Sensor Development for Harsh Environments

J. E. Hardy
Leader, Sensor and Instrument Research Group
Oak Ridge National Laboratory
SECA Core Technology Program
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Sensors Required for High Performance - To Improve Reliability and Control

• Goals for Sensor and Controls
  – Increase operational efficiency
  – Reduce emissions
  – Lower operating costs
  – Accelerate time to full-scale commercial implementation

• Numerous challenges exist
  – Extremely confined spaces
  – Harsh oxidizing and reducing environments
  – High temperatures (600 to 900 °C)
  – High electrical fields
  – Material issues (corrosion, deposition, etc.)
  – Long service life (5,000 hours in transportation; 40,000 hours for fixed site)
Sensor Measurement Requirements Are Very Challenging

- Flows (0 - 2 liters/min)
- Pressure (0 - 5 psig)
- Gaseous composition: steam, CO, CO\textsubscript{2}, H\textsubscript{2}, O\textsubscript{2}, H\textsubscript{2}S, CH\textsubscript{x} (0.1% up to 100%)
- Sulfur (ppm level to a few percent)
- Accuracy to within 1% of sensing range
- Best if non-intrusive or embedded in materials
SOFC Sensor Requirements Similar to CIDI/SIDI Engine Needs

- Items to be measured: $\text{O}_2$, $\text{CH}_x$, CO, Sulfur, Temperature, flow
- Environmental and operational conditions: temperature range essentially the same, low-cost, limited space, robust, accurate, high sensitivity, and low/no maintenance

National Labs have experience with auto industry in measurement technology development
National Laboratories Are Well-Suited for Sensor Development

• Multidisciplinary approach required to develop sensor systems
  – fundamental physics, material and joining sciences, measurement science, electronics, packaging, integration, and information/knowledge extraction

• History of dealing with harsh processing environments
  – radiation, corrosive chemicals, high temperatures, precision measurement and controls, safety and security
Sensor Development Programs Underway at Several National Labs

- **LANL** - electrochemical sensors for HC and CO gases, zirconia O₂ sensor, ultrasonic sensor for pressure
- **SNL** - acoustic wave HC gas sensor, micromachined catalytic gas sensors (CO, H₂, HCs), H₂ chemical resistance and optical sensor, MEMS pressure sensors
- **ANL** - HC ion mobility sensor, microwave sensor for NOₓ, acoustic and SAW for exhaust gas, flow, and temperature
- **PNNL** - O₂ and NOₓ sensors

Most of these sensors operate at temperatures < 500°C
ORNL’s Diversity and Multi-program Nature Results in Excellent Resources for Sensor Development

- Over 150 professionals in measurement science
  - engineers, physicists, material scientists, chemists, electro-optics researchers, and metrologists
- Advanced analog and digital electronics (ASICs, microprocessors, low-power designs, microbatteries)
- Signal and image processing for data flow, information, and intelligence
- Material synthesis & characterization for harsh environments
- Systems engineering for packaging, miniaturization, integration, and sensor networks (optical and wireless)
ORNL’s Diversity and Multi-program Nature Results in Excellent Resources for Sensor Development (continued)

- Facilities for developing, prototyping, testing, and characterizing sensor concepts, robustness, and sensitivities
  - micro and nanofabrication laboratories (multilayer clean room sensor fab/1000 sensors per year)
  - materials (catalysts) synthesis and characterization facilities
  - testing and characterization facilities (environmental effects including high temperature and multi- or single component gas mixtures)

Staff, experience, and labs create technology development path for robust, low-cost ($10s) sensor systems
ORNL Has Developed Harsh Environment Sensor Systems

- Vehicle exhaust gas flowmeter (650°C, 150 to 1 range, fast response, low ΔP)
- Liquid film probes (800°C, severe thermal shock)
- Drill bit monitor (high temp electronics)
- Chem/Bio Mass Spectrometer (radiation, vehicle operation, EMP, low power)
- Extraction of information from very noisy signals
ORNL Sensor Development for Automotive Applications that May Fit SOFCs

- \( \text{NO}_x, \text{O}_2, \) and \( \text{NH}_4 \) sensor development in progress
  - planar \( \text{O}_2 \) sensor developed with output proportional to partial pressure; response time diffusion barrier/geometry dependent
  - low-cost \( \text{NO}_x \) demonstrated to 400\(^\circ\)C; commercialization partner on board
  - resistive mixed potential sensors for \( \text{NO}_x, \text{NH}_4, \text{H}_2\text{S}, \) hydrocarbons with potential for lower cost and easier to produce
ORNL NO$_x$ Sensor Development

Sensor Type #1 (Gasoline lean burn engine)
Sensitivity: 100-200 ppm (potential lower detection limit for diagnostics)
Accuracy: +/- 20 ppm
Response Time: < 1 sec (0-90% full scale)
NO/NO$_2$: equally sensitive to NO and NO$_2$
Concerns: sulfur

Sensor Type #2 (Diesel application with urea)
Sensitivity: 20-300 ppm
Accuracy: +/- 20 ppm
Response Time: < 1 sec (0-90% full scale)
NO/NO$_2$: separately measure NO and NO$_2$
Concerns: soot, sulfur and urea(NH$_3$)
NOx Sensor Development at ORNL

Porous materials to control diffusion of exhaust gases

Non noble metal electrodes to eliminate NOx catalysis

Low dielectric constant insulators to reduce cross talk

Prototype materials developed

Modeling of sintering processes in multilayer bodies composed of materials with differing properties.

Developed and in production!

Alumina (Al2O3)

Zirconia (ZrO2)

Cavity

Zirconia (ZrO2)

Alumina (Al2O3)
Several issues need to be resolved before NOx sensors can be commercialized

<table>
<thead>
<tr>
<th>Primary Issues</th>
<th>Secondary Issues</th>
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<tbody>
<tr>
<td>• Response time (&lt;500 ms)</td>
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<tr>
<td>– monitoring vs control</td>
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<tr>
<td>• Sensitivity</td>
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<tr>
<td>– 10 ppm NO</td>
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<tr>
<td>– small signal (~10nA/ppm)</td>
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<tr>
<td>• packaging</td>
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<td>• electronics</td>
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<td>• Cost</td>
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| • Durability |
|             |
|   – drift    |
|   – aging    |
| • Poisoning  |
| • Selectivity |
|   – NO vs NO₂ |
|   – NH₃, O₂, H₂O, and HC interference |
Mixed Potential Sensors for High-Temperature Sensing

- Current development indicates need for resistive mixed-potential sensors for:
  - NO\textsubscript{x}, NH\textsubscript{4}, H\textsubscript{2}S, hydrocarbons
- These sensors offer: simpler designs and electronics, large signals, reduced cost
- However, they must operate at reduced temperatures (<600°C) and they may have prohibitively long response times
Several New Sensor Concepts Are Exciting Possibilities for Fuel Cells

- CO sensor based on oxidization - measurement of heat evolved leads to amount of CO present
- Fiber-optic thermophosphor temperature sensor based on fluorescence decay being proportional to temperature
- Micro-size laser absorption measurement systems using long wave IR for gas spectroscopy
- Microcantilever arrayed measurement system for gas detection
- H$_2$S sensor based on novel S conducting electrolyte
Fiber-Optic Coupled Phosphor Thermometer Offers Highly Reliable, Accurate Temperature Measurements

**Objective:**

- Development of a reliable, accurate, low-cost temperature sensor for monitoring and control of fuel cell systems
- YAG fiber-optic probe developed with high resistivity to corrosion and erosion to extend probe life
- Design robust mechanical interface to couple sensor to fuel cell
- Provide high sensitivity and quality signal conditioning electronics
- Develop a drift-free, high accuracy, robust optical thermometry system
- Sensor consists of a single crystal YAG fiber with a phosphor grown directly on the fiber tip
- Phosphor thermometry has been demonstrated by ORNL for turbine, steel processing, and automotive diagnostics over the past 10 years.
Hyper-spectral, Longitudinal Integrated Resonator Gas Sensor on a Chip

Objective:

- Develop integrated single chip gas spectroscopy system
- Measure CO, ammonia, H₂S, and SOₓ to better control fuel cells for enhanced performance
- MEMS fabrication of wristwatch size CO₂ laser and folded cavity approach for gas sampling cells
- Integrated laser and sampling cell to provide sensor-on-a-chip
MEMS-Based Hydrogen Sensors

- Enhance energy efficiency and safety of fuel cell fuel quality and leak detection
- Provide low-cost hydrogen sensor for fuel-cell process control and leak monitoring
- Develop platform that is expandable to sensing other gases such as CO and SO₂
- Utilize an economical micro-electro-mechanical system (MEMS) sensor developed for hydrogen sensing
- Demonstrated high-performance, stable output at temperatures and environmental conditions
- Develop reliable, sensitive low-cost electronic signal conditioning and readout
National Labs Well-Positioned for Developing Sensors for Harsh Environments

• Sensors for SOFCs are essential and development is very challenging

• National Labs have multidisciplined expertise and experience to address the issues - large cadre of experts in all aspects of measurement systems from the sensor concept, to materials & fabrication, microelectronics, signal processing, packaging, testing & characterization, and overall integration