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

NETL Contract FE0027918

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18th Annual SOFC Project Review Meeting, Pittsburgh, PA, June 12-14, 2017
Background

**Goals for wide adoption of SOFC**
- needs to improve cost-effectiveness
- enhance operation reliability

**Technical strategy**
- early diagnostics of potential upsets
- ability to operate cells at optimum conditions

Project objective

**Phase 1 activities:**
- develop sensing materials
- perform lab tests and field validation

**Phase 1 outcomes:**
- fundamental understanding of multivariable gas sensors at high temperatures
- enable cost-effective and stable sensors for SOFC applications

Technical approach

- implement new generation of gas sensors (multivariable sensors)
- leverage design rules of multivariable sensors for SOFC monitoring
- dynamic information about SOFC reforming gases

Gases in Phase 2: 15-20% H₂, 10-20% CO, 5-20% CO₂, 2-15% CH₄, 40-60% H₂O

Gases in Phase 1 are subset from Phase 2
Proposed sensor vs available offerings

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

In situ sensor
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

Sensor requirements
- High reliability (accuracy, stability)
- Low initial / operation cost
- Low power consumption
Commodity gas detection: 
Serving sensing needs in *established* markets

- Mature status-quo technology
- Widely available
- Interchangeable
- Inexpensive

Photo by Potyrailo
Commodity gas detection: Challenges outside established markets

Status quo of conventional sensors

Electrochemical

Non-dispersive IR

“The biggest headaches are caused by interfering chemicals…”

Existing sensors do not meet monitoring demands of new growing markets
Sensor arrays as accepted compromise

Compromise between selectivity of sensor system and system complexity

Stability of sensor arrays

20-sensor array

Normalized Prediction Error

Drift of each sensor (%)
Existing approaches for high value gas detection

- Environmental
- Homeland Security
- Industrial Hygiene
- Petroleum / Biofuel
- Chemical
- Agriculture
- Food & Beverage
- Pharmaceutical
- Forensic

Performance of competing approaches

Multi-analyzer
Portable MS
Portable GC

Modern approaches for detection of volatiles with high selectivity:
Solving demanding measurement needs with available tools
Breaking status quo: multivariable photonic gas sensors

Individual multivariable sensors:
• Several independent responses from individual sensor
• Disruptively overcome insufficient selectivity of existing sensors

Potyrailo et al.
Nature Photonics 2007
Nature Photonics 2012
Proc. Natl. Acad. Sci. USA 2013
Nature Communications 2015
Chemical Reviews 2016

Carpenter et al.
ACS Nano 2014
Nanoscale 2015
Physics of color formation: Value for multivariable photonic sensors

Combined effects of multilayer interference and diffraction produce iridescence in natural *Morpho* butterfly scales

Potyrailo et al. *Nature Communications* 2015
Bio-inspired gas sensors

Natural

Design rules for gas-selectivity control

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

Bio-inspired

System concept

- Multivariable resonant sensor
- Data analytics
- Sensor node
- System design

Potyrailo et al. Nature Communications 2015
Previous results for multivariable optical sensors

High temperature sensing materials with diverse gas response mechanisms

Unusually high vapor response selectivity of natural *Morpho* scales

Understanding of origin of selective vapor response

Design rules for bio-inspired highly selective gas sensors


Ben = benzene
ACN = acetonitrile
MEK = methyl ethyl ketone
MeOH = methanol
H2O = water

Potyrailo et al. *Nature Communications* 2015
Diversity of fabricated bio-inspired nanostructures

FIB CVD  Electron-beam lithography

CVD, UV litho, chemical etching  Selective etching of ALD material  Double-molding

laser interference litho  Conventional photolithography and chemical etching

Examples of 3D sensing materials utilized in this program

Innovative design of sensing structures for high selectivity gas detection
In-house built multi-channel vapor generation and mixing systems

Spectroscopy system

- Gas cabinets
- 8-channel gas-delivery system

Spectral imaging system

- CCD Spectrograph
- Sample Holder
- Lamp

- Computer control
- Flexible flow profiles
- Multi-gas mixing
Example of single-gas responses

Response to $\text{H}_2$

Response to $\text{CO}$

Response to $\text{CO}_2$

On track for needed response sensitivity and speed
Tools for data analysis of multivariable sensors: machine learning, data analytics, multivariate statistics

**Supervised learning**
- Artificial neural network
- Bayesian statistics
- Case-based reasoning
- Gaussian process regression
- Gene expression programming
- Group method of data handling
- Inductive logic programming
- Instance-based learning
- Lazy learning
- Learning Automata
- Learning Vector Quantization
- Logistic Model Tree
- Minimum message length
- Probably approximately correct learning
- Random Forests
- Support vector machines
- Symbolic machine learning

**Unsupervised learning**
- Expectation-maximization algorithm
- Vector Quantization
- Generative topographic map
- Information bottleneck method
- Self-organizing map
- Association rule learning
- Hierarchical clustering
- Single-linkage clustering
- Conceptual clustering
- Cluster analysis
- K-means algorithm
- Fuzzy clustering

**Semi-supervised learning**
- Generative models
- Low-density separation
- Graph-based methods
- Co-training

**Reinforcement learning**
- Temporal difference learning
- Q-learning
- Learning Automata

**Deep learning**
- Deep belief networks
- Deep Boltzmann machines
- Deep Convolutional neural networks
- Deep Recurrent neural networks
- Hierarchical temporal memory

Increasing role of data analytics in high performance sensing

Wikipedia.org
Toward selective and stable bio-inspired gas sensors for solid oxide fuel cells

System concept

Field test

Stability of multivariable sensor
Initial response stability
Example: H₂ gas

Baseline studies of sensor stability
Short-term responses of sensor: analyte, interference, their mixtures

Excellent short term response for selective analyte quantitation
Long-term responses of sensing nanostructure: analyte, interference, their mixtures

Reflectance vs. Time

WL #1

WL #2

Long term response exhibits strong baseline drift

WL = wavelength
BS = baseline
Predicted analyte concentrations from long-term responses

Corrected long term sensor baseline drift
Summary

• Design of bio-inspired sensing materials for simultaneous quantitation of several gases
• Refined material-design rules to operate at elevated temperatures
• Advancing fundamental understanding of multivariable gas sensors at high temperatures
• Initial stability tests started
Acknowledgements

- GE Fuel Cells SOFC Team
- GE Global Research Team
- SUNY Albany team
- Steven Markovich @ DOE/NETL

- Funding provided by the US Department of Energy through cooperative agreement FE0027918

This material is based upon work supported by the Department of Energy under Award Number FE0027918. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the authors and do not necessarily reflect the views of the DOE.