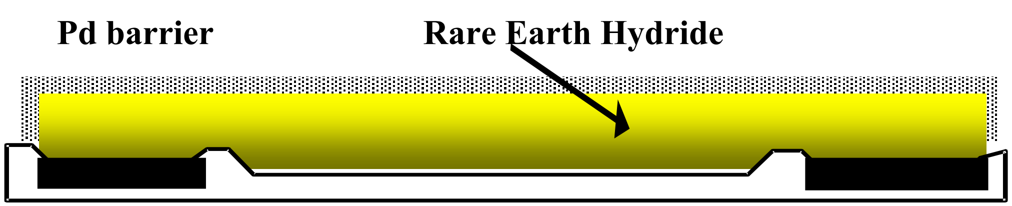
- Project Goals
  - Demonstrate the capabilities of micro machined H_2 and H_2S sensors
  - Develop an understanding of their performance
  - Critically evaluate the utility and viability of this technology for life safety and process monitoring
- Approach
  - MEMS based platform coupled with multilayer sensing films
  - Thermally controlled chemi-resistive transduction

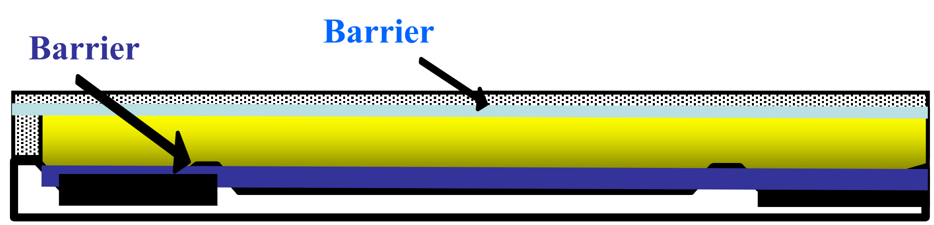




ATMI LEL Sensors

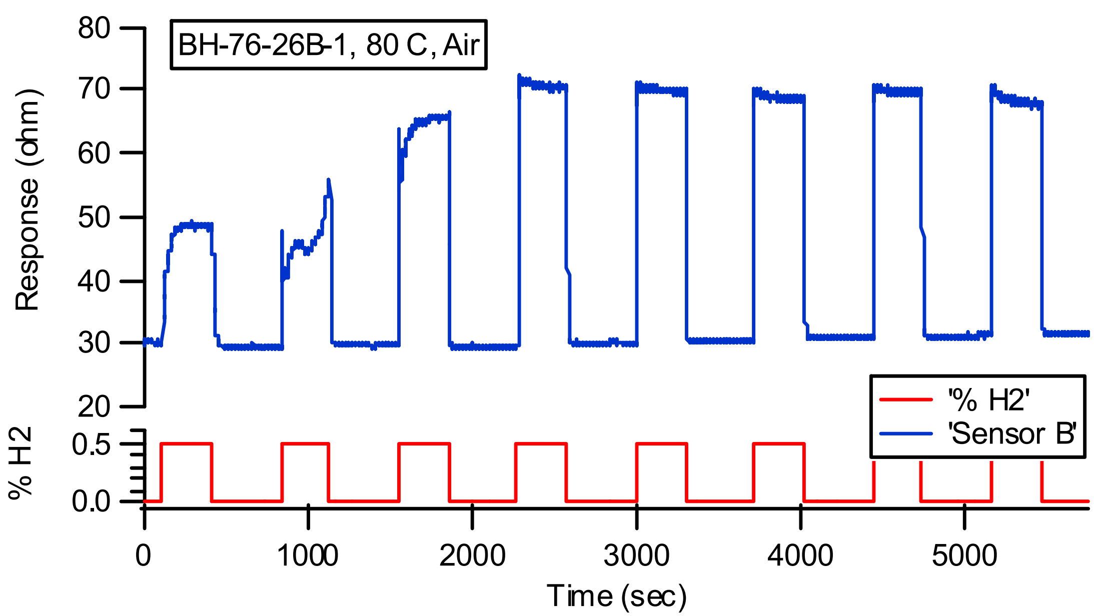
- **Hydrogen in ambient air – safety sensor**
  - 0.1 – 10% H2
  - -30 to 80 °C
  - Response time < 1 sec
- **Pd/Y bi-layer**
  - T_{90} < 2 sec
  - 8 to 10% per month baseline drift rate
- **Pd quad-layer**
  - 2.68% per month baseline drift rate





LEL Sensors – Pd Quad-layer

- Pd quad-layer
  - Air, 80°C
  - T_{90} < 2 sec
- Sensor in commercialization stage



ATMI

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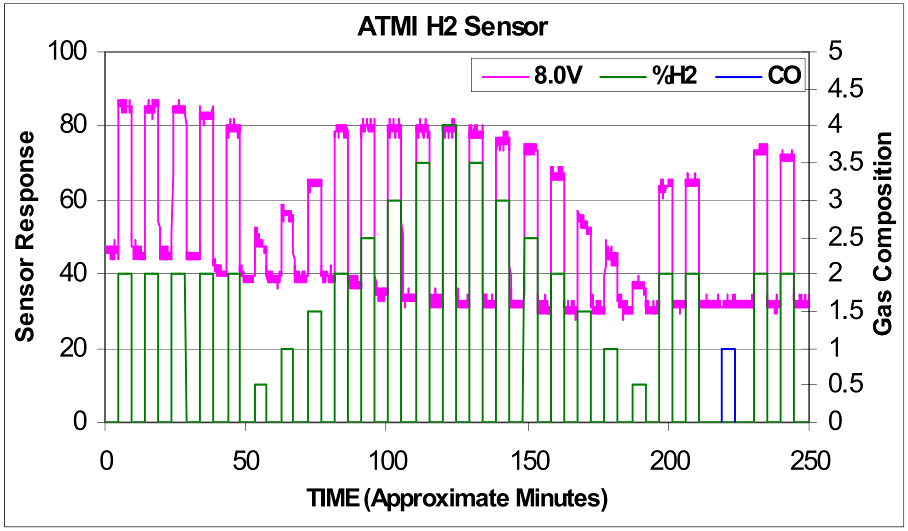
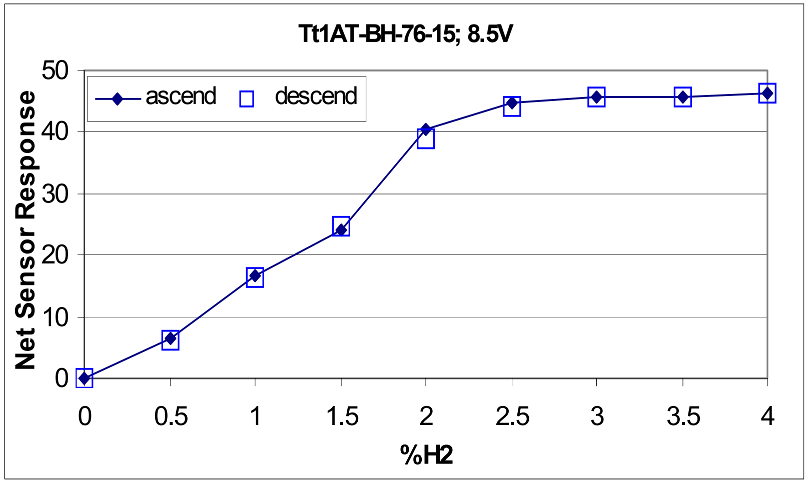
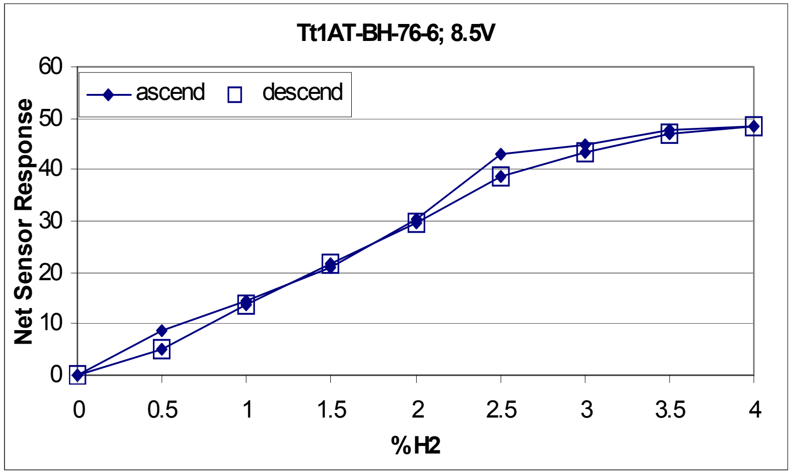
Pd Quad Layer – LEL Applications As Tested at IIT

- Quick response
  - T_{90} ~ 2 sec
- Good LDL
- 2.5% H_2 linearity
- Insensitive to 100 ppm CO
- Good Hysteresis

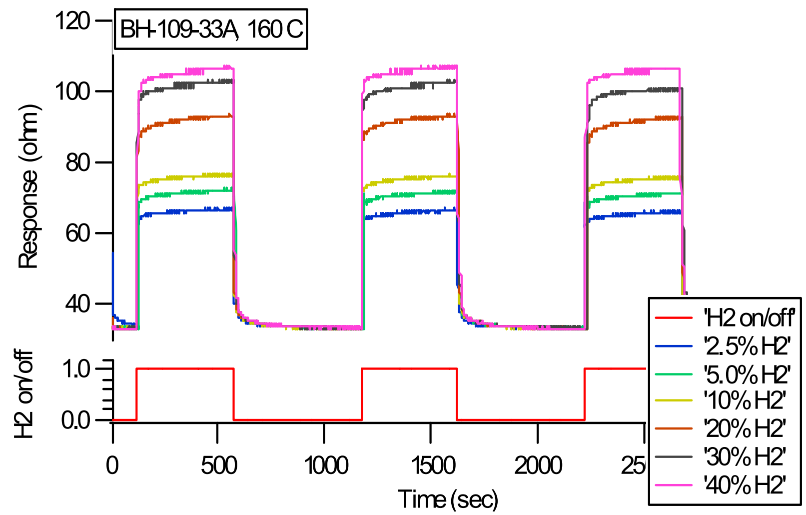


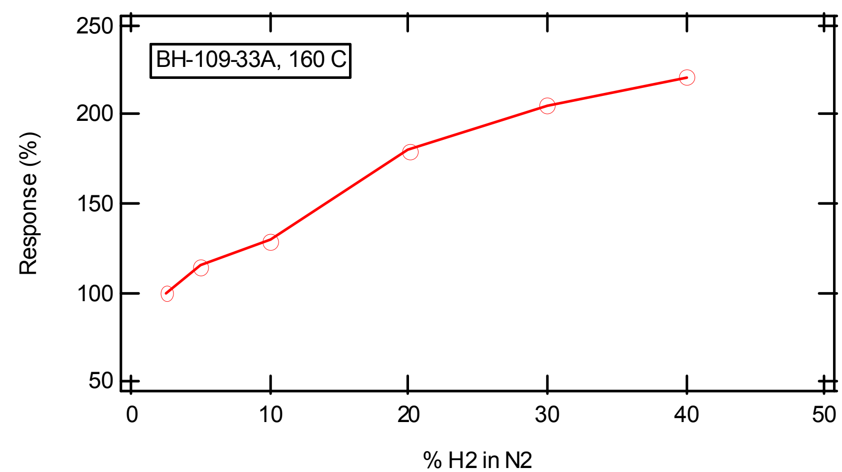




Stack Sensor -Thin Rh Quad-layer Dynamic Range

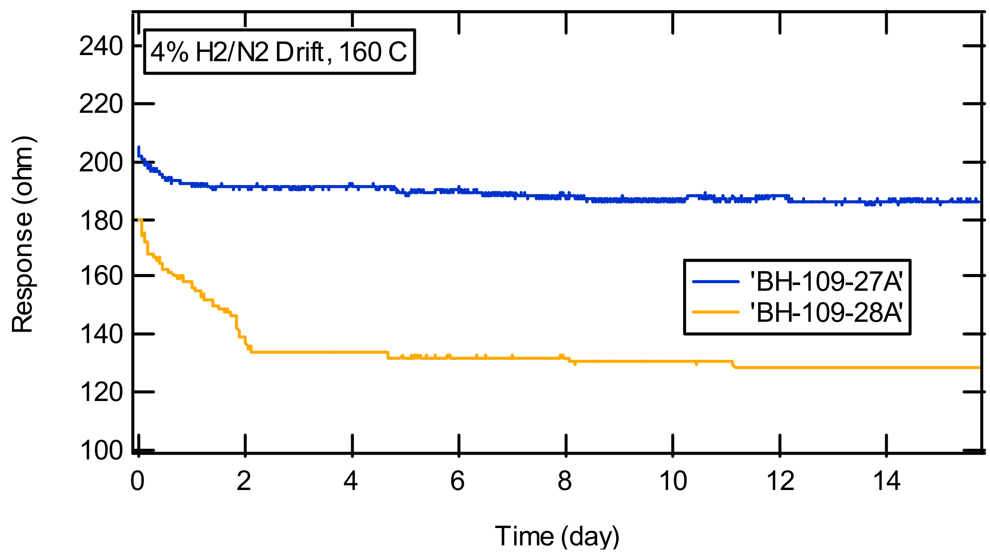
- Dynamic ranges
  - 160°C
  - 2.5 to 40% H_2
  - Linear responses
    - 2.5 to 20% H_2
    - 20 to 40% H_2
    - 2.4 to 40% H_2 in N_2

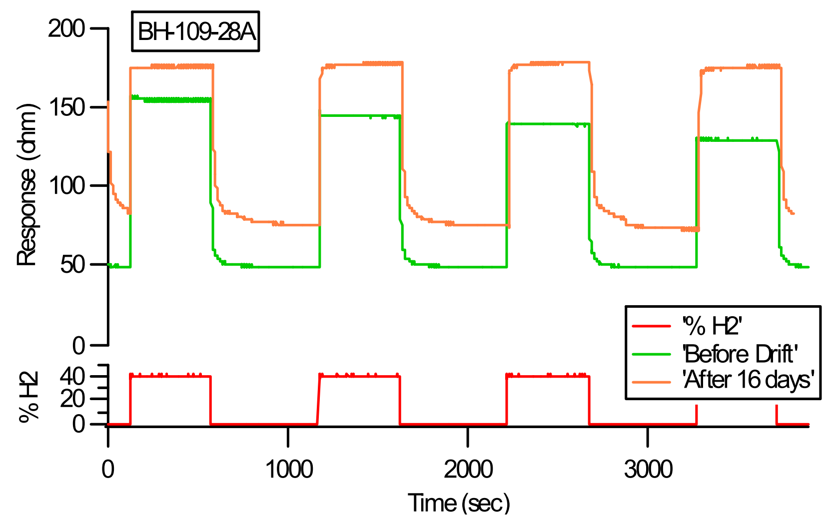




Stack Sensor – Thin Rh Quad-layer Long Term Performance

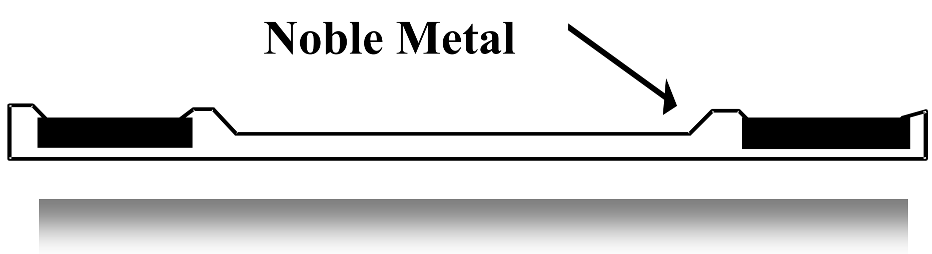
- 4% H_2/N_2
- 160 °C, 16 days
- Negligible drift
- Minor degradation





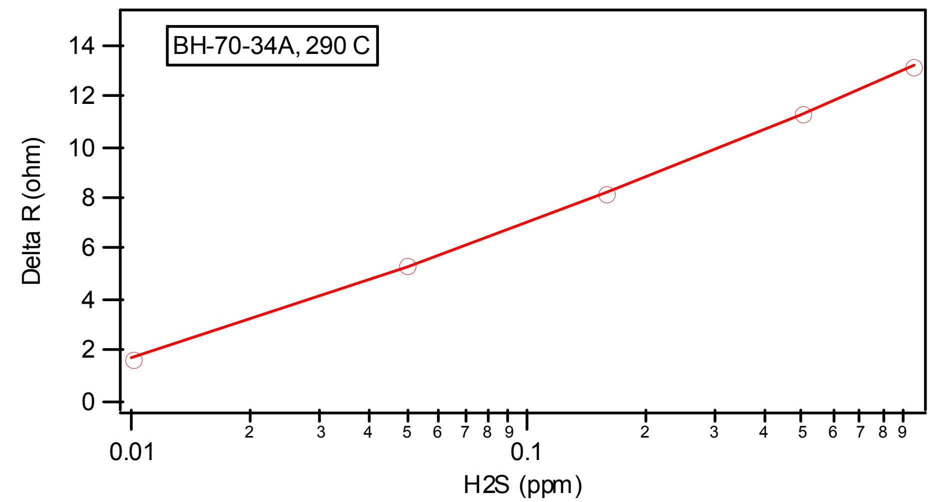
ATMI H_2S Sensor Development

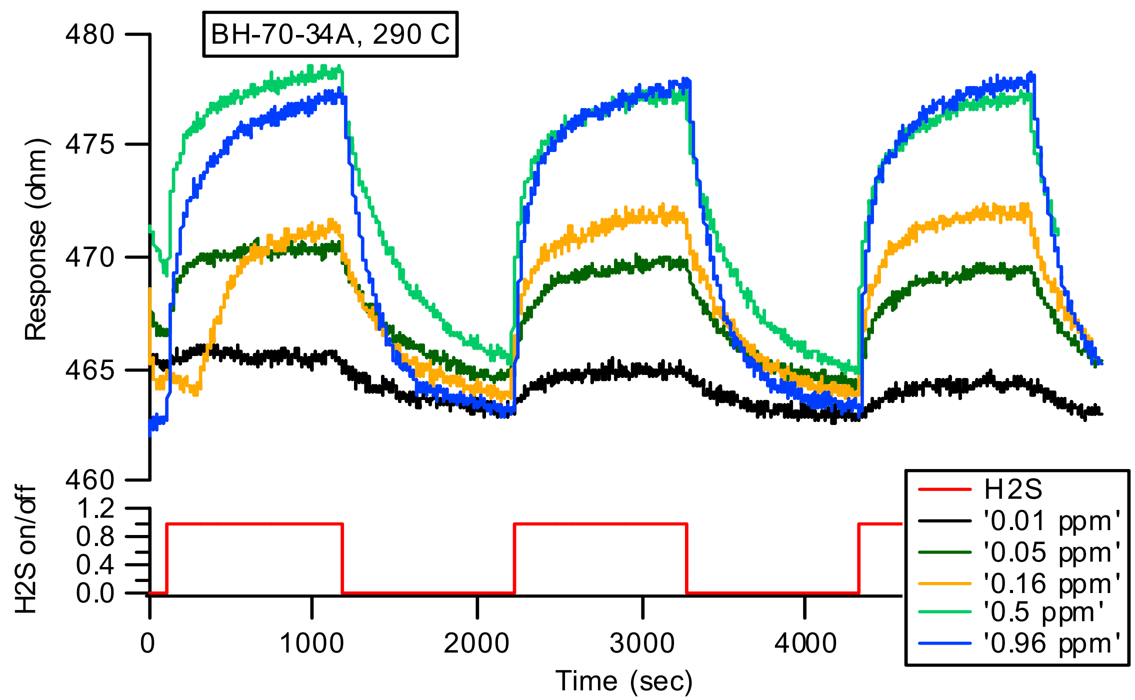
- Targets
  - Temp: 400˚C
  - Range: 0.05 ppm - 0.5 ppm
- Approach
  - Ultra thin (< 50nm) metal film deposition on micro hotplate platform
  - 25 nm and thinner are discontinuous
  - 50 nm films continuous with poor adhesion
  - Additional interlayer improves adhesion



Rh Sensor Performance

- 290°C operation
- 4% H_2/N_2 background
- **10 ppb H_2S detection**
- 15.5 min on
- 15.5 min off
- Logarithmic response
- Delta-R linear with log of H_2S concentration between 10 – 1000 ppb





NEXTECH MATERIALS

Summary of NexTech Accomplishments

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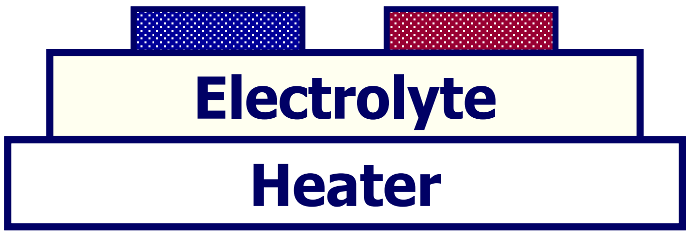
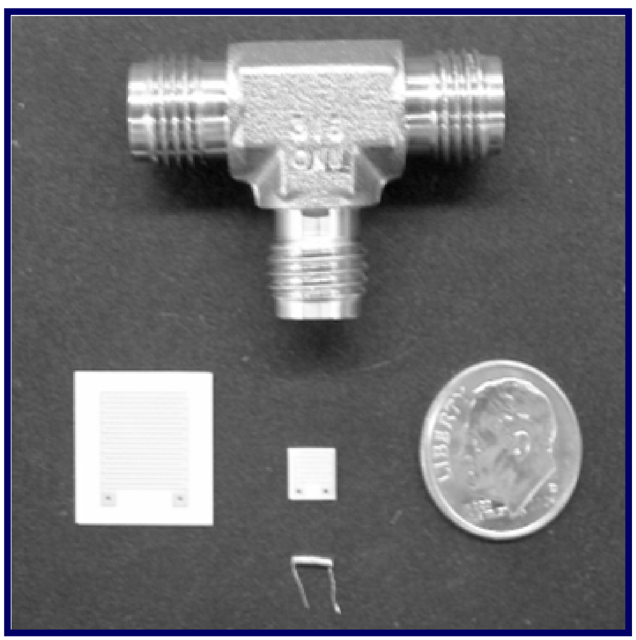
NEXTECH MATERIALS

NexTech Sensor Platforms



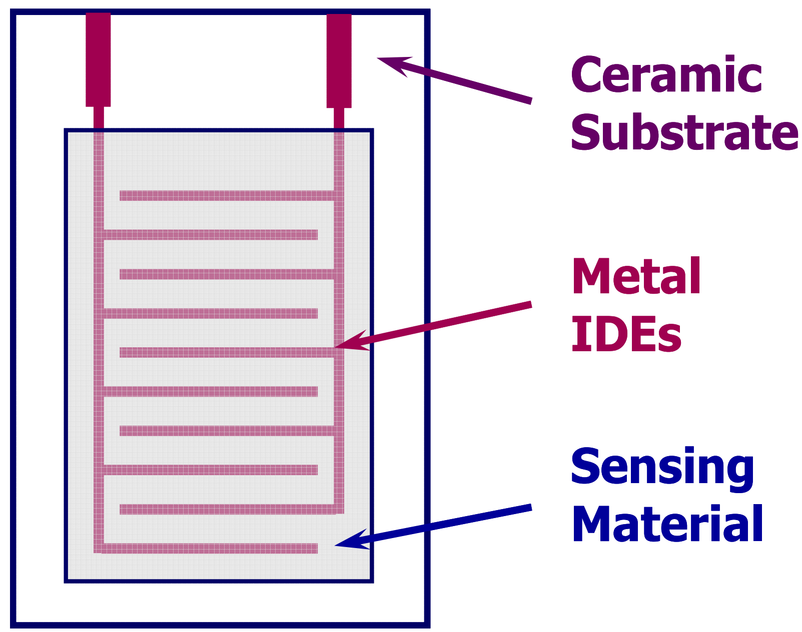
Mixed Potential Mode

Carbon Monoxide



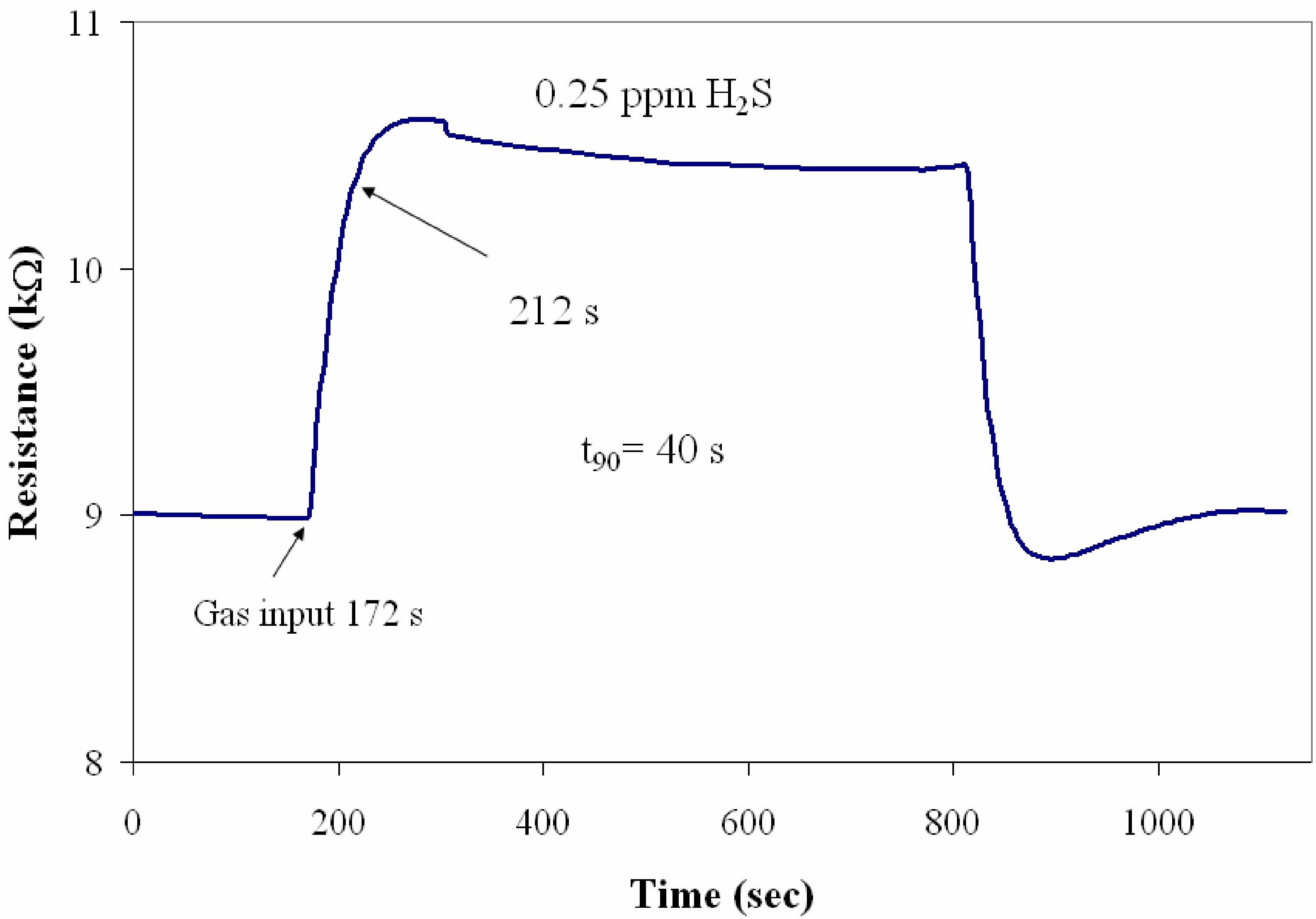
Chemi-Resistor

Carbon Monoxide
Hydrogen Sulfide

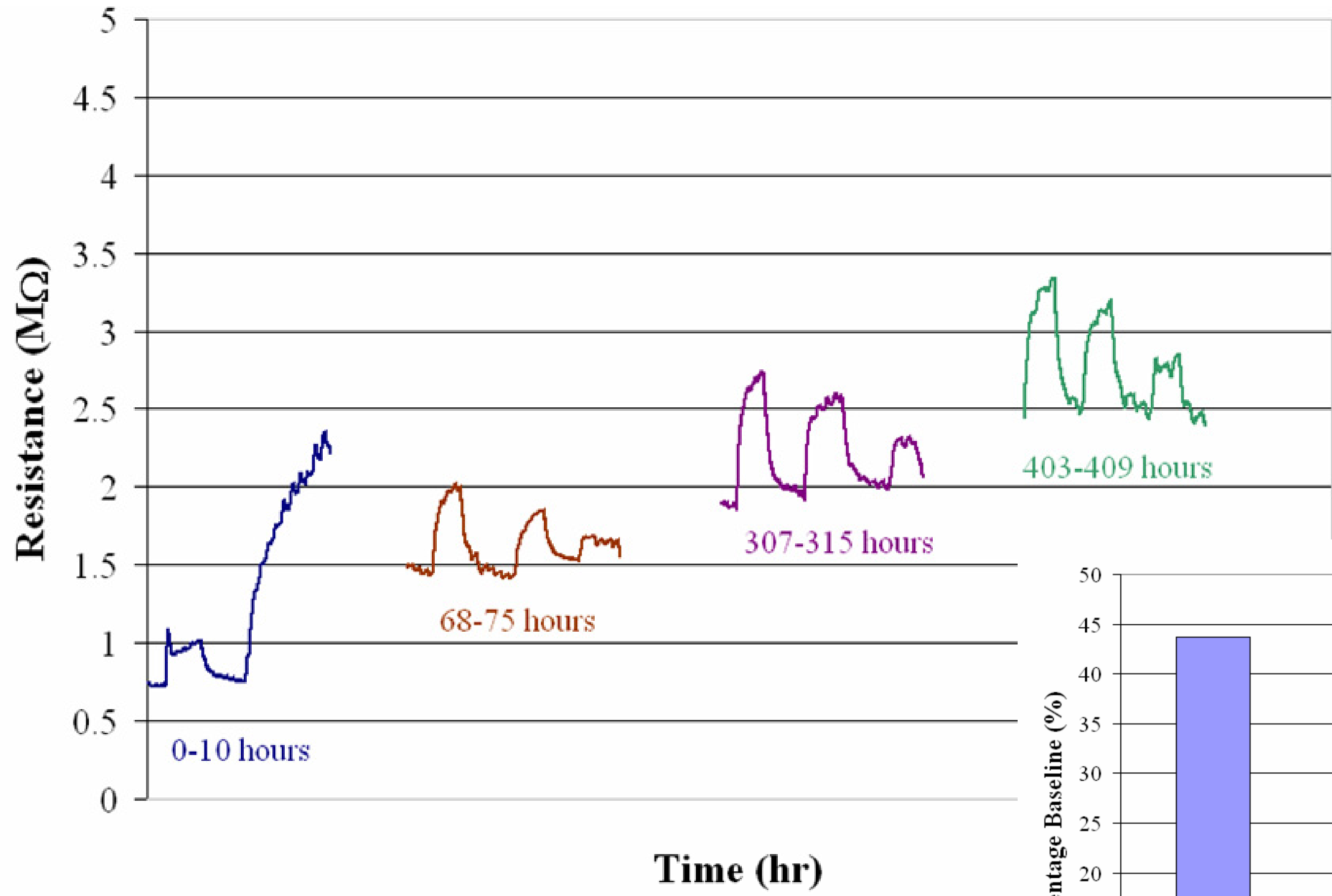


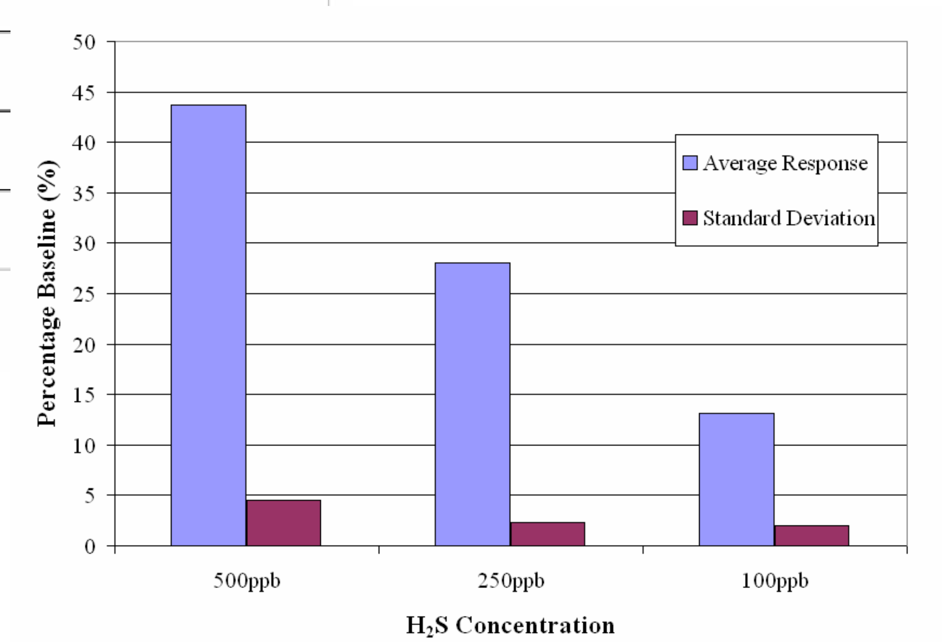
NEXTECH MATERIALS

Resistive-Mode H_2S Sensors



H_2S Sensor: Long Term Testing





Baseline drifting, but sensitivity is constant relative to baseline

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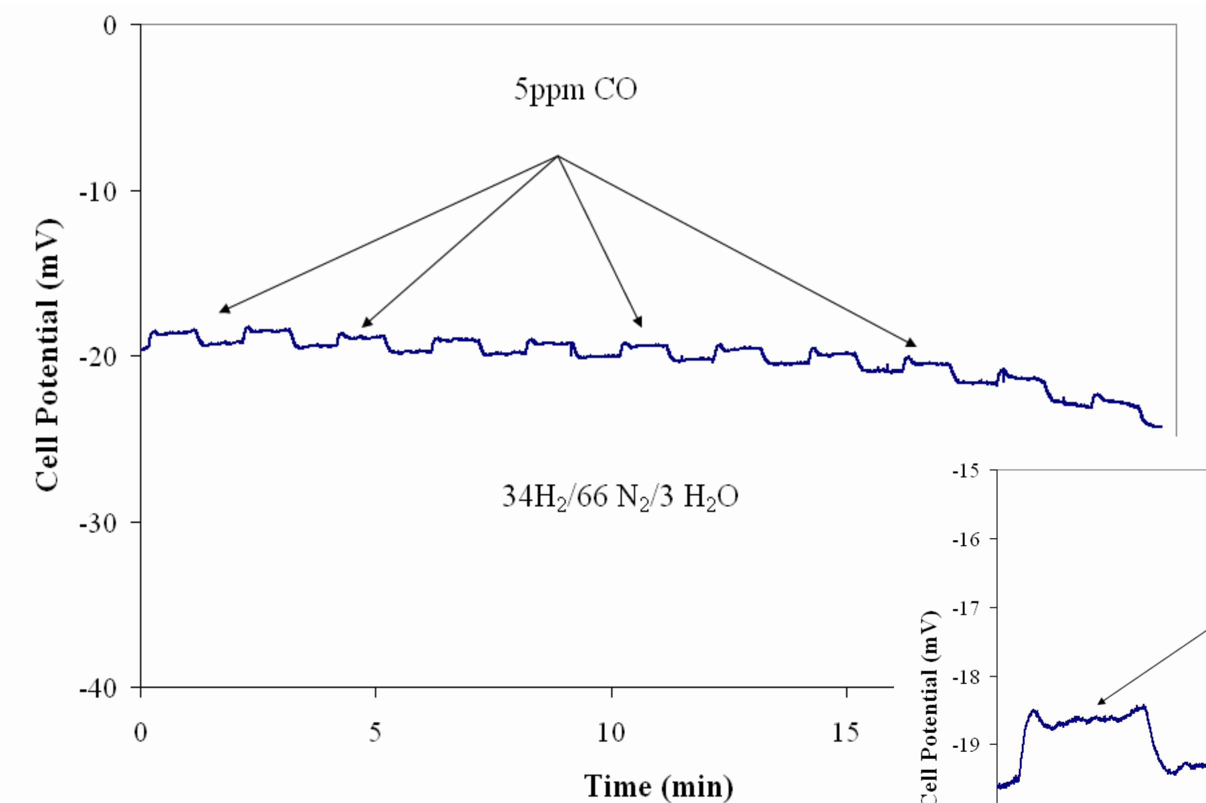
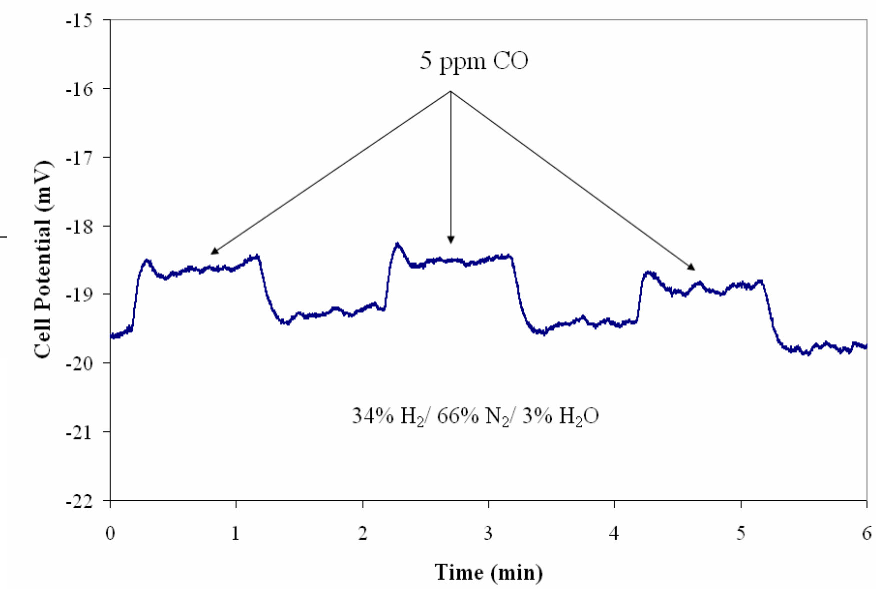
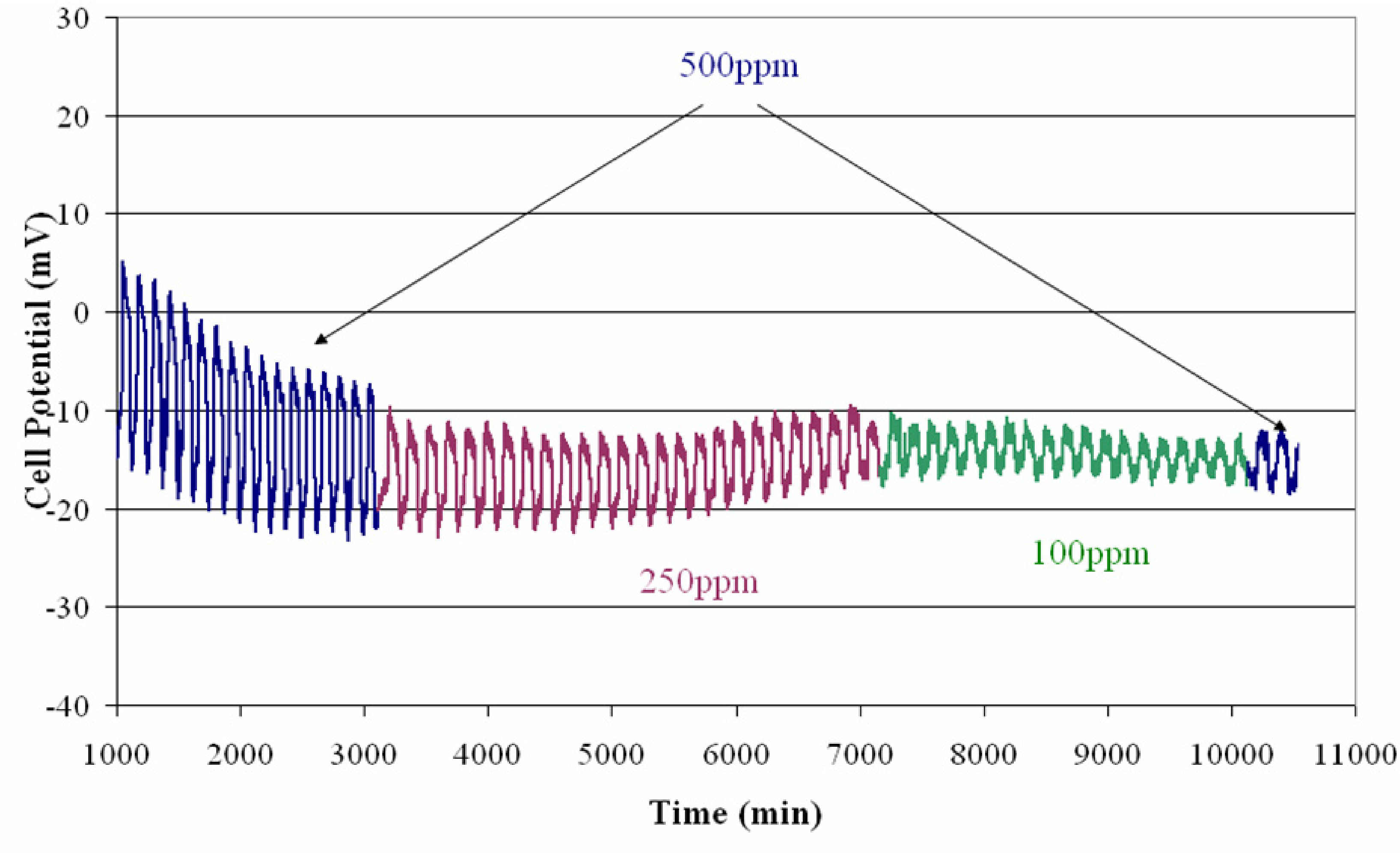
CO Sensor Response to Low Concentrations





Long-Term CO Sensor Testing



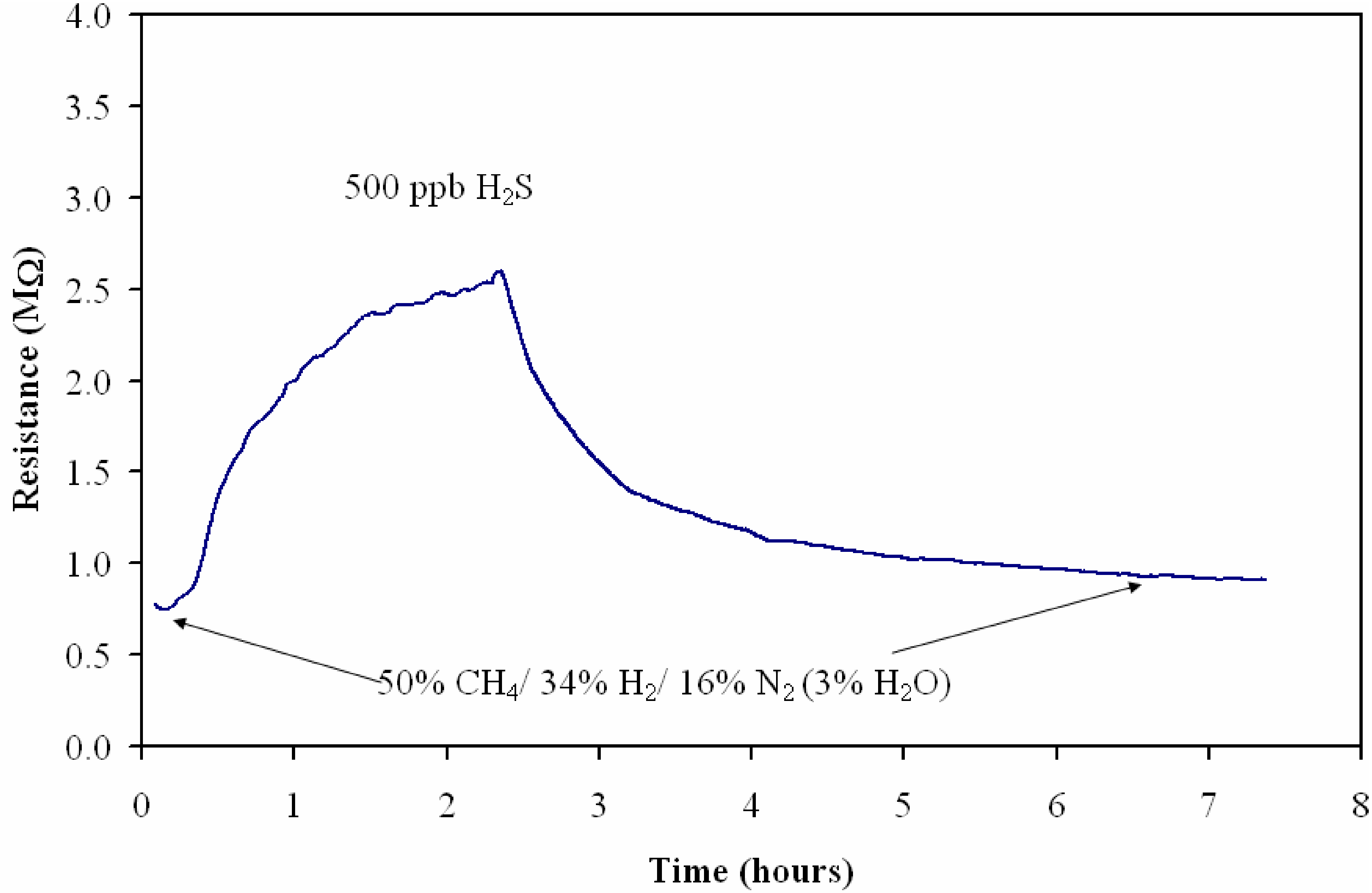
Low surface area electrodes minimize baseline drift, but possible loss of sensitivity to higher CO contents with cycling

NEXTECH MATERIALS

Los Alamos Collaboration

- LANL Contact: Dr. Rangachary Mukundan
- Testing agreement in place
- Ongoing collaboration on MP sensors
- Verification of LANL sensor performance in progress
- Initial tests show sensitivity at 25 ppm CO in $N_2/H_2/17vol\%\ H_2O$
- Need to address challenges of humidifying Nafion membrane

H_2S Sensor Response in Methane



Responses to Previous Year Reviewers' Comments

- Redundancy between IIT and UTRC facilities.
  - Two independent laboratories with emphasis on different chemical and physical sensors.
- Need to look at other sensor work
  - IIT is continually looking at other sensor technologies and updating the sensor database
- A clear manufacturer has not been identified
  - ATMI and NexTech, for example, are addressing design for manufacture.
  - ATMI has sold technology to a sensor manufacturer for commercialization.

Future Work

- Address CO baseline drift issues
- Poisoning
  - Run in fuel cell mode to oxidize CO in situ
  - Thermal cycling experiments (desorb CO)
- Evaluate sulfur cross-sensitivity of CO sensor
- Continue collaboration with LANL on CO sensor

- LEL sensors
  - Focus on pd quad layer
  - Continue to improve life time performance
- Stack sensors
  - Focus on Rh quad layer
  - Optimize materials design
  - Characterize short and long term behavior
- H_2S sensors
  - Focus on Rh ultra-thin films
  - Characterize short term concentration behavior
  - Look for cross sensitivities

Hydrogen Safety

The most significant hydrogen hazard associated with this project is:

- Gas mixtures containing up to 70% by volume of hydrogen will be utilized.
- The presence of hydrogen does present a hazard if a leak occurs in the gas piping system so that hydrogen can mix with laboratory air.

Hydrogen Safety

Our approach to deal with this hazard is:

- Flammable gas detectors were located in our laboratory; a relay opens and turns off power to solenoid valves on the H_2 supply at H_2 levels above 10% of LEL.
- The LabView-based control program senses the alarm, shuts off all other gases and purges all gas lines with N_2.
- All valves used in the experimental apparatus are explosion-proof.
- Pressure relief valves are used in all piping to prevent over-pressurization of components.