Highly Selective and Stable Multivariable Gas Sensors for Enhanced Robustness and Reliability of SOFC Operation

General Electric – FE0027918
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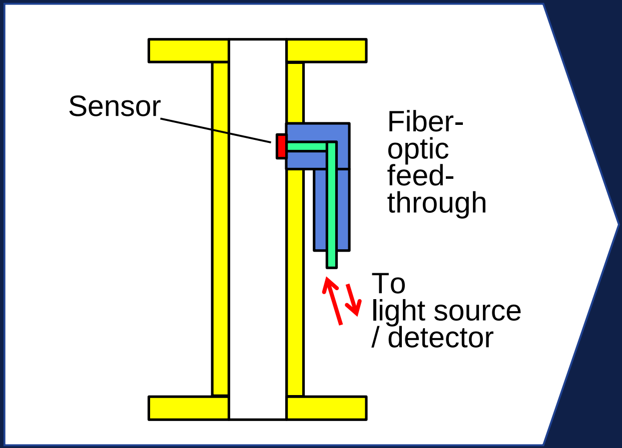
10:00 am – 11:30 am Kickoff Meeting Friday Nov. 18, Solid Oxide Fuel Cells FOA 1469

Photonic sensor development



Field validation

Highly Selective and Stable Multivariable Gas Sensors
for Enhanced Robustness and Reliability of SOFC Operation

18-month program
to develop and perform initial field validation of stable and gas-selective sensors
for in situ monitoring of gases produced with on-site steam reforming in SOFC systems.

The knowledge from this sensor will allow accurate SOFC control and will deliver a lower operating cost for SOFC customers.

Project Team Introduction/Description

GE
Global Research

- *Requirements flow-down from optical system design to multi-gas sensing,*
- *fabrication of GE sensors,*
- *lab tests for selectivity with gas mixtures,*
- *stability tests and optimization,*
- *sensors downselection,*
- *field validation*

SUNY
Polytechnic Institute

- *Fabrication of SUNY sensors,*
- *lab tests for sensitivity with individual gases,*
- *Nanoscale characterization of sensing films*

GE
Fuel-Cells

- *Sensor flange design*
- *sensor validation on 50 kW SOFC*
- *sensor benchmarking,*
- *recommendations for Phase 2 plan and deliverables*

Background

Goals for wide adoption of SOFC systems:

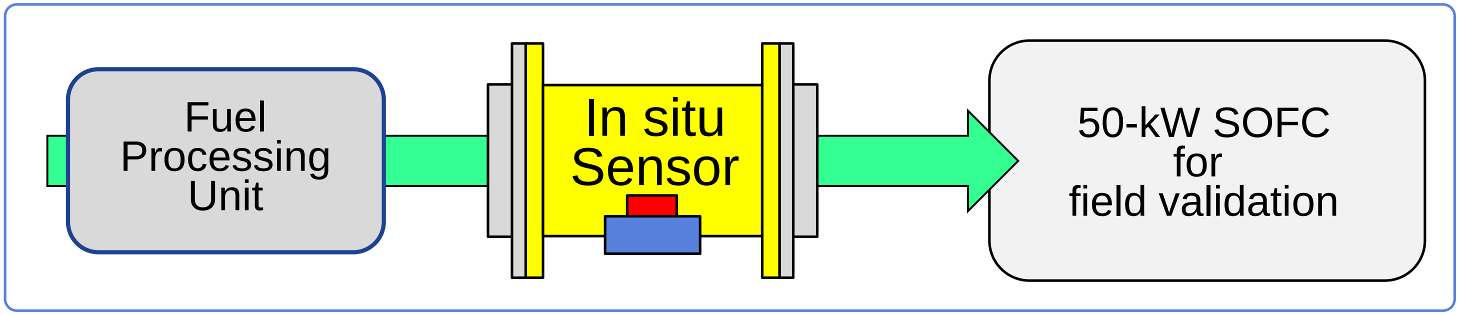
- needs to improve cost-effectiveness,
- enhance operation reliability,
- improve stack robustness to deliver a lower operating cost

Technical strategy:

- early diagnostics of potential upsets
- ability to operate the cells at their most effective conditions

Technical solution:

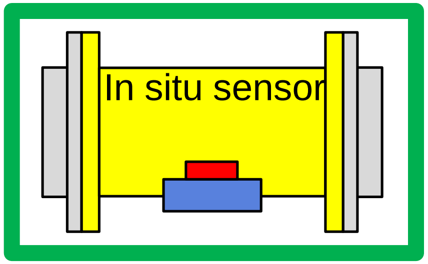
- real-time gas mixture composition measurements during operation
- feed of in situ inputs from gas sensors into SOFC system



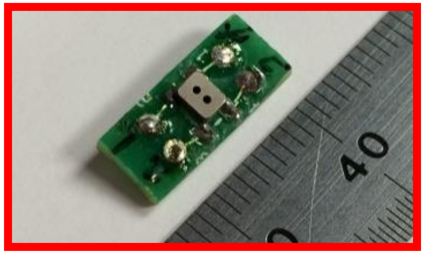
Proposed sensor vs available offerings

Cost

Available
$250,000 system,
high selectivity,
extensive sampling,
lab operation



Proposed
$10,000 - 20,000 system,
high selectivity,
in situ operation
at high temperature



Available
$5-10 sensor, $50 – 10,000 system
poor selectivity,
in situ operation
at ambient temperature

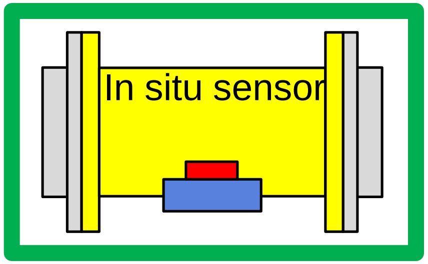
In Situ

Sampling

Proposed sensor vs available offerings

Cost

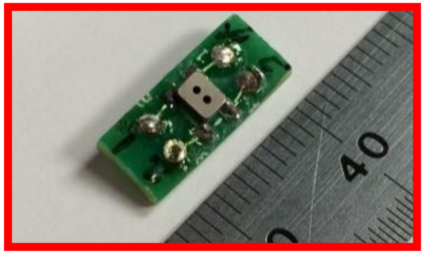
Available
$250,000 system,
high selectivity,
extensive sampling,
lab operation



Proposed
$10,000 - 20,000 system,
high selectivity,
in situ operation
at high temperature

Sensor requirements

- High reliability (accuracy and stability)
- Low initial / operation cost
- Low power consumption



Available
$5-10 sensor, $50 – 10,000 system
poor selectivity,
in situ operation
at ambient temperature

In Situ

Sampling

Technical approach

- Selective sensing of gases for SOFC application by implementing a new generation of gas sensors, known as multivariable sensors
- Leverage design rules of multivariable sensors for in-situ monitoring of SOFC reforming gases
- Leverage broad expertise in functional materials to design sensor with multi-response mechanisms to gases

Requirements for sensors
in the era of Internet of Things and Industrial Internet

Top 10
General sensor requirements

- High accuracy
- High selectivity
- Broad dynamic range
- Low initial cost
- Low operation cost
- Low power consumption
- Fast response time
- High sensitivity
- Small size
- High stability

Potyrailo, *Angew. Chem. Int. Ed.* 2006
Potyrailo, Mirsky, *Chem. Rev.* 2008
Potyrailo et al., *Chem. Rev.* 2011
Potyrailo, Naik, *Annu. Rev. Mater. Res.* 2013
Potyrailo, *Chem. Rev.* 2016

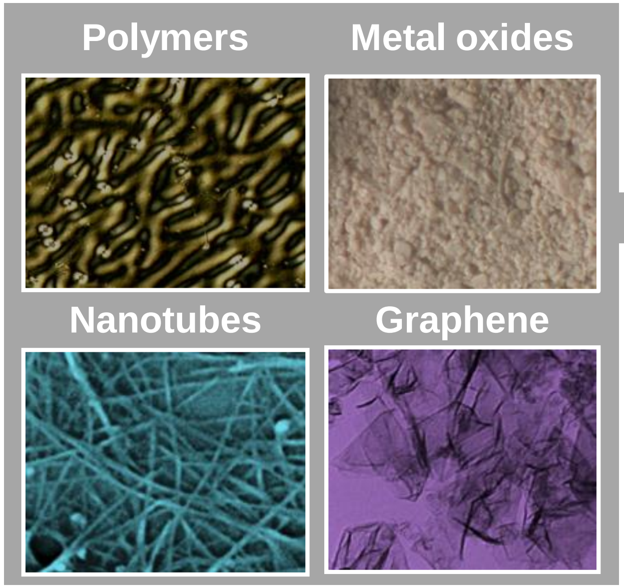
Top 3
Focused sensor requirements

- High reliability (accuracy and stability)
- Low initial / operation cost
- Low power consumption

Markets for Sensors in the Internet of Things 2014-2021
Markets for Sensors in the Industrial Internet, 2014
Potyrailo, *IDTech Internet of Things* 2014
Potyrailo, *TSensors Summit* 2015
Potyrailo, *Chem. Rev.* 2016

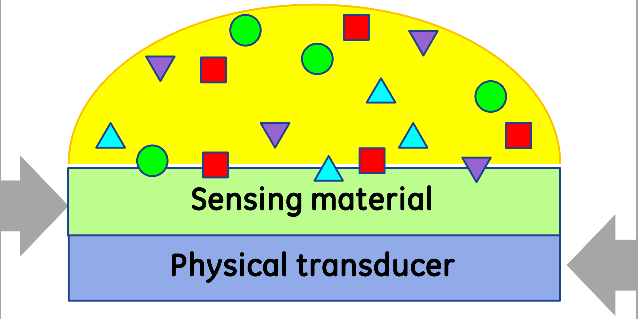
Our focus: enhanced reliability (accuracy + stability) of sensors at low cost
by development new transduction principles and data analytics

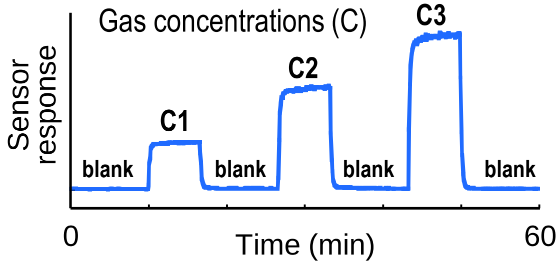
Anatomy of conventional gas sensors

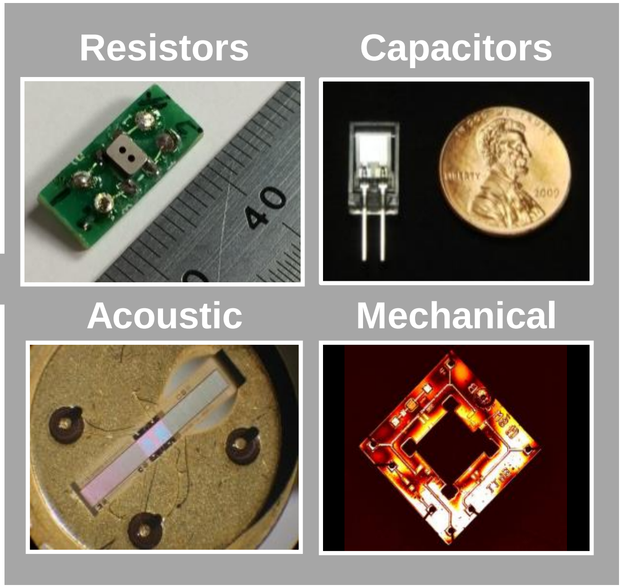


Potyrailo et al. *Sensor Lett.* **2004**
Potyrailo et al. *Chem. Rev.* **2011**

Sensor system



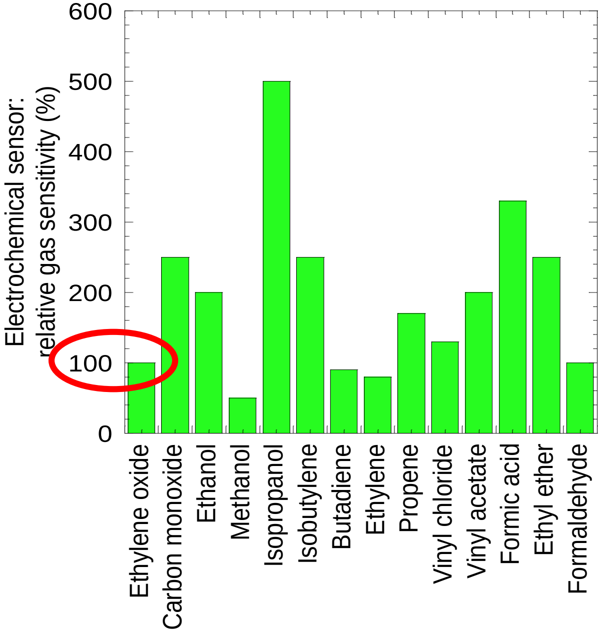




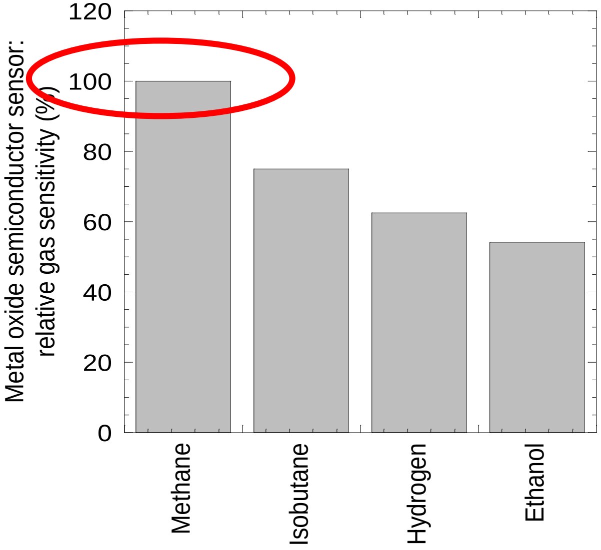
Potyrailo et al. *Annu. Rev. Mater. Res.* **2013**

Appropriate pairing of ***transducer + sensing material***
is the key for meeting detection requirements

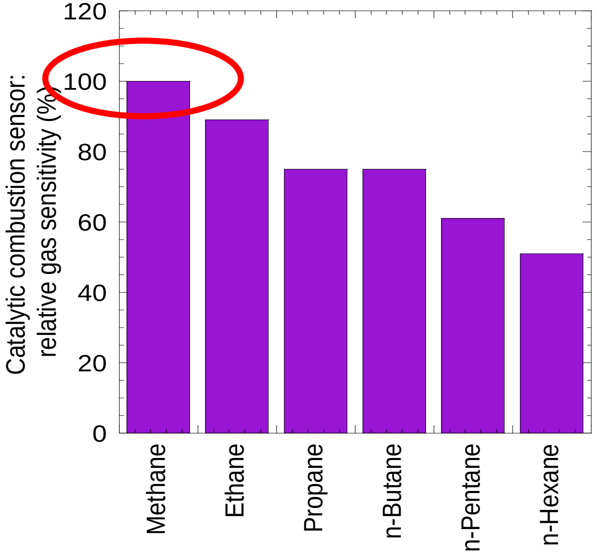
Selectivity challenges in major types of sensors



Electrochemical



Metal oxide



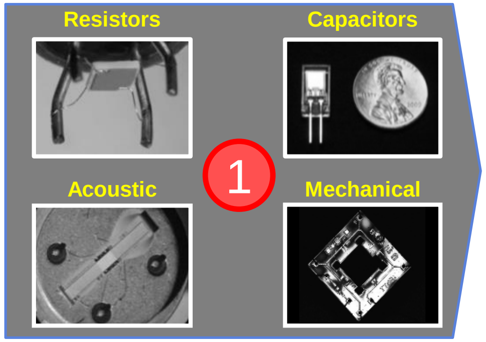
Catalytic

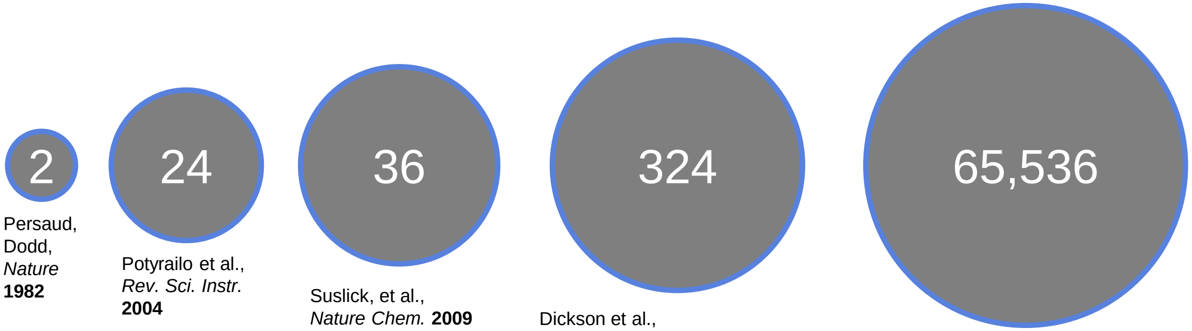
Non-selective response to different gases is
a significant accuracy limitation of conventional sensors

Origin: conflicting requirements for sensor selectivity vs. reversibility

Potyrailo *Chem. Rev.* **2016**

Sensor arrays as accepted compromise





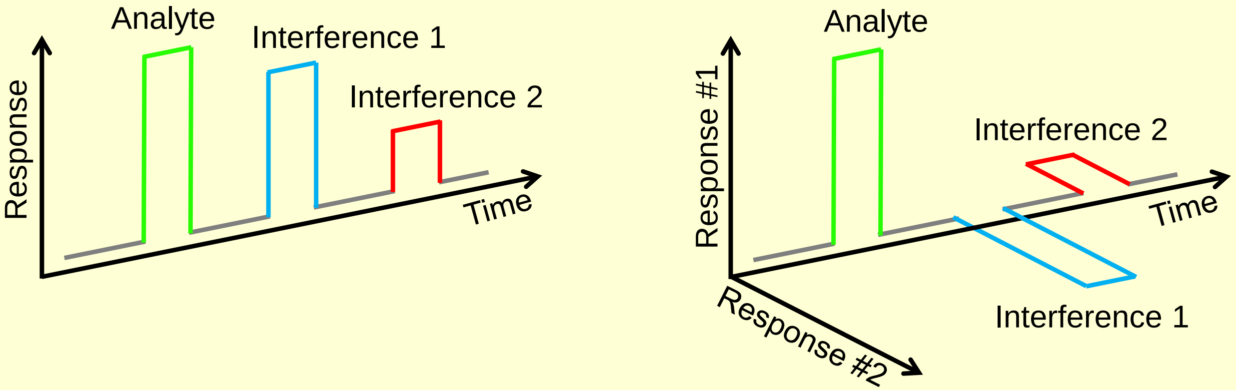
Persaud, Dodd, *Nature* **1982**

Potyrailo et al., *Rev. Sci. Instr.* **2004**

Suslick, et al., *Nature Chem.* **2009**

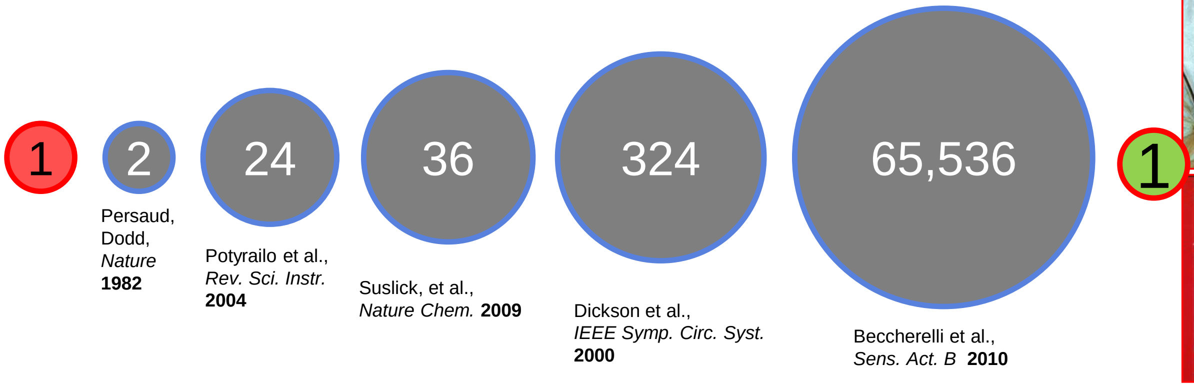
Dickson et al., *IEEE Symp. Circ. Syst.* **2000**

Beccherelli et al., *Sens. Act. B* **2010**



High dispersion of sensor response improves selectivity (= accuracy)

Breaking status quo: multivariable gas sensors



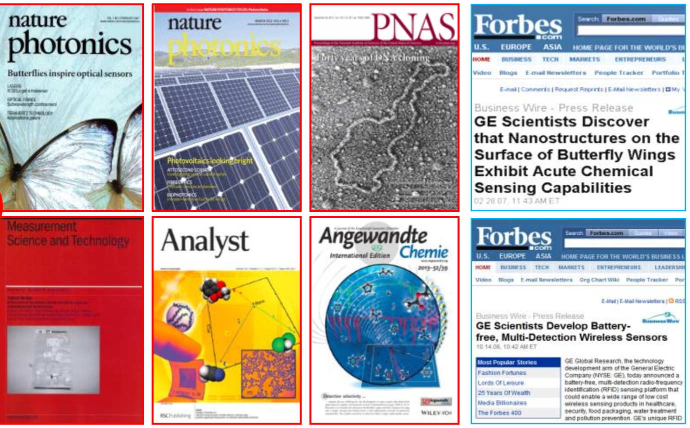
Persaud, Dodd, *Nature* **1982**

Potyrailo et al., *Rev. Sci. Instr.* **2004**

Suslick, et al., *Nature Chem.* **2009**

Dickson et al., *IEEE Symp. Circ. Syst.* **2000**

Beccherelli et al., *Sens. Act. B* **2010**



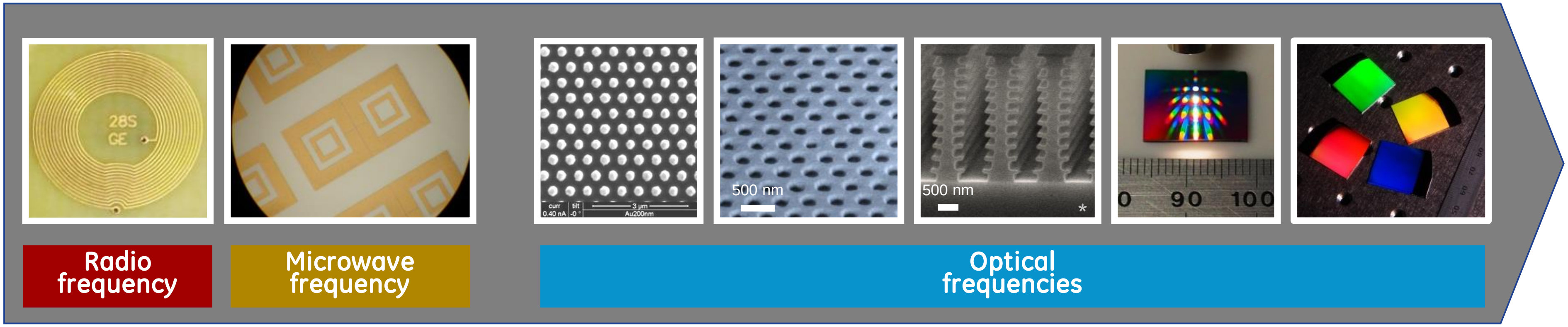
Selectivity:
~2,000,000-fold rejection of chemical interferences outperformed gas sensor arrays in side-by-side tests

Sensitivity:
part-per-million, part-per-billion, part-per-trillion

Individual multivariable sensors:

- Several independent responses from individual sensor
- Disruptively overcome insufficient selectivity of existing sensors

Roadmap for our electromagnetic resonant multivariable transducers



Radio frequency

Microwave frequency

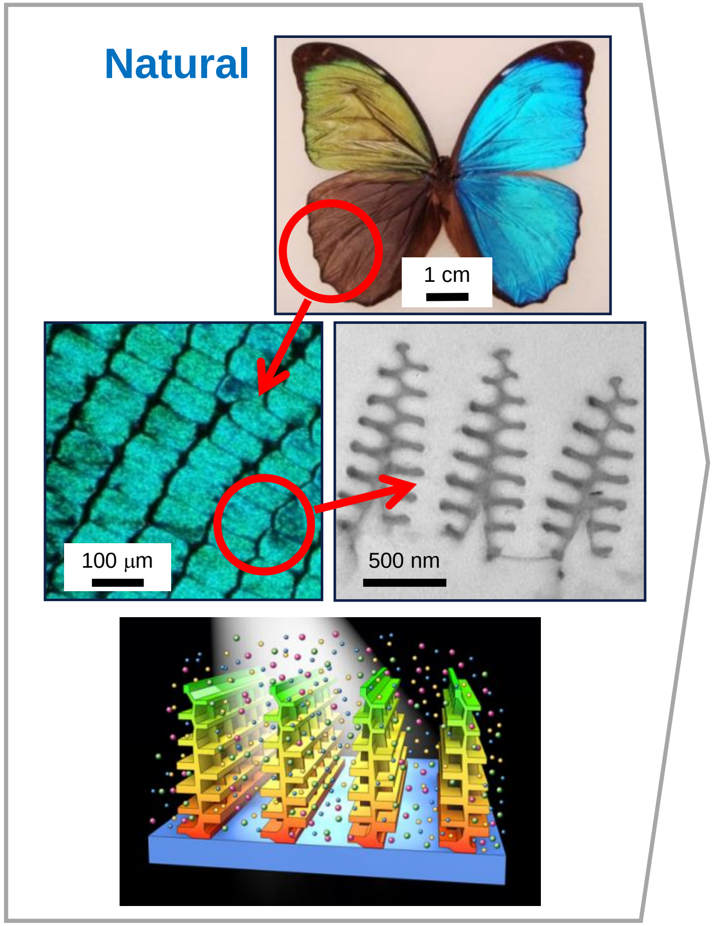
Optical frequencies

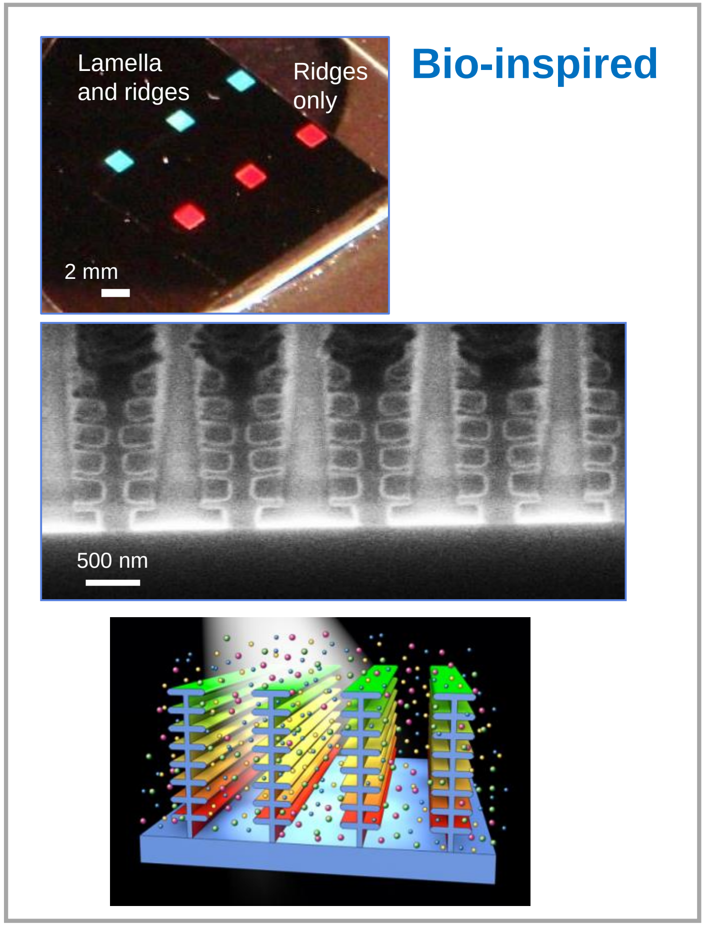
New philosophy for highly selective sensing

Potyrailo et al., *20+ Granted US Patents*

Potyrailo et al. *Nature Photonics* 2007
Potyrailo et al. *Chem. Rev.* 2011
Potyrailo et al. *Proc. Natl. Acad. Sci. USA* 2013
Potyrailo et al. *Annu. Rev. Mater. Res.* 2013
Potyrailo et al. *Angew Chem. Int. Ed.* 2013
Potyrailo et al. *Nature Communications* 2015 *

Bio-inspired gas sensors



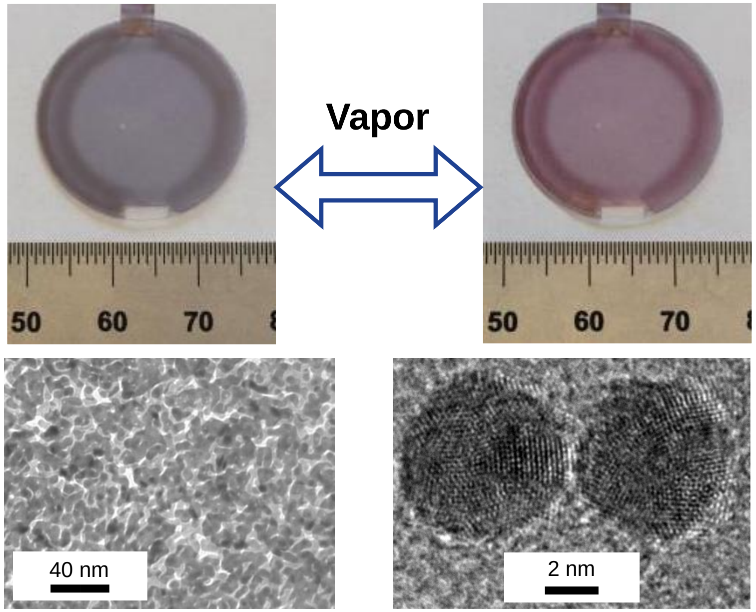


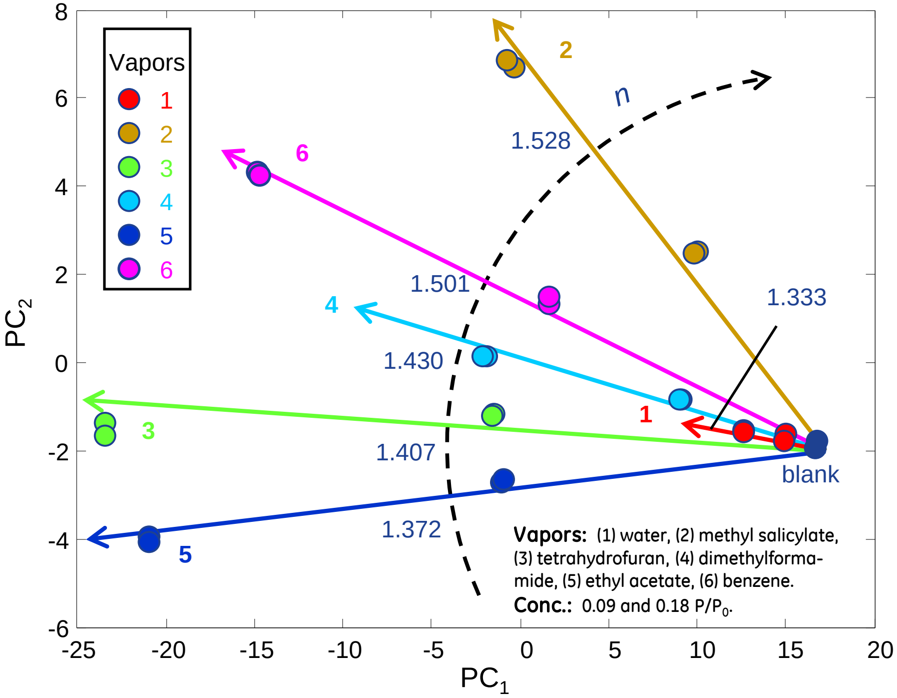
Design rules for gas-selectivity control:

- Spatial orientation of surface functionalization
- Chemistry of surface functionalization
- Extinction and scattering of nanostructure

Nature Photonics **2007**; *Proc. Natl. Acad. Sci. USA* **2013**; *Nature Communications* **2015**

Plasmonic resonant multivariable sensors



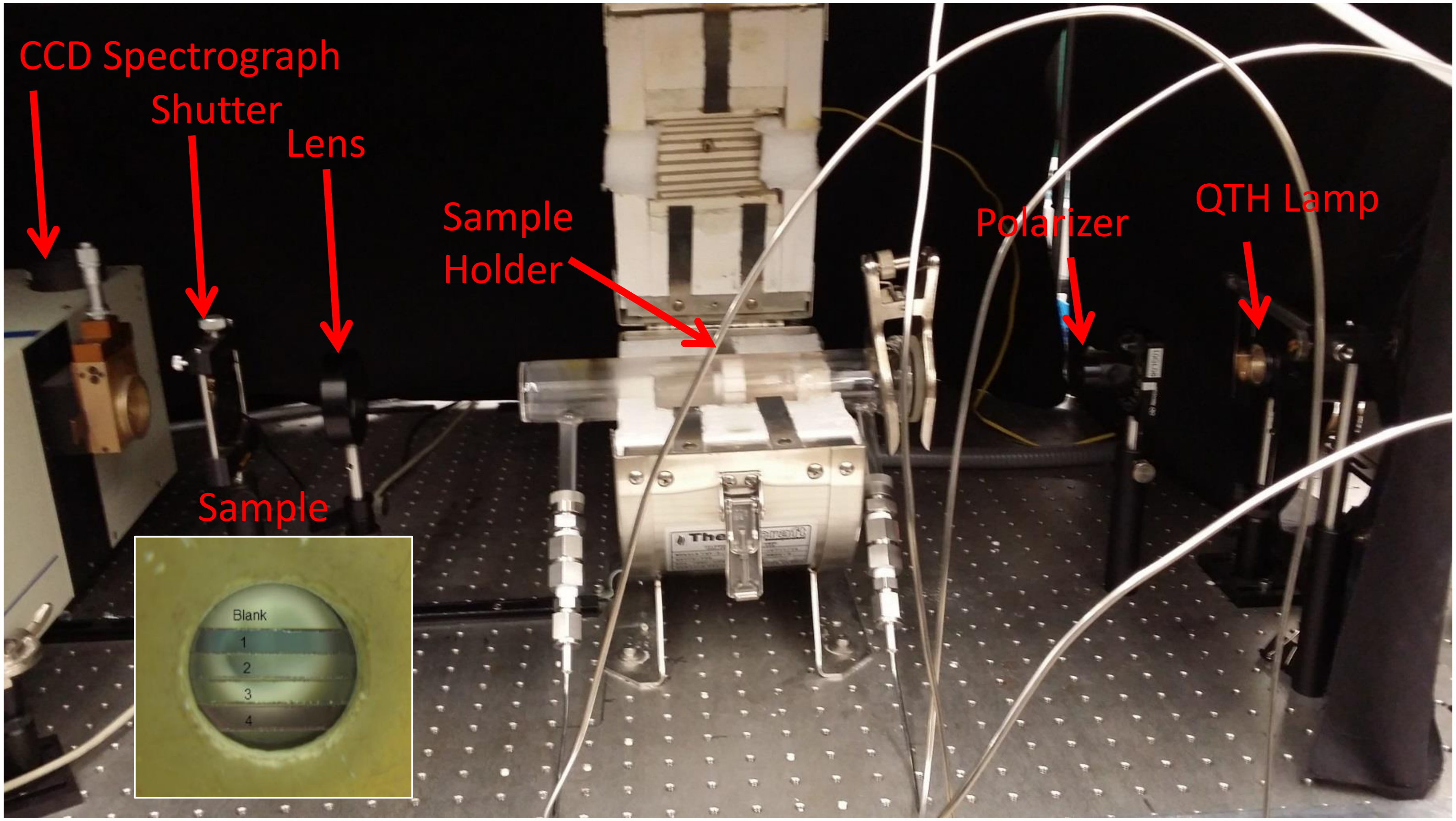


Vapors: (1) water, (2) methyl salicylate, (3) tetrahydrofuran, (4) dimethylformamide, (5) ethyl acetate, (6) benzene.
Conc.: 0.09 and 0.18 P/P_0.

Sensor selectivity is based on
interparticle spacing, dielectric constant, refractive index, and film reflectivity

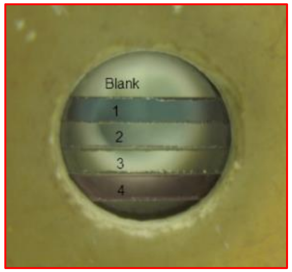
Angew. Chem. Int. Ed. **2013**

CCD imaging spectrograph built at SUNY



- CCD data acquisition for up to 8 samples on 1cm substrate simultaneously
- 300K to 1100K

Analysis of sensing materials using CCD imaging spectrograph



Element 1: MBE CeO_2 with implanted Au

- Ceria is 200nm thick
- Gold particle size ~30nm
- Au ~ 8 at. %

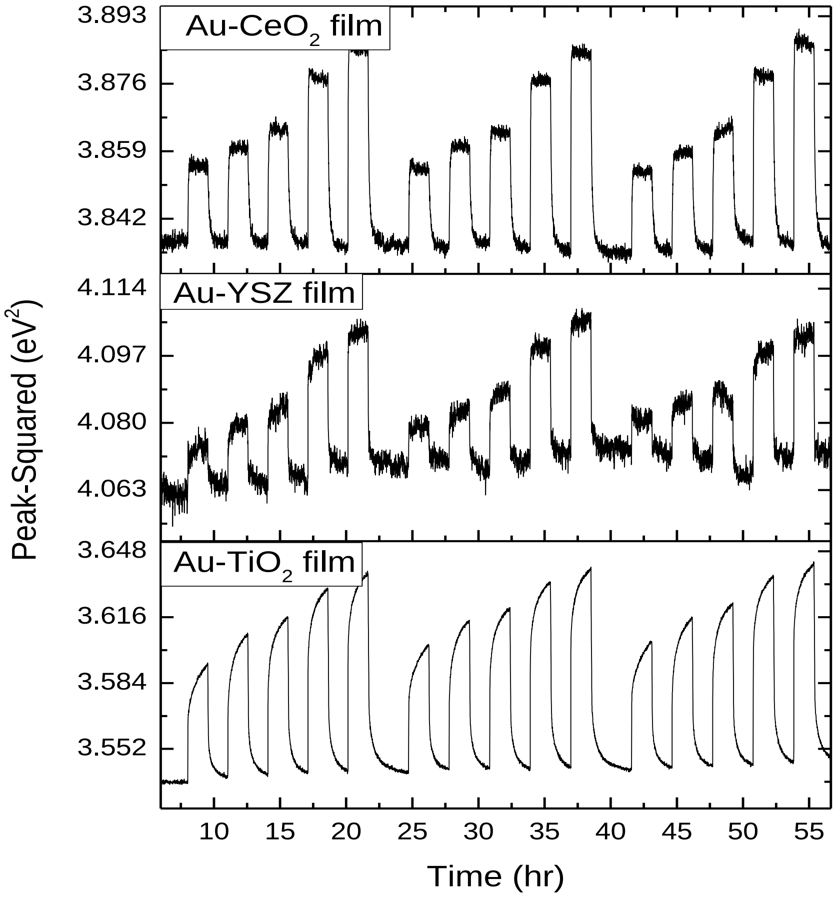
Element 2: PVD Au-YSZ

- ~30nm thick Au-YSZ
- Au particle size ~25nm
- ~10 at.% Au

Element 3: PVD Au-TiO_2

- ~30nm thick Au-TiO_2
- Au particle size ~25nm
- ~10 at.% Au

H_2 (200, 500, 1000, 5000, 10000 ppm) at 500 °C in air



Project objective

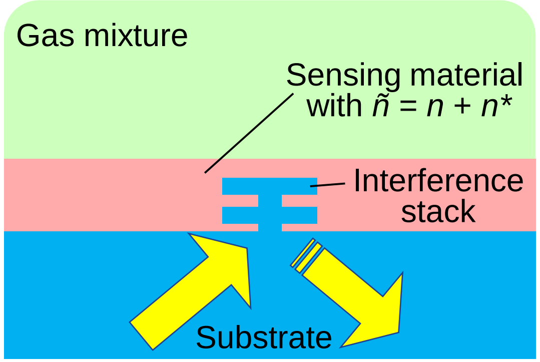
The program objective is to achieve the highly desired selectivity and stability of sensing of gases for SOFC application by implementing a new generation of gas sensors, known as multivariable sensors [1-6]. This program will culminate with field validation of developed sensors on GE SOFC systems.

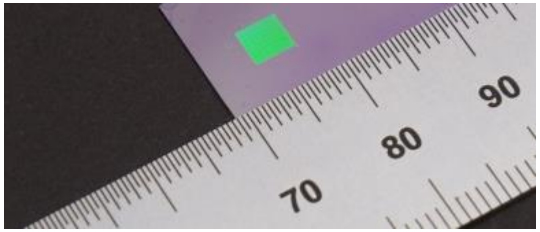
In Phase 1, we will develop sensing materials, perform lab tests for sensitivity and stability, downselect sensor designs, and perform field validation of developed sensors on a SOFC system at GE–Fuel Cells.

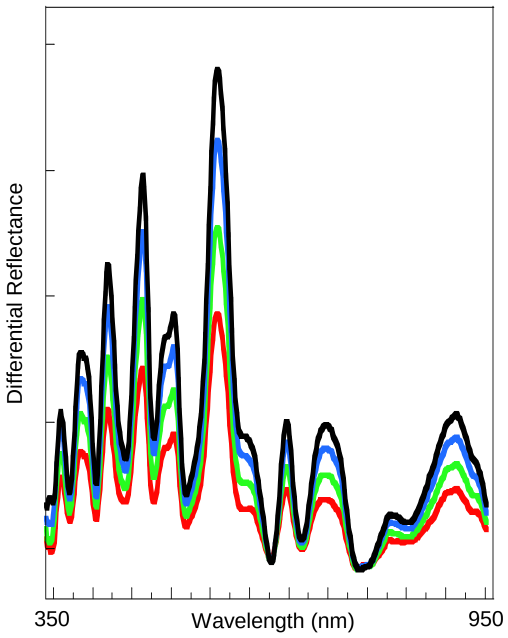
Phase 1 will advance fundamental understanding of multivariable gas sensing at high temperatures and will enable cost-effective and stable sensors for SOFC applications. In situ data generated by the sensors will allow development of recommendations for Phase 2 deliverables.

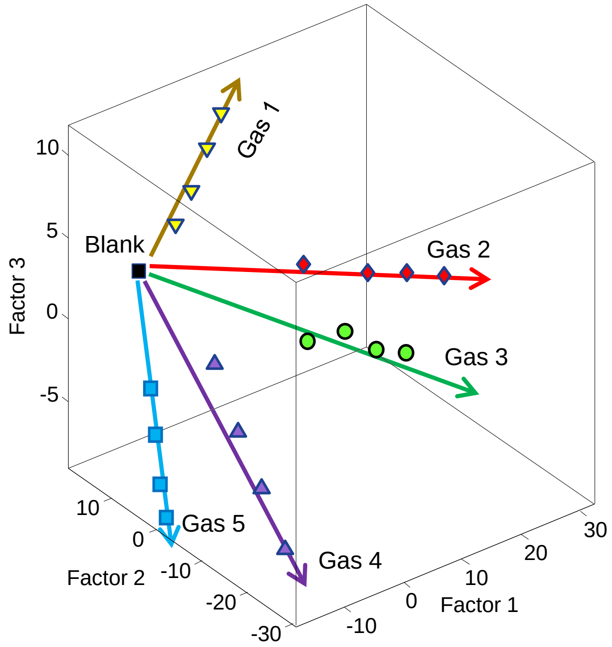
(1) Potyrailo et al. *Nat. Photonics* **2007**, *1*, 123-128
(2) Potyrailo et al. *Chem. Rev.* **2011**, *111*, 7315–7354
(3) Carpenter et al. *Anal. Chem.* **2012**, *84*, 5025-5034
(4) Potyrailo et al. *Proc. Natl. Acad. Sci. U.S.A.* **2013**, *110*, 15567–15572
(5) Potyrailo et al. *Nat. Commun.* **2015**, *6*, 7959
(6) Potyrailo *Chem. Rev.* **2016**

Proposed multivariable optical sensor based on interference stacks



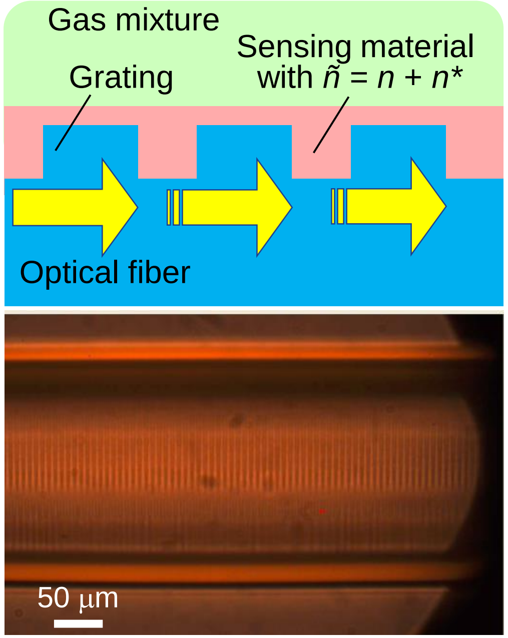


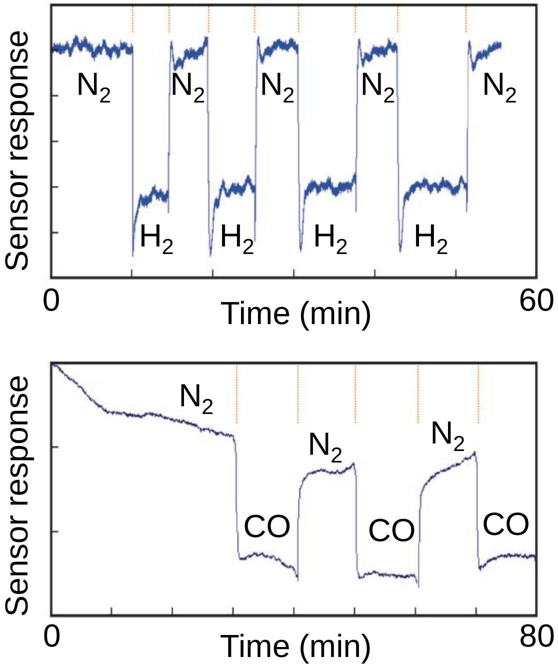


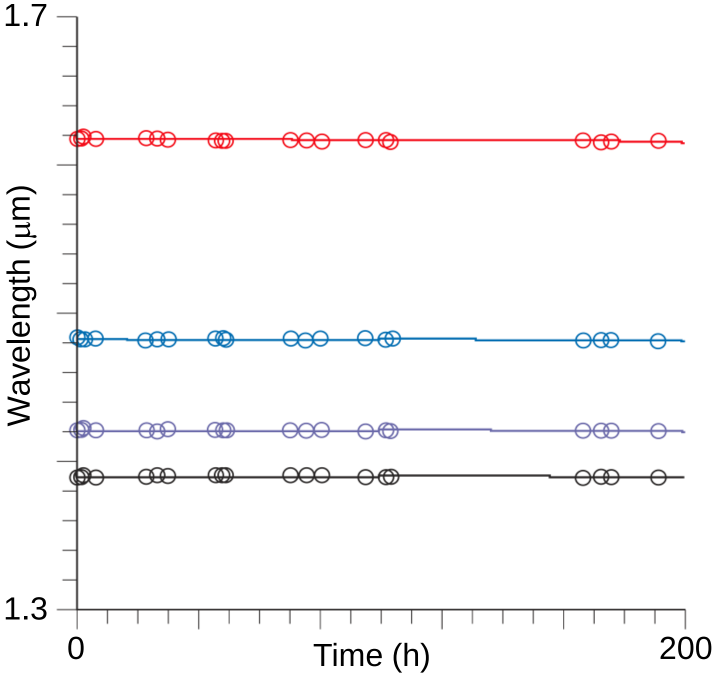


Proof-of-concept: Potyrailo et al. *Nature Comm.* **2015**

Proposed multivariable optical grating-based sensor

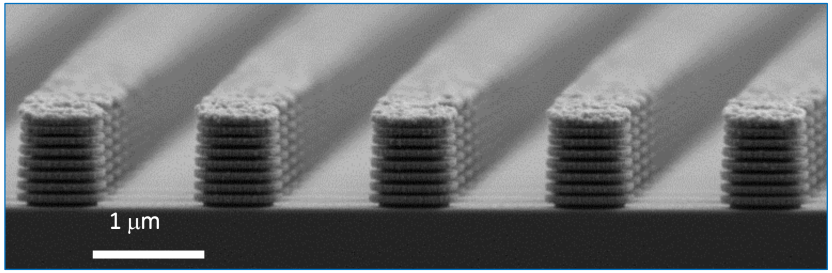


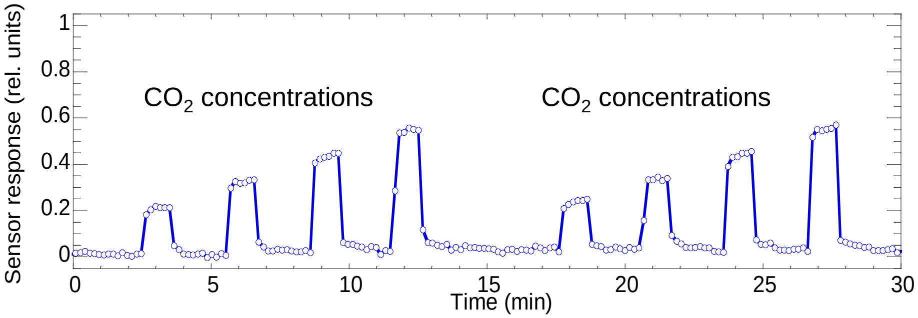




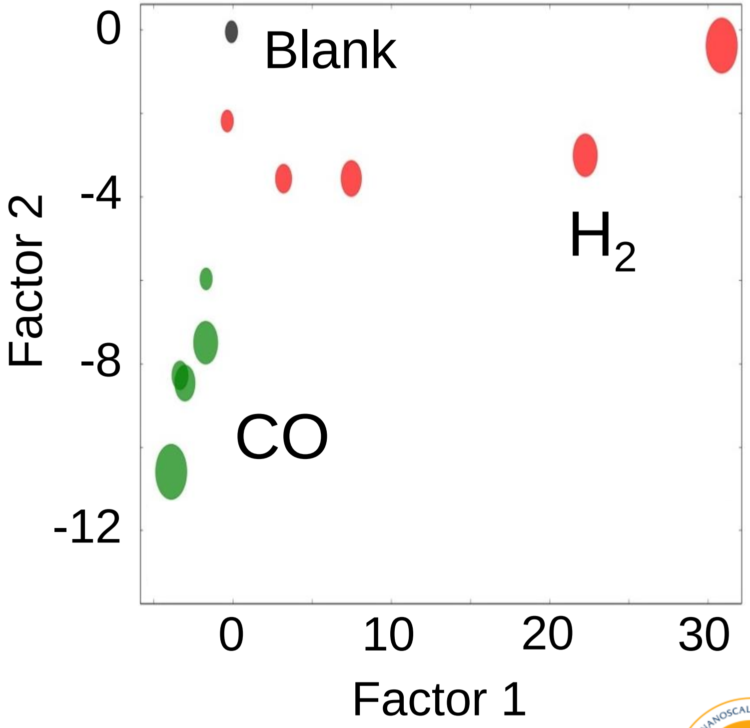
Proof-of concept: Wu, J., Distributed Fiber Optic Gas Sensing for Harsh Environment, Final Report, Department of Energy, NETL, Award DE-FC26-05NT42438 2008, http://www.osti.gov/scitech/servlets/purl/938805

Example of proposed sensing structures and materials for multivariable optical sensors





Proof-of-concept: GE



Proof-of-concept:
Carpenter et al. *Anal. Chem.* **2012**, *84*, 5025-5034.

Project structure

Task	Owner	Timing	Objectives
1. Project management, planning, and reporting	GE Global Research	Months 1-18	Defined by DOE; risk management, coordination, reporting
2. Validate selectivity of multivariable sensor system in laboratory conditions	GE Global Research SUNY Poly	Months 1-9	•Develop requirements for spectral dispersion for multivariable transducers and optical changes of sensing materials for gas monitoring at required levels •Establish gas-selectivity ranking of tested sensors
3. Validate stability of multivariable sensor system in laboratory conditions	GE Global Research	Months 10-15	•Establish protocol of sensor stability test, employ benchmarks on non-patterned surfaces •Establish stability ranking of tested sensors
4. Field-validate multivariable sensor system at GE–Fuel Cells factory	GE Global Research GE–Fuel Cells	Months 16-18	•Validate developed sensors in operation cycles of a 50-kW SOFC system •Develop recommendations for Phase 2 deliverables

Deliverables and milestones

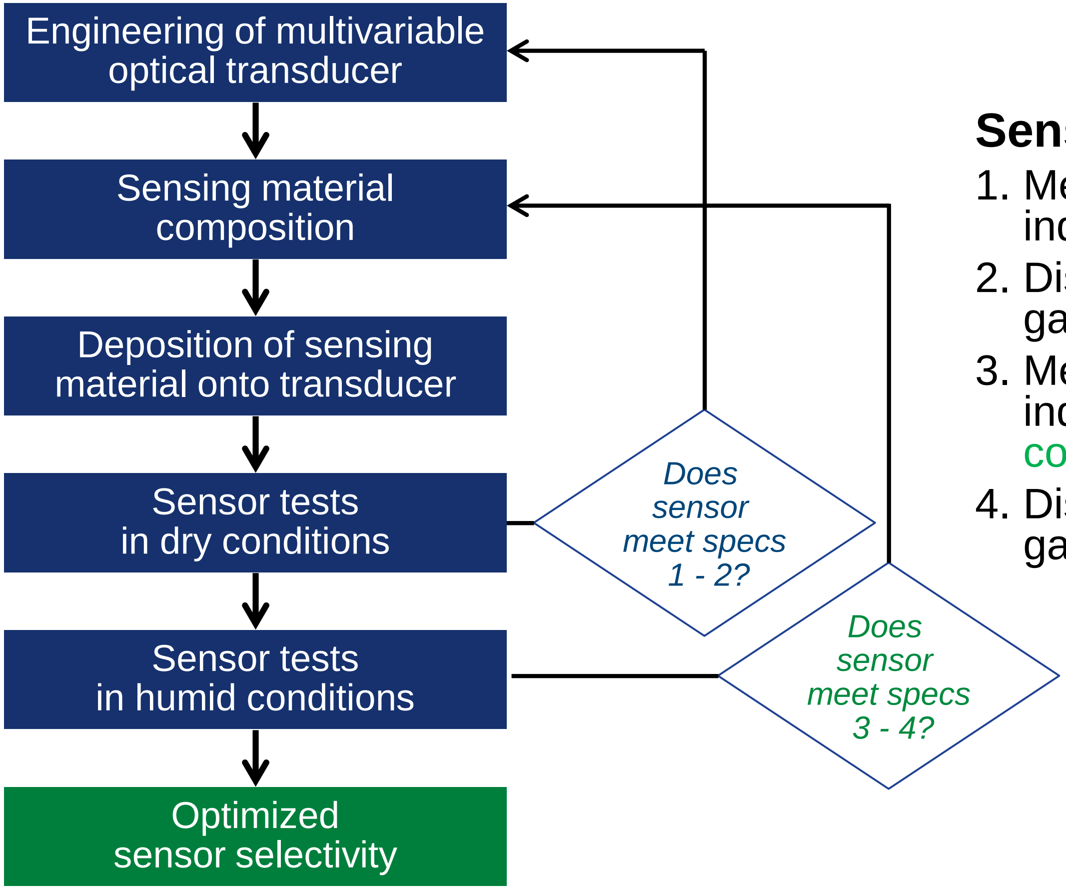
Deliverables

Task	Deliverable
1	Quarterly reports, updated risks, final report
2	Characterization data of sensing materials deposited on optical transducers
2	Sensor data and gas-selectivity ranking of transducer /sensing film systems
3	Characterization data of sensor aging
3	Sensor data and stability ranking of transducer /sensing film systems
4	Sensor data of field validation in a 50 kW SOFC system

Milestones Log

Task Number	Description	Planned Completion Date	Actual Completion Date
1	Updated Project Management Plan and Data Management Plan	10/15/2016	
1	Kickoff Meeting	10/15/2016	
2	Developed sensor systems demonstrate selectivity toward gases of interest	6/30/2017	
3	Developed sensor systems demonstrate performance stability of at least 2 weeks	12/31/2017	
4	Developed sensor systems operational in field tests with SOFC system for in-situ detection of gases	3/31/2018	

Selectivity optimization of multivariable optical gas sensors



Engineering of multivariable optical transducer

Sensing material composition

Deposition of sensing material onto transducer

Sensor tests in dry conditions

Sensor tests in humid conditions

Optimized sensor selectivity

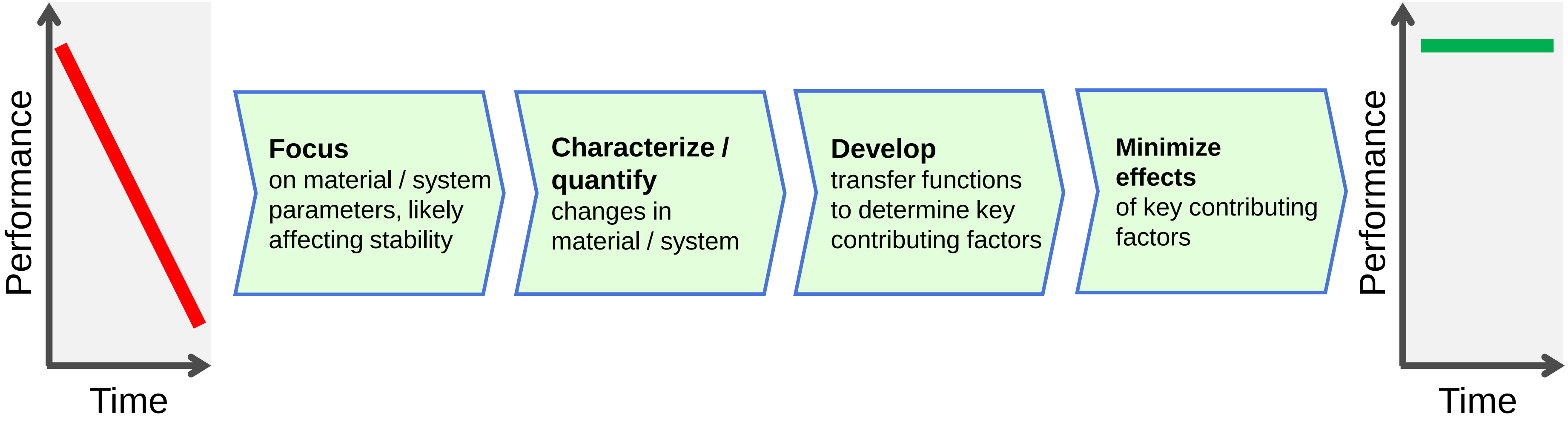
Does sensor meet specs 1 - 2?

Does sensor meet specs 3 - 4?

Sensor specifications:

1. Measurement dynamic range for individual gases in dry conditions
2. Discrimination between different gases in dry conditions
3. Measurement dynamic range for individual gases in humid conditions
4. Discrimination between different gases in humid conditions

Improvement of material and system stability using a four-step Six Sigma process



Focus
on material / system parameters, likely affecting stability

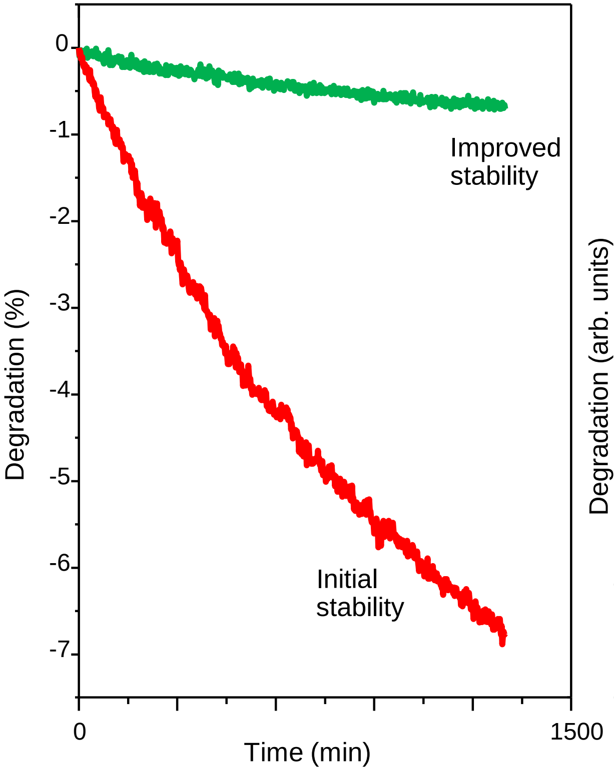
Characterize / quantify
changes in material / system

Develop
transfer functions to determine key contributing factors

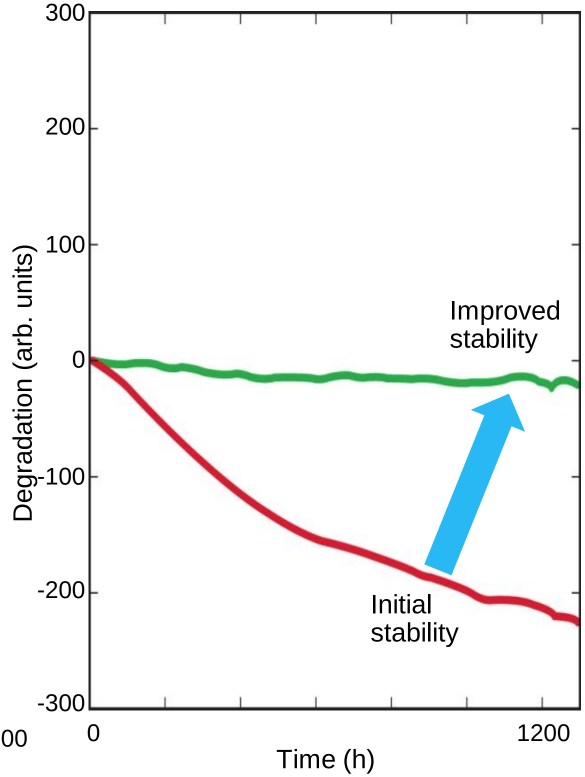
Minimize effects
of key contributing factors

Stability improvement of GE's materials and structures by implementing Six Sigma for product development

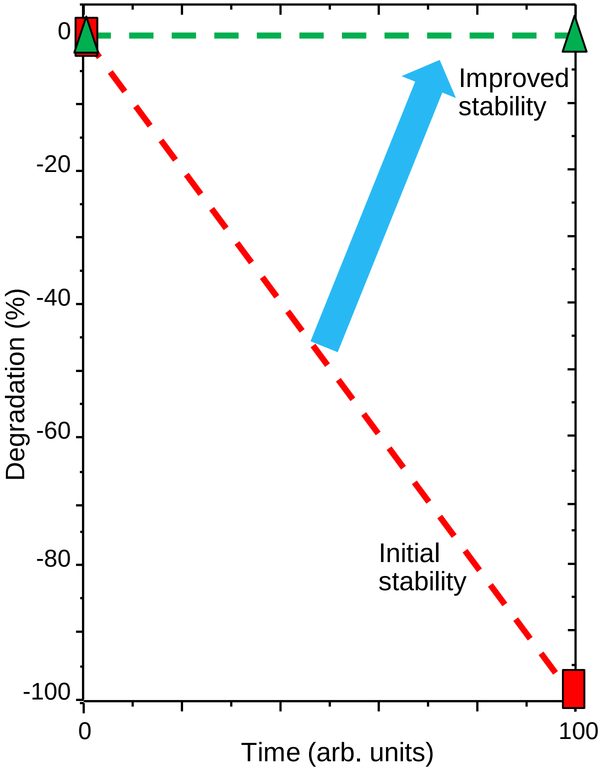
Inorganic material



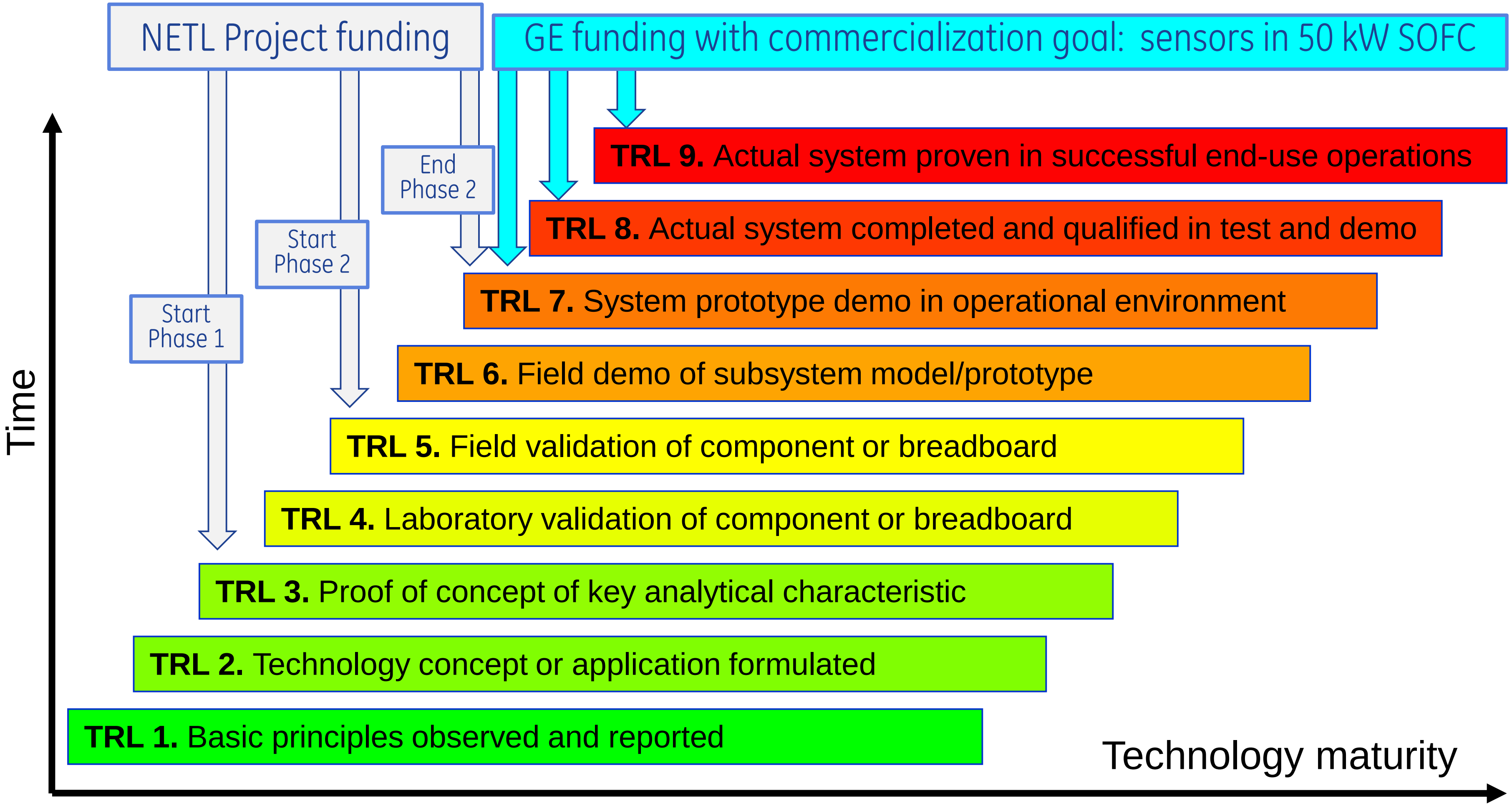
Inorganic structure



Polymeric material



Technology Readiness Level / commercialization goals



NETL Project funding

GE funding with commercialization goal: sensors in 50 kW SOFC

Start Phase 1

Start Phase 2

End Phase 2

TRL 9. Actual system proven in successful end-use operations

TRL 8. Actual system completed and qualified in test and demo

TRL 7. System prototype demo in operational environment

TRL 6. Field demo of subsystem model/prototype

TRL 5. Field validation of component or breadboard

TRL 4. Laboratory validation of component or breadboard

TRL 3. Proof of concept of key analytical characteristic

TRL 2. Technology concept or application formulated

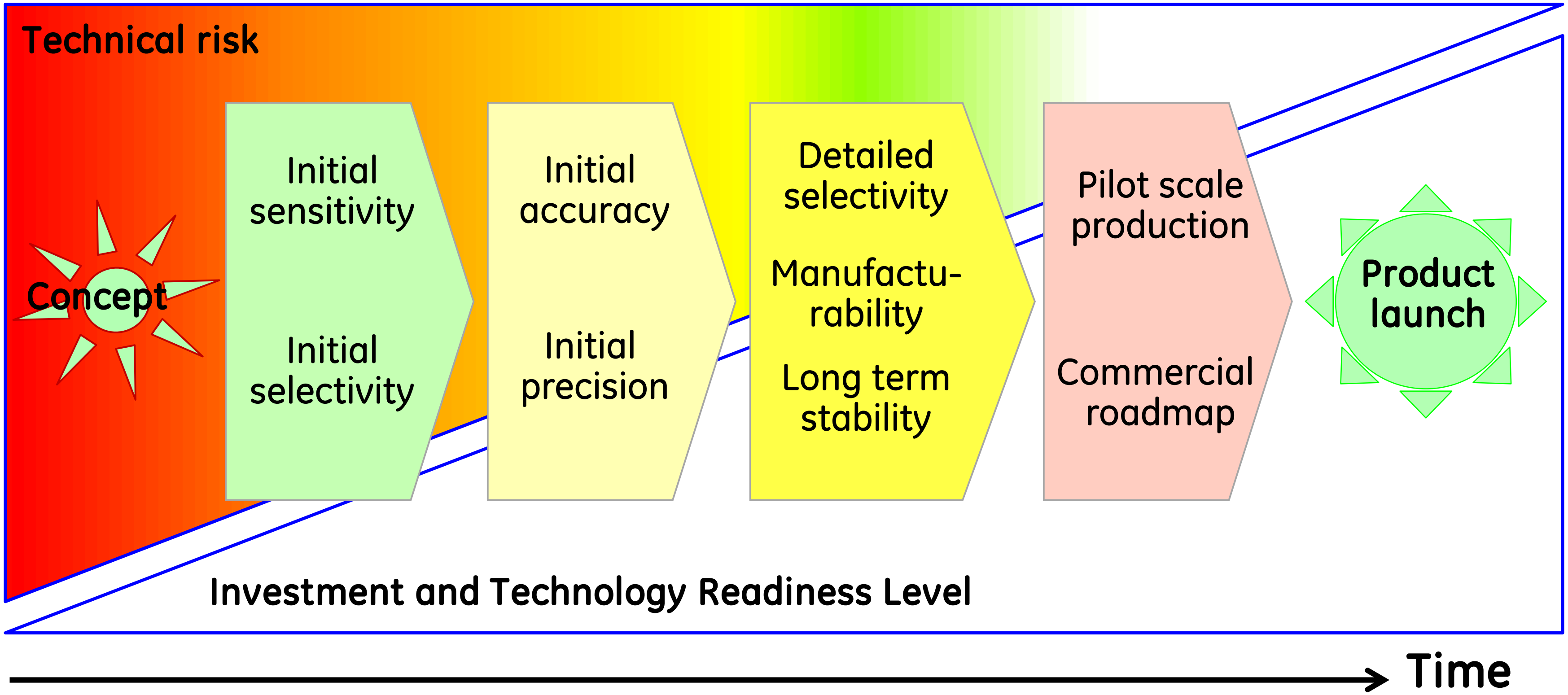
TRL 1. Basic principles observed and reported

Sensor commercialization process can include:

- technology readiness levels
- manufacturing readiness levels
- data readiness levels
- commercialization readiness levels

Potyrailo, in preparation

From sensor ideas to commercial products



Technical risk

Concept

Initial sensitivity

Initial selectivity

Initial accuracy

Initial precision

Detailed selectivity

Manufacturability

Long term stability

Pilot scale production

Commercial roadmap

Product launch

Investment and Technology Readiness Level

Time

Money investment: 1 : 10 : 100 : 1000

proof-of-concept → working prototype → pilot scale production → product launch

Time investment: several years

G.Whitesides, *Lab on a Chip*, **2013**; GE TrueSense Personal Water Analytics: The Prism Awards for Photonics Innovation Winners **2011**

Q & A