Optical Fiber Based Sensors for Future Fossil Energy Applications

Presenter: Dr. Paul R. Ohodnicki, Jr.

April 10, 2018
Other Key Technical Staff

Formal Staff Members on Tasks

• Benjamin Chorpening
• Michael Buric
• Bo Liu
• Yuhua Duan
• Yuning Wu
• Jeffrey Wuenschell
• Robert Fryer
• Kevin Chen (University of Pittsburgh)
• Mohamed Bayoumy (University of Pittsburgh)

Past Staff Members on Tasks and Collaborators

• Youngseok Jee
• Shiwoo Lee
• Harry Abernathy
• Greg Hackett
• John Baltrus
• Joseph Tylczak
• Gordon Holcomb
• Ping Lu
• Juddha Thapa
• Ting Jia
Presentation Overview

- NETL R&IC Sensor Material and Optical Fiber Sensor Program Overview
  - Fossil Energy Needs Driving Advanced Sensors
  - Enabling Materials for Harsh Environment Sensing
  - Current Capabilities, Research Thrusts, and Partnerships
- Highlights of Recent Results and On-Going Activities
  - H₂ Sensing Materials
  - Multi-Component Speciation Through Broadband Interrogation
  - O₂ Sensing Materials
  - SOFC Applications of Optical Fiber Sensors (Embedding and Interrogation)
  - Existing Plant Applications of Optical Fiber Sensors (Boiler Application Field Validations)
  - Theoretical Investigations of High Temperature Oxide Sensor Materials
  - Sapphire Fiber Growth and Cladding Research
  - UCR Fellow / Outreach Program on SAW Sensor Devices
- Summary and Conclusions
Fossil Energy Needs Driving Advanced Sensors

Increased Visibility Through Embedded Sensor Technology Can Improve Reliability, Resiliency, and Efficiency Across the Fossil Energy Infrastructure.
Fossil Energy Needs Driving Advanced Sensors

Short Term Focus

<table>
<thead>
<tr>
<th>Coal Gasifiers</th>
<th>Combustion Turbines</th>
<th>Solid Oxide Fuel Cells</th>
<th>Advanced Boiler Systems</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperatures</td>
<td>Up to 1600°C</td>
<td>Up to 900°C</td>
<td>Up to 1000°C</td>
</tr>
<tr>
<td>Pressures</td>
<td>Up to 1000psi</td>
<td>Pressure Ratios 30:1</td>
<td>Atmospheric</td>
</tr>
<tr>
<td>Atmosphere(s)</td>
<td>Highly Reducing, Erosive, Corrosive</td>
<td>Oxidizing and Reducing</td>
<td>Oxidizing</td>
</tr>
<tr>
<td>Examples of Important Gas Species</td>
<td>H₂, O₂, CO, CO₂, H₂O, H₂S, CH₄</td>
<td>O₂ Gaseous Fuels (Natural Gas to High Hydrogen), CO, CO₂, NOₓ, NO, SOₓ, Hydrogen from Gaseous Fuels and Oxygen from Air</td>
<td>Steam, CO, CO₂, NOₓ, SOₓ</td>
</tr>
</tbody>
</table>

SOFC Temperature: 700-800°C
Anode Stream: Fuel Gas (e.g. H₂-Containing)
Cathode Stream: Air or O₂

Example: Solid Oxide Fuel Cells
Internal Gas and Temperature Distribution

Incompatible with Traditional Sensing Technologies
1) Limits of High Temperature Electrical Insulation
2) Limited Access Space
3) Requires Multi-Point Sensing
4) Electrified Surfaces
5) Flammable Gas Atmospheres

In-House Efforts Have Exploited the SOFC Technology as a Demonstration Platform for Harsh Environment Embedded Sensors in Electrified Components.
Challenges in Existing Coal Fired Power Plants

- Local tube overheating
- Ammonia slip
- Combustion control and air in-leakage
- Mill performance
- Water / WW chemistry
- Controls optimization

Cross-section of John W. Turk Jr. USC Plant. Courtesy of Babcock & Wilcox. All rights reserved.
Enabling Harsh Environment Sensor Materials

System Properties: Gas Species, T, P (Input Variables)

Functional Thin Film: Electrical, Optical, Electrochemical (Sensing Element)

Sensor Technology: Electrochemical, Chemi-Resistive, RF, Optical (Transducer)

Sensor Response (Sensitivity, Selectivity, Stability)

Key Challenge #1: Functional Sensor Materials

Key Challenge #2: Materials for Device Stability
Emphasis on Optical Fiber Based Sensors

> Eliminate Electrical Wiring and Contacts at the Sensing Location
> Tailored to Parameters of Interest Through Functional Materials
> Eliminate EMI and Potential Interference with Electrical Systems
> Compatibility with Broadband and Distributed Interrogation

Optical Fiber Based Sensors are Particularly Well-Suited for Harsh Environment and Electrified System Applications.
Recent Activity Focused on Wireless Sensors

More Recent Activity Has Been Initiated on Surface Acoustic Wave Based Sensors Compatible with Wireless Interrogation.

Surface Acoustic Wave Devices for Harsh Environment Wireless Sensing

David W. Greve\textsuperscript{1,2,*}, Tao-Lun Chin\textsuperscript{1,2}, Peng Zheng\textsuperscript{1,2}, Paul Ohodnicki\textsuperscript{1}, John Baltrus\textsuperscript{1} and Irving J. Oppenheim\textsuperscript{1,3}

*Sensors 2013, 13, 6910-6935; doi:10.3390/s130606910
Collaborative Interactions with Universities


NETL On-Site Sensor Material / Device Research

Crosscutting Program Extramural Funded Programs

The NETL Research & Innovation Center Seeks Opportunities to Engage with Partners Funded Through the Crosscutting Program to Promote the Goals and Missions of NETL.
Unique Facilities of the Project Team

Custom Sensor Development Reactors

Custom Sensor Development Reactors Simulate:

- Power Generation and Combustion Systems
- Subsurface / Geological Environments
- Pressurized Gas and Oil-Based Systems


Unique Sensor Fabrication Facilities

Laser Heated Pedestal Growth System for Fabricating Single Crystal Fibers

Commercial and Custom Optical Interrogator Systems for Optical Fiber Sensors
Unique Facilities Available at NETL

**High-Pressure Combustion Facility (Aerothermal Rig)**
- Simulates hot gas path of a turbine
- Natural gas or hydrogen fuel
- Capable of 2 lb/s air flow @ 10atm
- Temperature: up to 1300°C
- Optically-accessible combustor and test sections

**Hybrid Performance Facility (Hyper)**
- A 300kW solid oxide fuel cell gas turbine (SOFC-GT) power plant simulator
- 120 kW Garrett Series 85 APU with single-shaft turbine, 2-stage radial compressor, and gear driven generator
- 100+ process variables measured including rotational speed (1,200Hz; 40,500 rpm), air/fuel flow, temperature (turbine: 637°C; SOFC: 1133°C), pressure (up to 260kPa), etc.

Au-Nanoparticle Incorporated Oxides

Gas Stream Response

Temperature Response

High Electronic Conductivity Oxides

Au-Nanoparticle / Oxide and High Electronic Conductivity Oxide Based H$_2$ Sensing Materials Leveraging the Fiber Optic Sensing Platform for SOFC Relevant Applications (~700-800°C).
Functional Thin Films for High Temperature Sensing

We Have Recently Discovered that Direct Thermal Emission Monitoring of the Functional Sensor Layer as Well as Characteristic Absorption of the Silica Fiber Can Be Used for Sensing.
A Primary Advantage of Optical Based Sensors Lies in the Capability for Multi-Variate Analysis of Broadband Wavelength Signals Which is an Emerging Trend Being Explored.
More Recent Work is Targeting LSM and Related Perovskite Oxides for High Temperature $O_2$-Sensing. Responses are Consistent with p-Type Electronic Conductivity of Oxides.
We are developing and applying computational methodologies and techniques with a goal of obtaining high temperature functional properties from first principles.
Temperature effect on electronic structure:
- electron-phonon interaction
\[ \epsilon_{k\nu}(T) - \epsilon_{k\nu}(0) = \frac{1}{N_q} \sum_{q,\nu} a_{q,\nu}^{(2)} \left[ \frac{1}{2} + n_B(\omega_{q\nu}, T) \right] + \cdots \]
  - Allen-Heine-Cardona (AHC) theory
  - Finite displacement method (FD)
- Lattice thermal expansion
  - Quasiharmonic approximation

- Electron-phonon interaction is the major contribution.

Example #1: Temperature Dependent Bandgap of TiO\(_2\) and SrTiO\(_3\).
Computational Methods Applied to Sensor Materials

- Current DFT theory to calculate the dielectric constants does not include electron-phonon coupling.
- We propose a statistical method based on atomic displacements.

\[
u_n = \sum_{q,i} u_{n,q,i} = \sqrt{\frac{\hbar}{m_n}} \sum_{q,i} n_{q,i} e^{i(q \cdot R_n + \phi_{q,i})} \sqrt{\left(\frac{\hbar \omega_{q,i}}{k_B T} - 1\right)} \omega_{q,i}\]

1. Generate a set of configurations according to the phonon dispersion.
2. A random phase is added to each phonon modes.
3. Calculate the dielectric constants for each configuration.
4. Configurational average.

- Curves of optical properties get smoothed as temperature increases.


Example #2: Finite Temperature Extrapolation of Optical Constants for TiO\(_2\).
Example #3: Optical Properties of Complex Perovskites and Defect Chemistry.
Enhanced Temperature and $\text{H}_2$ Stability of OFDR Rayleigh Based Interrogation of Optical Fibers Associated with Engineered Voids Within the Silica Network.
High Temperature Distributed Sensing in Silica Fibers

Elevated Temperatures Near the Anode Stream Inlet Due to the High Thermal Conductivity of the Fuel Gas Stream and Elevated Temperatures Relative to Cell Operating Temperature.

Additional Studies of Silica Fiber Sensor Packaging and Potential Exploration of Alternative Fiber Materials are Required

Enhanced Backscattering Processing Methodologies Have Enabled Successful Temperature Profile Measurements Throughout an Operational SOFC Anode and Cathode Stream.
Additive Manufacturing Embedding of Silica Fibers

University of Pittsburgh

LENS Embedding Within a High Temperature Ti-Alloy Part

CT Scanning Capabilities Leveraged to Explore Structure of Embedded Sensors

Embedding of Silica Based Optical Fiber Sensors in High Temperature Metals is Being Explored Through the Exploitation of Additive Manufacturing Techniques Such as LENS.
Planned Field Validations: Temperatures Across the Boiler Tube Wall

100+ temperatures from one optical fiber

Measure temperatures from every tube
- Expected spatial resolution 1 inch (200 ft long)
- Identify local hot spots on tube wall
- Outside wall for initial effort (silica fiber in air 1000°F)
- Sapphire fiber later in hotter locations

New Task
- CRADA being negotiated for test site

Planned Field Validations: Temperatures Across the Boiler Tube Wall
New Research Efforts Currently Being Initiated Will Target Research and Development of Cladding Layer Approaches for Sapphire Based Fibers.
Alternative Optical Fiber Material Investigations

Laser Heated Pedestal Growth Processing

**Alternative Optical Fiber Material Investigations**

Significant Accomplishments Include (1) Optimized Process Control for Long Sapphire Growth and Custom Shapes and (2) fs-laser Processed Sapphire Fibers for Distributed Interrogation.
More Recently, The Crosscutting Program University Outreach Program Has Begun to Initiate Formalized Collaborations Between the NETL Research & Innovation Center and Partners.

Promoting Development of High Temperature Wireless Sensor Technology

- New Project Activity on Sensing Layers
- Collaborating on Materials for Device Stability
- Seeking Opportunities to Support UCR Projects
  - Characterization Support
  - Access to Unique NETL Facilities

Dr. Robert Fryer, ORISE Researcher
The Collaboration is Focused on (1) Developing New Sensing Materials for High Temperature SAW Sensing and (2) Collaborating with Partners to Leverage NETL Expertise and Facilities.

\[
\frac{\Delta v}{v_0} \approx \frac{1}{V_p} \left( \frac{\delta v}{\delta I} \Delta I + \frac{\delta v}{\delta \epsilon} \Delta \epsilon + \frac{\delta v}{\delta E} \Delta E - \frac{\delta v}{\delta \sigma} \Delta \sigma + \frac{\delta v}{\delta m} \Delta m + \frac{\delta v}{\delta p} \Delta p + \ldots \right)
\]

- \(\Delta v\) = change in velocity
- \(v_0\) = velocity without surface layer
- \(K^2\) = electromechanical coupling coeff.
- \(\sigma_s\) = sheet conductivity of sensing layer
- \(\epsilon_{\text{eff}}\) = effective dielectric permittivity

Contributions from varying surface layer’s film conductivity:

\[
\frac{\Delta v}{v_0} = -\frac{K^2}{2} \frac{\sigma_s^2}{\sigma_s^2 + (v_0 \epsilon_{\text{eff}})^2}
\]
Key Successes to Date Include Screening of Several Candidate Sensing Layers for SAW Sensing Applications and Establishment of New Laboratory Capabilities.
Summary and Conclusions

• NETL Has a Well Established Focus Area in Enabling Materials for Harsh Environment Sensing Applications
• NETL Has Excellent Capabilities for High Temperature and Harsh Environment Sensor Development
• Functionalized Optical Fiber Sensors Show Great Promise for a Range of Energy Related Applications
• NETL R&IC Has Active In-House Research In a Broad Range of Areas
  • Power Generation
  • Subsurface CO₂ Storage / Oil & Gas
  • Natural Gas Infrastructure
  • Electricity Infrastructure
• We are Always Interested in Collaboration Opportunities as Well as Joint Technology Development and/or Licensing of Patented Concepts

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.