Low Cost Sensors for Hydrogen and CO in Fuel Cells

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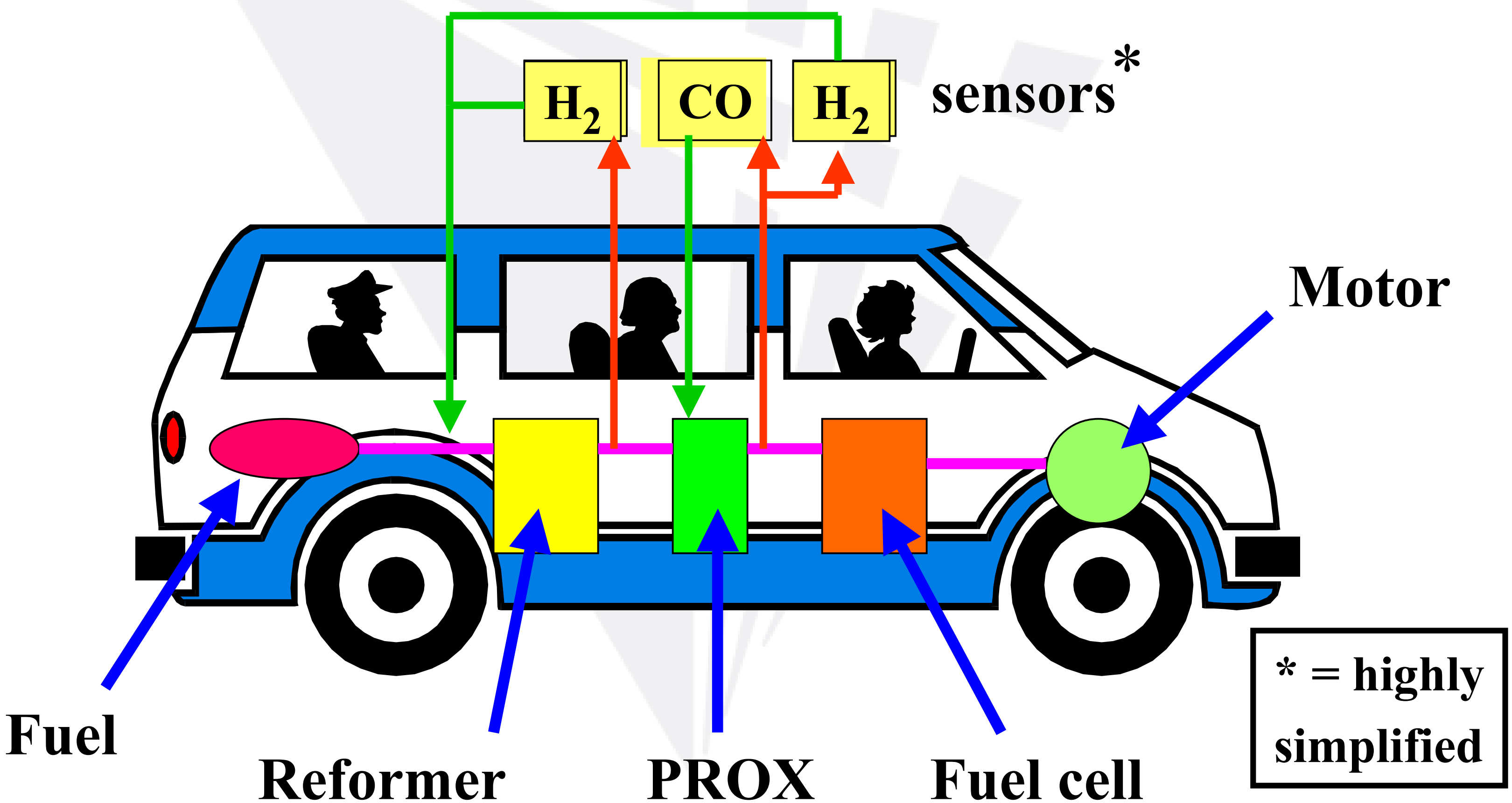
Project Structure

- **Illinois Institute of Technology**
  - **administration, scientific leadership, sensor R&D, prototype production, and delivery**
  - **P.I.: J.R. Stetter, W.R. Penrose, S. Yao, Y.-T. Chao, S.-W. Roh)**
- **SensorTek, Inc., J&N Enterprises**
  - **industrial partner, production scale-up, in-service testing, parts, molds and use thereof, application reviews**

Chemical Sensors Are Essential in FCVs

as feedback elements in power system, and for safety



Goals Updated for 2001

Hydrogen Process Sensor

- 0 to 100% in reformate matrix
- 10 – 30 mol % water
- 3 atm total pressure
- 0.1 – 1.0 s response time
- 70 to 150°C

Hydrogen Sulfide Sensor

- 0.05 – 0.5 ppm in reformate
- Up to 400°C
- Response time < 1 min

Hydrogen Safety Sensor

- 0 to 10% in air
- 10 – 98 % RH
- 1.0 s response time
- -30 to 80°C
- Lifetime 5 yr
- Selectivity vs hydrocarbons

Goals Updated for 2001 (Cont'd)

CO Lo-Range Sensor

- Pre-stack protects catalyst
- 1 to 100 ppm in reformate matrix
- 10 – 30 mol % water
- 3 atm total pressure
- 0.1 – 1.0 s response time
- 70 to 150°C

CO Mid-Range Sensor

- 100-1000 ppm in reformate matrix
- 250°C

CO High-Range Sensor

- Raw reformate: controls reformer operation
- 0.1 to 2.0% CO in reformate matrix
- 10 – 30 mol % water
- 3 atm total pressure
- 0.1 – 1.0 s response time
- 250-800°C

CO Safety Sensor

- 0-1000 ppm
- Ambient conditions

Achievements

- Ag/AgCl reference electrode in liquid-electrolyte cell:
  - eliminates long-term drift due to hydrogen
  - reduces response time by 5-fold
- Polymer barrier limits access to cell
  - increases range of hydrogen sensor to > 1 atm.
  - eliminates CO interference in hydrogen measurements
  - barrier good to 300 °C, can be used with any sensor
- Response times reduced using dynamic response
  - Using Rate of change of signal gives T_Rs of ~3 sec
- Stable signal for CO in presence of high hydrogen

Achievements (cont'd)

- Solid-state sensors based on NASICON sodium conductor
  - Very fast response times to nitrogen oxides, hydrogen
  - Extremely pure NASICON phase by proprietary method
  - Tunable selectivity by varying electrode materials and doping with inorganic salts
  - Potentiometric mode
  - Operating range of 50 to 700 °C

Achievements (cont'd)

- Data collection system for reformate gases at Argonne
  - long-term logger for testing sensor responses in 24/7 system
- Sensor Technology User Facility
  - Tests sensors in gases of arbitrary composition
  - Temp range 25 to 400 °C
  - Pressure range ambient to 3 atm
  - Flow rates 0 to 800 cc/min
  - Script-driven experiments permits totally flexibility in experimental protocol
  - Available for use by non-IIT personnel as user facility

Achievements (cont'd)

- Low surface area gold electrode gives much higher signal-to-noise ratio than conventional hydrogen-sulfide sensor electrodes
  - slightly reduced response times not considered important for H_2S
  - electrode made in mass numbers by sputtering and fits into standard low-cost sensor housing
  - high-purity gold eliminates CO interference
  - ppb detection limits achieved
- Targets for low cost have been maintained by using uniform parts originally designed for low cost for all sensor types.

Approach

- Understand the basis of selectivity in sensor catalysts
- Build and test the catalysts in sensor bodies
- Implement, building a product in conjunction with commercial partner

Status Re: Specifications

- Low cost sensor design – COMMERCIAL TEST
- Sensor stability – STABLE IN HIGH HYDROGEN
- Lifetime – > 2 YEARS IN COMMERCIAL PKG.
- High concentrations – TO 1 ATM.
- Selectivity – H_2 IN CO; CO IN H_2, H_2S IN H_2
- High temperatures – BEGUN, SOME PROGRESS
- Response times – BEGUN, ~3 SEC AT HIGH CONC
- Testing in real fuel cell environments – BEGUN

Critique from 2001 Review

"This work replicates prior art"

Response:

- **Today's porous-electrode amperometric gas sensors have serious failings, especially in fuel cell applications:**
  - **Interferences (cross-sensitivities)**
  - **Instability in high concentrations of hydrogen**
  - **High cost**
  - **Limited temperature ranges (-20°C to +60°C)**
  - **Slow response times (>20 s)**
- **Significant improvements have been made, and patents and publications pending**

Critique from 2001 Review

"Approach to future development not well outlined"

Response:

- **Aggressive pursuit of improved catalysts for selective CO sensors**
- **Exploration of poisoning phenomenon as a means of measuring low CO in high-hydrogen streams**
- **Aggressive investigation of solid-state sensors for all temperature ranges**
- **Two new test facilities to investigate sensors under harsh fuel cell conditions**

Critique from 2001 Review

"Work in fuel cell environment, especially wet gases"

Response:

- **User facility at IIT being modified to accommodate high partial pressures of water, at high temperature – design nearly complete**
- **Beginning experiments at Argonne's fuel cell test facility, which includes all elements of PEM system (reformer, shift, PrOx, stack)**

Critique from 2001 Review

"Interact with other sensor developers and users"

Response:

- **Solicitation of clients for the SSTUF user facility**
- **Working with Argonne National Laboratory fuel cell program**
- **Ongoing relationship with J&N Enterprises, Valparaiso, IN, in support of new sensor development and commercial-ization of new sensor products and improvements**

Critique from 2001 Review

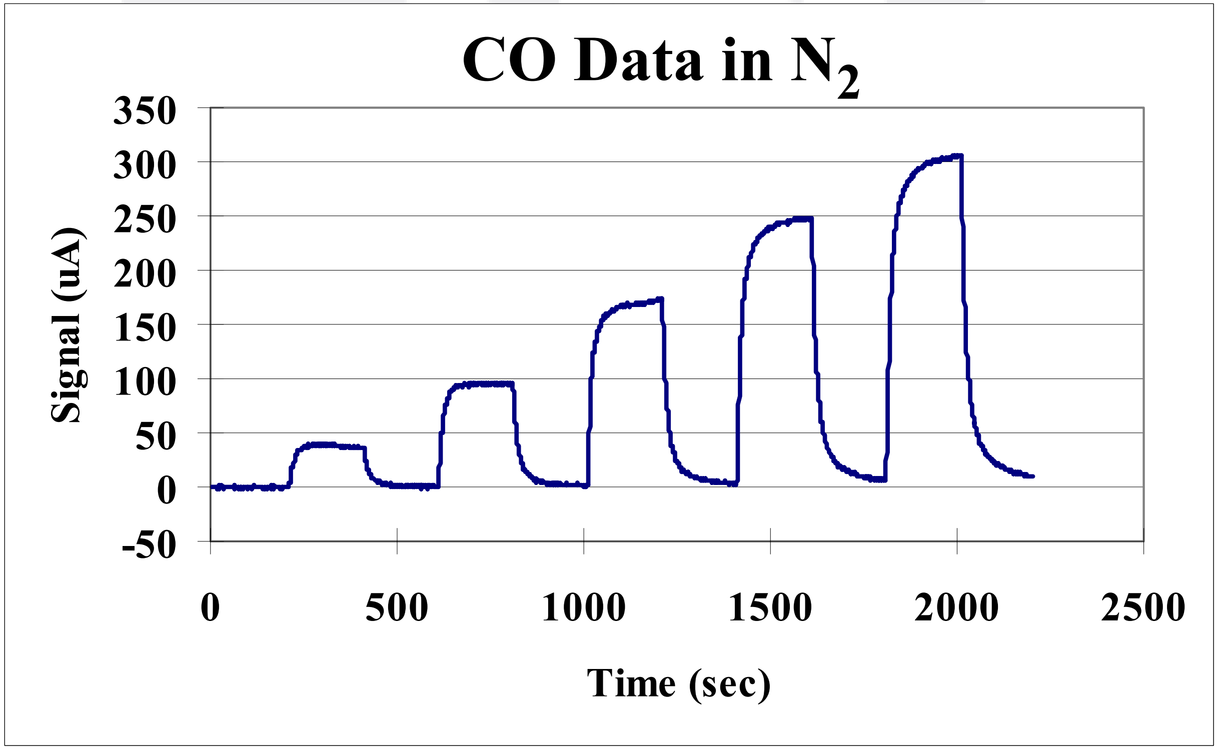
"Environmental hydrogen-in-air sensors available"

<u>Response:</u>

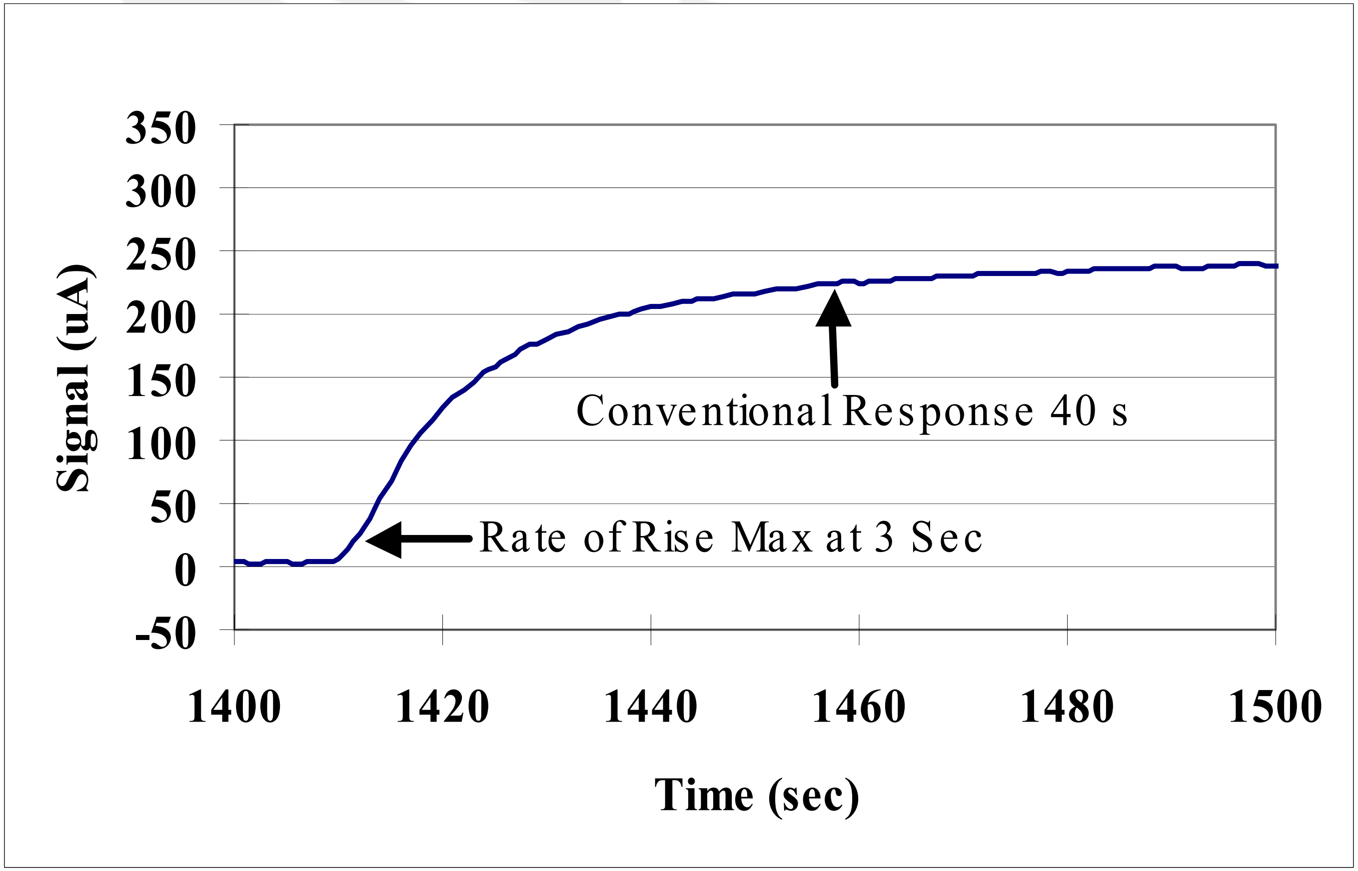
- **Stability, lifetime, and low cost are not simultaneously available**
- **Existing sensors have poor selectivity; interferences from alcohols, hydrocarbons, and many other common gases**
- **Existing sensors exhibit large drifts on continuous exposure**
- **Existing sensors have either limited temperature range (electrochemical) or high power requirements (metal oxide)**
- **Inexpensive side-product of development of sensor for hydrogen in anaerobic environments**
- **Faster response times through new reference electrodes**

New H_2 and CO Sensors

with Ag/AgCl Reference and Polymer Barriers Do Not Fatigue and Are Linear to Very High Concentrations

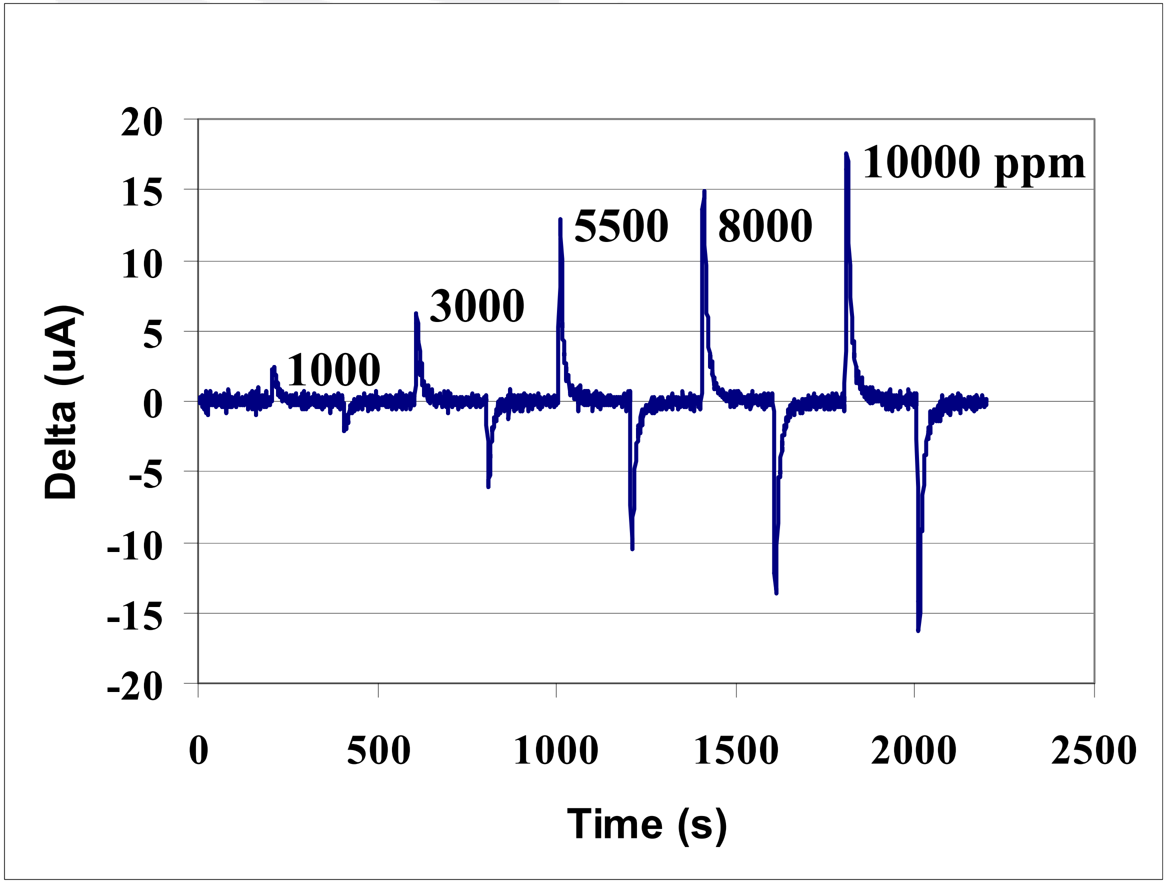


Faster Response Through Data Processing



Differential Signal Yields Faster Data

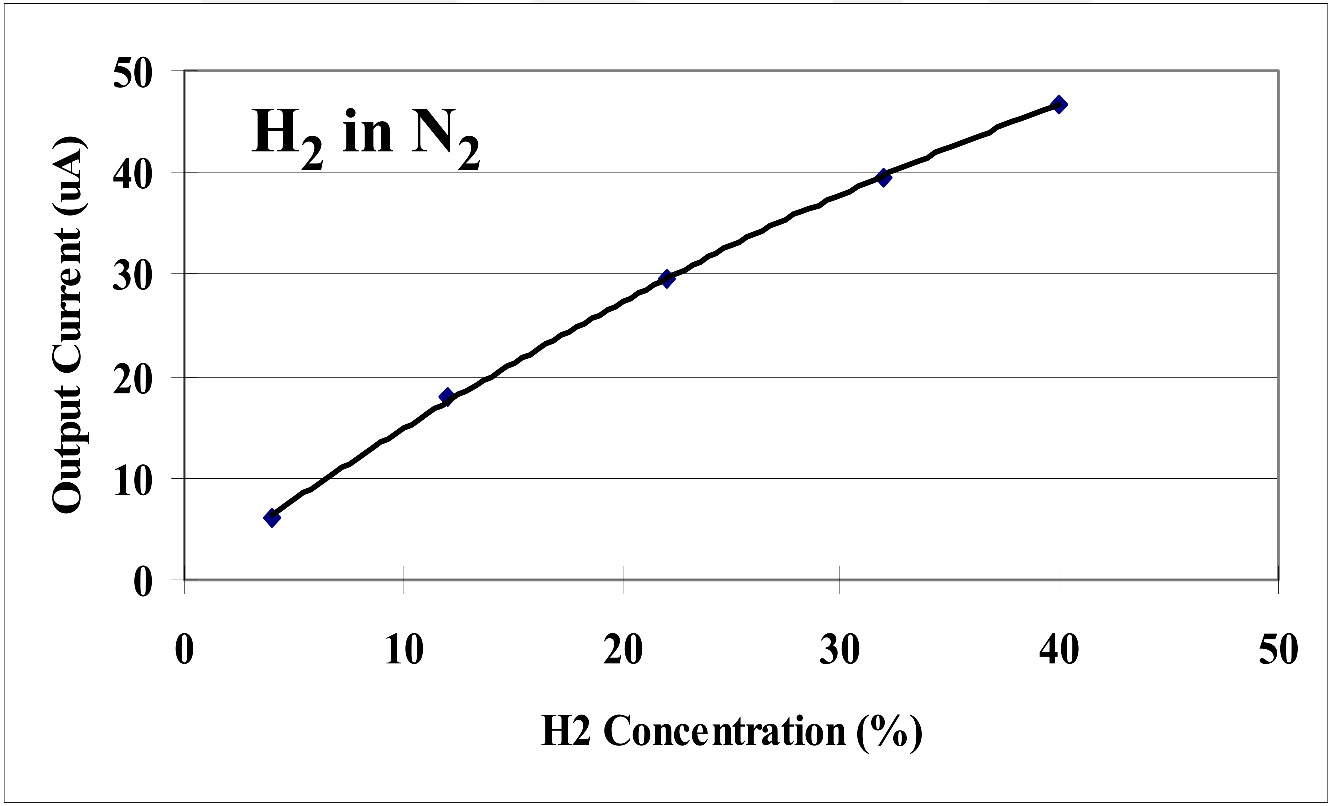
CO Data Available At 3 s



H_2 Response

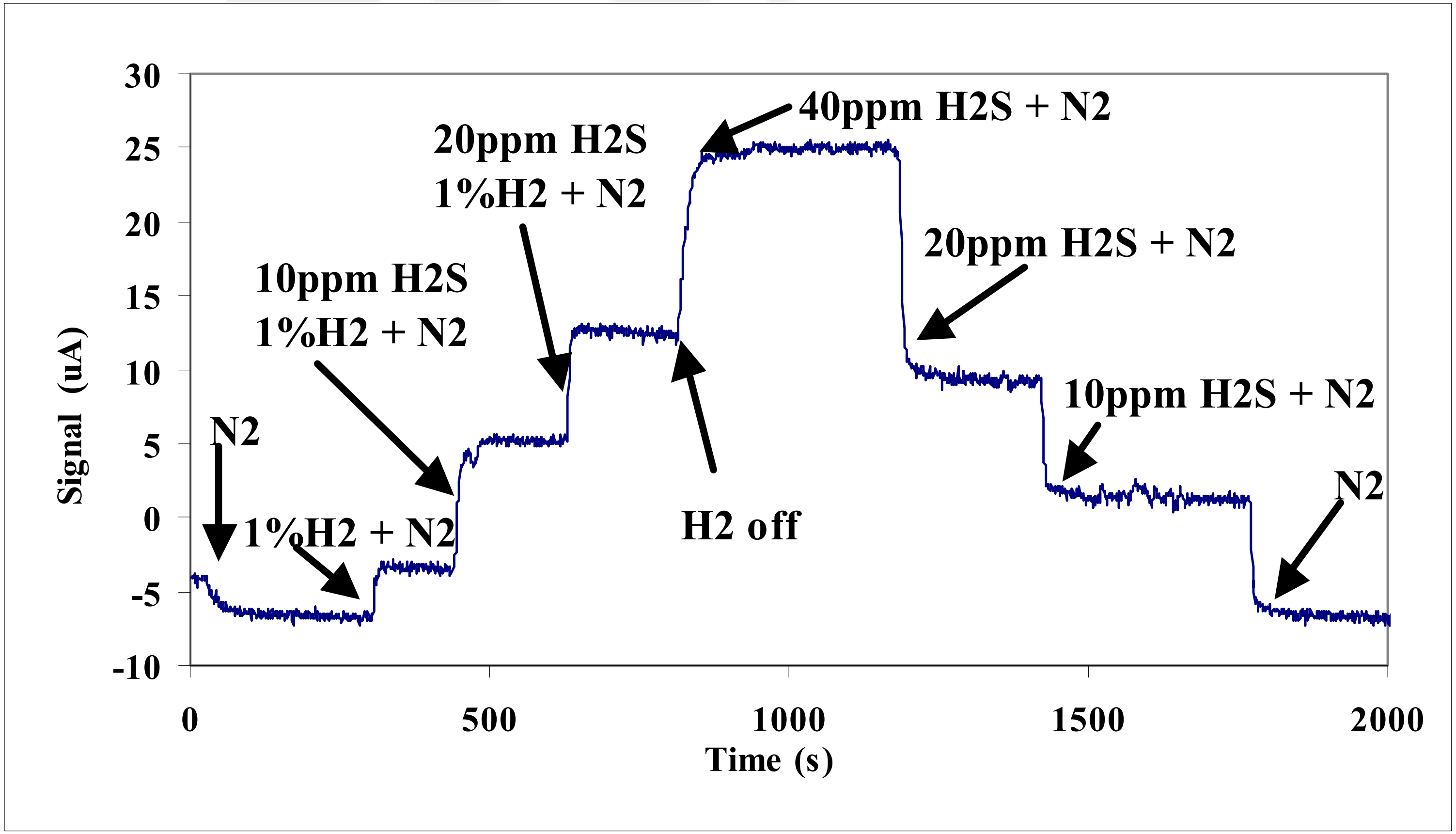
with Ag/AgCl Reference and Polymer Barrier

No Fatigue in Anoxic Matrix; Wide Linearity



Hydrogen Sulfide on Sputtered Gold Electrode

(Anaerobic, Some H2 Interference)



Working With Argonne

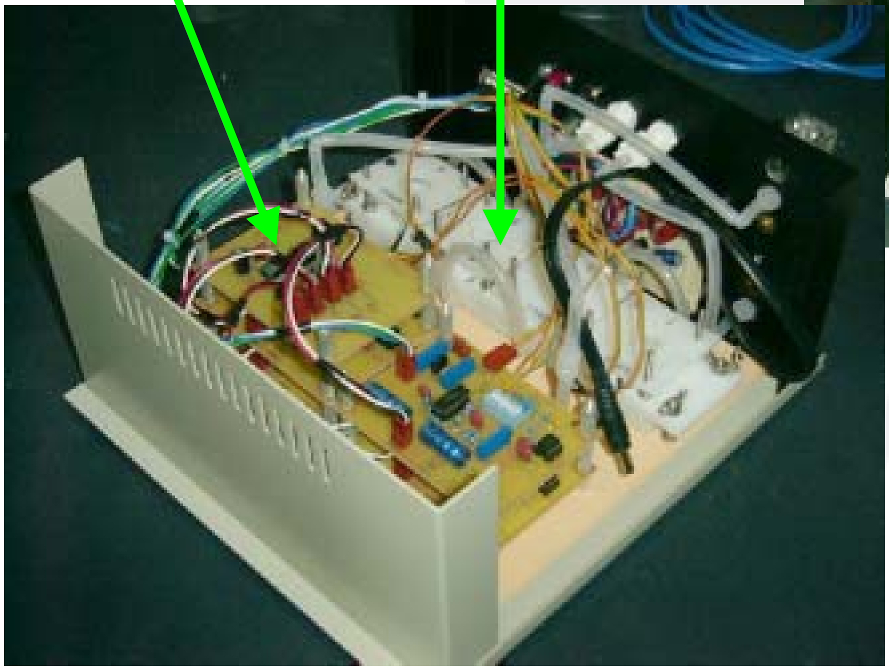
- Waited until prototype sensors were fully tested in the lab
- Needs to be unobtrusive so as not to interfere with ongoing research
- Long term measurements on authentic reformates
- Portable datalogger and sensor management console
- Experiments beginning now (mid-April)

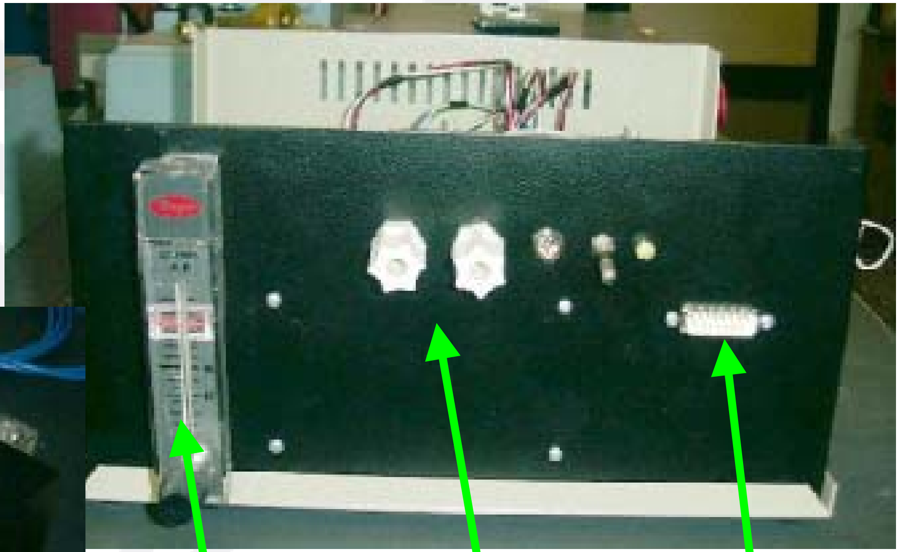
Datalogging System for ANL Installation

Sensor Management Console for ANL

Manifold

Potentiostats





Flow-meter

Gas In/out

Data

Shared Sensor Technology User Facility (SSTUF)

- Funded by ANL
- Facility to test sensors for fuel cell applications under conditions approximating in-service use
- For use by staff for subscribers or clients, or by subscribers
- Tests run by disinterested third-party agents under standard conditions to produce data that can be compared with other manufacturers
- Confidentiality
- Reconfigurable for different sensor types and conditions

Specifications

- **Test chamber 10 cm diameter x 25 cm cylindrical**
- **Temperatures RT to 450 °C**
- **Pressures 0 to 4 atm gauge**
- **Gases: nitrogen, hydrogen, carbon dioxide, and carbon monoxide in any proportion at 200 to 800 scc/min**
- **Gas composition programmable**
- **Water vapor partial pressure variable over wide range**
- **System operates from script file that controls most variables in very flexible way**

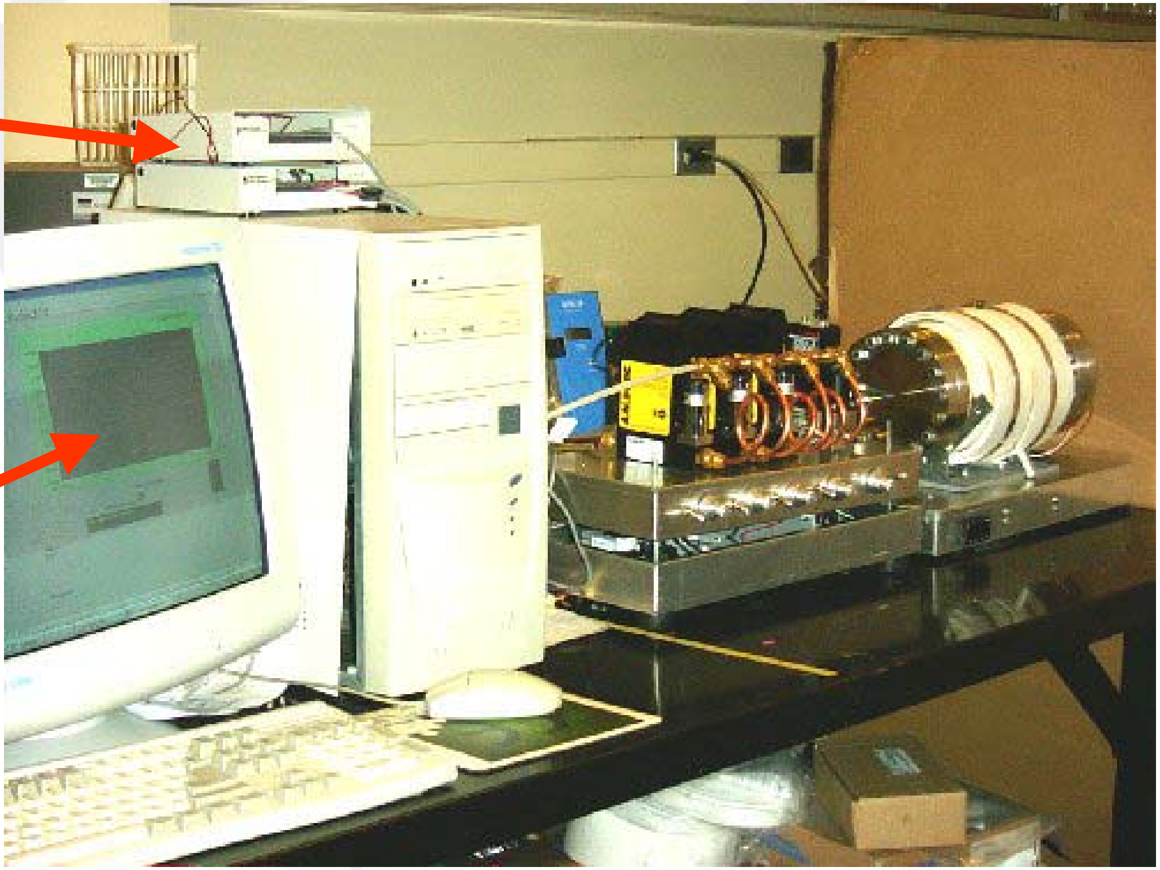
SSTUF System – Part I

16 analog in

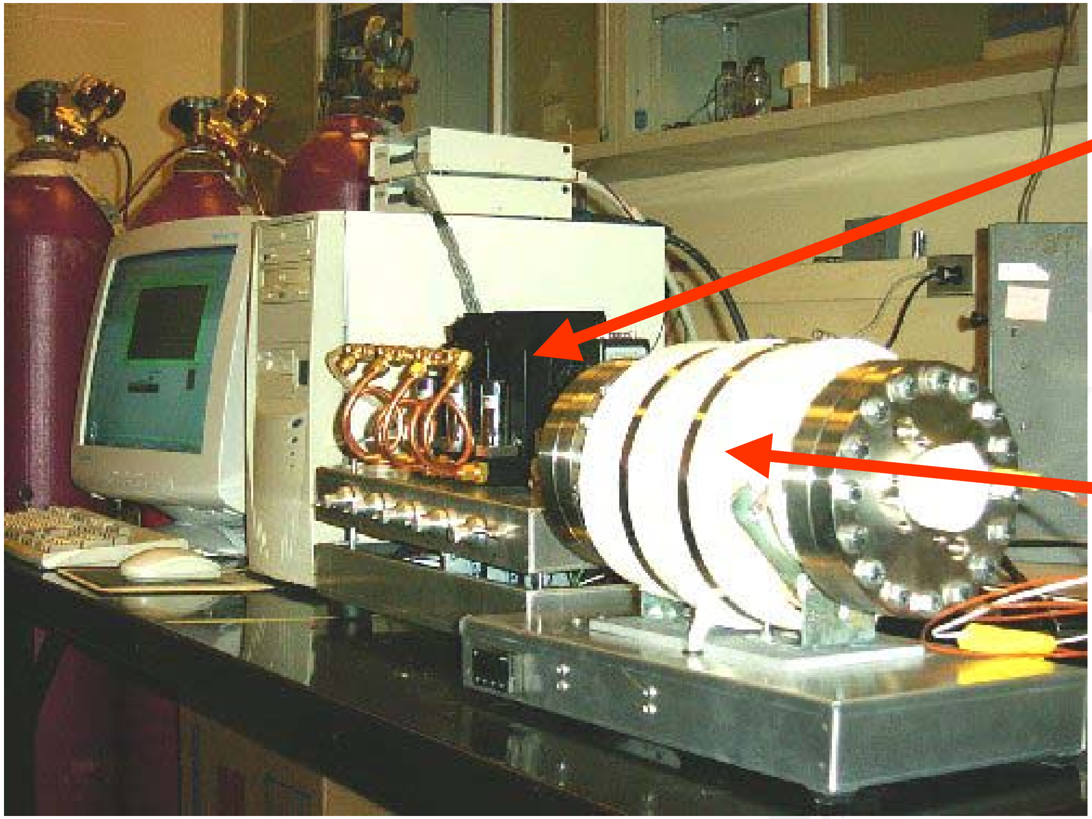
10 analog out

16 digital I/O

Labview
operating
program



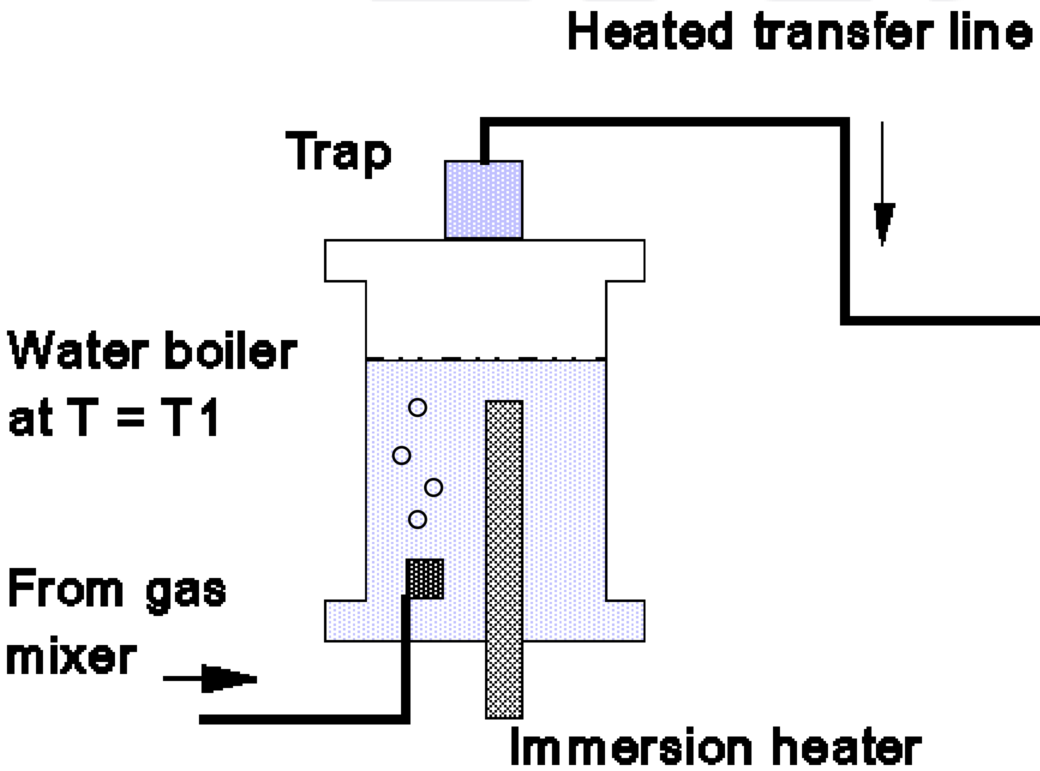
SSTUF System – Part II



Four channel gas mixer and pressure control

Oven and 950 W of heaters

Control of Water Vapor Partial Pressure
(Design Only)



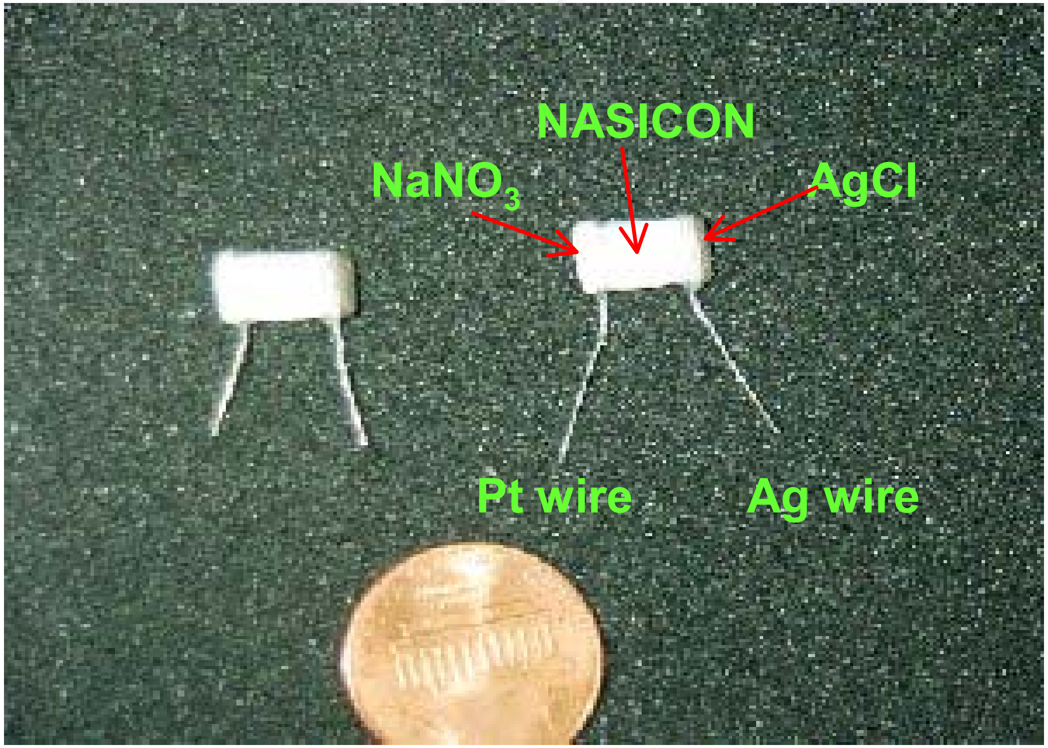
Partial pressure of water is vapor pressure at T1 when T1 < T2

High-Temperature Sensors

- NASICON-based “high-temperature” sensors
- Proprietary method for making purest NASICON as measured by XRD
- Sensors are active in “intermediate” temp range of 50 to 300°C (too high for porous-electrode sensors and too low for other solid-state sensors) where many fuel-cell sensors are needed
- Electrodes and doping provide selectivity
- Fast response

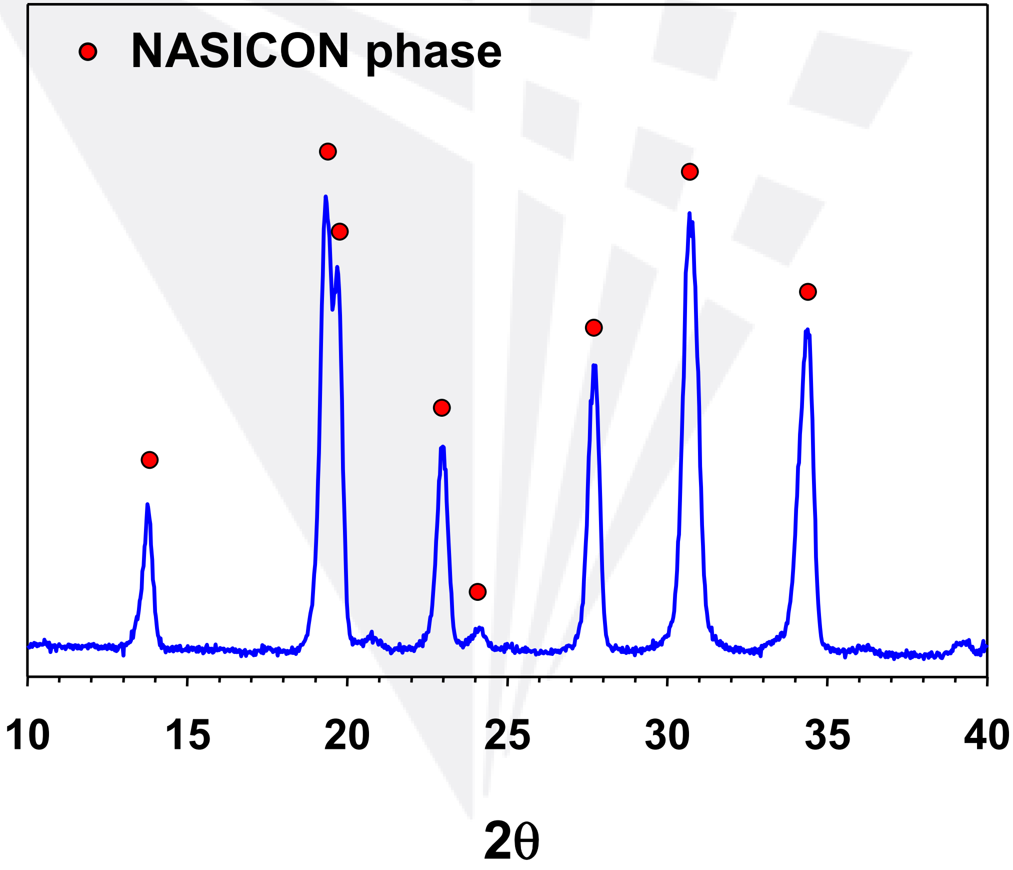
NO_x Sensors Based on NASICON

Using Ag/AgCl Reference Electrode

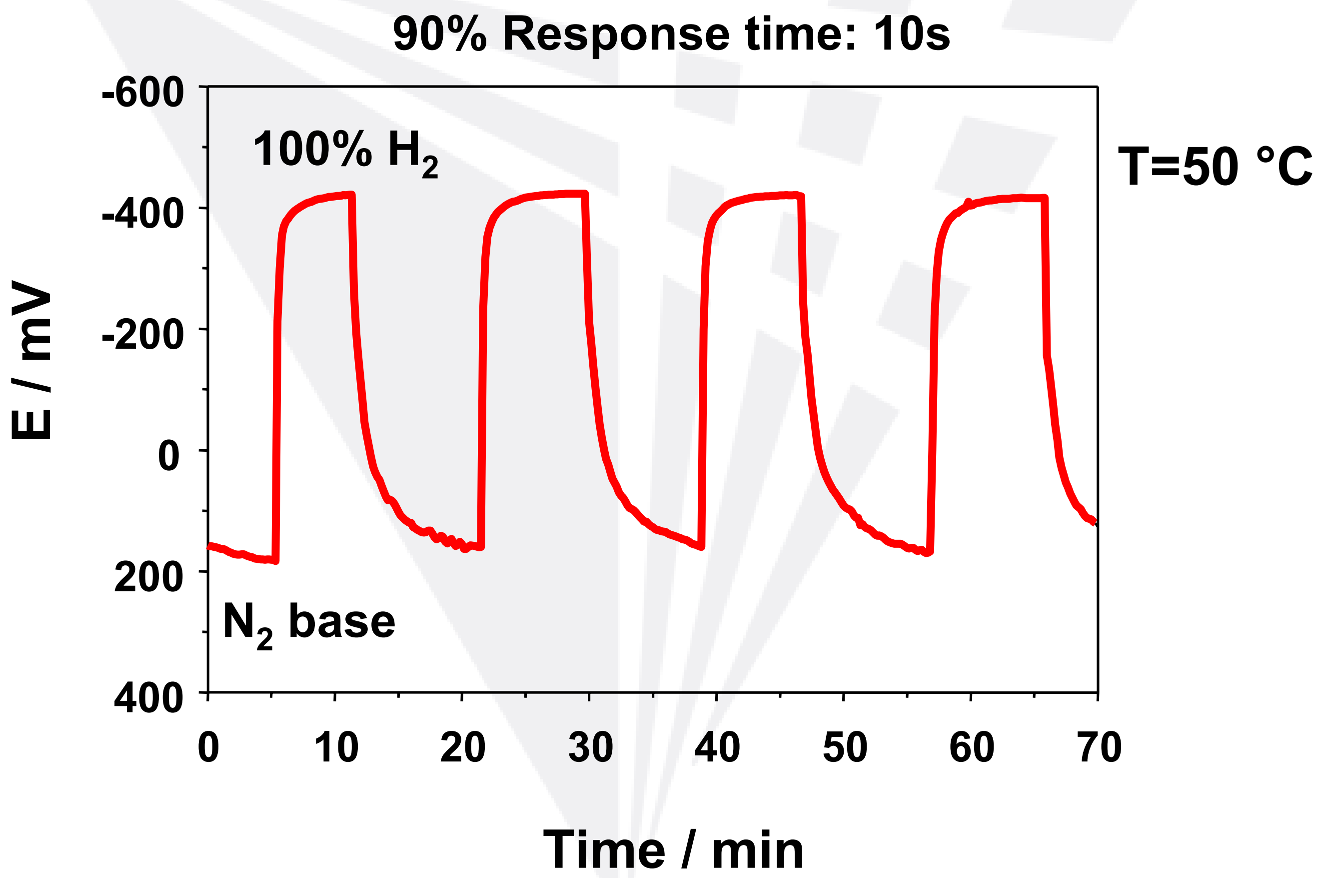


NASICON: Na Super Ionic CONductor ($Na_3Zr_2Si_2PO_{12}$)
Made by Solid-Phase Reaction Method

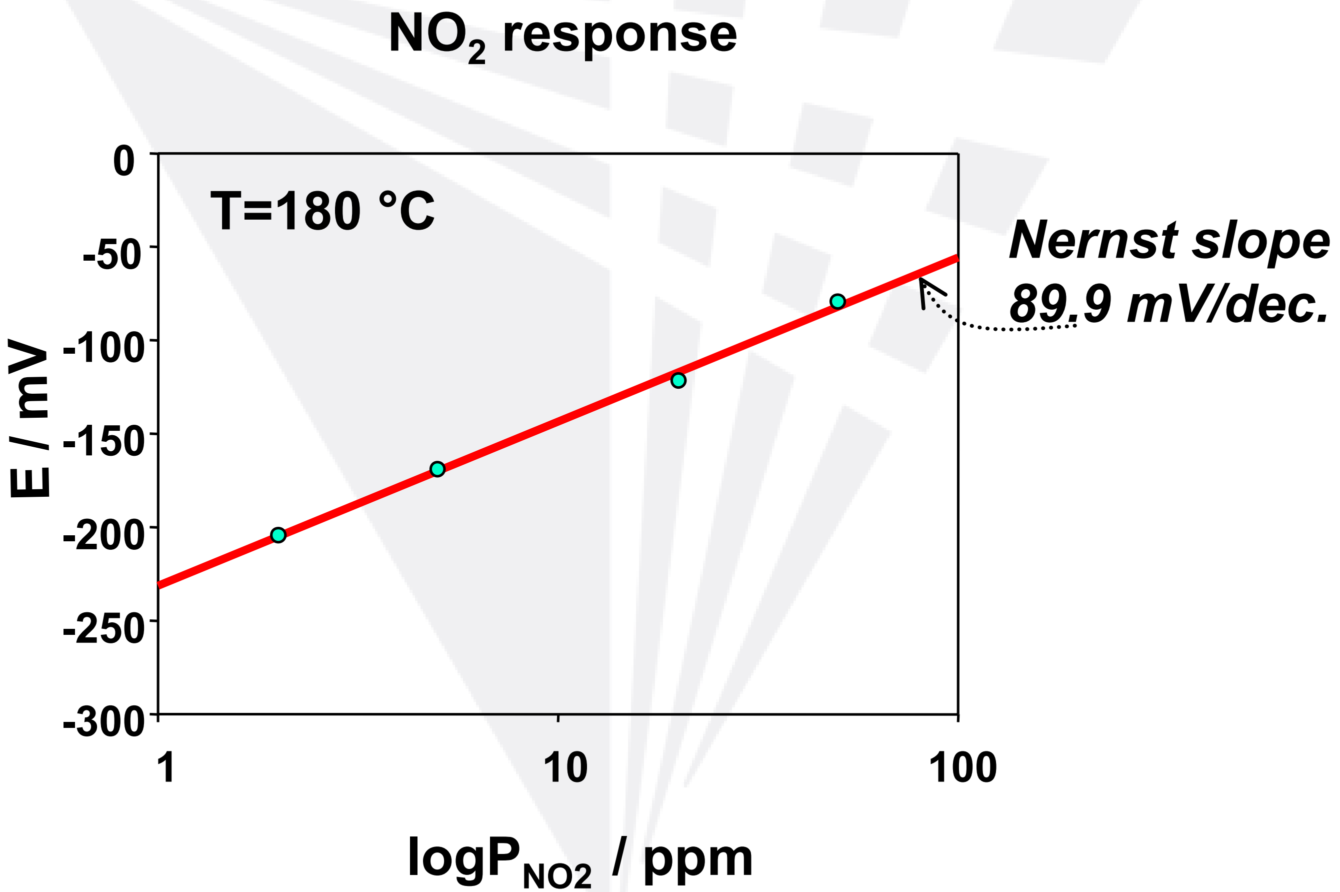
XRD:



Response of NASICON Sensor



NASICON Sensors in Potentiometric Mode



Summary

- We have addressed the concerns of last year's review
- New knowledge has been incorporated into products without delay
- We have achieved substantial improvement in sensor properties
- We have patents and publications pending
- Sensors for CO and H_2S are in commercial use with corporate partner, with hydrogen due out soon

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Future Focus

- **Newly-developed sensors will be tested at Argonne on 24/7 fuel cell pilot plant**
- **Shared Sensor Technology User Facility (SSTUF) will work with sensor developers to test sensors under harsh conditions**
- **Continued improvements in response times and temperature ranges**
- **Continued research into causes and control of cross-sensitivities**
- **Continued movement of developments into commercial applications**
- **Completion of final deliverables by May 2003, including completed sensors**