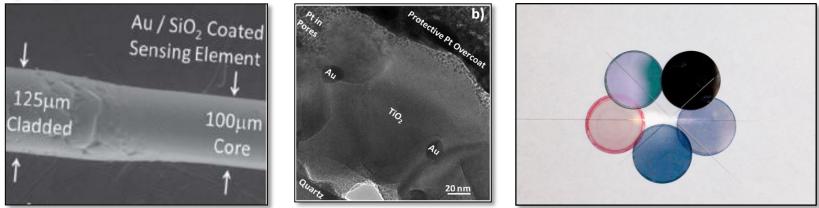


#### NATIONAL ENERGY TECHNOLOGY LABORATORY

#### Optical Material Enabled Harsh Environment Sensors



## Sensor Materials and Fiber Optic Sensors for Harsh Environment Sensing Applications at NETL

#### Dr. Paul Ohodnicki, Materials Scientist / Technical Portfolio Lead

**Functional Materials Team** 



Materials Engineering & Manufacturing Directorate

NETL Research & Innovation Center



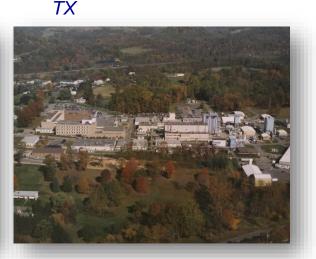




Oregon



**Fairbanks**, AK



# PennsylvaniaWest VirginiaNATIONAL ENERGY TECHNOLOGY LABORATORY

Sugar Land,

# **Relevant Research Focus Areas in R&IC**

- Material and Device Research Focus Area
  - Overview of Research Focus Area at NETL
  - Example of Cross-Disciplinary Integrated Research
- NETL R&IC Sensor Material and Optical Fiber Sensor Program Overview
  - Energy Related Harsh Environment Sensing Needs
  - Current Capabilities, Research Thrusts, and Partnerships
- Highlights of Recent Successes and On-Going Activities
  - H<sub>2</sub> Sensing Materials for SOFCs
  - Theoretical Investigations of High Temperature Oxide Sensor Materials
  - Thermal Emission Based High Temperature Sensing
  - Optical Fiber Materials Research and Development
  - Embedding of Sensors for High Temperature Applications
  - pH and CO<sub>2</sub> Sensing Materials for Subsurface Applications
- Summary and Conclusions

# **Materials and Device Research Focus Area**

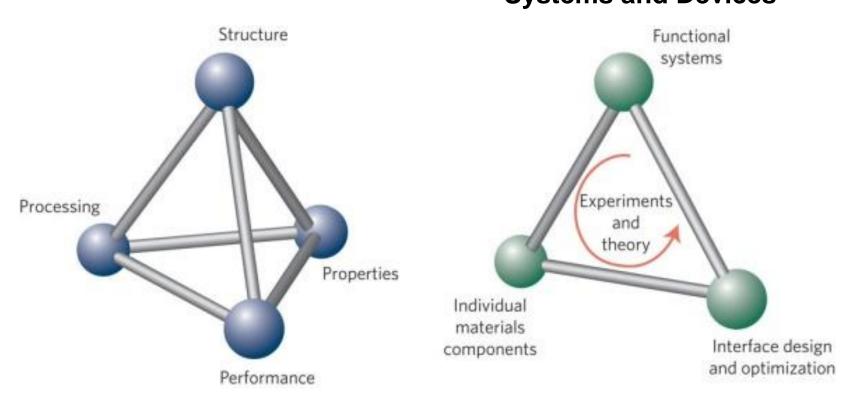


### **Functional Material Development for Devices and Systems**

#### Classic Materials Science Paradigm

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Emerging Paradigm Materials Interface with Functional Systems and Devices

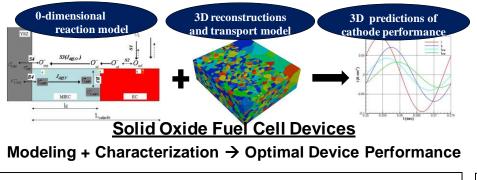


Materials Research Targeted at Device and System Level Benefits



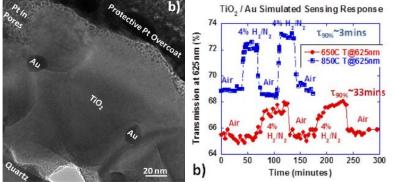
## **Materials and Device Focus : Functional Material Team**

#### **Current Fiscal Year 2016**



Solid Oxide Fuel Cell Materials / Devices Function and Durability

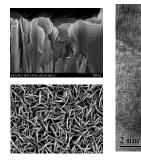
#### **Current Fiscal Year 2016**

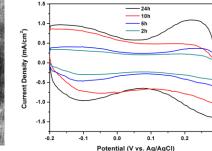


Sensor Materials / Devices Chemical and Temperature Sensing

#### **Ended Fiscal Year 2014**

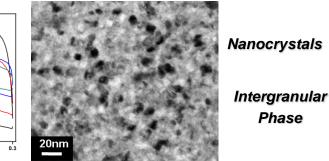
0.148 nm





Energy Storage Materials / Devices Enhanced Performance

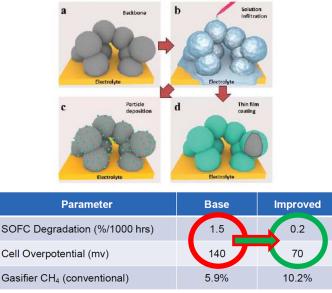
#### **Current Fiscal Year 2016**



Soft Magnetic Materials / Devices Inductors and Sensors

## **Solid Oxide Fuel Cell Material / Device Development**

#### SOFC Materials Engineering for Improved Device Figure of Merits



Kristin Gerdes, "Advanced Coal Power Systems: Competing in Multiple Market Scenarios," 13<sup>th</sup> Annual SECA Workshop, July 24, 2012, Pittsburgh, PA

#### Supports DOE NETL SECA Program

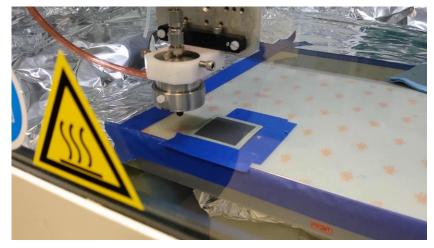
- *Reduce* cell production / operation costs
- Enhance cell activity / efficiency
- Improve cell lifetime (40+ khr)

#### Key Success = Cathode Infiltration

Commercially scalable

process developed at NETL :

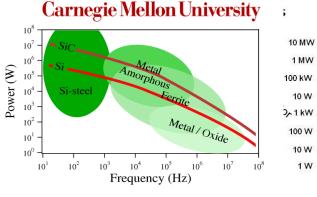
10%  $\uparrow$  in peak power, 33%  $\downarrow$  in degradation, 200%  $\uparrow$  in lifetime



On-going Industrial Collaborations Demonstrating Performance Improvements on Commercial Cells

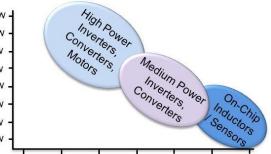
SOFCs Also Offer Many Advantages at Distributed Generation Scale

## **Soft Magnetic Material / Device Development**





**Power and Energy Applications** 



60 Hz 1 kHz 10 kHz 100 kHz 1 MHz 10 MHz 100 MHz



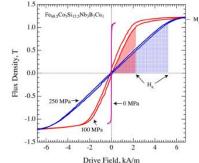
Previously Supported by ARPA-E Solar ADEPT

#### **Currently Supported by DOE EERE SETO**

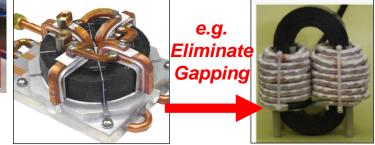
- Manufacturing Research of alloys and magnetic cores
- Transformer / Converter functionality, cost, and efficiency
- Current / Field Sensor functionality, cost, and telemetry

#### Key Success = Tunable

#### Permeability Alloys



Tunable Permeability Enables New Device Innovations



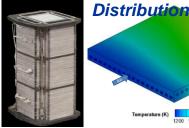
On-going Alloy and HF Transformer Development

Overall Capabilities are Housed Across CMU, NETL, and NASA GRC

# Harsh Environment Sensor Material / Device Development

	Short Term Focus			
	Coal Gasifiers	Combustion Turbines	Solid Oxide Fuel Cells	Advanced Boiler Systems
Temperatures	Up to 1600°C	Up to 1300°C	Up to 900°C	Up to 1000°C
Pressures	Up to 1000psi	Pressure Ratios 30:1	Atmospheric	Atmospheric
Atmosphere(s)	Highly Reducing, Erosive, Corrosive	Oxidizing	Oxidizing and Reducing	Oxidizing
Examples of Important Gas Species	H <sub>2</sub> , O <sub>2</sub> , CO, CO <sub>2</sub> , H <sub>2</sub> O, H <sub>2</sub> S, CH <sub>4</sub>	O <sub>2</sub> ,Gaseous Fuels (Natural Gas to High Hydrogen), CO, CO <sub>2</sub> , NO <sub>x</sub> , SO <sub>x</sub>	Hydrogen from Gaseous Fuels and Oxygen from Air	Steam, CO, CO <sub>2</sub> , NO <sub>3</sub> , SO <sub>X</sub>

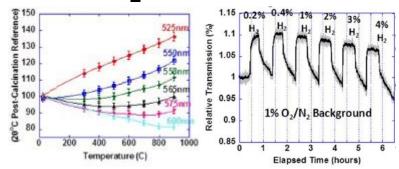
#### Example : Solid Oxide Fuel Cells Internal Gas and Temperature



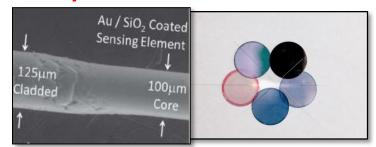
- Incompatible with Traditional Sensing Technologies
- 1) Limits of High Temperature Electrical Insulation
  2) Limited Access Space
- 3) Requires Multi-Point Sensing
- 4) Electrified Surfaces
- 4) Electrified Surfaces
- 5) Flammable Gas Atmospheres

## <u>Key Success = In-Situ Anode</u>

#### Stream H<sub>2</sub> and Temp. Sensor



#### Low-Cost, Multi-Parameter (H<sub>2</sub>, T), Compatible with Distributed



#### Supports DOE NETL Crosscutting Program

- Enabling / demonstrating new embedded sensor technology
- Accessing high-value process information

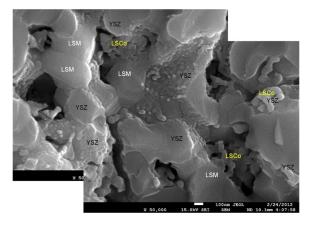
On-going Technology Development and Testing in Operational SOFCs

Sensor Development for Distributed, Multi-Parameter Monitoring



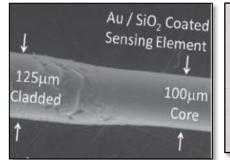
### **Example of Cross-Disciplinary Research**

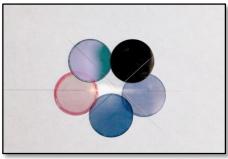
SOFC Materials Engineering for Improved Device Figure of Merits



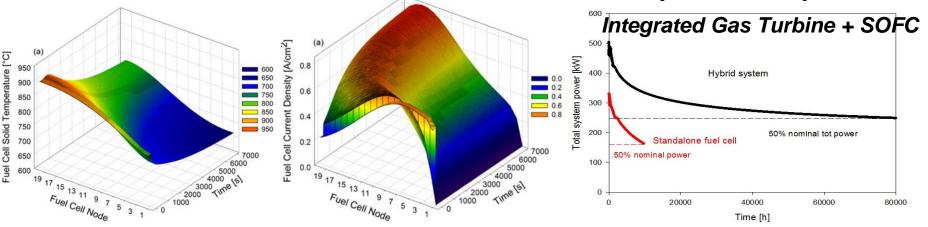
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Sensor Materials Engineering to Enable Harsh Environment Sensors for Embedded SOFC Monitoring





Hybrid Power Systems



Combining Device Performance and Embedded Sensing Information with Advanced Controls in Hybrid Power Systems to Maximize Efficiency / Lifetime / Flexibility.

### High Temperature Functional Electroceramic Oxides and Integration with Devices

Computational Chemistry: Density Functional Theory, Bandstructure, Thermodynamics

Synthesis and Processing: Bulk, Thin Film, Single Crystal Growth, Infiltration

Electrochemical Properties: Surface and Bulk Reaction Thermodynamics / Kinetics

Functional Properties: Electronic, Optical, and Magnetic

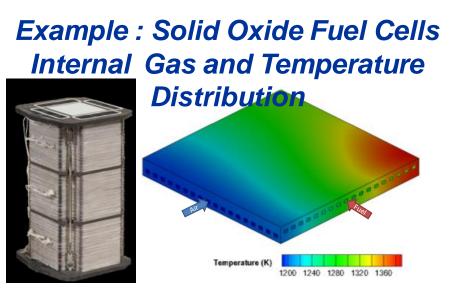
Device Integration and Application Relevant Testing

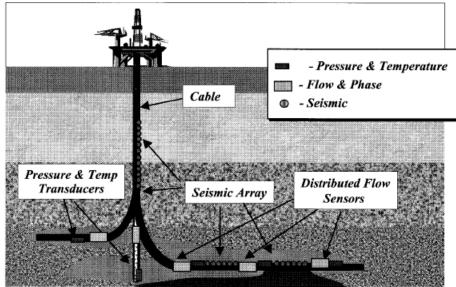
Research Efforts in Functional Oxide Material Research Spanning Use-Inspired Basic to Application Relevant Device Testing

# NETL Sensor Material and Optical Fiber Sensor Program Overview



## **NETL Needs / Capabilities in Harsh Environment Sensing**



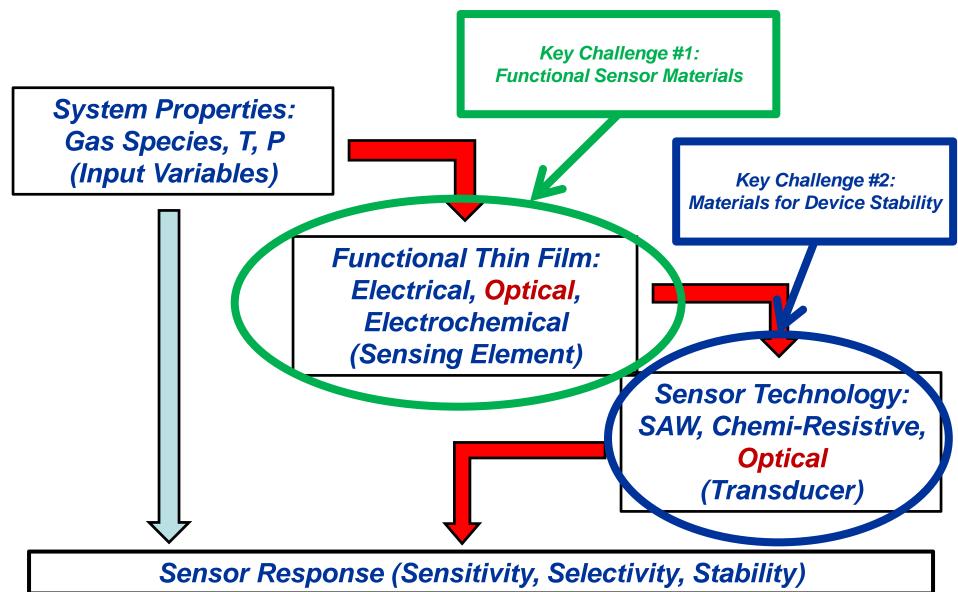


High Temperature Power Generation Systems

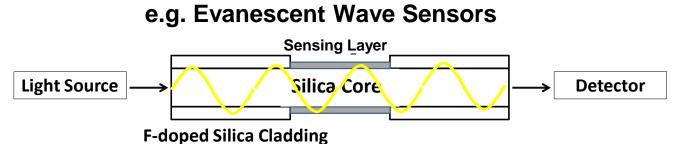
High Temperature, High Pressure Subsurface Wellbores and Geological Formations

NETL Has Needs, On-going Funded Projects, and In-House Research Activity in Harsh Environment, Low Cost Sensing for a Broad Array of Applications

### **Sensor Materials in Harsh Environment Sensing Applications**



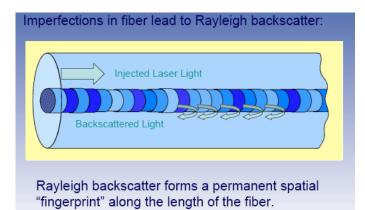
### **Emphasis on Optical Based Sensing Platforms / Materials**



- → Elimination of Electrical Wiring and Contacts at the Sensing Location
  - → Can Be Tailored to Particular Parameters of Interest Through Integration with Functional Materials
- → Eliminate EMI and Potential Interference with Electrical and Electrified Systems
  - Compatibility with Broadband and Distributed Interrogation

#### Optical Backscattering Based Reflectometry



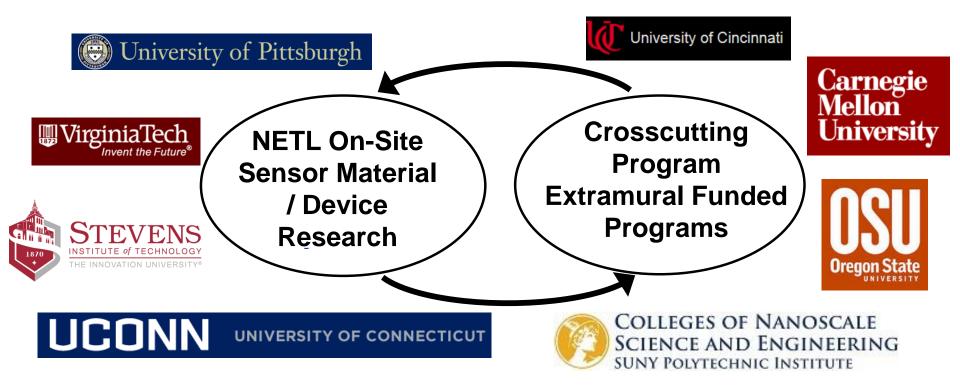


Optical Fiber Based Sensors are Particularly Well-Suited for Harsh Environment and Electrified System Applications.

#### **Leveraging Partnerships with Extramural Funded Projects**

10 – Joint Publications (U. Pitt, U. Albany, OSU, U. Conn. VA Tech)

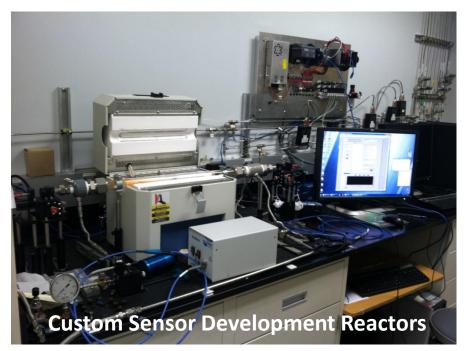
4 – Joint Patent Applications (U. Pitt., Stevens, OSU)



NETL On-Site Research Efforts Both Benefit From and Provide Additional Value to Extramural Solicited Programs in Related Areas.

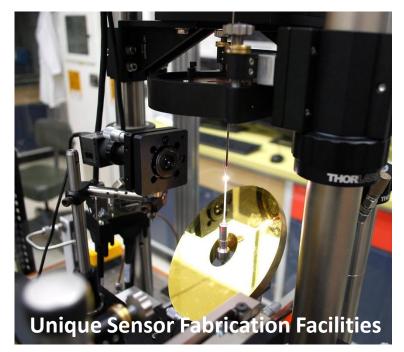
NETL Manages Major Extramural Research Activity in Harsh Environment Sensing.

#### **Unique Facilities of the On-Site Research Team**



**Custom Sensor Development Reactors Simulate:** 

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





NETL On-Site Research Has Developed Capabilities for Necessary for Sensor Material and Optical Fiber Sensor Device Development and Optimization for Harsh Environment Applications.

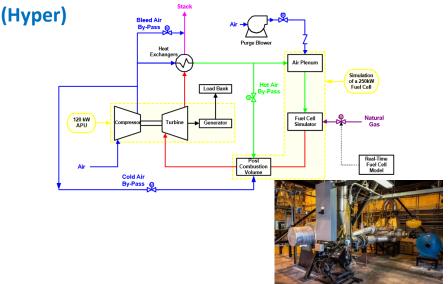
## **Pilot-Scale Combustion, Turbine, and SOFC Facilities at NETL**

#### 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**



- 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.

Sensor Development Efforts Benefit from Access to Pilot Scale Facilities for Demonstration

of Prototype Sensor Devices in Near-Application Environments.

### **On-Site Research Targets Embedded Sensing**

### Internal Gas and Temperature



Gas and Temperature Distribution SOFCs: Incompatible with Traditional Sensing Technologies

1) Requires High Temperature Electrical Insulation

2) Limited Access Space

Temperature : 700-800°C Anode Stream : Fuel Gas (e.g. H<sub>2</sub>-Containing) Cathode Stream : Air or O<sub>2</sub>

3) Only Single-Point, Single-Parameter Sensing

Gradients in Temperature and Composition of Gas Stream Internal to an SOFC are Critical Process Parameters for Maximized Efficiency / Lifetime.

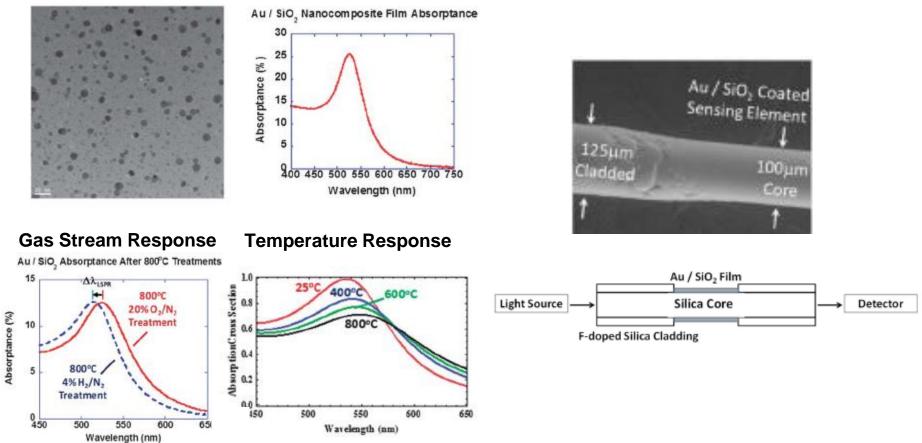
In-House Efforts Have Exploited the SOFC Technology as a Demonstration Platform for Harsh Environment Embedded Sensors in Electrified Components.



# Highlights of Recent Successes and On-going Activities



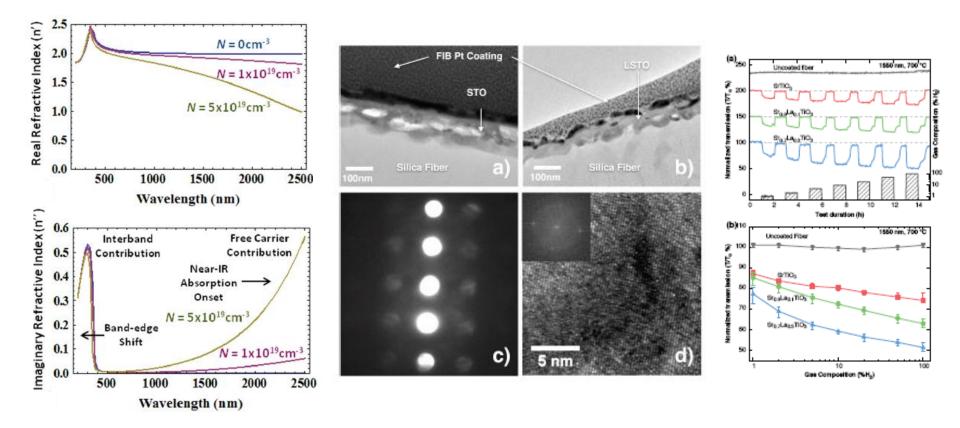
### **Plasmonic Nanocomposites for Optical Sensing**



Au-Nanoparticle Incorporated Oxides Have Been Integrated with the Optical Fiber Sensing Platform to Functionalize for Temperature and Gas Stream Composition.

Broadband Wavelength Interrogation Allows for Multiparameter Monitoring Using a Single Sensor Element at Temperatures Relevant for Operational SOFCs (700-800°C).

#### **Plasmonic Oxides for Optical Sensing**

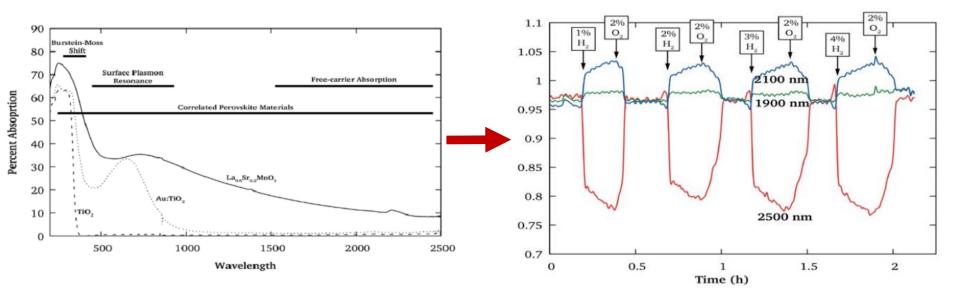


High Electronic Conductivity Oxides Have Been Demonstrated to Show Enhanced Sensing Responses as Compared to Traditional Sensing Oxides.

Perovskite Oxides Traditionally Used for SOFC Electrode Materials Have Been Leveraged as Sensing Materials in the Same Technology Platform.

#### **Correlated Perovskite Oxides for Optical Sensing**

La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub> and Related Perovskite Sensor Materials



Nanophotonic Materials XII, edited by Stefano Cabrini, Gilles Lérondel, Adam M. Schwartzberg, Taleb Mokari, Proc. of SPIE Vol. 9545, 954501 · © 2015 SPIE · CCC code: 0277-786X/15/\$18 · doi: 10.1117/12.2188924

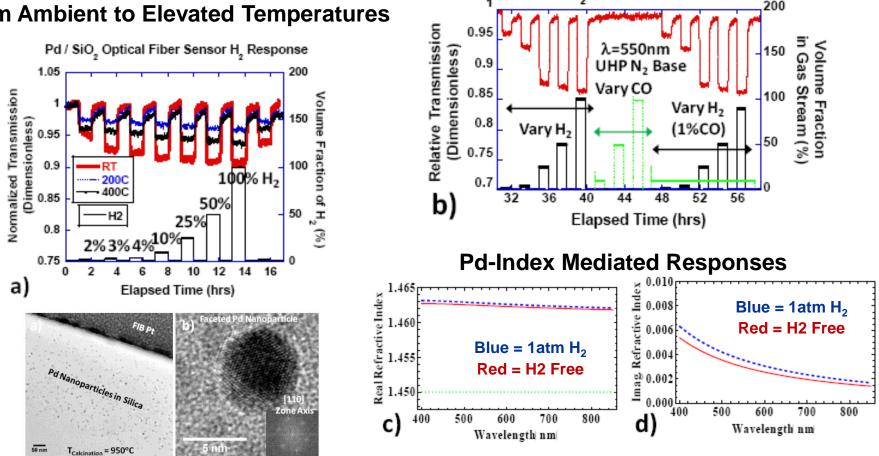
#### Correlated Perovskite Oxides are Currently Being Investigated in More Recent Efforts with Interesting Preliminary Results

Basic Optical Properties in this Class of Oxides are Not Well Understood Due to Strong Electron – Electron Correlations

### **Pd-Nanoparticle Incorporated Oxides for Optical Sensing**



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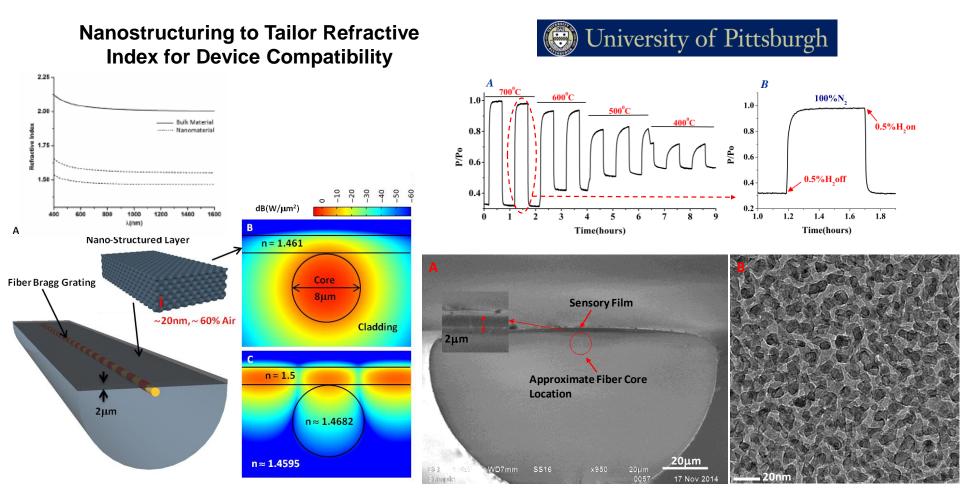


Optical Transmission Modifications for Pd-SiO2 and Related Systems are Associated with Changing Real and Imaginary Refractive Indices of Pd Nanoparticles Due to H2 Absorption in Bulk Lattice.

NATIONAL ENERGY TECHNOLOGY LABORATORY

Pd / SiO, Optical Fiber Sensor

### **Nanostructuring of Functional Oxides for Optical Sensing**

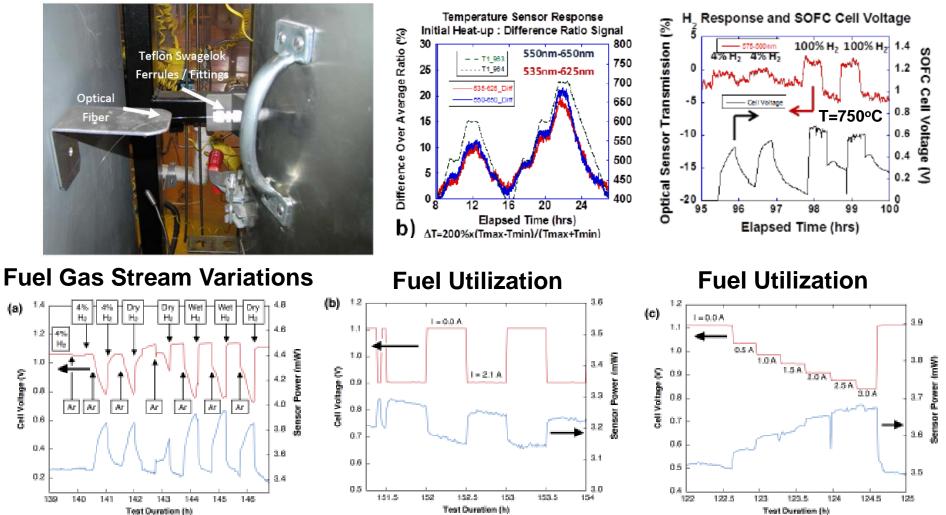


For Oxide-Based Functional Sensor Layers, Engineering of Sensing Layer Porosity can Enhance Responses for Thick Film Sensing Layers.

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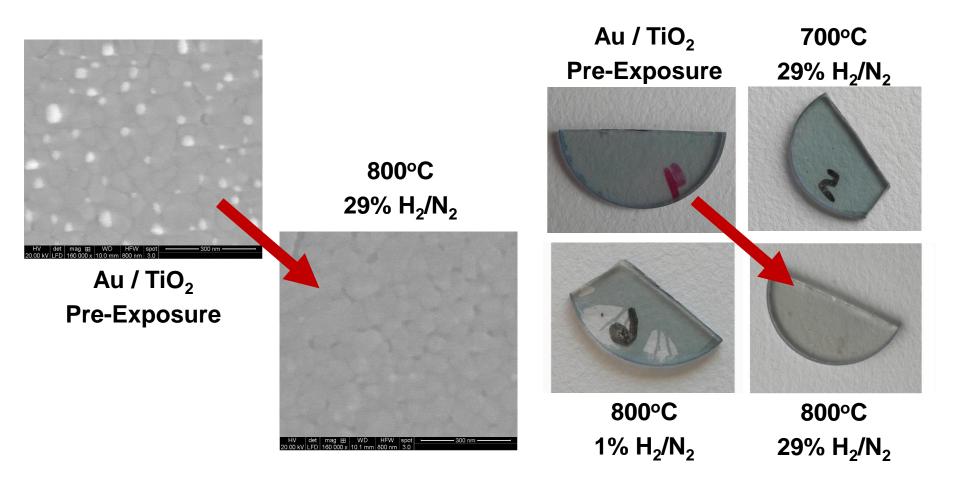
#### **Demonstrations in Operational SOFC Systems**



Optical Fiber Sensors Have Been Demonstrated for Temperature and H<sub>2</sub> Concentration in Operational SOFCs with Correlations to Electrochemical Potential and Fuel Utilization.

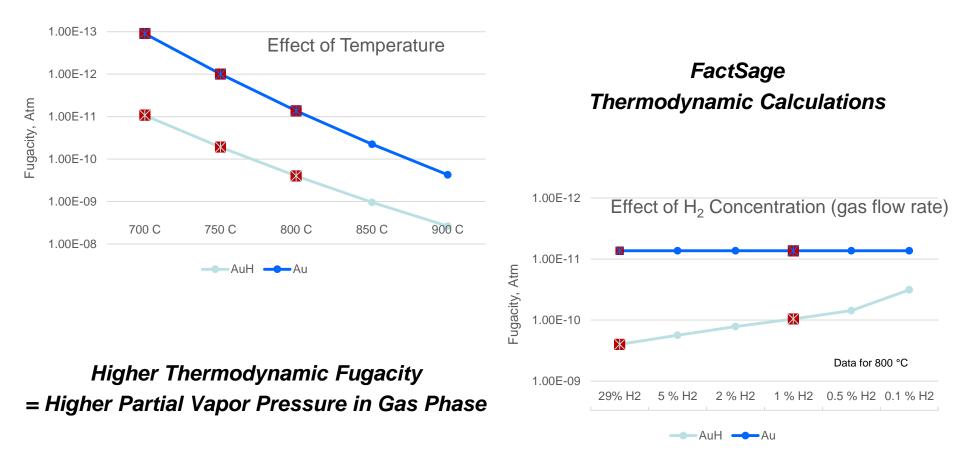
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#### "Realistic" Exposure Testing of Sensor Materials

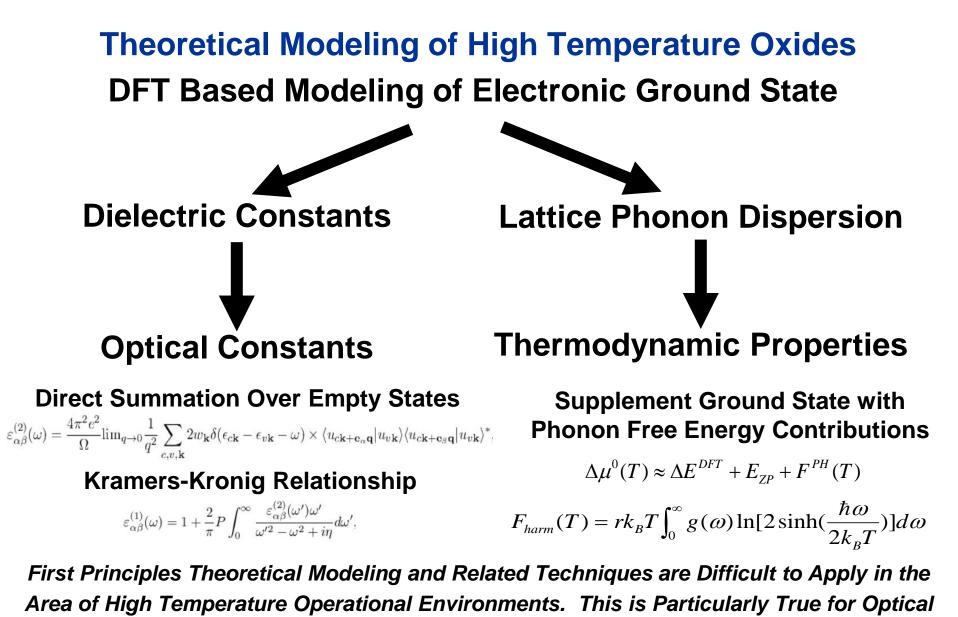


Application Relevant Exposures Illustrate Gas Composition Dependent Instabilities with Mass Loss of Au From the Substrate for Week-Long Exposures at ~800°C.

### "Realistic" Exposure Testing of Sensor Materials

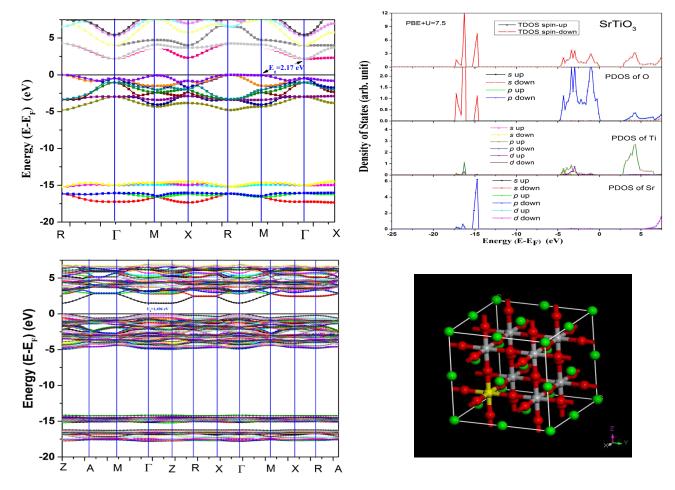


The Mechanism Has Been Confirmed as Reactive Evaporation Based on Thermodynamic Calculations and Mitigation Strategies Are Being Developed.



and Electronic Properties of Materials Which are Related to Bandstructure.

### **Theoretical Modeling of High Temperature Oxides**



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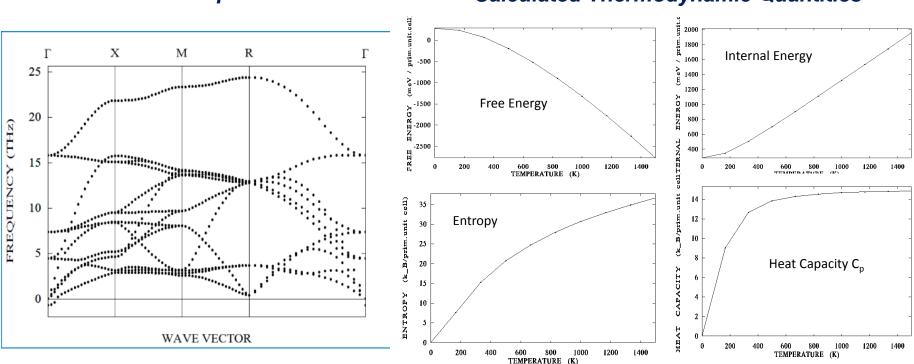
DFT+PBE+GGA+U U(Ti(3d))=7.5 The calculated band-gap: 2.17 eV (indirect) 3.03 eV (direct)

Adjusted U-Parameter for Greatest Consistency with Experiment

La – Doping Adds an Electron to the Conduction Band and is Predicted to Result in Spin Polarization

SrTiO<sub>3</sub> and Doped Variants are a Starting Point for the Calculations Due to Relative Simplicity and a Large Number of Previous Investigations.

## **Theoretical Modeling of High Temperature Oxides**



**Phonon Dispersion** 

**Calculated Thermodynamic Quantities** 

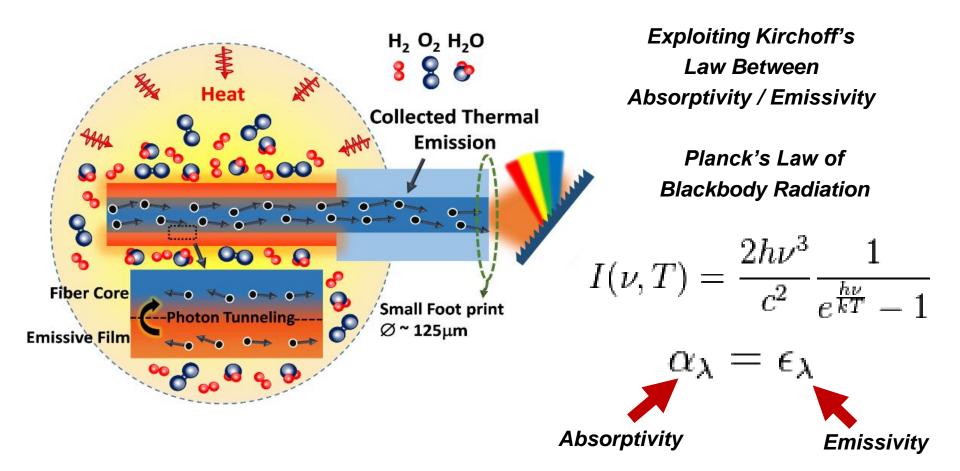
1 f.u. in primitive cell. N=5 3N vibrations with 15 branches

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Derived from DFT Electronic Ground State

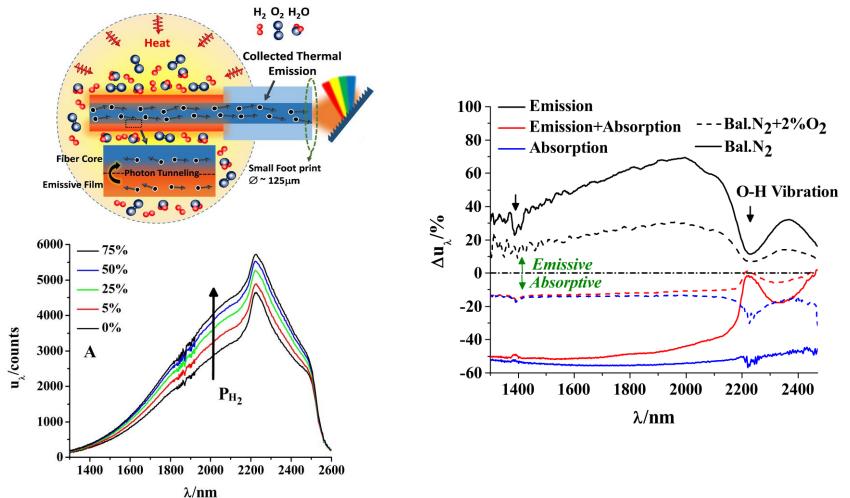
Phonon Dispersion for SrTiO<sub>3</sub> Has Been Calculated and is Being Used to Estimate Thermodynamic Parameters for Finite Temperature Simulations.

#### **Thermal Emission Based Sensing**



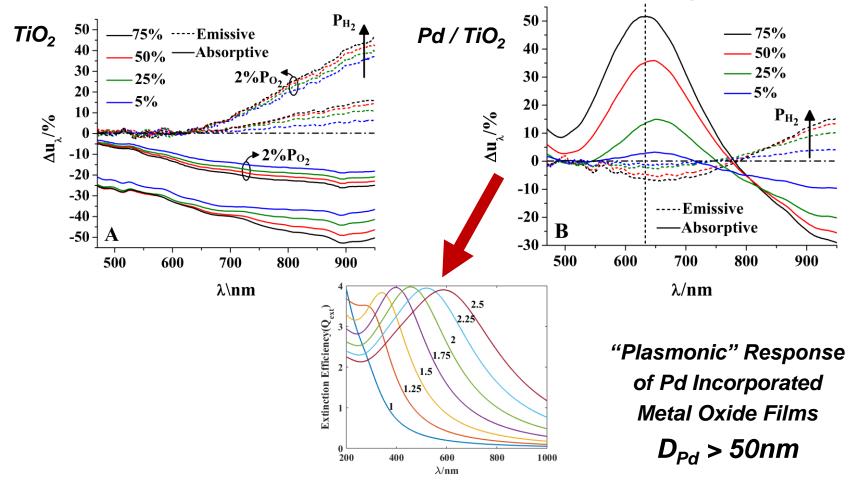
Thermal Energy Harvesting "Source-Free" Based Fiber Optic Chemical Sensors are Now Possible By Leveraging Thermal Emission Properties of Sensing Materials. We are Working to Understand How This Discovery Can Be Fully Leveraged.

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#### **Thermal Emission Based Sensing**

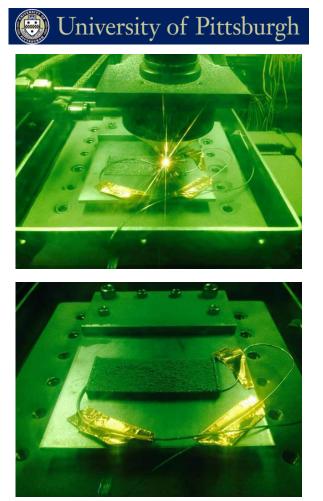


Thermal Emission Based Sensing Responses Can Be Observed in the Visible Range, Albeit Reduced in Magnitude Relative to Near-IR Emission Based Responses.

We Believe that Visible Range "Plasmonic" Sensing Activity was Observed for Pd / TiO2, and Are Working to Confirm with Films Deposited on Planar Substrates.

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### **Additive Manufacturing Based Sensor Embedding**



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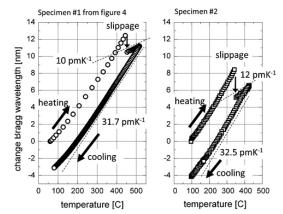


Fig. 5. Measured Bragg wavelength over temperature during temperature cycling for two samples where slippage occurred.

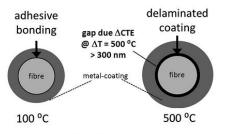


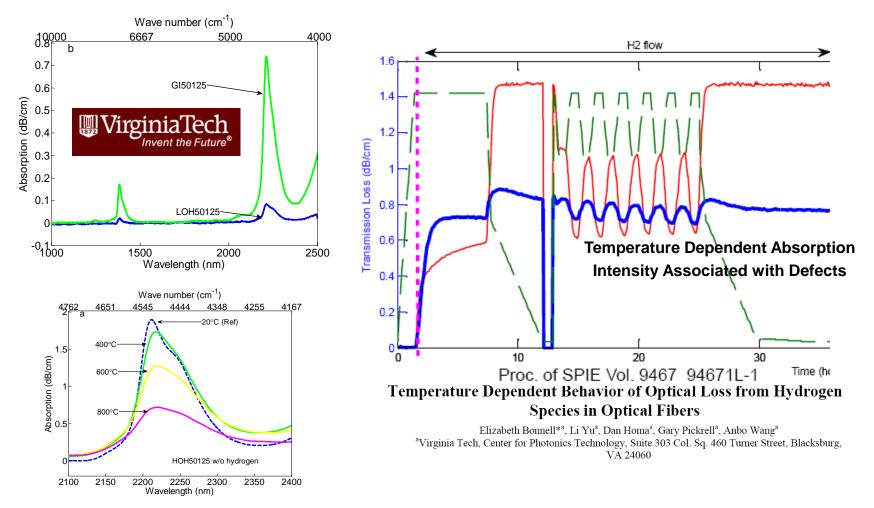
Fig. 6. Schematic visualisation of the delamination of the nickel coating from the silica fibre. Due to different CTE, estimates indicate gaps of more than 300 nm between fibre and metal coating.

Temperature and Strain Measurements With Fiber Bragg Gratings Embedded in Stainless Steel 316

Dirk Havermann, Jinesh Mathew, William N. MacPherson, Robert R. J. Maier, and Duncan P. Hand JOURNAL OF LIGHTWAVE TECHNOLOGY, VOL. 33, NO. 12, JUNE 15, 2015

Techniques for Embedding of Temperature and Strain Sensors Using Additive Manufacturing and Compatible with High Temperature Operational Environments are New Efforts for the Team Moving Forward. NATIONAL ENERGY TECHNOLOGY LABORATORY

## **High Temperature Stability of Silica Based Optical Fibers**

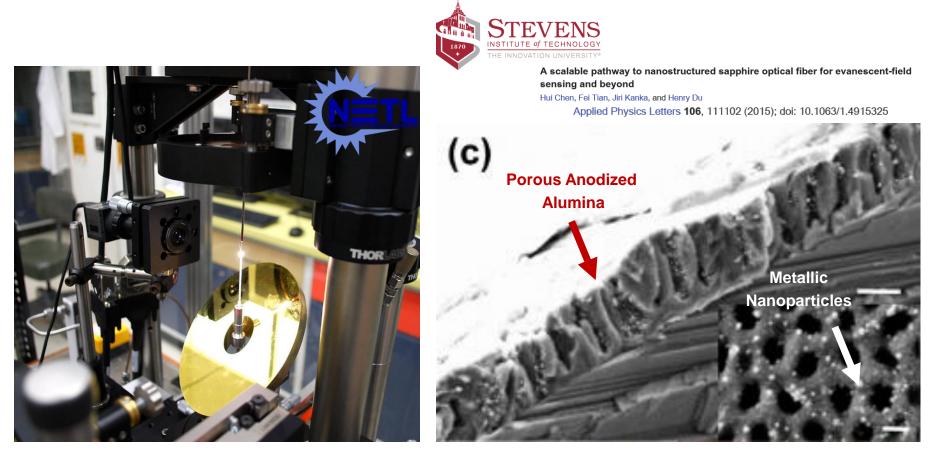


Understanding the Stability of Silica Based Optical Fiber Sensors Under High Temperature and Non-Ambient Conditions is an Area of Important Investigations.

OH- Defects Play an Important Role in the Near-Infrared Wavelength Range.

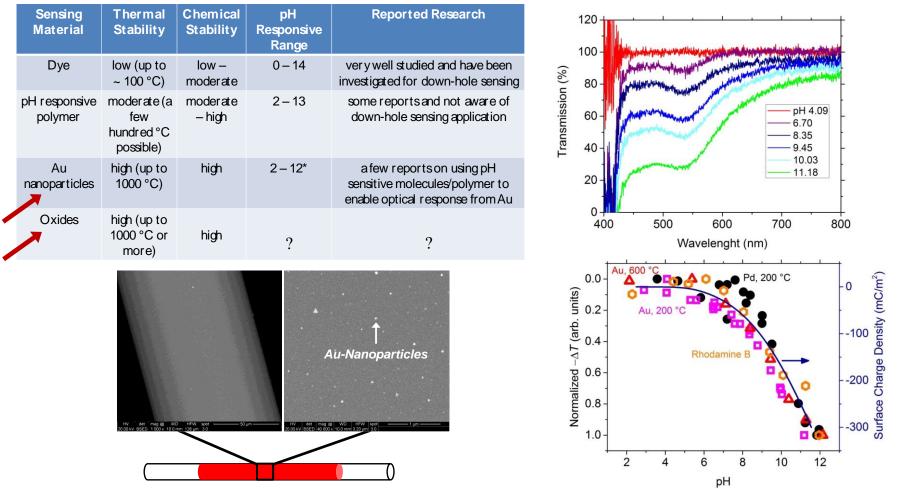
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### **High Temperature Stable Alternative Fibers and Claddings**



Investigation of New High Temperature Stable Optical Fiber Materials and Associated Claddings is an Area for Significant Future Research within the Group. Current Collaborative Research is On-Going in the Area of Anodized Aluminum Oxide Based Claddings and Associated Functionalization.

### Subsurface pH Sensing in Geological Formations



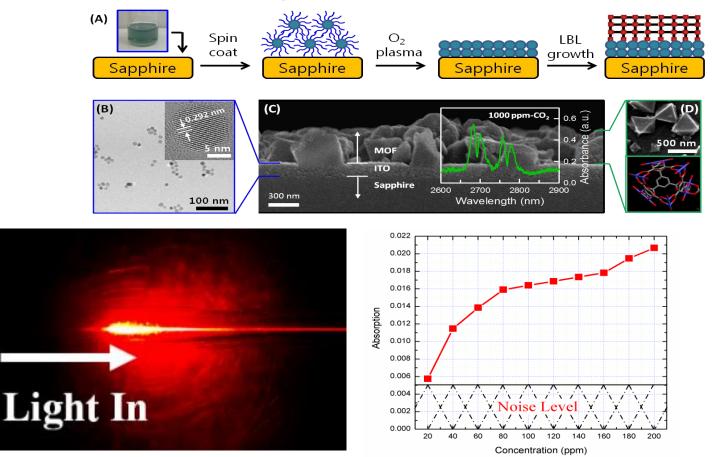
Optical Sensing Responses Associated with the Surface Charging Behavior of Metal Oxide Nanoparticles Has Been Demonstrated to Yield Reversible pH Sensing.

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Experimental Work Combined with Optical Waveguide Modeling Suggests the Observations are Associated with Ionic Adsorption at Sensor Layer Surfaces.

### **Subsurface CO<sub>2</sub> Sensing in Geological Formations**

Metal-organic framework (MOF) thin films



Metallorganic Framework Materials Have Been Pursued for Direct CO<sub>2</sub> Sensing Applications, and Combined with Plasmonic Nanoparticles in Some Cases. Investigations are Underway to Explore New Metallorganic Framework Materials and to Minimize Impacts of Water on CO<sub>2</sub> Sensing Responses.

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Oregon State

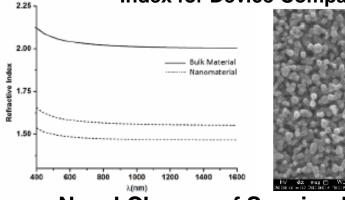
# **Summary and Conclusions**

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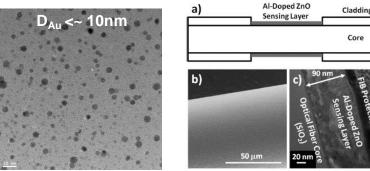


### **Collaboration and Licensing Opportunities**

Nanostructuring to Tailor Refractive Index for Device Compatibility



**Novel Classes of Sensing Materials** 



Sensor Material Approaches for Harsh Environment Sensing



Novel Sensor Applications in a Solid Oxide Fuel Cell Environment

A Significant Patent Portfolio Has Been Established and Collaboration / Licensing Opportunities Exist.

The Team is Always Interested in Engaging in Collaborative Relationships That Can Help us Move the Technology Forward and Into the Commercial Sector.

### **Summary and Conclusions**

- NETL Has a Well Established Focus Area in Materials and Devices Applied to a Range of Energy Related Problems
- NETL Has Excellent Capabilities for High Temperature and Harsh Environments Sensor Material and Device Development and Testing
- Functionalized Optical Fiber Sensors Show Great Promise for a Range of Energy Related Applications
- NETL Has Active In-House Research In a Broad Range of Areas
  - Power Generation
  - Subsurface CO2 Storage / Oil & Gas
  - Natural Gas Pipelines



• We are Always Interested in Collaboration Opportunities as Well as Joint Technology Development and/or Licensing of Patented Concepts

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