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CO Sensors for Fuel Cell Applications

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Objectives

- Development of CO sensors that can detect carbon monoxide in a hydrogen containing gas stream
- DOE Requirements
 1. 1-100 ppm CO at $<150^{\circ}\text{C}$
 2. 100-1000 ppm CO at 250°C
 3. 0.1-2% CO at $250^{\circ}\text{C}-800^{\circ}\text{C}$
- These sensors can be used to control the air bleed into the fuel cell anode
- These sensors could also be used to control the oxygen input of the PROX reactor

Budget and Technical Barriers

- This project had a budget of \$200,000 in FY03 (0.7FTE)
- The technical barrier for sensors is:

Automotive-type sensors are required that meet performance and cost targets for measuring physical conditions and chemical species in fuel cell systems. Current sensors do not perform within the required ambient and process conditions, do not possess the required accuracy and range, and/or are too costly.
- Currently, there are no commercial sensors that can sense CO in a H₂ containing stream

Technical Targets

1. 1–100 ppm reformate pre-stack sensor

Operational temperature: $<150^{\circ}\text{C}$

Response time: 0.1–1 sec

Gas environment: high-humidity reformer/partial oxidation gas: H_2 30%– 75%,
 CO_2 , CO , N_2 , H_2O at 1–3 atm total pressure

Accuracy: 1%–10% full scale

2. 100–1000 ppm CO sensor

Operational temperature: 250°C

Response time: 0.1–1 sec

Gas environment: high-humidity reformer/partial oxidation gas: H_2 30%– 75%,
 CO_2 , CO , N_2 , H_2O at 1–3 atm total pressure

Accuracy: 1%–10% full scale

3. 0.1–2% CO sensor 250° – 800°C

Operational temperature: 250° – 800°C

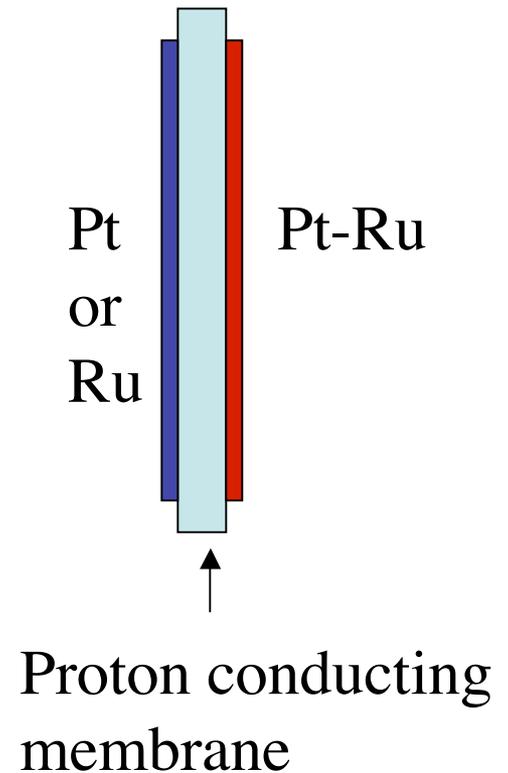
Response time: 0.1–1 sec

Gas environment: high-humidity reformer/partial oxidation gas: H_2 30%– 75%,
 CO_2 , CO , N_2 , H_2O at 1–3 atm total pressure

Accuracy: 1%–10% full scale

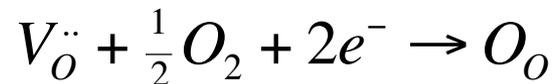
Approach (Low Temperature)

- Low temperature amperometric device based on CO inhibition of hydrogen oxidation kinetics
 - Use Nafion[®] as the proton conducting membrane
 - Use Pt or Ru electrode as working electrode
 - Electrode is sensitive to CO poisoning
 - Use Pt-Ru electrode as a counter electrode
 - Electrode is tolerant to the presence of CO



Approach (High Temperature)

- Potentiometric CO sensor based on the mixed-potential developed at an oxide electrolyte/metal electrode interface



CO sensor in air



CO sensor in H_2



- Use YSZ(zirconia) and CGO(Ceria) electrolytes
- Use various (Pt, Pd, Au, Ni) metal electrode combinations

A. Hashimoto et al. *Electrochem. and Solid State Letters*, **5(1)** H1-H3 (2002)

Project Safety

- The Los Alamos “Integrated Safety Management” practice was followed:



Major Hazards:

CO is toxic and H₂ is flammable
Test Station have CO and H₂ detectors

Will automatically shut off when
CO exceeds 50ppm or H₂ exceeds
the LEL

Problems:

CO sensor has cross interference
to H₂. Small H₂ leaks can cause
the CO sensor to alarm

Project Timeline

Fy01

Fy02

Fy03

Fy04

Project begins

Low temp CO sensor
prototype developed
Sense 100-1000ppm CO in
H₂

High temp CO sensors
first prototypes made
Sense 1-500ppm CO in
Room Air

Oxide proton conductor thin film
technology developed

Improved Low Temperature
sensor
Works at Room Temperature
Stable response to 10-200ppm CO
in H₂

High temp CO sensors
optimized
Electrodes and electrolytes have
been optimized to yield stable
responses at the lower CO
concentrations

Low temp CO sensor
prototype developed
Sense 1-100ppm CO in H₂
at 80-90°C

High temperature CO sensor
Heater has been incorporated into
these sensors

CO sensor tested
After PrOx reactor
(Fuel stream to power
5-10kW fuel cell)

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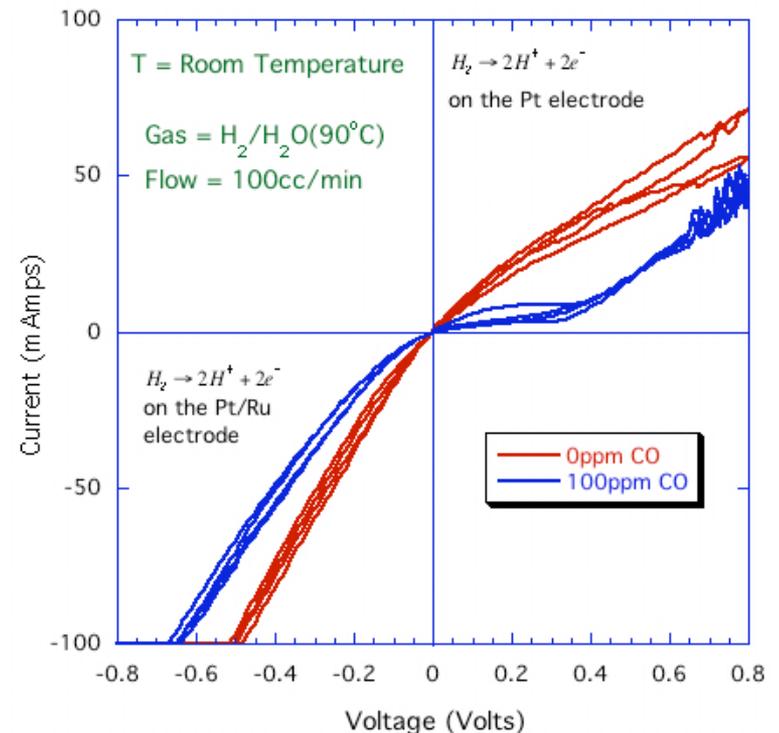
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Accomplishments (previous)

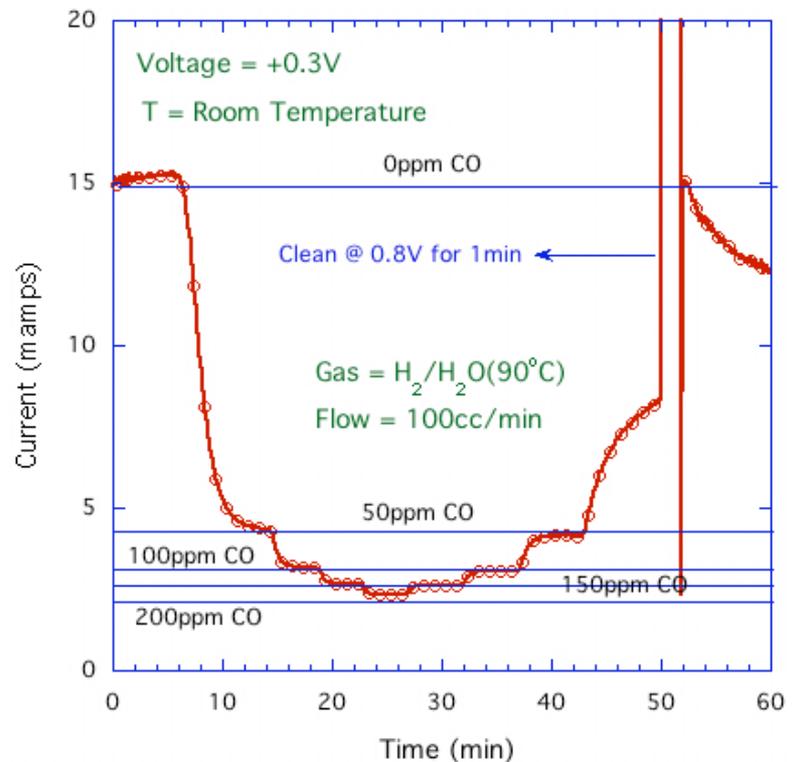
Low
Temperature

- Working Electrode
 - Pt/Nafion : 10mg/cm² of Pt
- Counter Electrode
 - Pt-Ru/Nafion : 10mg/cm² of Pt-Ru (50/50) alloy
- Electrolyte
 - Nafion 117
- Both the Pt and Pt/Ru alloy electrodes are good for H₂ oxidation
- There is very little effect of CO on the Pt/Ru alloy electrode
 - This electrode serves as a pseudo-reference electrode
- The Pt electrode reaction gets poisoned by the CO which can easily be cleaned at voltages > 0.4V



Accomplishments (previous)

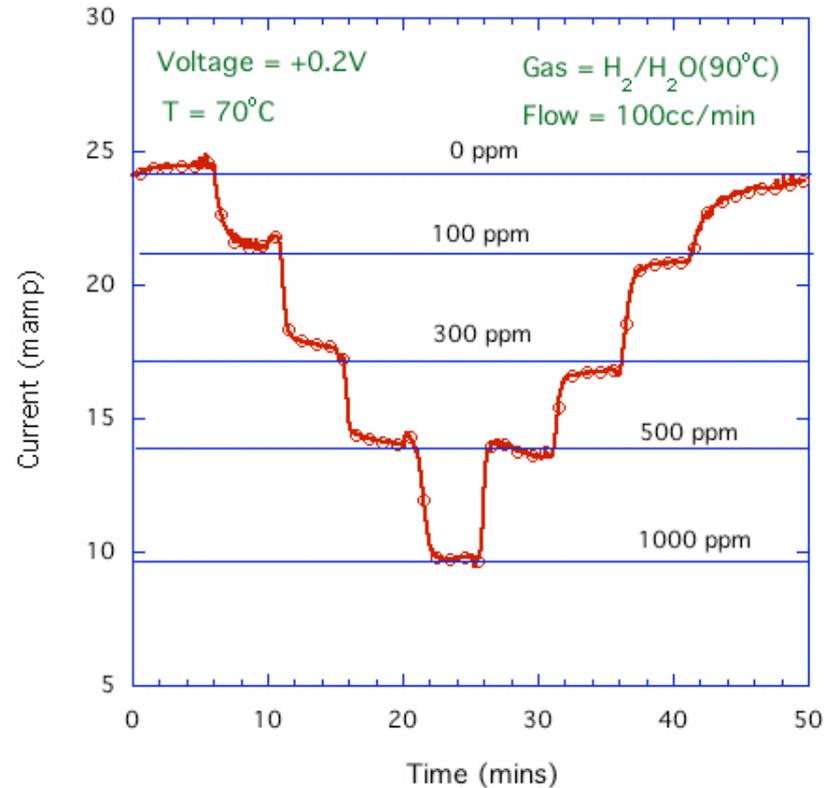
- The extent of poisoning on the Pt electrode can be used to give a useful sensor response
- The current at 0.3V decreases from 15mamps to <5mamps when the CO content in the H₂ stream is increased from 0 to 50ppm.
- The final CO can be cleaned by applying a 0.8V potential for approx. one minute
- **Slow response time (>5 mins) when CO is introduced**



Accomplishments (previous)

Low
Temperature

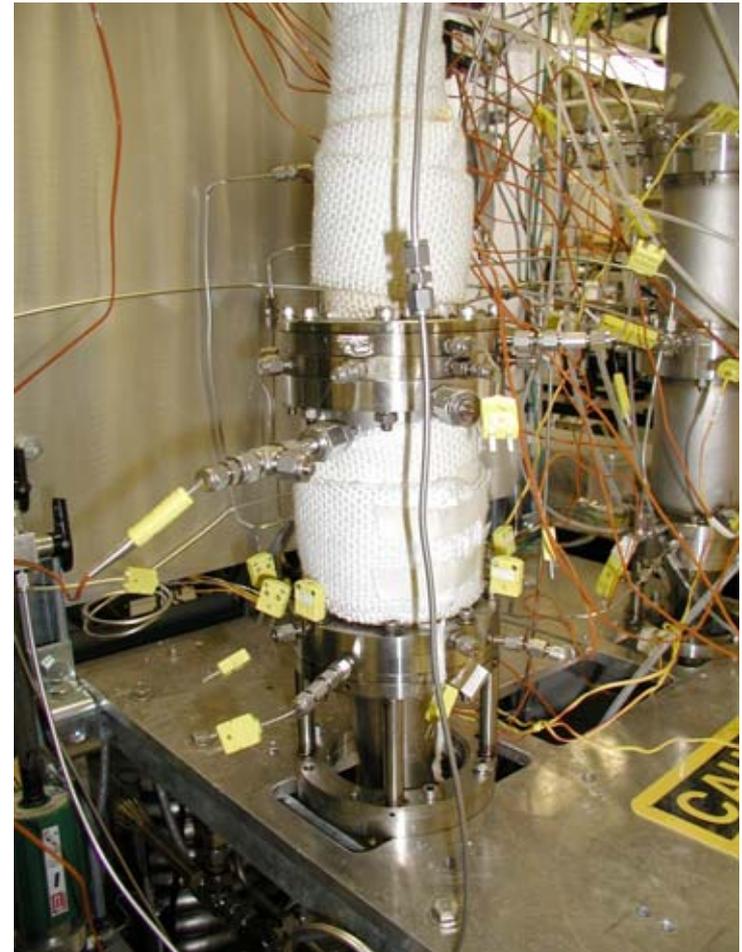
- Stable response obtained at 70°C
- Elevated temperature improves the response of the sensor
- No CO cleanup is required
- Response time : 1 - 2mins
- Sensor sensitivity is less:
 - 100 ppm of CO
 - 80% change at room temperature
 - 16% change at 70°C
- Baseline recovery is still slow



Useful to protect fuel cell from spikes

Sensor Testing Post PrOx Reactor

- Sensor was placed downstream of the PrOx reactor
- The temperature of the gases was 70-90°C
- Typical flow rates:
 - $\text{H}_2 \approx 100\text{L}/\text{min}$ (40%)
 - $\text{N}_2 \approx 70\text{L}/\text{min}$ (25%)
 - $\text{CO}_2 \approx 50\text{L}/\text{min}$ (17.5%)
 - $\text{H}_2\text{O} \approx 0.7\text{gm}/\text{sec}$ (17.5%)
- System pressure was 10 psi

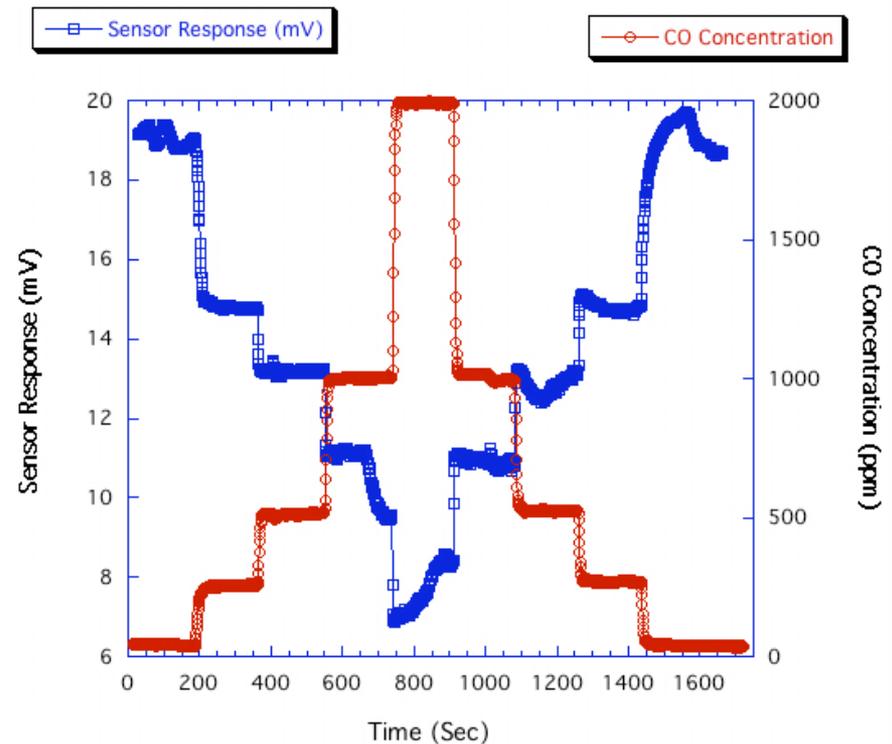


Sensor Response (Post PrOx Reactor)

Low
Temperature

- Working Electrode (+ve)
 - Pt/Nafion : 10mg/cm² of Pt
- Counter Electrode (-ve)
 - Pt-Ru/Nafion : 10mg/cm² of Pt-Ru (50/50) alloy
- Electrolyte
 - Nafion 117
- Gas diffusion layer (both sides)
 - E-Tek double sided carbon teflon GDL
- Can sense 100-2000 ppm CO at 80°C
- Response time is 1 sec at the high concentrations and <1 min at the low concentrations (1 sec between data points)
- Response time at high CO concentrations is adequate while that at low concentrations has to be improved by signal processing
- Response time of commercial IR sensor is 10 sec

Sensor operated at 0.1V



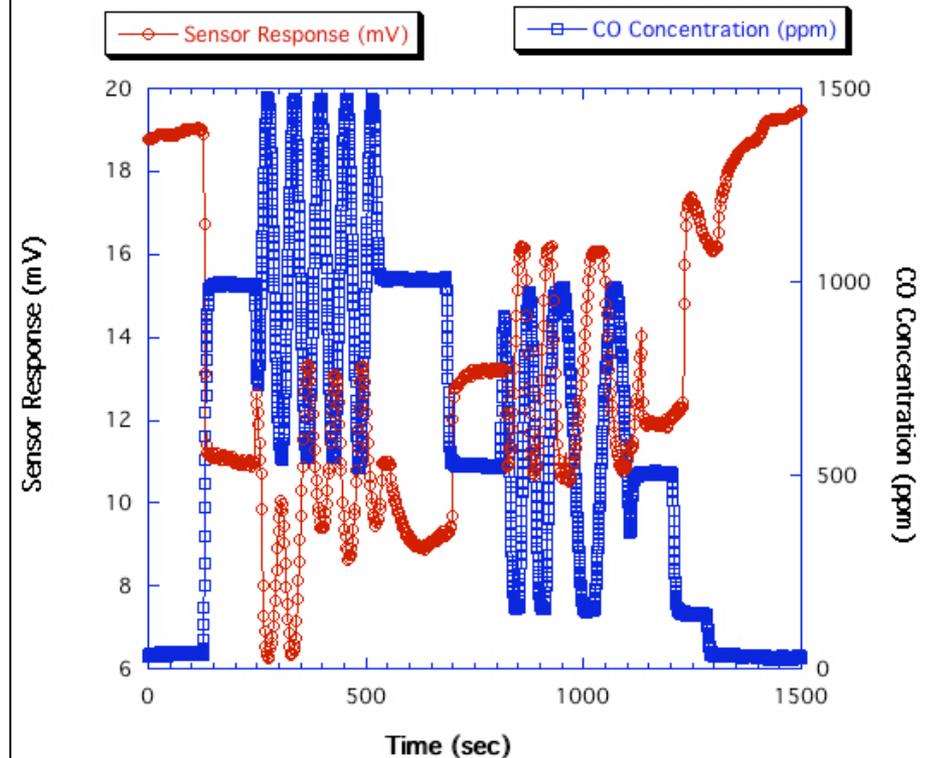
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Sensor Cycling Tests

- Same Conditions as previous test
- The sensor was able to track the cycling of CO concentration in the 100-1500 ppm range.
- The cycling period was 1 min in most cases (one 2 min cycle)
- The performance of the sensor was comparable to an analytical IR CO analyzer in most circumstances
- There are some fluctuations in the sensor current due to varying moisture content of the gases
 - Sensor will need to be calibrated for various temperatures and humidity contents

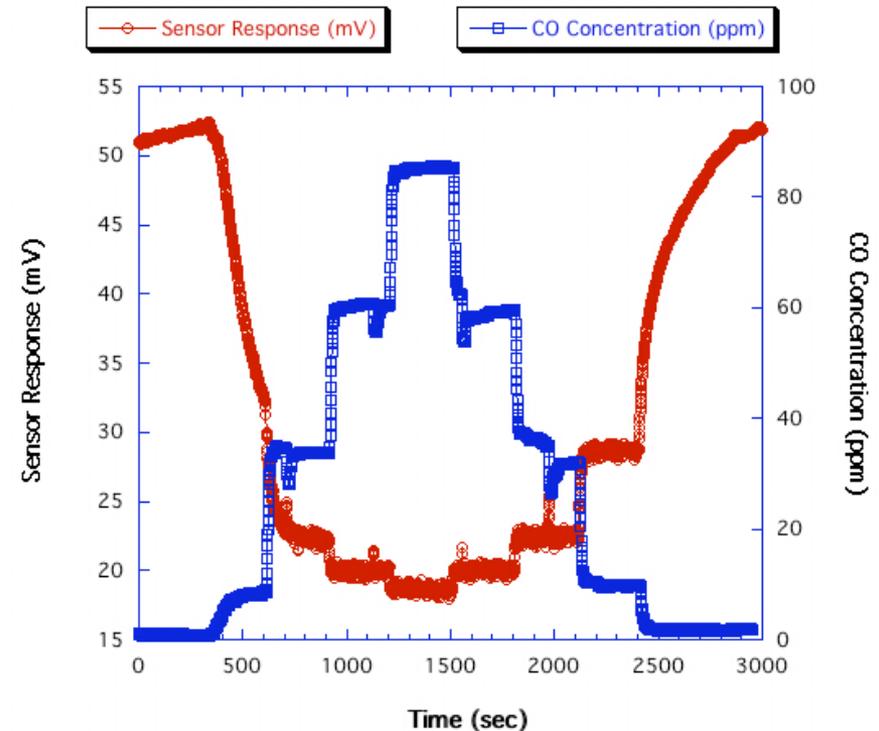
Sensor operated at 0.1V



Improved Sensor

- Working Electrode (+ve)
 - Pt/C/Nafion : 0.2mg/cm² of Pt
- Counter Electrode (-ve)
 - Pt-Ru/Nafion : 10mg/cm² of Pt-Ru (50/50) alloy
- Electrolyte
 - Nafion 112
- Gas diffusion layer (both sides)
 - E-Tek double sided Carbon PTFE GDL
- Can sense 25-100 ppm CO at 85°C
- Response time is 1 sec at the high concentrations and <10 sec at 25-50 ppm CO (1 sec between data points)
- Response time from 0-25 and 25-0 ppm is slow and needs to be improved (signal processing)
- This sensors meets all (except response time) the DOE targets for the low concentration CO sensor

Sensor operated at 0.3V

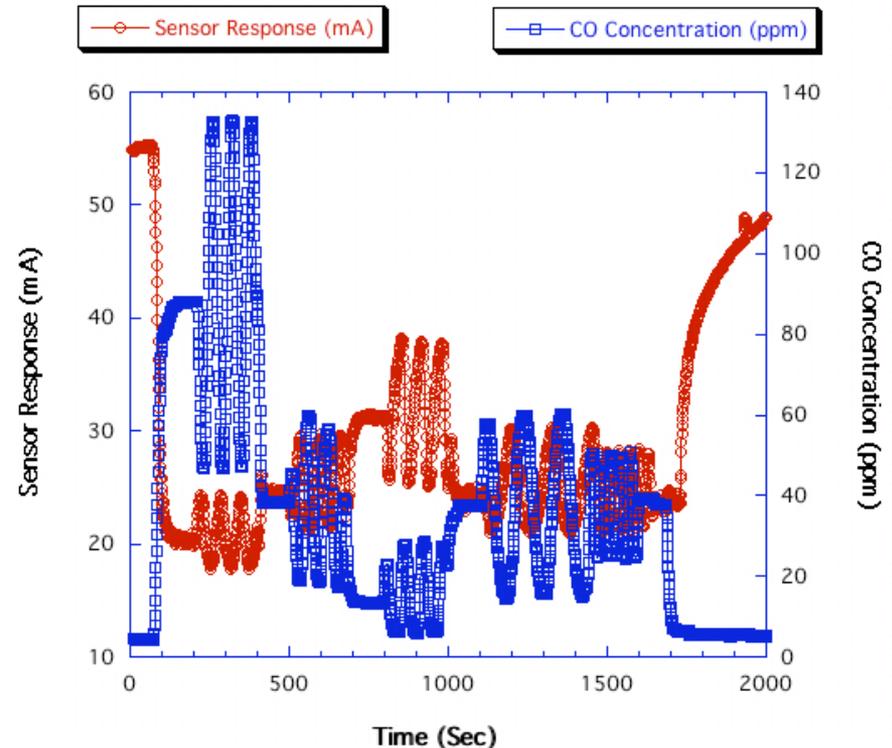


Lower catalyst loading leads to improved sensitivity

Sensor Cycling Tests

- Same Conditions as previous test
- The sensor was able to track the cycling of CO concentration in the 0-100 ppm range.
- The cycling period was 1 min in most cases (some 30sec cycles)
- The performance of the sensor was comparable to an analytical IR CO analyzer in most circumstances
- The return to baseline of the sensor is slow and may need to be improved by the application of a stripping voltage ($\approx 0.8V$) for a short duration
- Sensor is more stable than the sensor with high loadings

Sensor operated at 0.3V

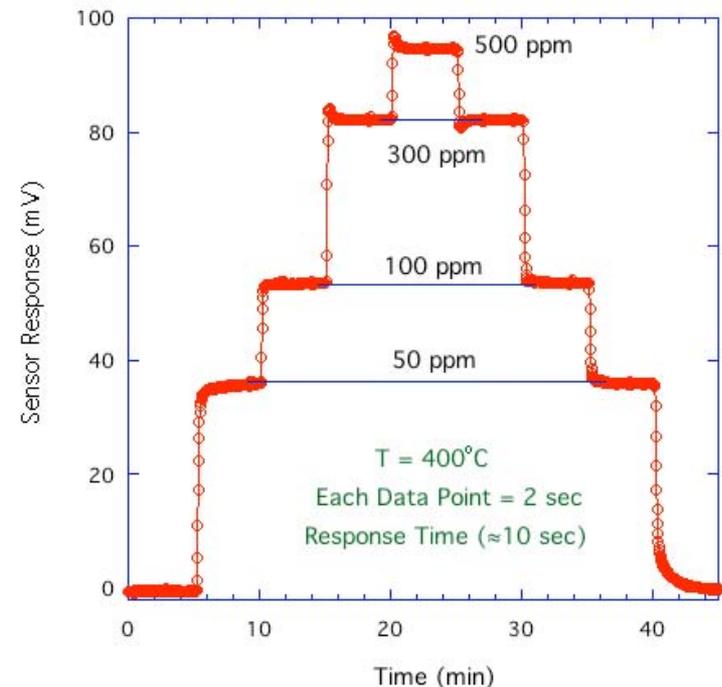


Accomplishments (previous)

High
Temperature

- Electrolyte
 - 8mole% YSZ ($\text{Zr}_{0.85}\text{Y}_{0.15}\text{O}_{1.93}$) or 20mole% CGO ($\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$) or
 - 20mole% EBO ($\text{Bi}_{0.8}\text{Er}_{0.2}\text{O}_{1.9-\delta}$)
- Electrodes
 - Pt, Au
- Kinetic Control (Electrode morphology)
- Stable CO response in Air (tested for up to 2 months)
- Response time < 10sec
- Reproducible results from multiple sensors

Pt / $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ / Au



Patent application filed

May 25, 2004

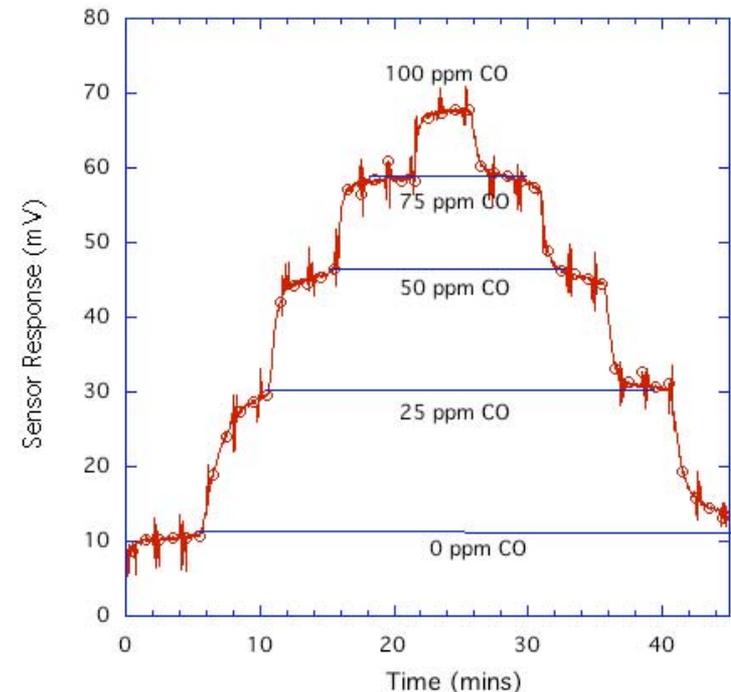
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Accomplishments (previous)

High
Temperature

- Electrolyte
 - 3mole% YSZ
- Electrode
 - Pd paint and Ni (1 μm sputtered)
- Lowered operating temperature (185°C)
- Response of 60mV @ 100ppm CO (10 fold increase)
- Stable baseline
- Approx. 1 minute response time
- High noise (need to average)
- Stability and Reproducibility?

Base Gas = 70% H_2 /30% CO_2 (H_2O)



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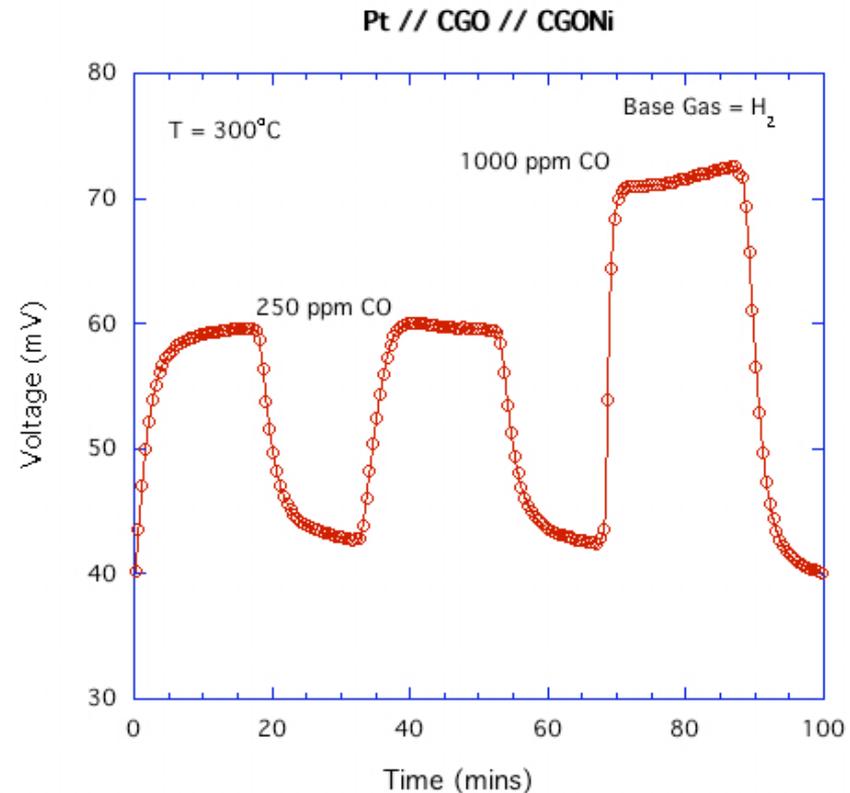
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Newly Developed Sensor

Requirements

- Previously developed
1-100ppm at 150°C
- This sensor
100-1000ppm at 250°C
- The Pt // CGO // CGO,Ni
sensor operates at 300°C
and can detect 100-1000
ppm CO in a H_2 stream

Have to study durability and
repeatability



Heater

Photolithography Mask

- Used on 1/2 - 3/4" YSZ and CGO substrates
- Test heaters were made on sapphire substrates to study the power requirements
- The maximum power required was < 5 watts
 - 3/4" sapphire substrate at 300°C
- The actual power will be determined by the size of the substrate, the operating temperature of the sensor, and flow rate and temperature of the test gases



Interaction and Collaborations

- Extensive collaborations within the LANL team
 - Involved members from hydrogen fuel cell, direct methanol fuel cell, fuel processing and sensor teams
- NexTech Materials, Ltd
 - Non Disclosure Agreement signed
 - Results of our low temperature sensor tests have been shared
 - Potential for technology transfer is being studied

Reviewer's Questions

- Status of Commercially available CO sensors?
 - Not available, Several patents have been issued. However, sensor configuration and measurement electronics are complicated. (US Patent 6,001,499 and 6,488,836)
- Stability of metal electrodes at high temperatures?
 - These metal electrodes have been found to be stable for at least 2 months of continuous operation (US Patent 6,605,202)
- Define power requirements to these sensors
 - The power requirement for the high temperature sensor will be <5watts (the actual power will depend on the final sensor configuration)
 - The power requirement for the low temperature sensor will be a few mW. It is mainly the power required to operate the measurement electronics and control system (Apply a voltage of <0.5V and measure a current of <100mA)

Future Work (FY 04)

Study effect of impurities like H₂S on the sensor response of both the high and low temperature systems

Safety requirements are being met in order to use highly toxic H₂S gas

Stability of high temperature sensors when exposed to high CO concentrations for prolonged periods

Explore possibilities of technology transfer to industry

Identified critical need for safety sensors that can discriminate between H₂ and CO.

CO safety sensors that have minimal cross interference from H₂

Conclusions

- PEM based CO sensors have stable reproducible response to 25-2000ppm of CO at 80-90°C
 - Low Pt loading(0.2mg/cm²) of the working electrode results in a sensor that can detect 1-100 ppm CO in the fuel inlet stream of a fuel cell stack
 - High Pt loading(10mg/cm²) of the working electrode results in a sensor that can detect 100-2000 ppm CO in the inlet stream of a PrOx reactor
- Oxide based sensors can be used to measure 25-1000ppm CO in H₂/CO₂/H₂O mixtures at 150-300°C
 - Stability and response time need improvement

Acknowledgements

- Bryan Pivovar, Piotr Zelenay and Piotr Piela for help with unsupported MEAs with high catalyst loadings
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