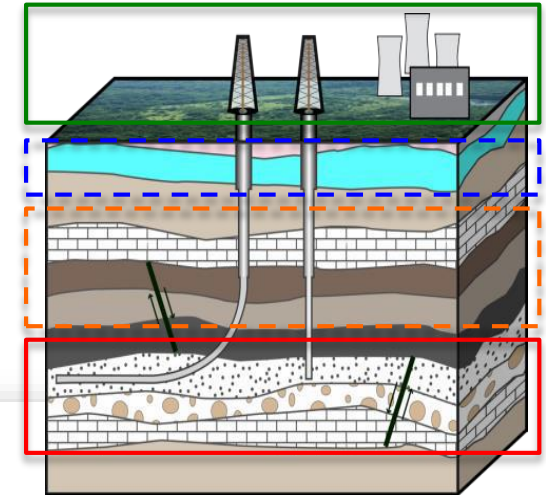
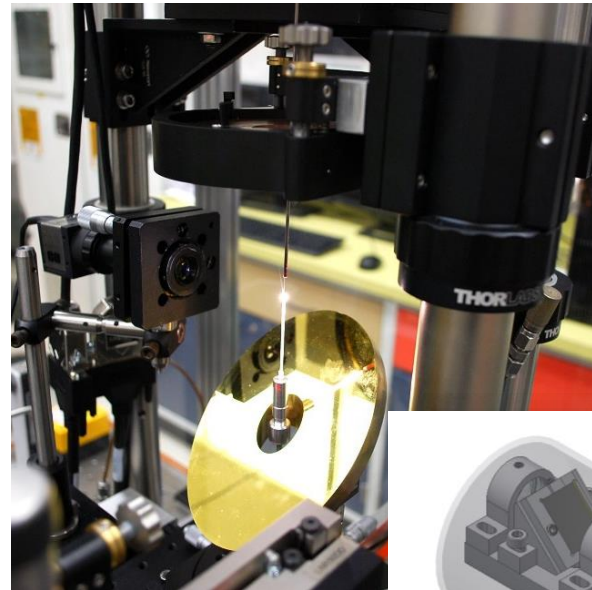
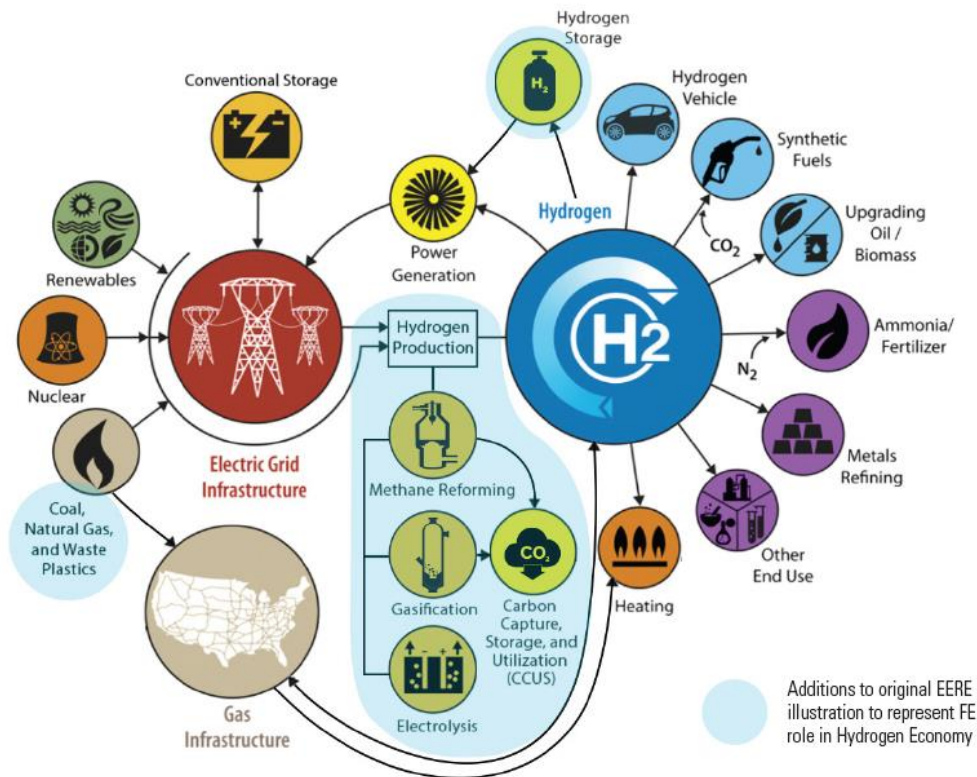


Advanced Sensors and Controls for Hydrogen with Carbon Management Applications

NETL FWP-1022427 and FWP-1022456

Sam Bayham

Technical Portfolio Lead, NETL



Project Overview



Agreement #: FWP-1022427 and -1022456

Funding: \$2,550,000 (FY23 funding)

Cost Share: \$0

Project Objective

- Support reduction of CO₂ emissions across the energy sector by developing sensors, instrumentation, controls, and other novel energy concepts to improve the operating flexibility of fossil energy and carbon management (FECM) systems so they may operate in an integrated manner with renewable energy and energy storage technologies to provide clean, efficient, and reliable power, with the ultimate goal of net-zero carbon dioxide emissions by 2035.

NETL PIs

Michael Buric, Benjamin Chorpening, Yuhua Duan, Dustin McIntyre, David Tucker, Rigel Woodside

Supporting Staff

Lee Aspitarte, Chet Bhatt, Michael Bowen, Jordan Chapman, Jared Charley, Leebyn Chong, Scott Crawford, Daniel Hartzler, Farida Harun, Gary Lander, Geunsik Lim, Danylo Oryshchyn, Hari Paudel, Marcus Poyer, Dan Sorescu, Jennie Stoffa, Juddha Thapa, Jeffrey Wuenschell, Biao Zhang, Nana Zhou

Project Oversight

- Eva Rodezno (FECM/HQ), Rin Burke (NETL Tech Manager), Nate Weiland (NETL Senior Fellow), Aaron Lyons (PM)

Advanced Sensors and Controls

High Level Goals of FWP

- Develop advanced sensors and controls to support development of Hydrogen with Carbon management (HCM) technologies
- Enable optimized monitoring and management using novel sensors and controls
 - Increase operational flexibility
 - Maintain or improve efficiency/availability
 - Sharply reducing carbon emissions
- Cultivate novel “outside the box” ideas for next-generation sensing or net-zero power generation



Sensors and Control Needs for HCM

[Kemper County Integrated Gasification Combined Cycle \(IGCC\) Power Plant, Mississippi - Power Technology \(power-technology.com\)](https://www.power-technology.com)

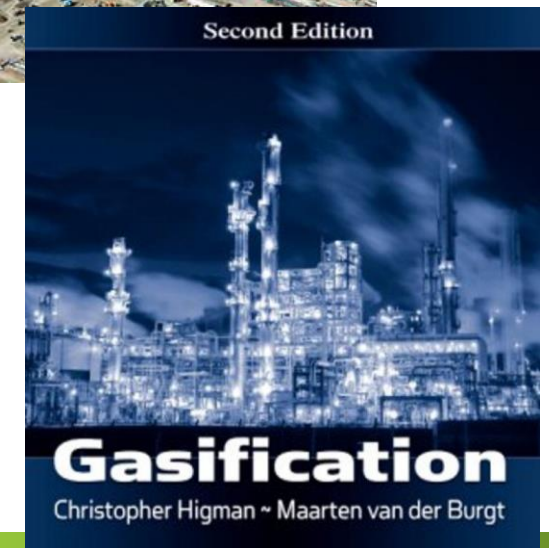
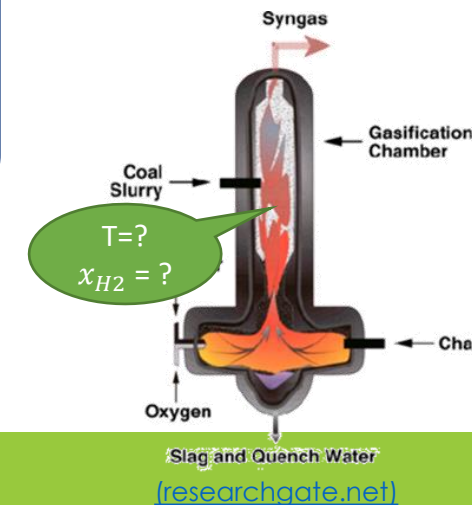


“For process control purposes, where ratios between fuel, oxygen and/or steam are known, the temperature can be calculated. This is an important aspect, as **temperatures in slagging gasifiers can only be measured with great difficulty and are generally not very trustworthy.**” – Higman and van der Burgt (2007) Gasification, 2nd edn., p. 22

We need robust sensors to measure temperature, concentration in harsh environments to ensure high efficiency, uptime, and control!

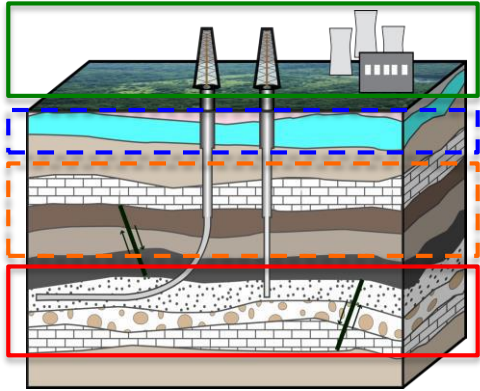
“Ensure time is allotted during the design phase to evaluate the **effect of startup, shutdown, and other transient operating scenarios such as extended turndown operation** on process design, equipment design, and controls design.” – Kemper County Gasification Final Report (2019), p. 618

We need new paradigms to study non-steady state scenarios and advanced control schemes for finer control of integrated systems



Technology Areas

Focus: Hydrogen with Carbon Management



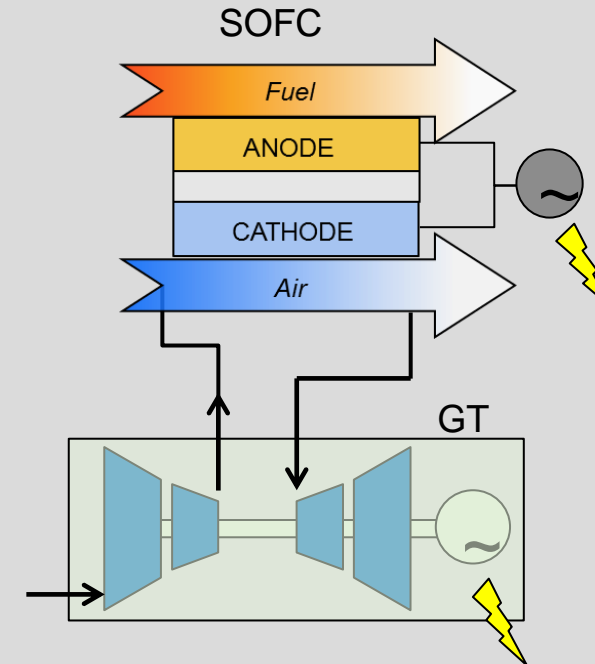
Carbon Storage and Subterranean chemistry

- Assure CO₂ storage stability
- At the Wellhead
- Downhole
- High pressure water or brine



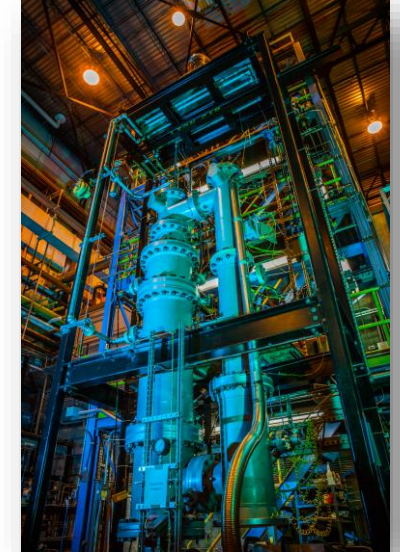
Hydrogen Production and Utilization

- Modular gasification
 - waste plastics / MSW
 - Sustainable biomass
 - Coal waste deposits
- Microwave fuel reforming
- Hydrogen/Blend GT
- SOEC
- Ammonia systems



Hybrid NG/Hydrogen Systems

- 800°C in SOFC
- 1,500°C in GT
- Transient controls
- + CO₂ storage



Novel Systems

- Direct Air Capture
- Supercritical CO₂ cycles
- Chemical Looping

Portfolio Overview

Sensors & Instruments

- High temperature optical fiber sensors
 - Crystalline fiber
 - Sensing materials
 - Interrogation
- Real-time gas composition analysis of hydrogen blends
- LIBS for subterranean sensing of fluid migration

Controls

- Cyber-physical systems as a zero-carbon integrated energy system development acceleration tool
- Online System Identification for power plants (ended)
- Cyber Physical Historian Development

Novel Concepts

- AI for screening and design of functional materials
- Quantum sensors for FECM applications
- Direct Power Extraction

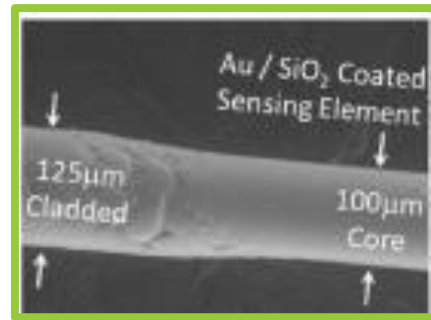
Sensors

Optical Fiber Sensing for Harsh Environments

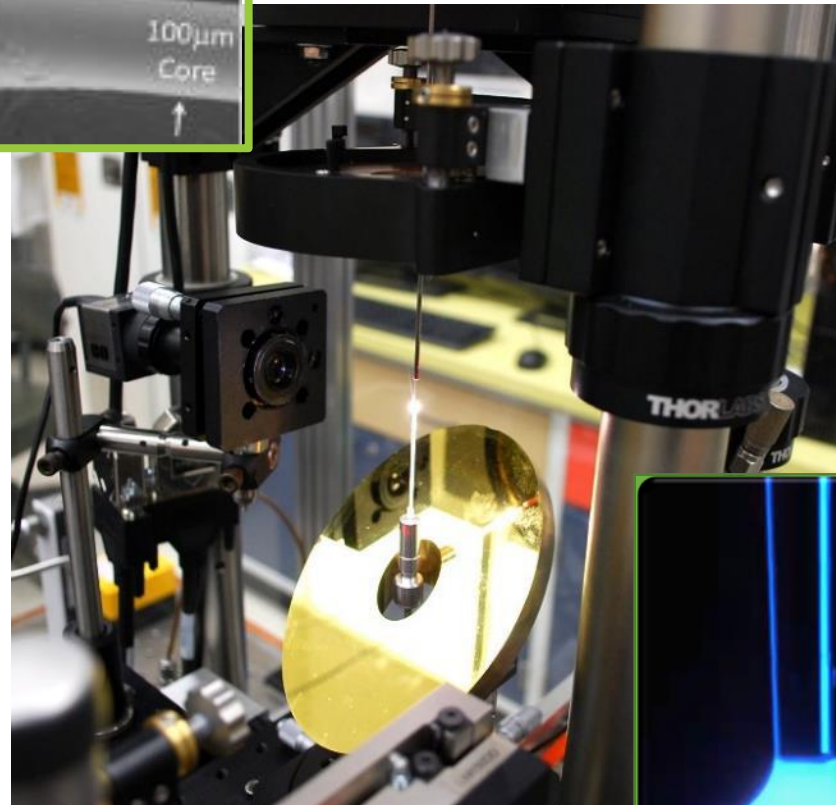
Objectives

PI: Michael Buric (michael.buric@netl.doe.gov)

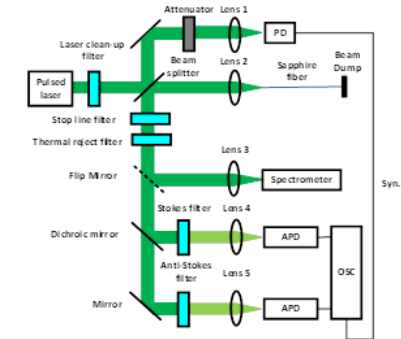
- Develop materials and methods for spatially resolved optical fiber-based sensing under harsh conditions ($>800^{\circ}\text{C}$)
- Develop low-cost **functional coating**
- Develop economic fabrication process for durable optically clad **sapphire** fiber and interrogation system



Functional nanomaterials

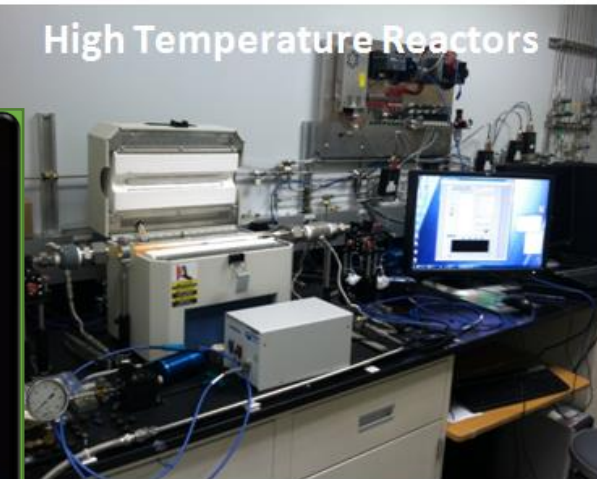


Laser Heated Pedestal Growth system



Commercial and novel multipoint interrogation

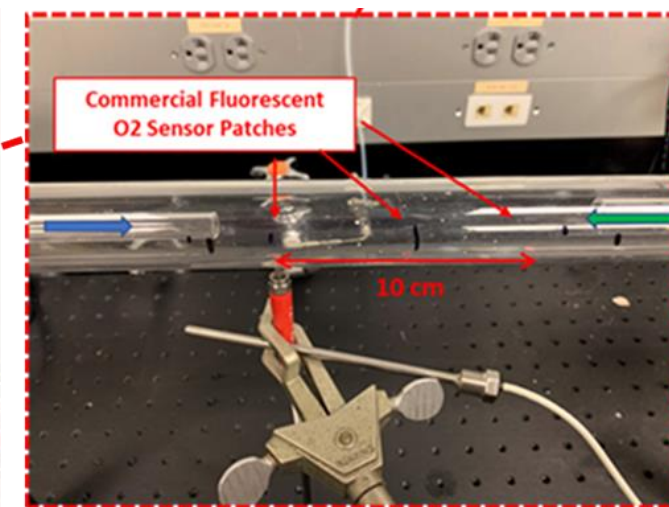
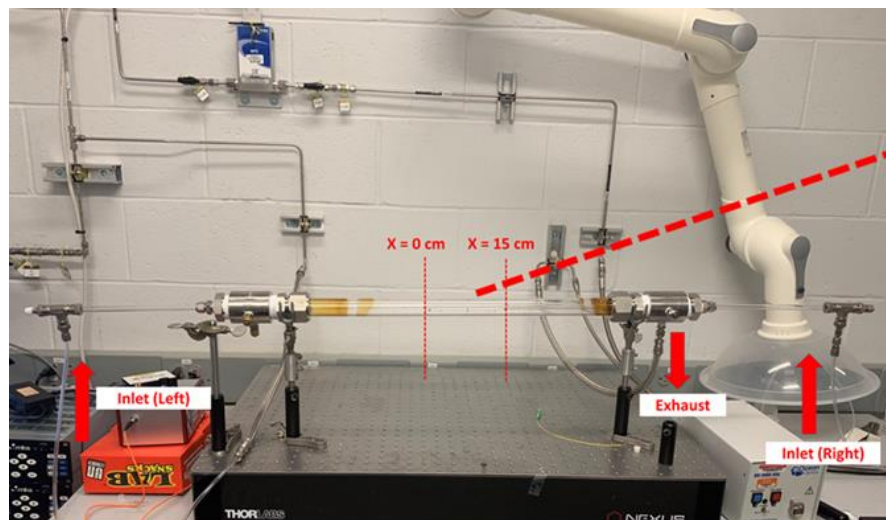
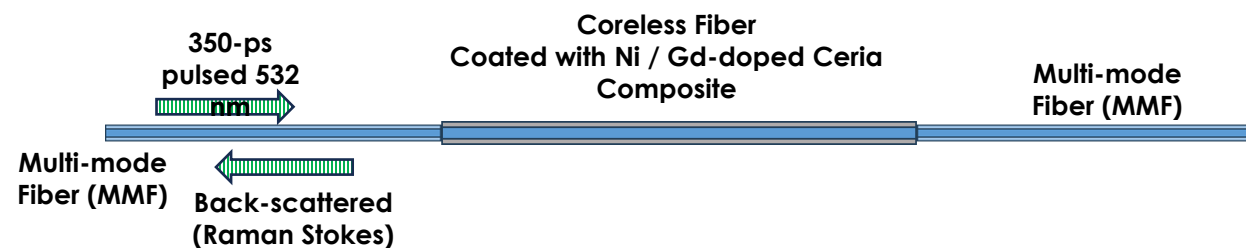
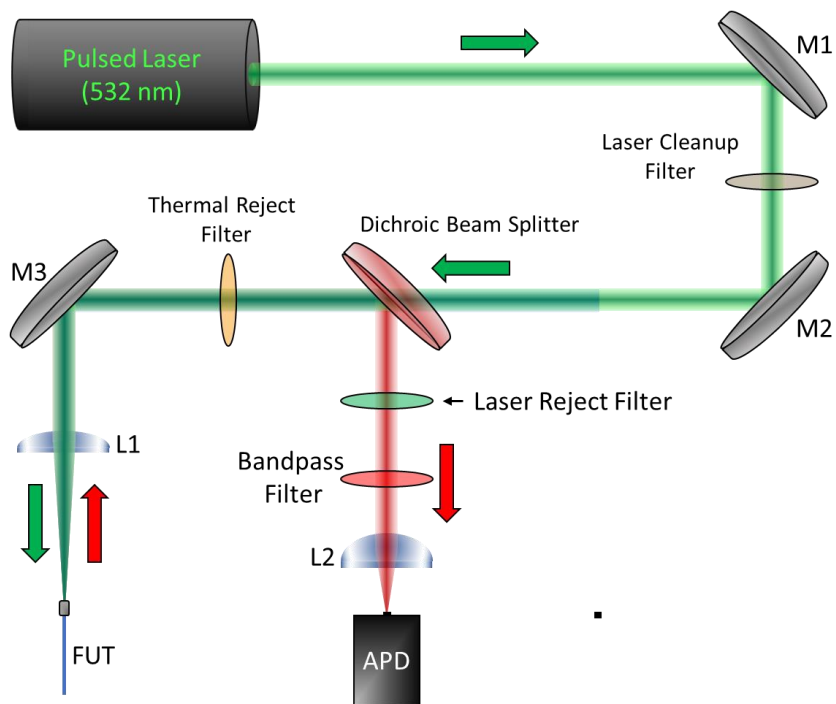
High Temperature Reactors



Fossil energy relevant gases

Optical Fiber Sensing for Harsh Environments

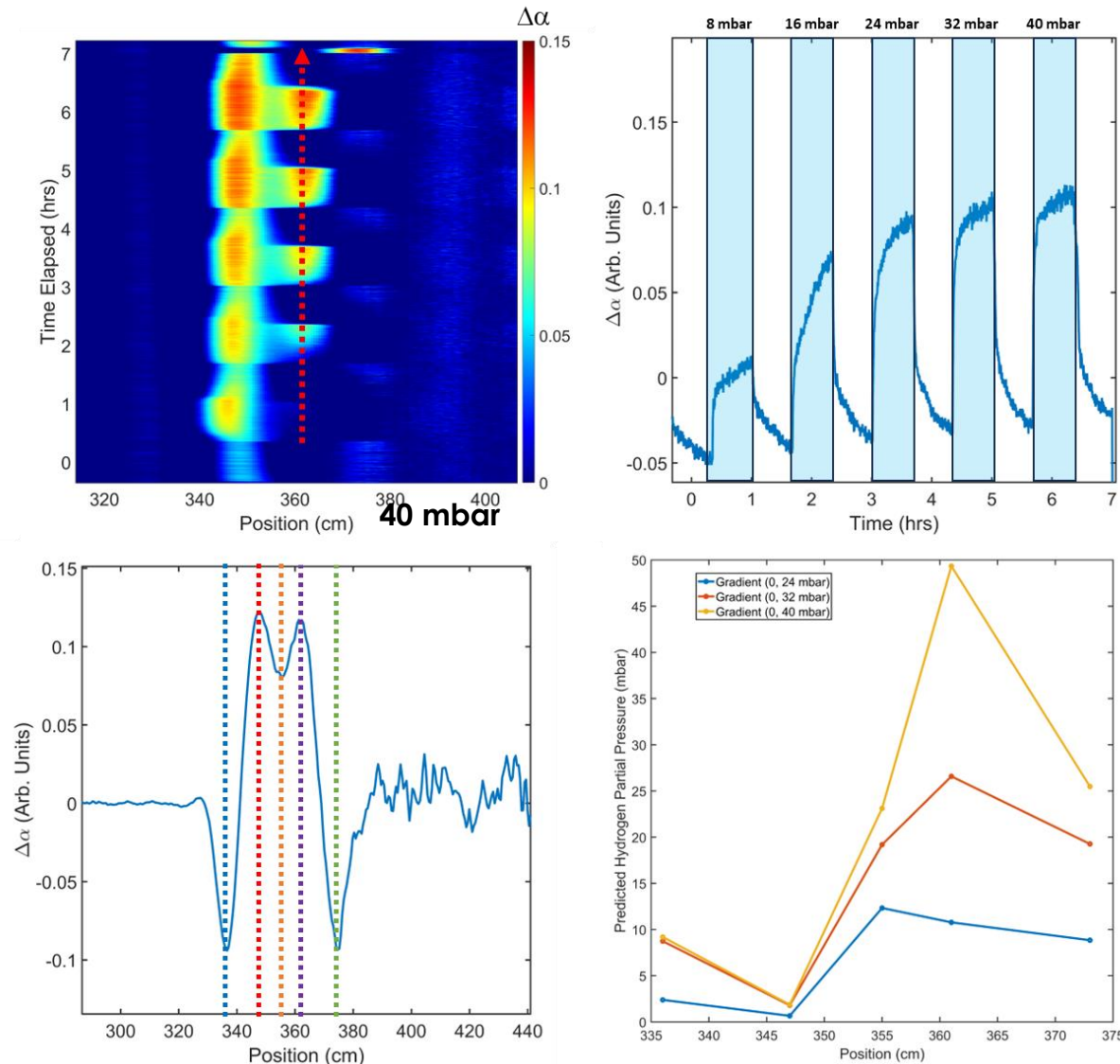
Progress



- Five different coatings tested for distributed hydrogen sensing at 700 °C
- Distributed H₂ sensing with ~40-cm of coreless silica MMF coated with Ni / Gd-doped Ceria, coated via dip coating followed by calcination.
- Tested in custom-built gas reactor for setting up gas concentration gradient.
- Interrogated with Raman optical time domain reflectometry (approximately 5-cm spatial resolution).

Optical Fiber Sensing for Harsh Environments

Progress

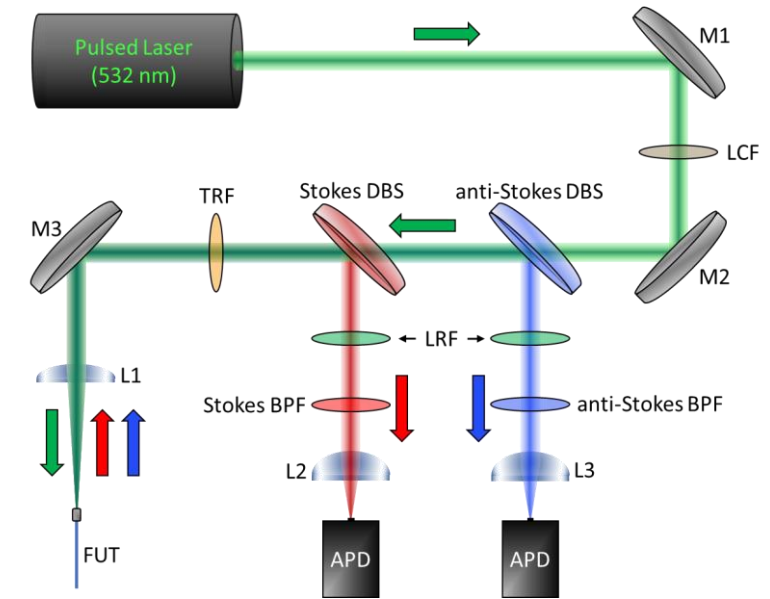
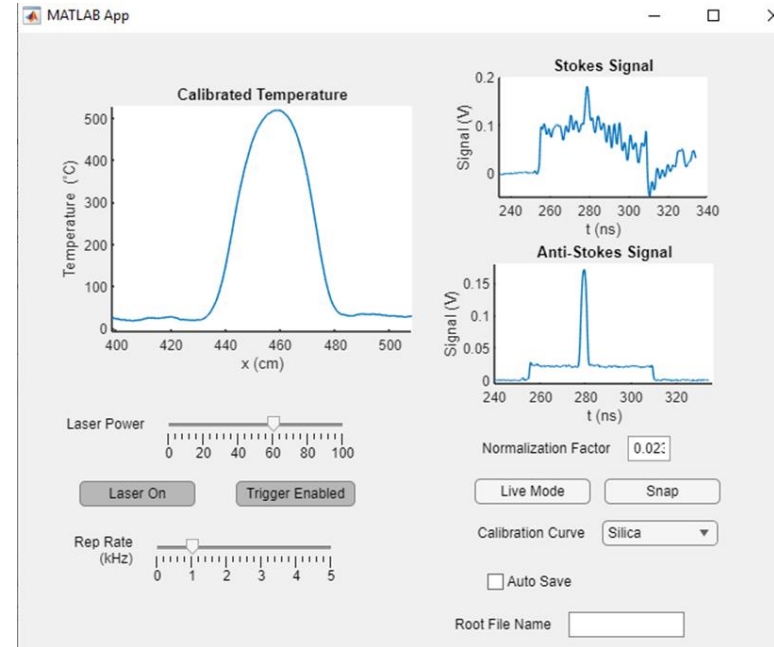


- Calibration curves were used to estimate concentration gradient across cell
- Absorptive loss vs. hydrogen partial pressure curves were generated
- Improving sensing range, sensitivity, and response time by changing coating and sintering parameters
- Test distributed hydrogen/temperature sensing in a tubular solid oxide fuel cell at NETL in May 2024

For more details, please see our SPIE proceedings paper!

Optical Fiber Sensing for Harsh Environments

Raman Distributed Temperature Sensing (DTS) System Upgrades



- Design completed for improved portability and field use: timing electronics and laser control integrated into main box
- GUI built to control all internal components and provide real-time, calibrated output of temperature vs. position for fiber sensors.
- System designed for additional features which are being added as software is refined

Optical Fiber Sensing for Harsh Environments

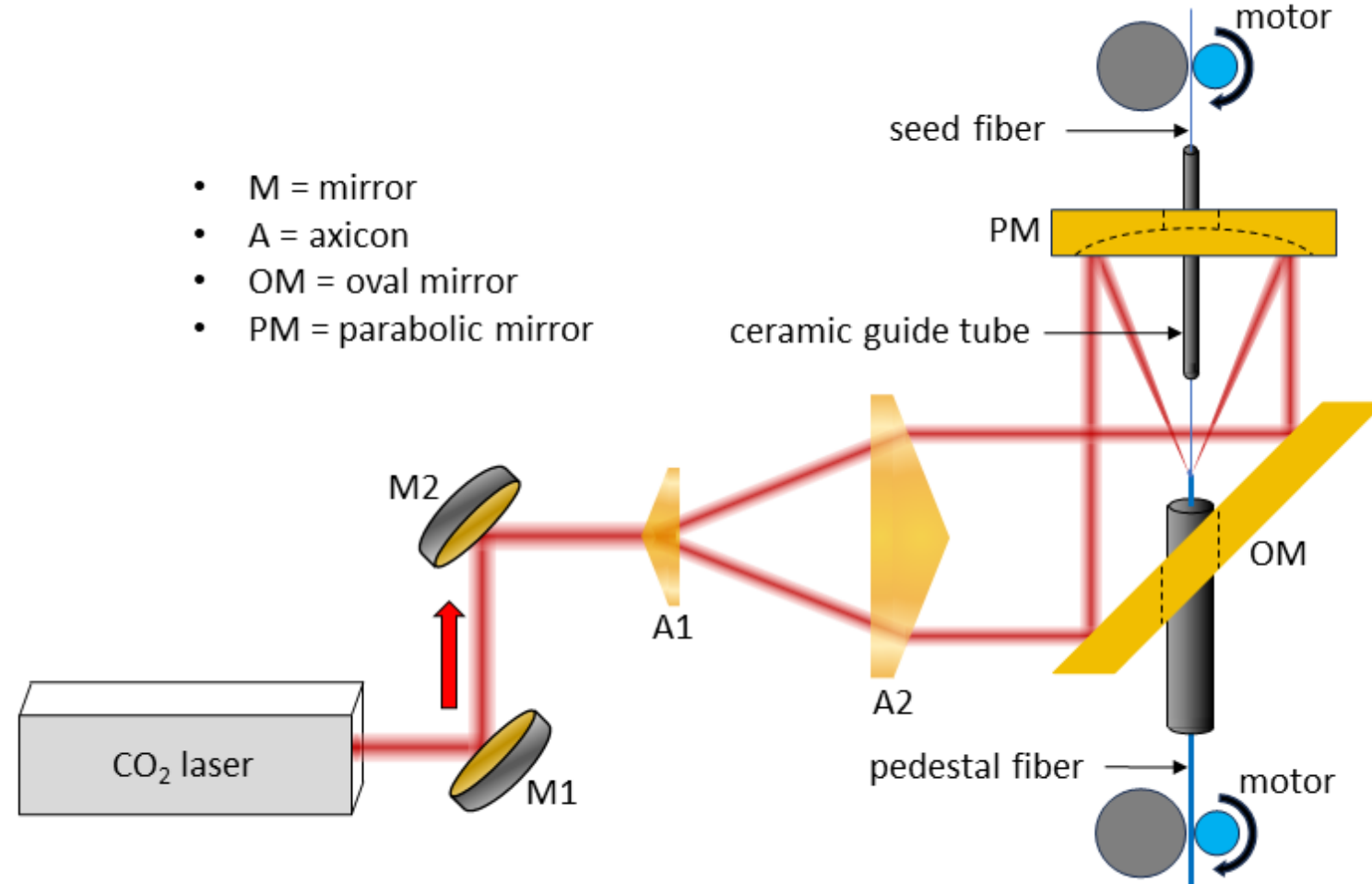
Progress

Laser Heated Pedestal Growth

- Grow, dope, and regrow these fibers to drive dopants into the fiber.
- Finished fibers evaluated with numerical aperture, loss, and EPMA

Accomplishments:

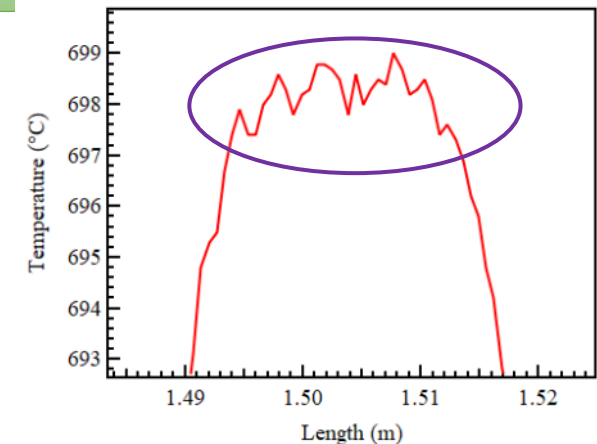
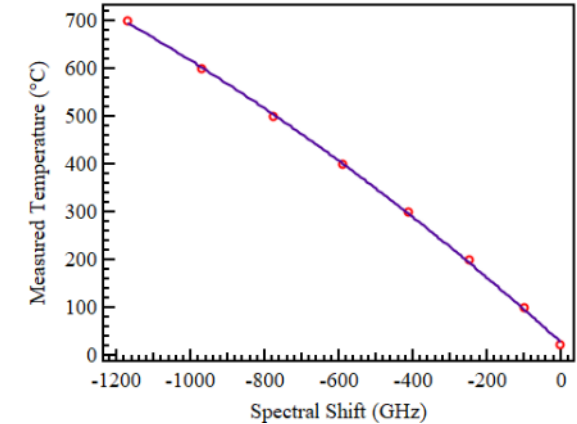
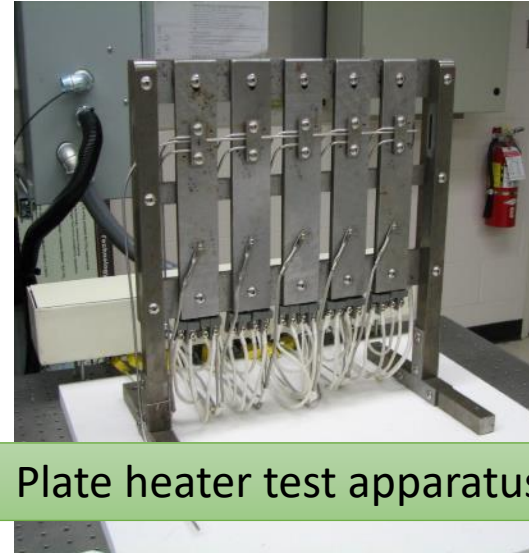
- Presented LHPG and interrogator work at UPISC collaboration workshop on Nov. 8, 2023.
- Conference paper submitted for SPIE DCS.
- Established recipes for ~300 um YAG fiber
- Grown a dozen small pieces (<10 cm) of YAG and Ce-doped YAG fiber and performed EPMA analysis.



Microwave Temperature Measurement Using OF

Objectives PI: Benjamin Chorpening (benjamin.chorpening@netl.doe.gov)

- Apply optical fiber temperature measurements in NETL microwave reactor facility (ReACT)
- Attempt measurement from multiple fibers in reactor bed
- Design and construct higher spatial resolution temperature measurement test apparatus
 - Better match to microwave reactor testing

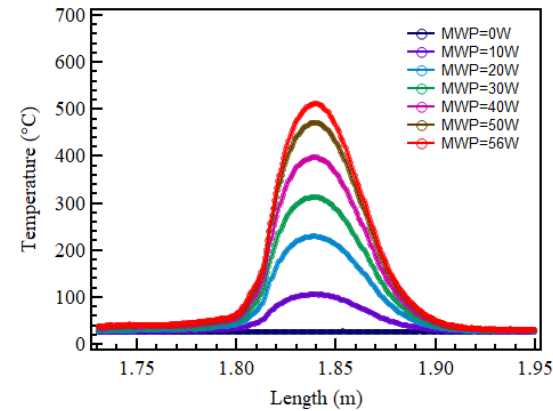


Microwave Temperature Measurement Using OF

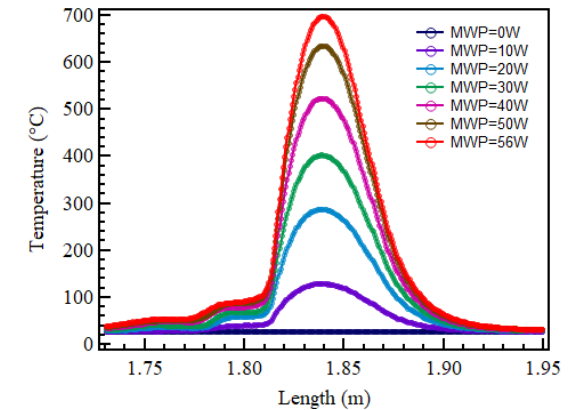
Accomplishments

- Temperature profiles measured along two optical fibers passed through catalyst bed
- At least four different powders tested. Both E-field and H-field reactor testing, using a couple grams of catalyst
- First-of-a kind experiments aid in microwave reactor development and provide insight into internal temperatures during operation in the microwave reactor
- Internal temperatures sometimes differ considerably from external surface pyrometer

Test with SiC Powder in Fixed Frequency Microwave Reactor



Fiber passes near outer surface of catalyst bed



Fiber passes through centerline of catalyst bed

Temperature profiles from an experiment, and illustration of the arrangement of optical fibers passing through the microwave reactor bed.

See the poster!

Juddha Thapa, Pranjali Muley, Ashraf Abedin, Xinwei Bai, Daniel Haynes, Christina Wildfire, Dushyant Shekhawat, and Benjamin Chorpeneing, "Distributed temperature profiles of silicon carbide catalyst bed in a microwave reactor using fiber-optic sensor", poster for the FECM/NETL Spring R&D Project Review Meeting, April 23-25, 2024, Pittsburgh.

Raman Gas Analyzer

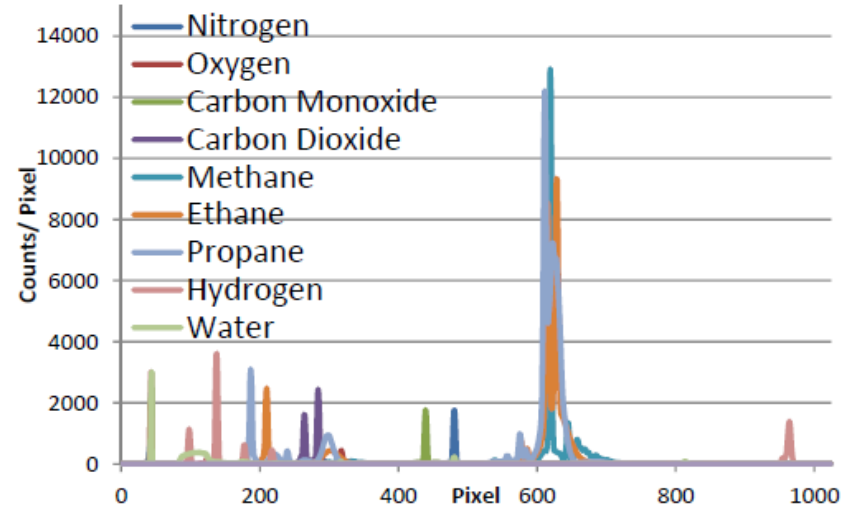
Objectives

PI: Benjamin Chorpening (benjamin.chorpening@netl.doe.gov)

- Program and test smaller prototype and prepare for field testing
- Identify opportunities for incremental improvements and advance the TRL
- Support field testing and on-site use of the RGA and tech transfer activities



US Patent 8,674,306,
NETL and Pitt



No commercial technology has this combination of speed, accuracy, and multi-gas capability.

- Applications to **low carbon power generation** (e.g. hydrogen blend turbines)
- Prototype tested in pilot scale laboratory applications
- Fast - 1 second measurement time
- Species concentrations measured to 0.1%
- Optical waveguide technology boosts Raman signal more than 1000X
- No recalibration needed in normal operation

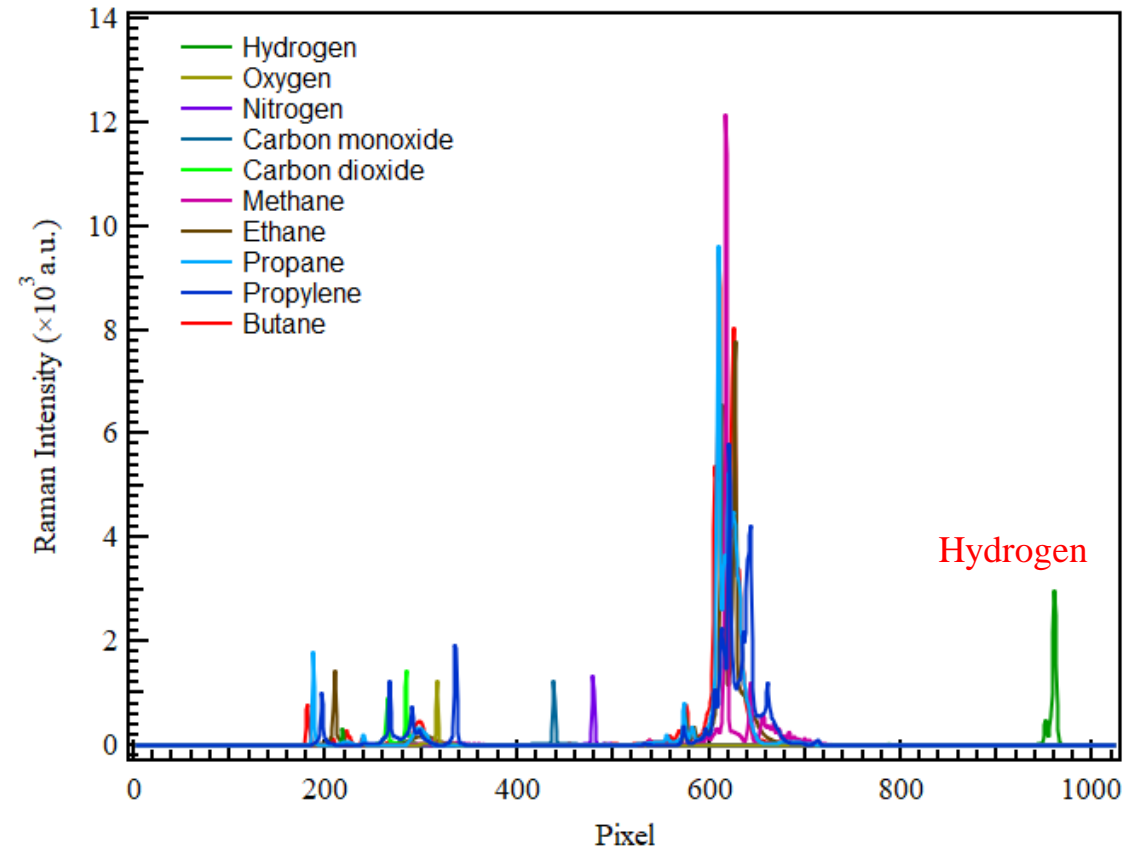
Raman Gas Analyzer

Progress

- Software upgrade completed (Win7 → Win10)
- Patent application filed for NETL developed capillary coating process
- Lab improvements completed to make initial calibration simpler
- Prototype recalibrated with major gas species

Next Steps

- Complete debugging
- Calibration and lab testing of cRGA
- Compare performance cRGA with RGA2
- Hydrogen Hub / H2 blend application testing
- Improve user interface for field testing



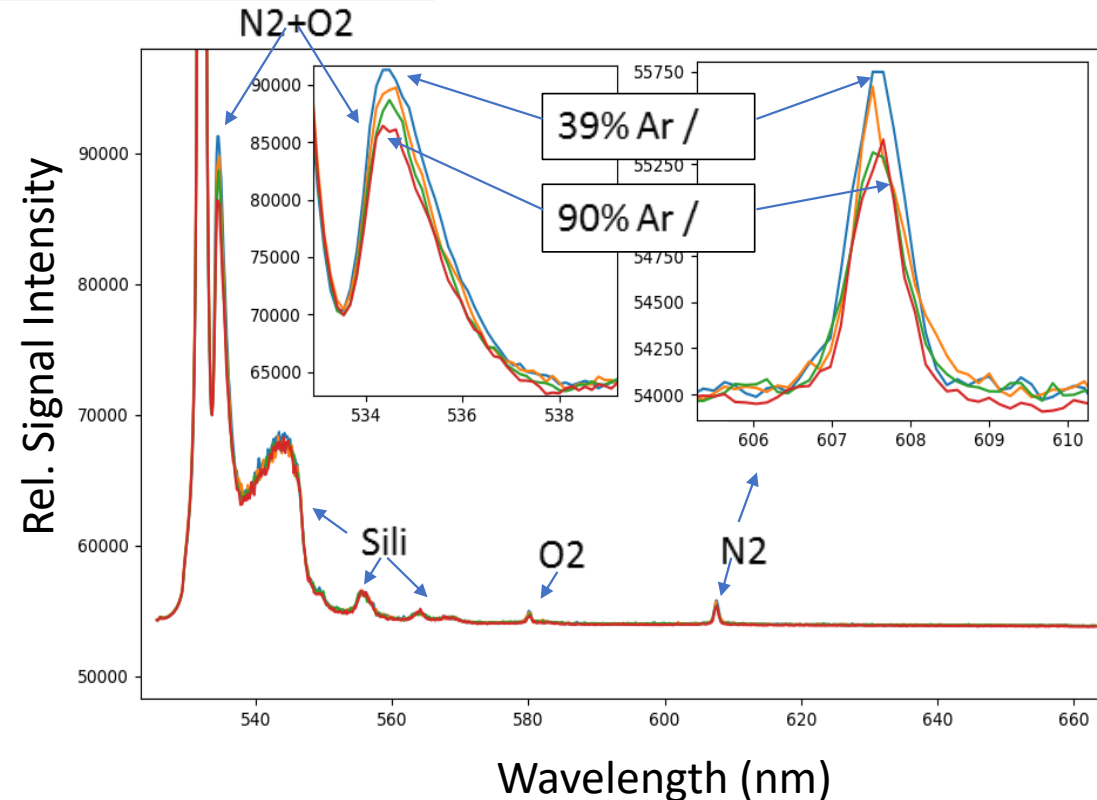
RGA calibration data 2024, Raman spectra of various gas species 150mW laser head power, 1s integration time and average of 100 spectra for each gas species. Wavelength varies on x-axis.

Ultrafast Laser Measurements for Harsh Environments

Objectives

PI: Dustin McIntyre (dustin.mcintyre@netl.doe.gov)

- Scheimpflug light detection and ranging does not rely on pulsed lasers or fast, gated detectors, having potential to be less expensive than traditional pulsed LIDAR.
- Explore as an alternative approach with lower equipment costs
- Spatially resolved measurements in gasifiers or other large industrial systems
- Assemble higher resolution prototype using existing laser, detector, and optics
- Test and apply to field measurements



Laser-based measurement of species/temperature along a line of sight with spatial resolution and single point access

Ultrafast Laser Measurements for Harsh Environments

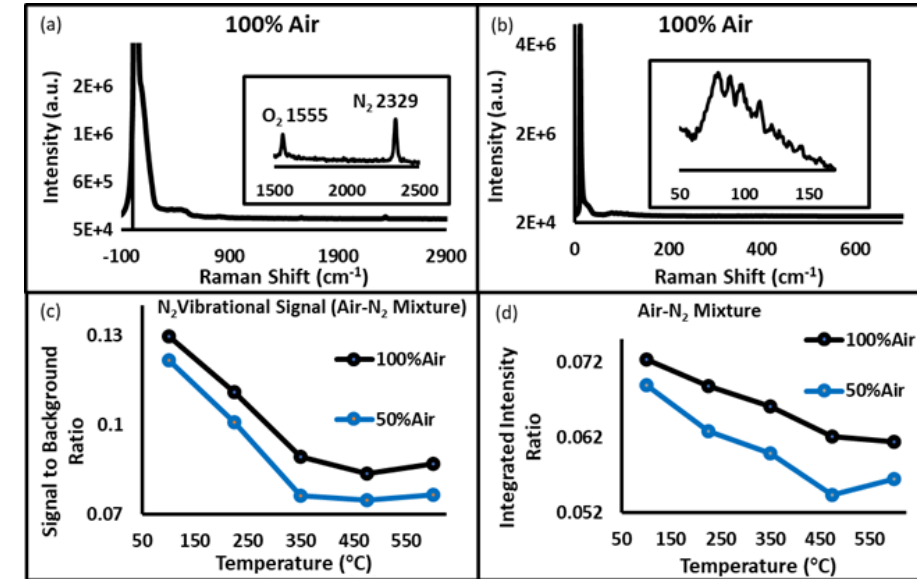
Progress Highlights

- Scheimpflug LIDAR was demonstrated to be able to quantify both gas temperature and composition at temperatures up to 600 °C.

	Vibrational Raman <i>inelastic scattering from molecular bond vibrations</i>	Rotational Raman <i>light scattering from molecular bond rotations</i>
Advantages	Well-separated and well-defined spectral lines	30x stronger signal, highly temperature sensitive
Disadvantages	weak signal, weak temperature dependence	strong spectral overlap between gas species, requires high spectral resolution, spectrally close to excitation laser

Products

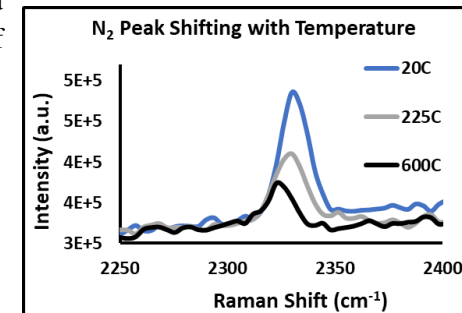
- Draft manuscript on gas sensing using the Raman S-LIDAR approach is complete.
 - Scheimpflug LIDAR for Gas Sensing at Elevated Temperature – Bhatt et. al.



Top: Vibrational (a, c) and Rotational (b, d) signals of varying mixtures of N₂ & O₂.

- 100% air = 78% N₂ & 21% O₂
- 50% air/N₂ = 89% N₂ & 10.5% O₂

Right: N₂ vibrational signal peak shifting with increasing temperature.



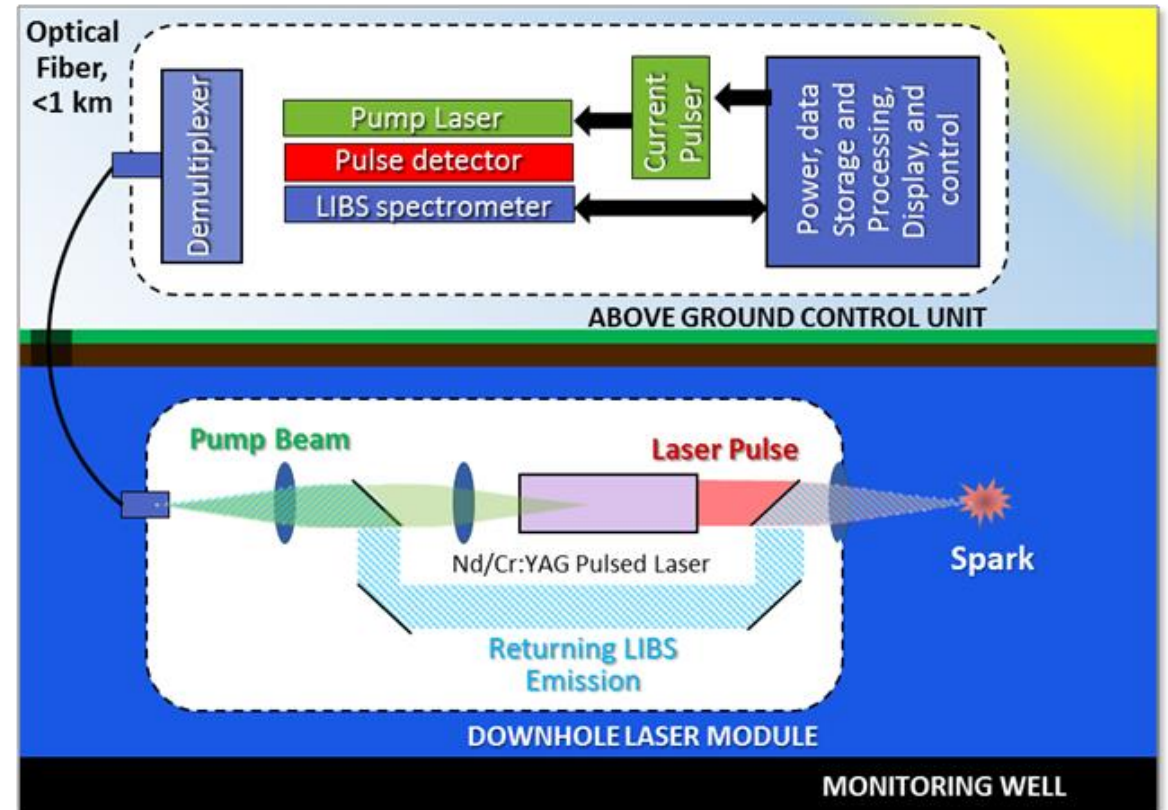
LIBS for Subterranean Sensing

Objectives

PI: Dustin McIntyre (dustin.mcintyre@netl.doe.gov)

- Develop a deployable miniaturized LIBS system for subterranean chemical sensing
- Improve design with the submersible probe, based on field testing
- Identify and arrange applications tests
- Add Raman measurements via engagement with MetroLaser Inc. through SBIR/TTO
- Focus on laboratory bench testing prior to construction or modification of fieldable systems

2019 R&D
100
Award
Winner



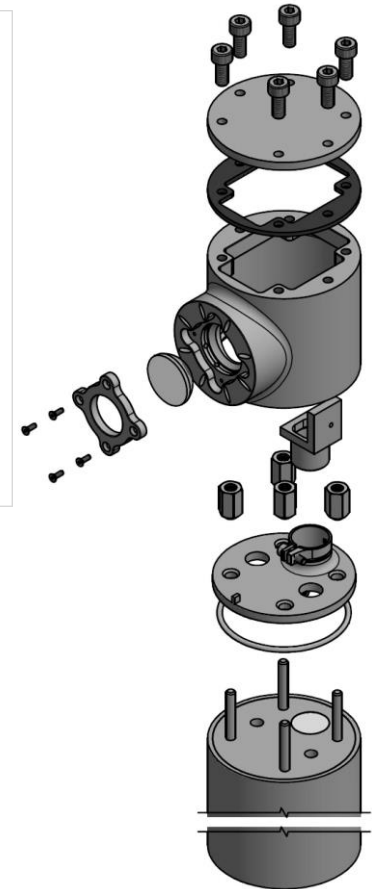
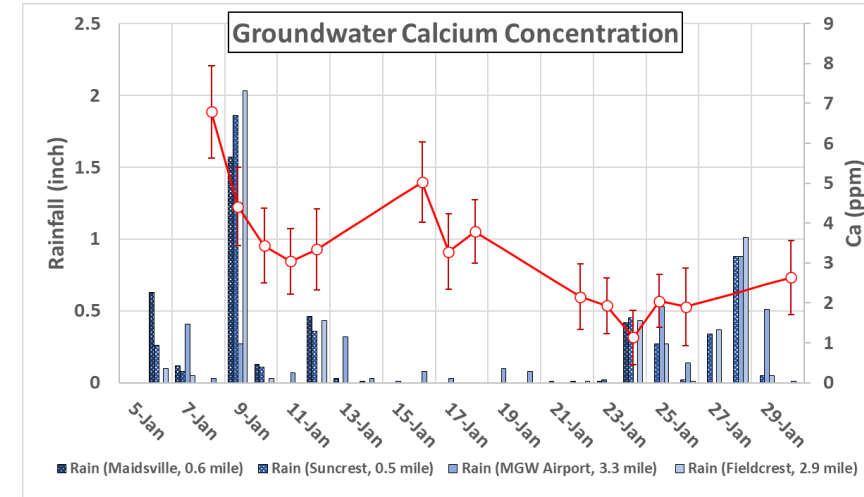
LIBS for Subterranean Sensing

Progress Highlights

- Angled adapter has been installed to address issues with groundwater outgassing, preventing correct signal measurement
- Modified prototype deployed into a monitoring well on the Morgantown site
- No issues regarding trapped air or gas bubbles
- Adapter lens experienced large shift in focal length upon immersion into water
- Lens replaced with one less susceptible to this issue and the modified probe is ready for testing

Products

- A more reliable field deployable sensor prototype has been developed.
- Patent executed: High Power Actively Q-Switched Downhole LIBS Analysis Systems (US Patent 11,953,443)



90 DEGREE ADAPTER
EXPLODED VIEW
SCALE 1:1

See the poster!

Controls

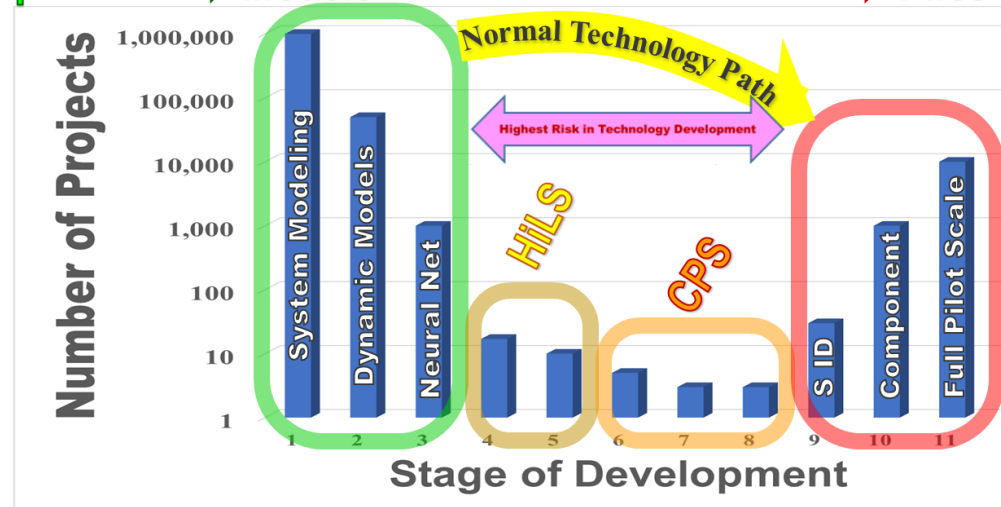
Cyber-Physical Systems for Integrated Energy Systems

Objectives

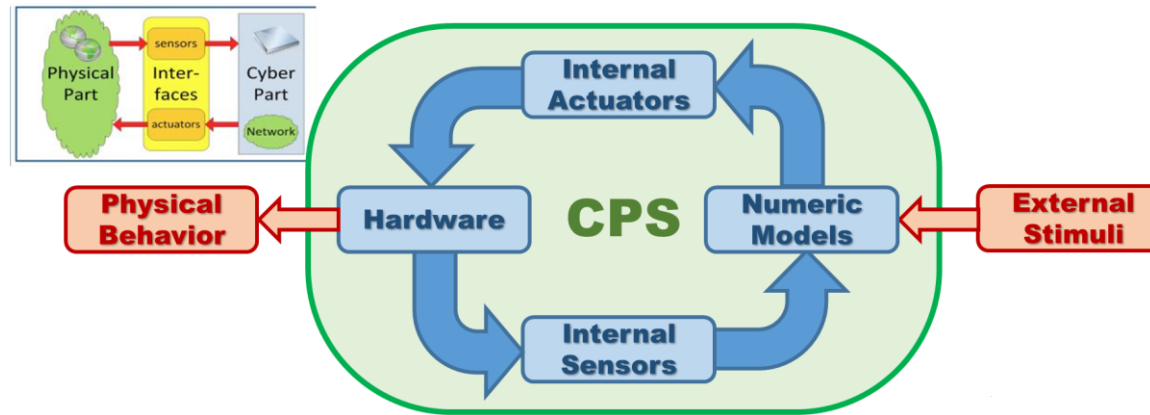
PI: David Tucker (david.tucker@netl.doe.gov)

- Develop cyber-physical paradigm to accelerate technology development
- Conceptual design of hybrid system that includes
 - Blue hydrogen
 - Solid fuel gasification
 - Post-C carbon capture
- Evaluate operability of the concepts using the HyPer facility in future years

Concept → Models → Pilot → Commercial



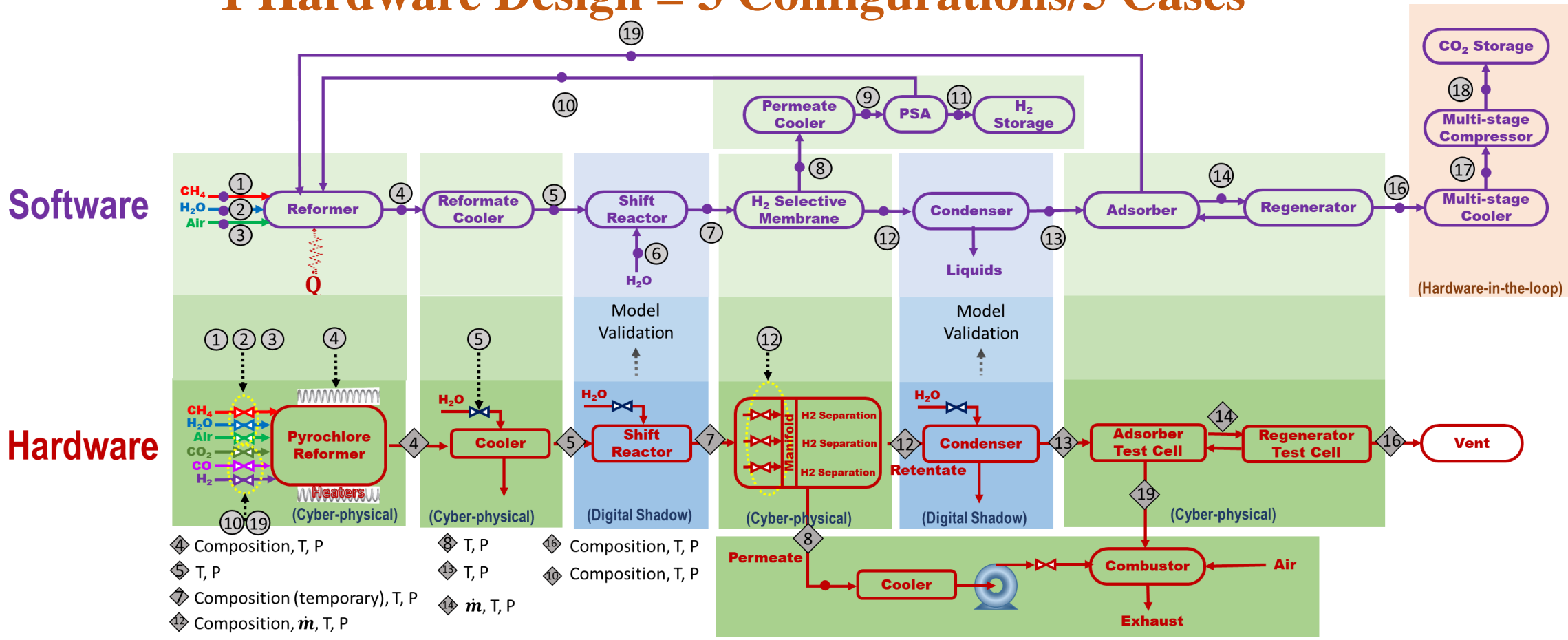
CPS Approach:
Key component under development represented as a real-time model, whereas the rest of the system is physically represented



Cyber Physical Systems are used to replace physical components that:

1. Are irreplaceable
2. Are expensive
3. Can't meet performance targets
4. Don't exist...yet

1 Hardware Design = 3 Configurations/5 Cases



Cyber-Physical Systems for Integrated Energy Systems

Configuration I:

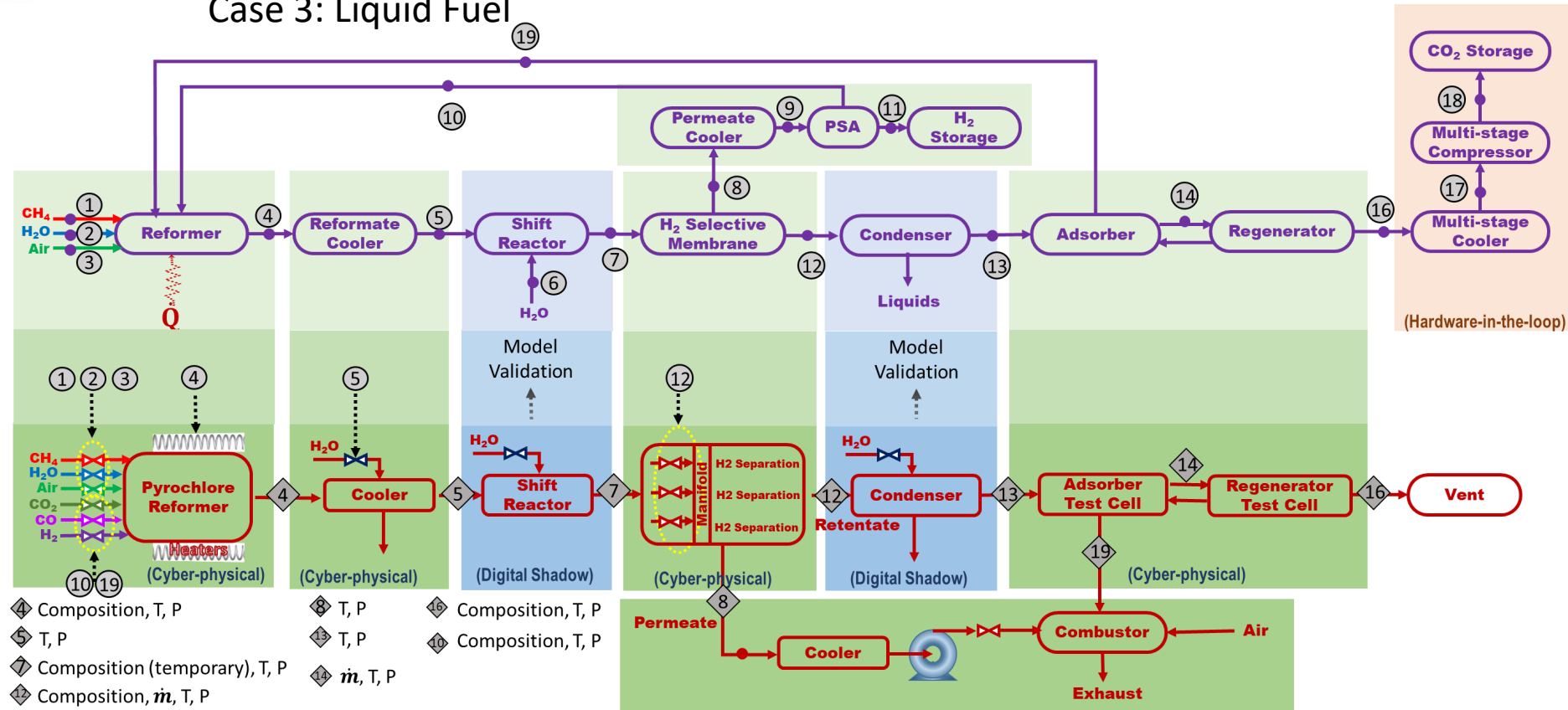
Blue Hydrogen Production with Carbon Management (NG or Liquid Fuels)



- Case 1: Natural Gas
- Case 2: Syngas with methane
- Case 3: Liquid Fuel

Software

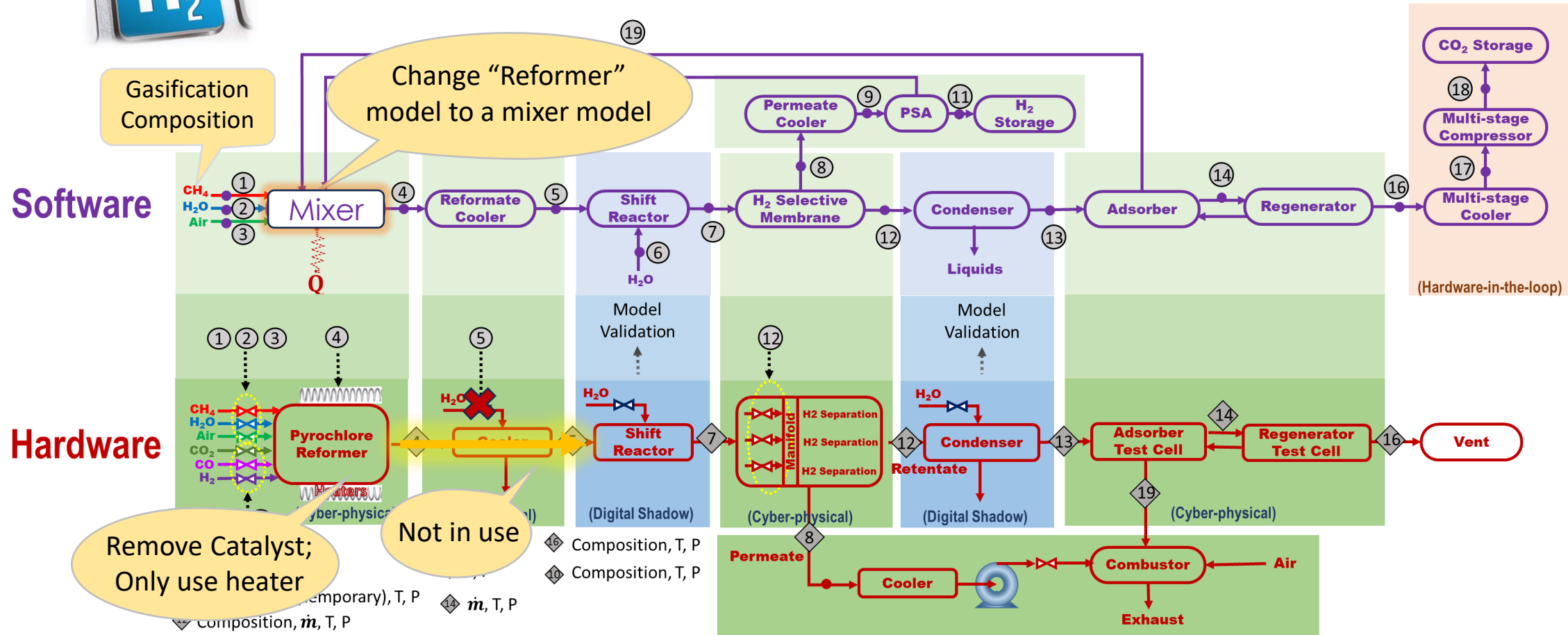
Hardware



Cyber-Physical Systems for Integrated Energy Systems

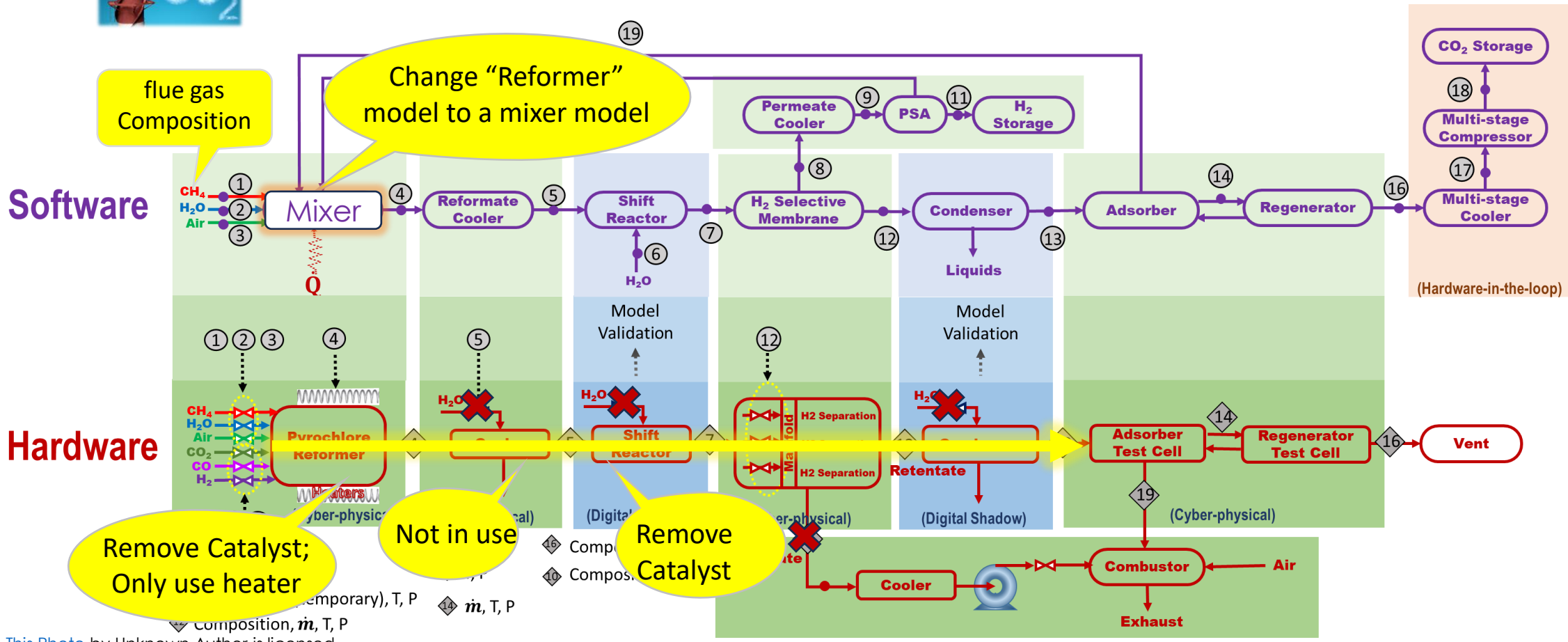
Configuration II: Blue Hydrogen Production with Carbon Management (Coal or Solid Fuels- Gasification)

Case 4: Syngas without methane



Configuration III: Carbon Capture for **Post-Combustion Gas**

Case 5: Combustion production/flue gas



Software

Hardware

Remove Catalyst; Only use heater

Not in use

Remove Catalyst

This Photo by Unknown Author is licensed under CC BY

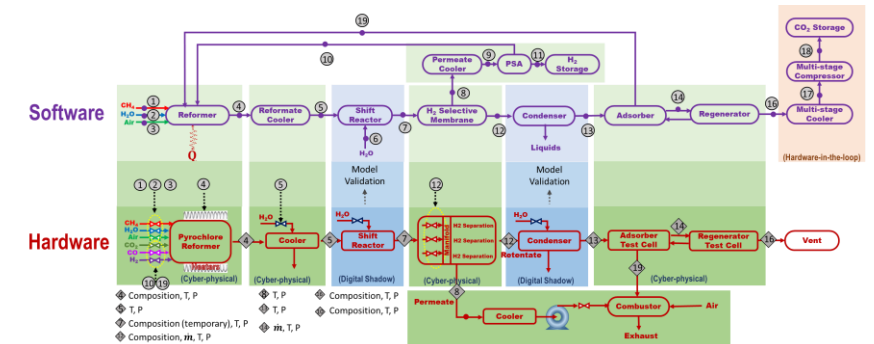
Progress



Achievement in EY23

- ✓ Completed preliminary design for one cycle/case
- ✓ Identified the possibility to use one design to investigate 3 configuration/5 cases studies

1 Hardware Design = 3 Configurations/5 Cases



Proposed Work in EY24

- Completed preliminary design and control assessment for all 3 configuration/5 cases of cyber-physical carbon capture systems
- Complete construction and shakedown of cyber-physical reformer system
- Develop AI/ML-based optimized energy system control under transients
- Provide support for understanding the real-time economics of flexible and responsive carbon capture system

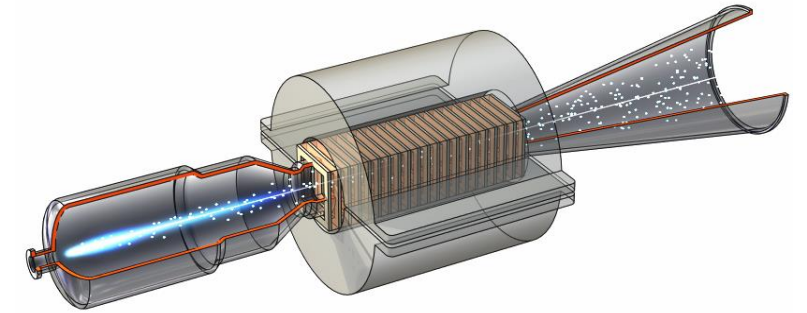
Novel Concepts

MHD channel testing and simulation

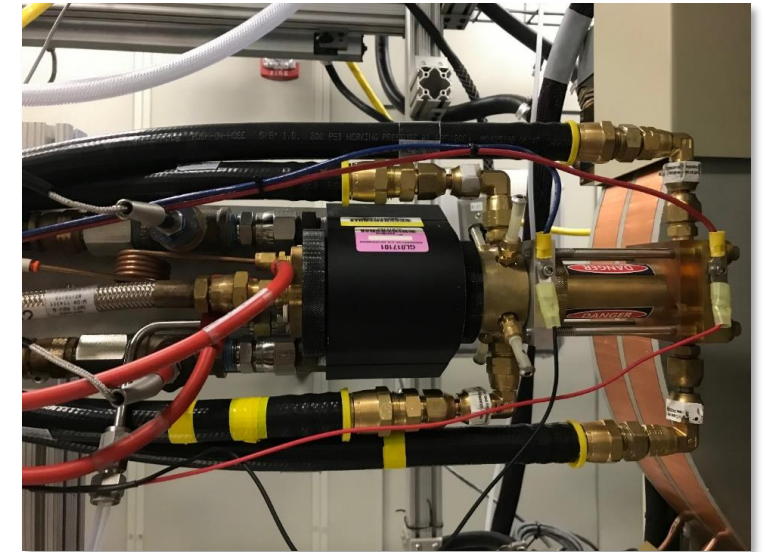
Objectives

PI: Rigel Woodside (rigel.woodside@netl.doe.gov)

- **Motivation for developing a MHD power cycle**
 - Enables high process efficiency with CCUS¹
 - Fuel flexible and resilient to particles as compared to turbines
 - Mixed fuel source capable (fossil + biomass + plastics)
- **EY2023 Progress Summary**
 - Completed photoionization experiments & analysis
 - Developed improved emulsions for consistent plasma production for laboratory MHD testing
 - Began TEA for new system with MHD topping cycle that uses bio-materials as seed
 - Article published on MHD materials characterization
 - Michael S. Bowen, David P. Cann, C. Rigel Woodside; "Application of the van der Pauw Method for Electrical Conductivity Measurements at High Temperatures Using an Insulating Compressing Ring; Review of Scientific Instruments, 94, November 06 2023.



MHD generator sketch (not to scale)

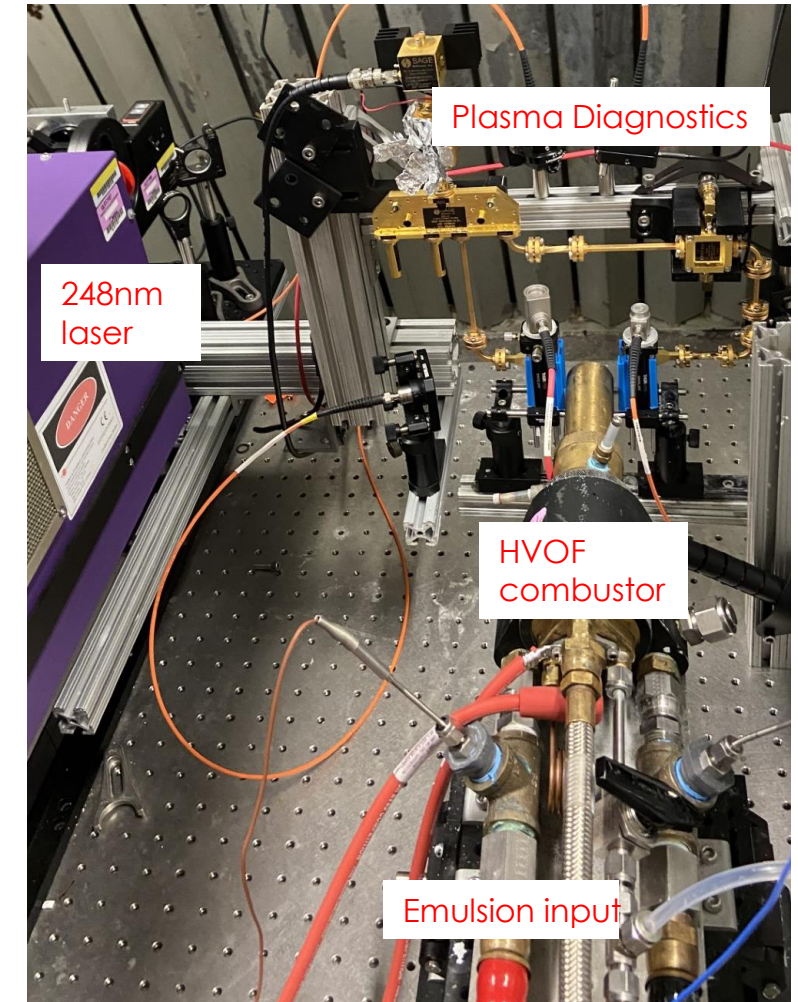


laboratory MHD generator

MHD channel testing and simulation

Experiments with photoionization enhanced MHD Power generation

- General concept: laser creates non-equilibrium plasma to enhance electrical conductivity
 - Potentially viable if MHD power extraction can exceed laser power input (net positive)
 - Experimentally investigated with combustion system, emulsions, pulsed laser and electron-ion recombination rate measurement
- Recombination rate measured with developed ~90 GHz based diagnostic
 - rate found to be different than values expected from literature
 - hypothesize measured rates due to superoxide formation
- Analysis using experiential results shows photoionization enhanced power could be viable between ~1000K and ~2000K
 - Could extend lower operational temperature of MHD generators
 - Could be useful to mitigate power loss in cooler boundary layers
- **finding expected to be published in 2024**

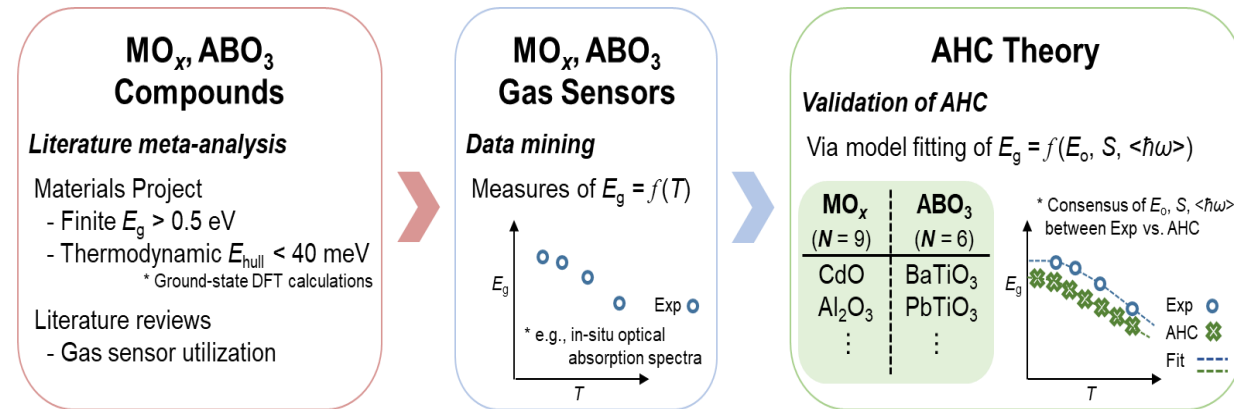
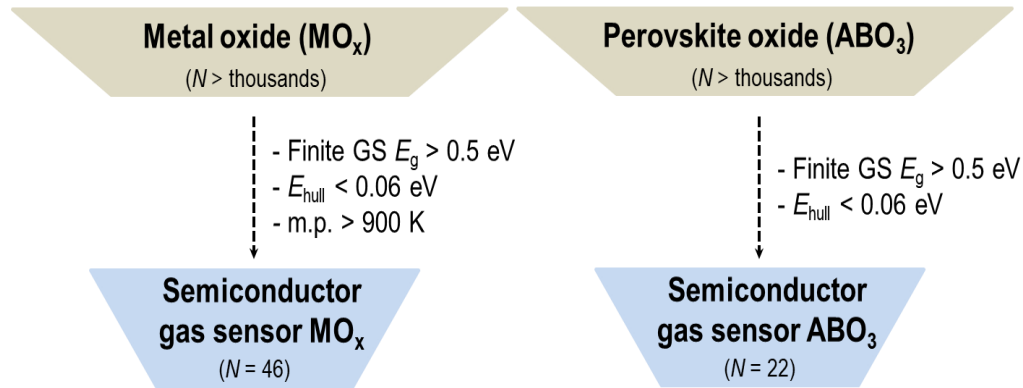
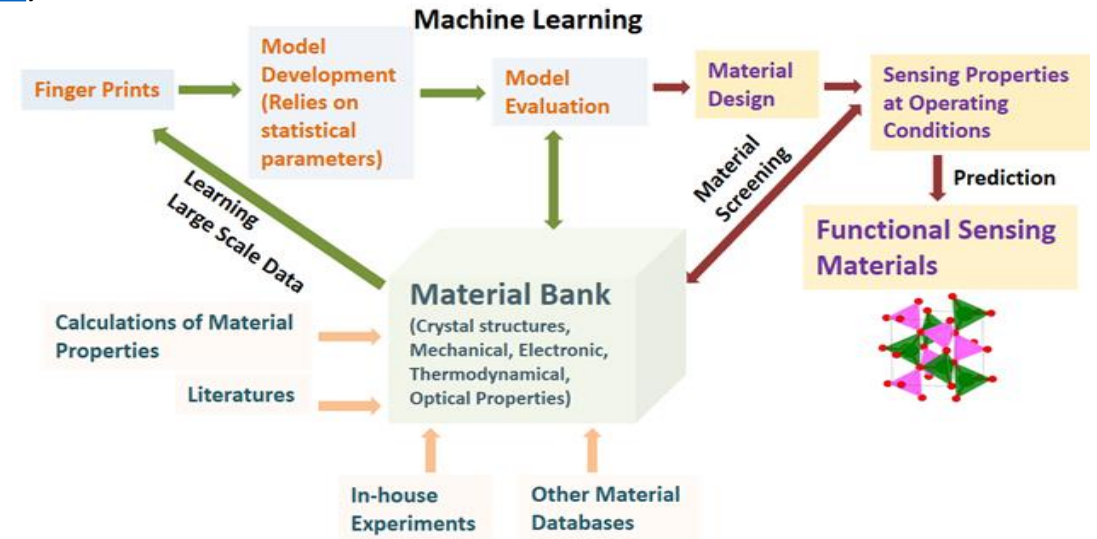


Sensing Materials and Machine Learning

Objectives

PI: Yuhua Duan (Yuhua.duan@netl.doe.gov)

- Develop ML-based models to screen and design sensing materials
- Boost development of gas sensor materials to detect gas molecules involved in technologies that function in harsh environments
- Understand temperature dependence of sensing materials, and sensing responses with mechanisms, in harsh environments



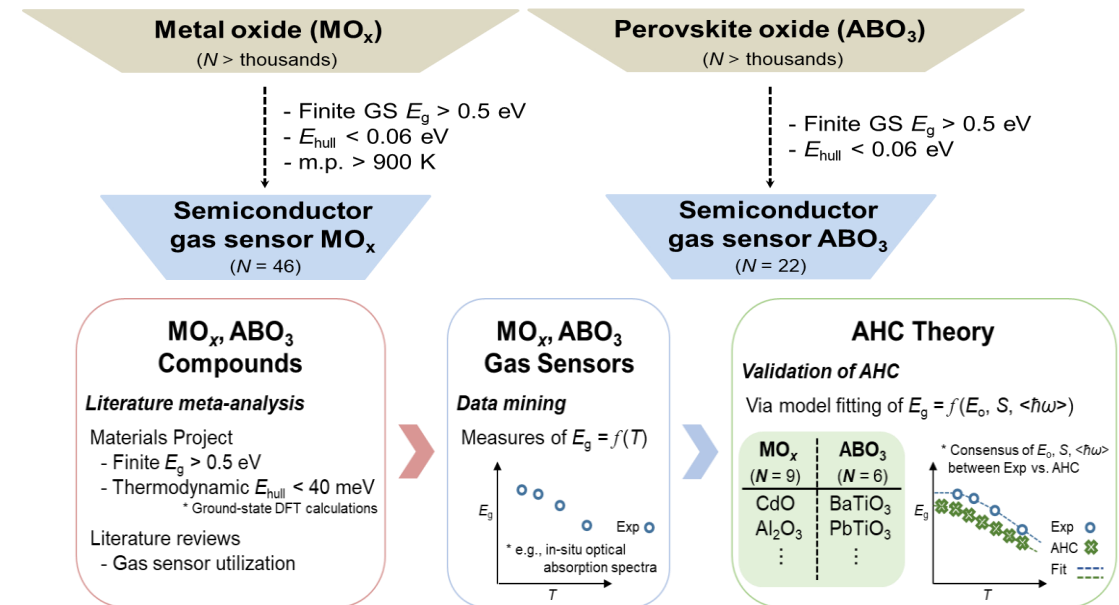
- Principal component analysis applied to combine 37 features into one reduced feature for each parameter in the O'Donnell model

$$E_g = E_0 - S \langle \hbar\omega \rangle \left[\coth \left(\frac{\langle \hbar\omega \rangle}{2k_B T} \right) - 1 \right].$$

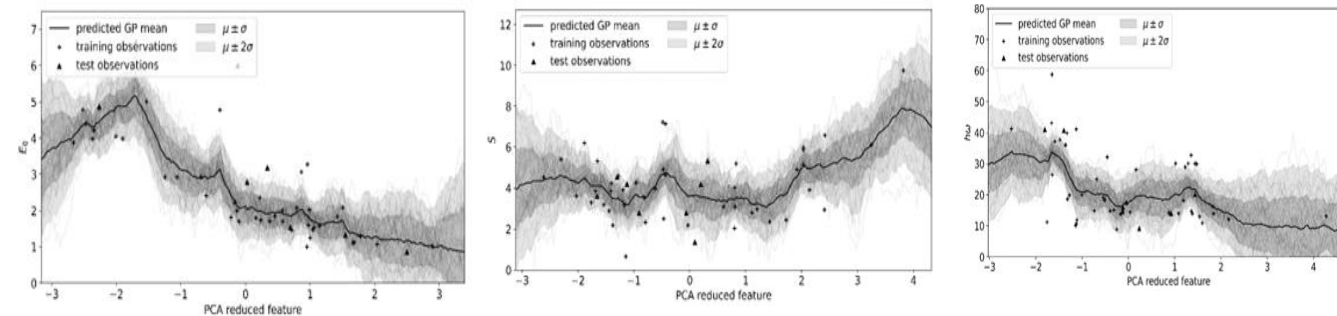
E_0	S	$\langle \hbar\omega \rangle$
Formation energy , molar density, melting point	Atomic mass , EP Debye temperature , thermal conductivity, heat of vaporization, speed of sound, boiling point, melting point	Entropy of formation , heat capacity, volume, density

- Bolded features were found to have the highest relative importance in their respective principal component
- Gaussian process (GP) regression models were trained separately for each of the three parameters

Database construction



ML prediction results



- Nandi, Chong, Park, Saidi, Chorpeneing, Bayham, Duan, **AIP Advances** 14(2024)035231.

Sensing Materials and Machine Learning

Progress

- Developed ML model for band gap shift prediction in metal oxides
- Explored O₂ and H₂ sensing mechanisms of perovskites (Sr, La, Mg-doped titania)
- Identified changes in optical, electronic properties due to oxygen, Sr vacancies
- Probed optical, electronic properties of perovskites containing neutral H atom, O atom
- H and O diffusion and recombination in the sensing materials
- Experimentally verified temperature-dependent band gap shifts and optical responses

See the poster!

$$E_g = E_0 - S \langle \hbar\omega \rangle \left[\coth \left(\frac{\langle \hbar\omega \rangle}{2k_B T} \right) - 1 \right]$$

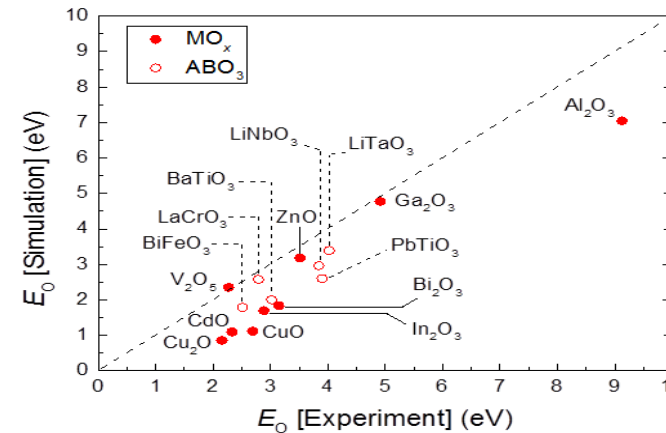
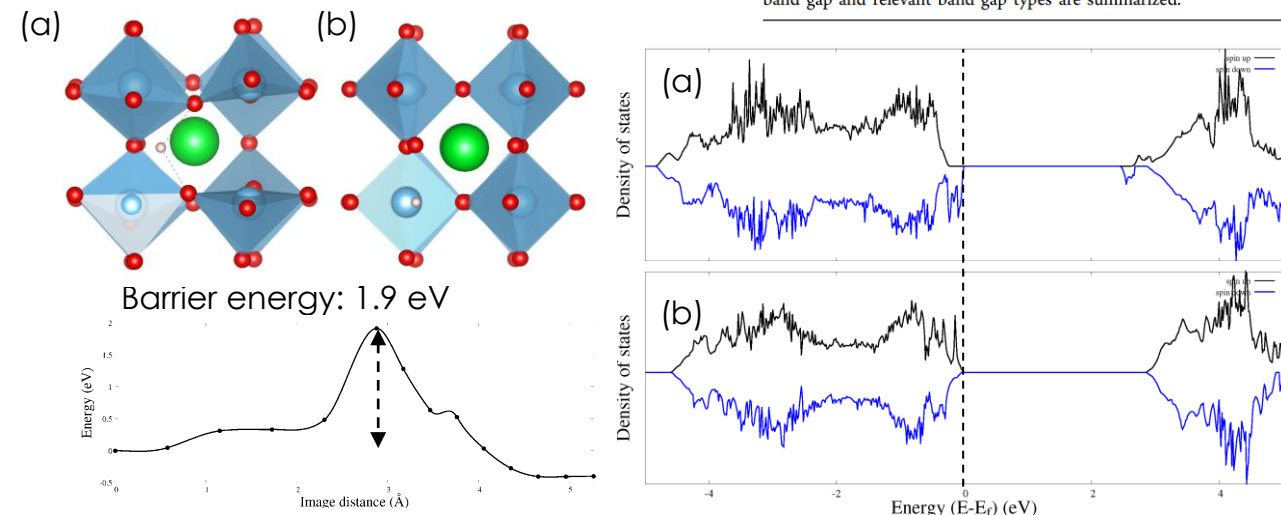


Table 1. List of MO_x and ABO₃ Materials Set with the Corresponding Ambient-Temperature Phases^a

material	phase (space group)	measurement method	band gap type
Metal oxides MO _x			
CdO	cubic (<i>Fm3m</i>)	absorption spectra ⁵¹	direct
CuO	tetragonal (<i>P4₂/mmc</i>)	absorption spectra ⁵²	indirect
Cu ₂ O	cubic (<i>Pn3m</i>)	absorption spectra ⁵³	direct
ZnO	hexagonal (<i>P6₃mc</i>)	absorption spectra ⁵⁴	direct
Al ₂ O ₃	rhombohedral (<i>R3c</i>)	exciton reflectivity ⁵⁵	direct
Bi ₂ O ₃	monoclinic (<i>P2₁/c</i>)	thermo-reflectance ⁵⁶	indirect
Ga ₂ O ₃	monoclinic (<i>C2/m</i>)	photoemission spectra ⁵⁷	indirect
In ₂ O ₃	cubic (<i>Ia3</i>)	absorption spectra ⁵⁸	indirect
V ₂ O ₅	orthorhombic (<i>Pmmn</i>)	absorption spectra ⁵⁹	indirect
Perovskites ABO ₃			
BaTiO ₃	tetragonal (<i>P4mm</i>)	absorption spectra ⁶⁰	indirect
BiFeO ₃	rhombohedral (<i>R3c</i>)	absorption spectra ⁶¹	indirect
LaCrO ₃	orthorhombic (<i>Pnma</i>)	absorption spectra ²⁹	direct
LiNbO ₃	rhombohedral (<i>R3c</i>)	absorption spectra ⁶²	indirect
LiTaO ₃	rhombohedral (<i>R3c</i>)	absorption spectra ⁶³	indirect
PbTiO ₃	tetragonal (<i>P4mm</i>)	absorption spectra ⁶⁴	indirect

^aExperimental measurement methods of the temperature-dependent band gap and relevant band gap types are summarized.



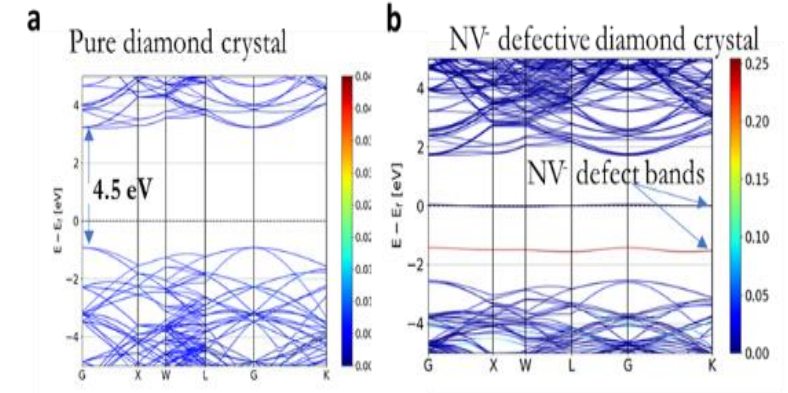
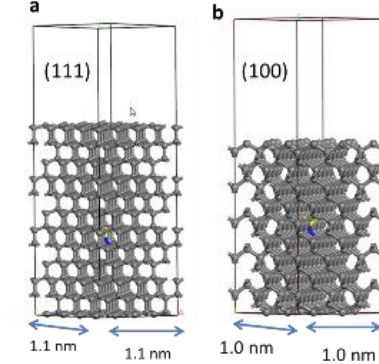
Quantum Sensing for FECM Applications

Objectives

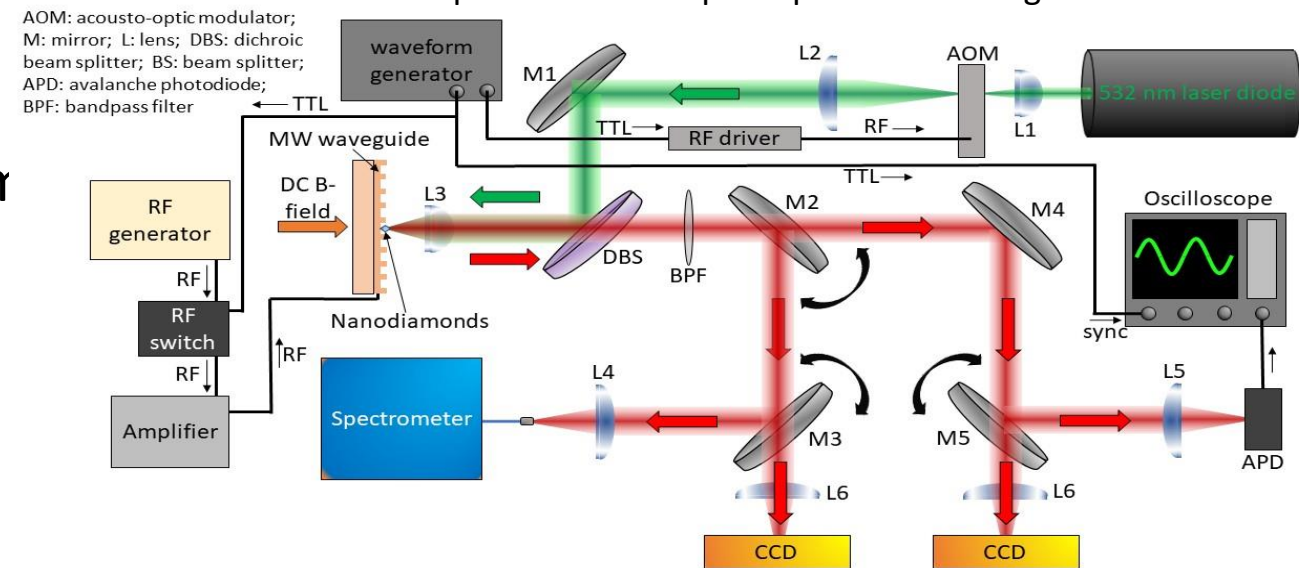
PI: Yuhua Duan (Yuhua.duan@netl.doe.gov)

- Use quantum optics and quantum sensing to realize performance in advanced sensing instrumentation
- Explore electronic, magnetic, and optical properties of nitrogen-vacancy (NV) defective nanodiamonds (ND) as quantum sensor materials.
- Write a review describing current and emerging commercially-available quantum sensing technologies and energy sector applications

NV center surfaces



Experimental set up for quantum sensing

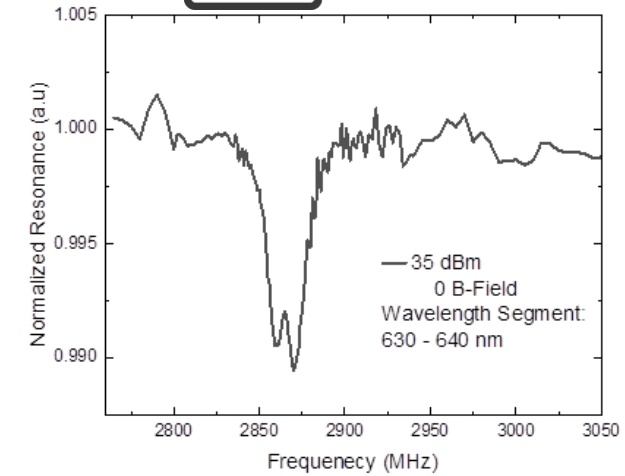
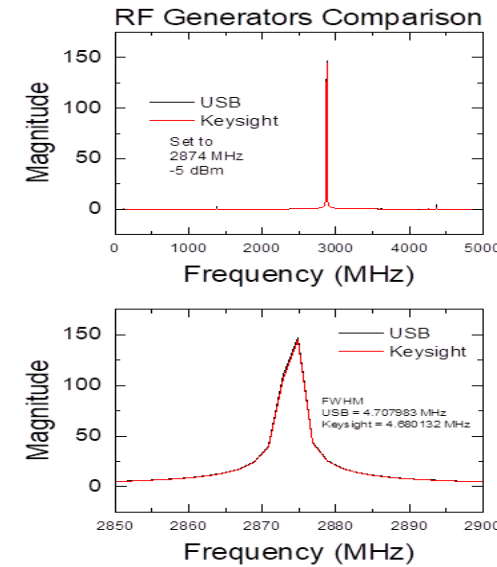


Quantum Sensing for FECM Applications

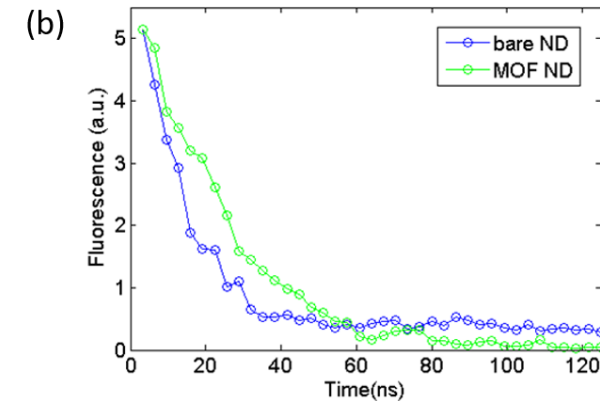
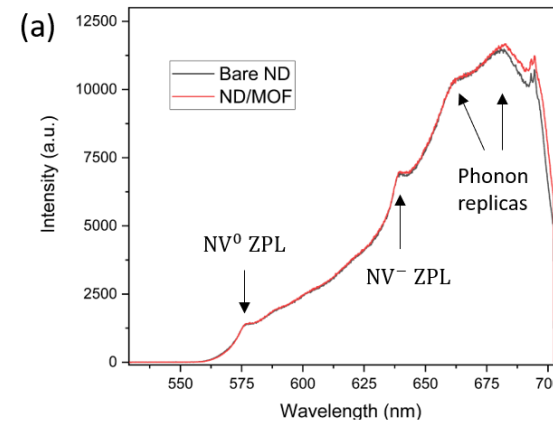
Accomplishments

- Analyzed charge distribution and electronic bands in nanodiamond with nitrogen vacancy center as pressure and magnetic field sensing devices
 - Quantum pressure transmitter for hydrogen or CO2 storage applications?
- Completed building experiment for spin relaxometry and optically-detected magnetic resonance (ODMR) measurements.
- Review manuscript in progress

See the poster!



ODMR of NV center



Fluorescence spectrum (a) and loss of carrier population (b) in NV center of nano-diamond

Advanced Sensors and Controls

- Continuing to make progress on key sensing technologies for FECM applications
 - Economic and robust optical fiber formulations and measurement systems
 - Development of compact prototypes for Raman gas analyzer, LIBS
 - Ultrafast laser measurement techniques for distributed gas/temp sensing
- Unique control strategies being developed
 - to accelerate technology development and allow for controls improvement in new or existing facilities
- Developing next-generation sensing technologies using quantum sensing and machine learning approach
- Drafted/published at least four papers and technical reports
- Closing out two tasks and incorporated DPE into portfolio

Questions & Discussion

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