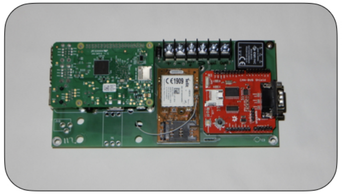
Natural Gas Infrastructure

Additive Manufacturing

Internet of Things



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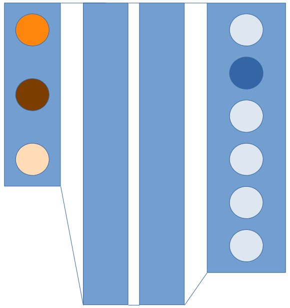


Solid-state Mixed Potential Electrochemical Sensors for Natural Gas Leak Detection and Quality Control (DE-FE0031864)

- **Lok-kun Tsui**,[1] Sleight Halley,[1] Kannan Ramaiyan,[1] Kamil Agi,[2] and Fernando H. Garzon[1]
- [1] Center for Micro-Engineered Materials, University of New Mexico, Albuquerque, NM, USA
- [2] SensorComm Technologies Inc, Albuquerque, NM, USA

CENTER FOR MICRO-ENGINEERED MATERIALS

SCT SENSORCOMM TECHNOLOGIES

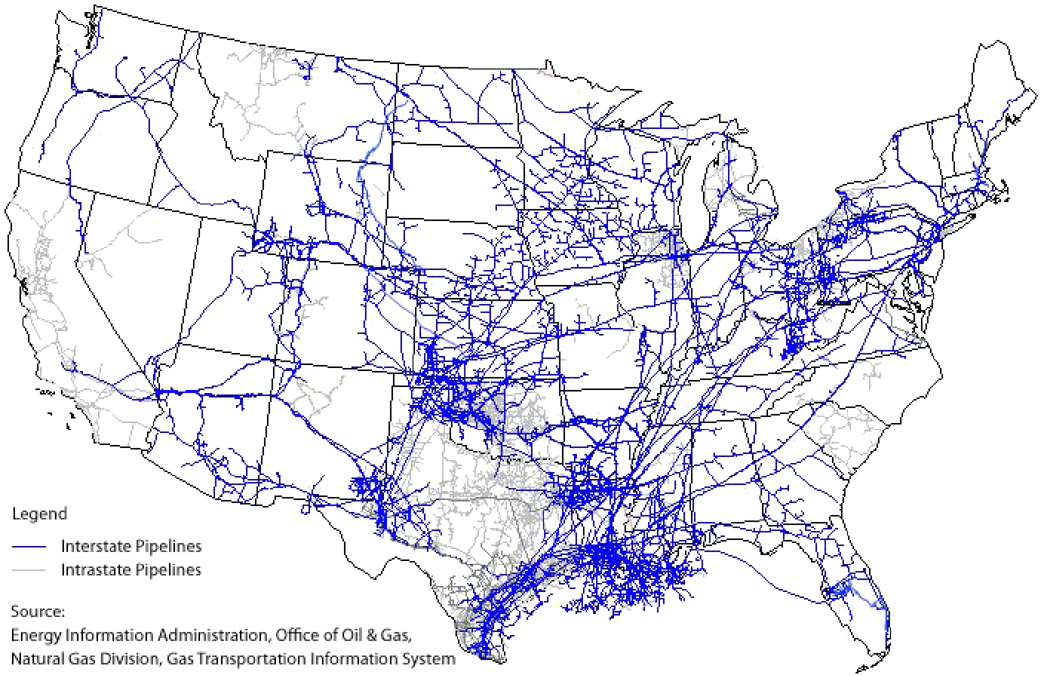
US Department of Energy
National Energy Technology Laboratory
2021 Carbon Management and Oil and Gas Research Project Review Meeting

Presentation Outline

- Motivation: Sensors for Natural Gas Detection
- Technical Status
  - Sensor Manufacturing by Ceramic AM
  - Machine Learning for Quantification and Identification
  - Data Acquisition using I-o-T Platform
- Accomplishments to Date
- Lessons Learned
- Synergy Opportunities
- Project Summary

Motivation: The Scope of the Natural Gas Emissions Problem

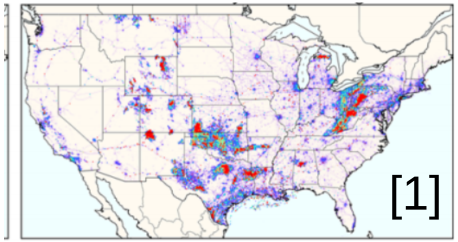
- Over 300k miles of pipeline used to transport natural gas. [1]
- Economic Cost of Methane Leaks: 2 billion dollars per year. [2]
- Powerful Greenhouse Gas– Emissions in US accounted for 1.624×10^8 Metric Ton CO_2 Equivalent.[3]
- Increased regulatory scrutiny of industrial emissions creates a greater need for monitoring technology.

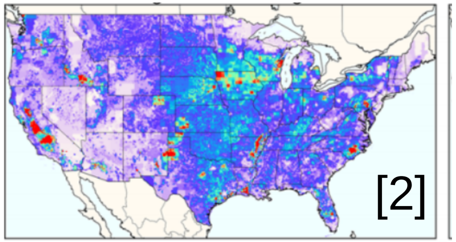


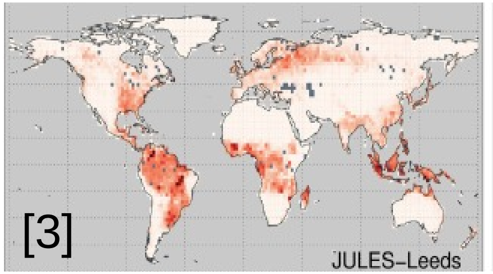
[1] https://afdc.energy.gov/fuels/natural_gas_distribution.html
[2] A.J. Marchese, *et al*. Science. 7204 (2018) eaar7204.
[3] Kort, E. A.; Frankenberg, C. Costigan, K.R.; Lindenmaier, R.; Dubey, M. K; Wunch, D. Geophys. Res. Lett, 2014, 41, 19, 6898

Sources of Methane Emissions (2019)

Nat. Gas Infrastructure	Livestock	Coastal Wetlands
156 mt/yr [1]	62 kt/yr [1]	153 kt/yr [1]







A sensing system for CH_4 monitoring must differentiate between these sources.

[1] EPA Inventory of US GHG Emissions and Sinks: 1990-2019
[2] J.D. Maasakkers, *et al.*, Environ. Sci. Technol. 50 (2016) 13123–13133.
[3] Parker et al. Remote Sensing of Enviornment, 211 (2018), 261-275.

Current Methods of CH_4 Monitoring

Technology	Satellite / Aircraft	Lab (GC/MS/ CRDS)	Portable IR	Catalytic Gas Sensors	SC Gas Sensors	Mixed Potential Sensors
Cost	Very High	High ($100k+)	Med ($30k)	Low	Low	Low
Area Resolution	Square Miles	Square Feet	Square Feet	Square Feet	Square Feet	Square Feet
Sensitivity	ppb	ppb	ppb	~1% LEL level	ppm	ppm (100 ppb using PDT)
Robustness	N/A	Low	Low	Med	Med	High
NG component gas selectivity	Yes	Yes	Yes	No	No	Yes
Stability	N/A	Requires frequent maintenance	Optical paths must be kept clean	Sensor drift	Sensor drift	High stability over 1000s of hours.
Size,weight, power	Very Large	Large, 3-20kg,10-100s W	Medium,kg,10s W	Small,g,W	Small,g,W	Small, g, W

Our Technology

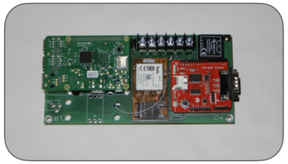
[1] EPA Inventory of US GHG Emissions and Sinks: 1990-2019
[2] J.D. Maasakkers, *et al.*, Environ. Sci. Technol. 50 (2016) 13123–13133.
[3] Parker et al. Remote Sensing of Enviornment, 211 (2018), 261-275.

Technology Approach

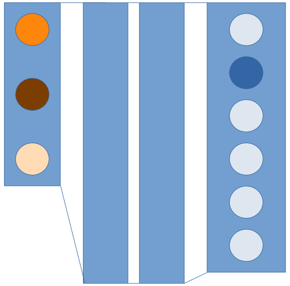
Natural Gas Infrastructure

AM

Internet of Things

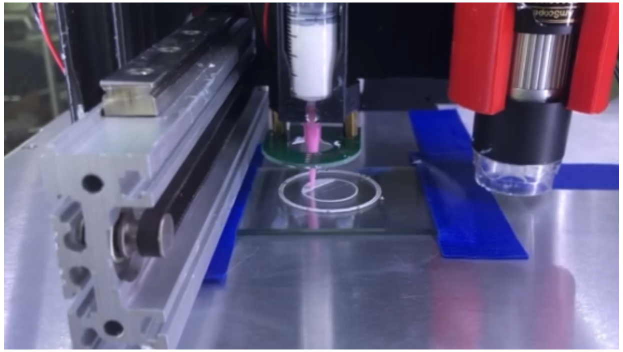


ML/AI

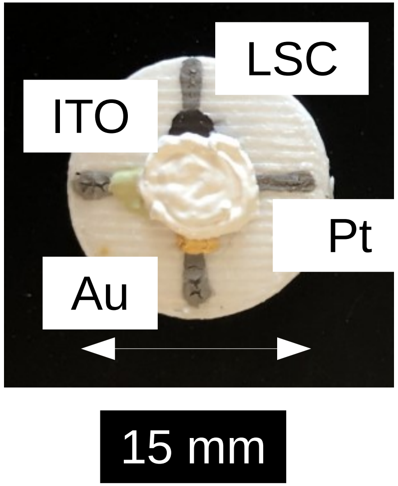


Multi-element MPE Sensors

- MPES devices rely on a difference in catalytic activity to generate a voltage upon exposure to test gases.
- Selectivity can be tuned by material selection, geometry, applied current bias.
- Low cost, robust, and well suited for mass-fabrication.
- Combined with ceramic additive manufacturing to enable rapid prototyping of materials for sensitivity.
- Sensor Composition:
  - Indium Tin Oxide (ITO): CH_4
  - $La_{0.87}Sr_{0.13}CrO_3$ (LSC): C > 1 Hydrocarbons
  - Au: NH_3
  - Substrate: YSZ (Gen 1-4) → CSZ; MSZ (Gen 5)
  - Electrolyte: Porous YSZ

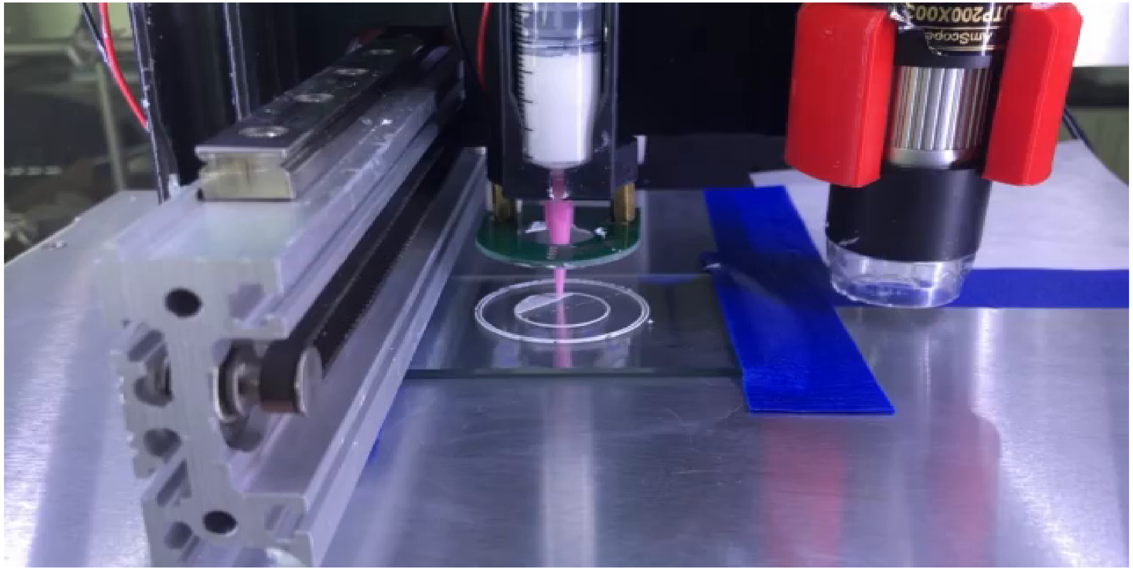


Additive Manufacturing of Sensor Substrate



A Four Electrode Sensor

Video



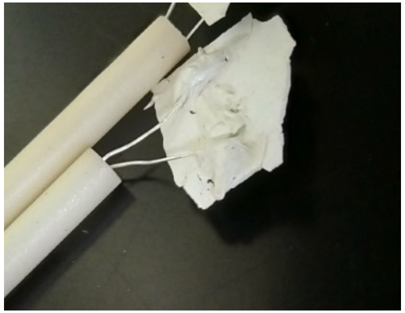
Sensor Evolution

Spring 2020

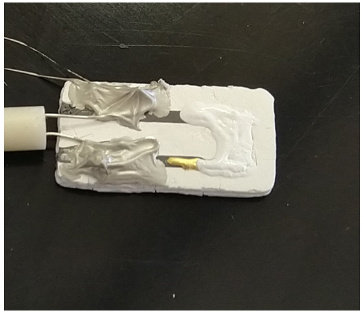
Fall 2020

Spring 2021

Summer 2021



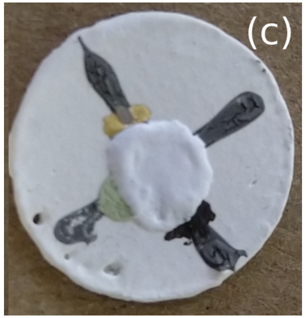
Generation 1:
Razor blade cast substrate. Parts are very brittle.



Generation 2:
3D printed substrate. Substantially increased robustness. Used as demonstration for Au/Pt electrode

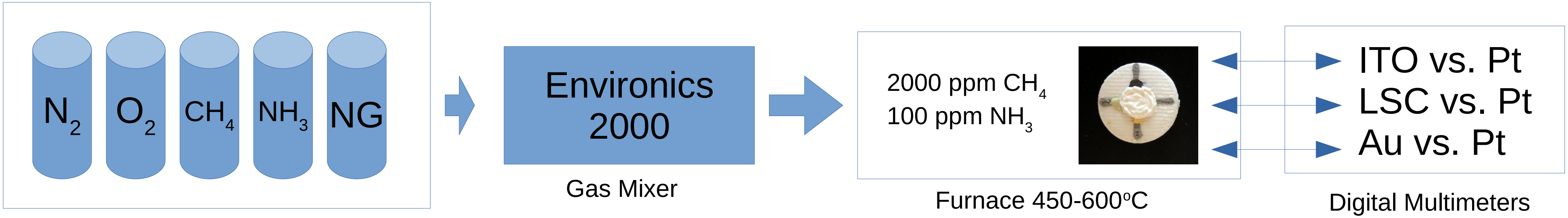
Generation 3:
First 4 electrode design incorporating Pt, LSC, Au, and ITO electrodes on one substrate

Generation 4:
Radial configuration to equalize electrode areas.



Generation 5:
Robocasted low ionic conductivity (CeO_2-ZrO_2) substrates for enhanced sensitivity

Sensor Test Procedure



Gas Manifold

Data Collection:

- Flow Rate: 150 CCM
- O_2 Content: 21%
- Balance gas: N_2

CH_4	BMAT1028	NH_3	Mix CH_4/NH_3	Mix NG/NH_3
Wetlands	Natural Gas		Bovine Methane	
1000-4000 ppm	1000-4000 ppm CH_4	50-250 ppm	1000-4000 ppm CH_4 75-325 ppm NH_3	1500-4000 ppm CH_4 75-250 ppm NH_3

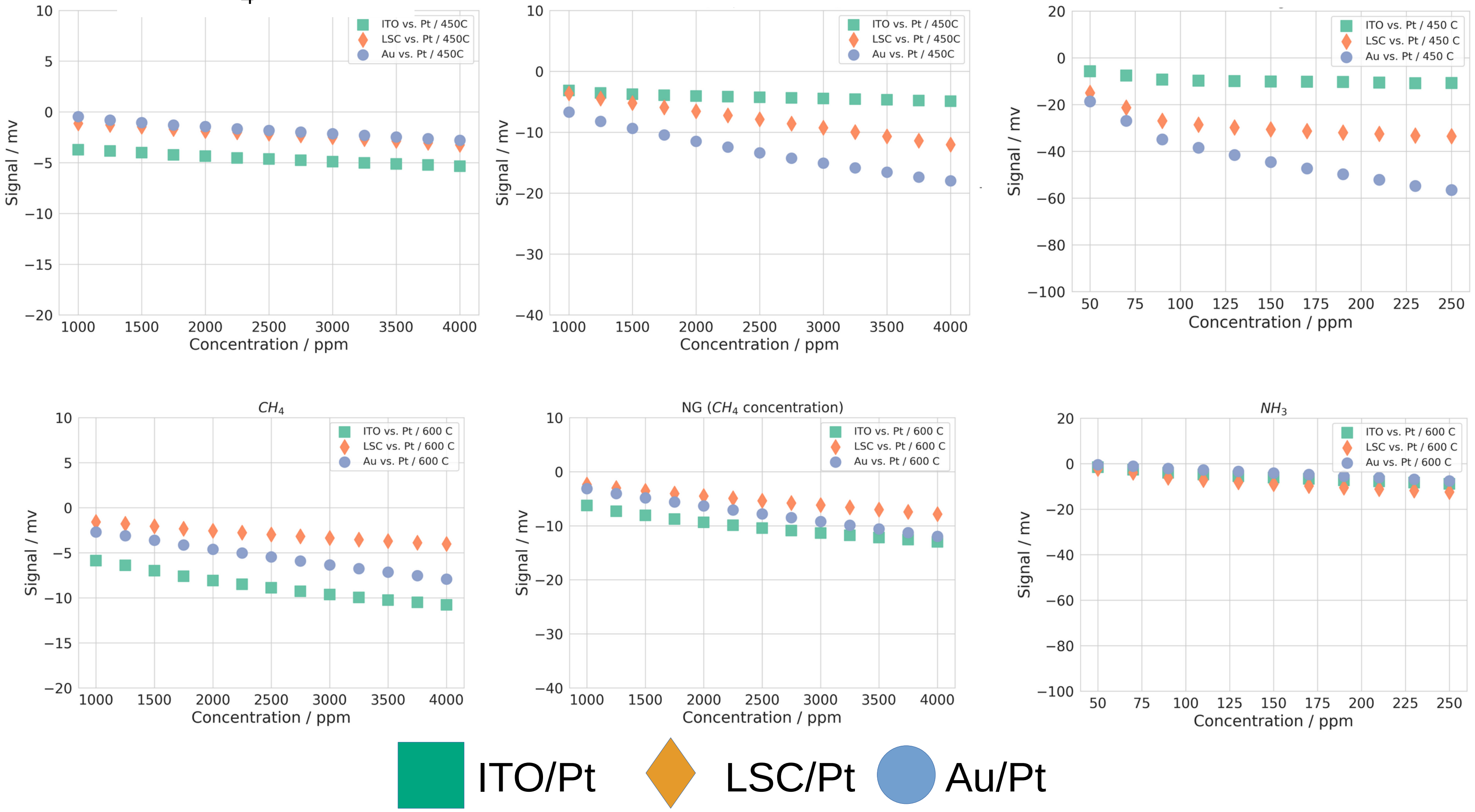
CH_4 Only | Natural Gas | NH_3

450°C

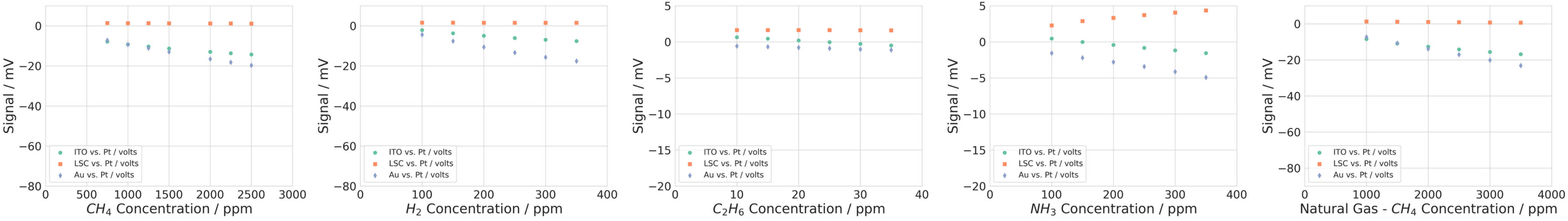
- Differentiated response CH_4 vs. NG
- Strong NH_3 Sensitivity.

600°C

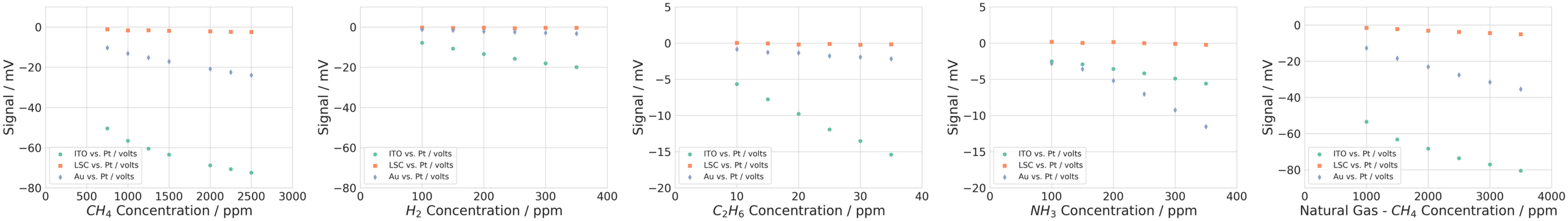
- Stronger sensitivity for both CH_4 and NG but lower response selectivity.
- Weakened NH_3 sensitivity



Ytttria-Stabilized-Zirconia (YSZ) Substrates



Ceria-Stabilized Zirconia (CSZ) Substrates



Using CSZ produces up to 3.5x enhancement in sensitivity to CH_4 and C_2H_6

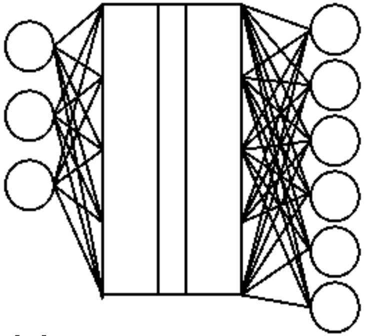
Machine Learning Approach

- ML Needs: Identification and Quantification
- ML process: Artificial Neural Networks
  - Mimics the interconnected networks of biological neurons which can automatically learn relations between inputs and outputs.
  - Does not require human to define functional form → helps to automatically resolve difficult to predict cross interference effects with complex mixtures.
  - Can be readily deployed on portable computing hardware.
- Train separate artificial neural networks for identification and quantification.

Fully Connected, Feed Forward ANN

Input

Sensor Signals



Hidden Layers

Output

Identification

OR

Quantification

Gas

Sensor Signal

Identification Process

Quantification Process

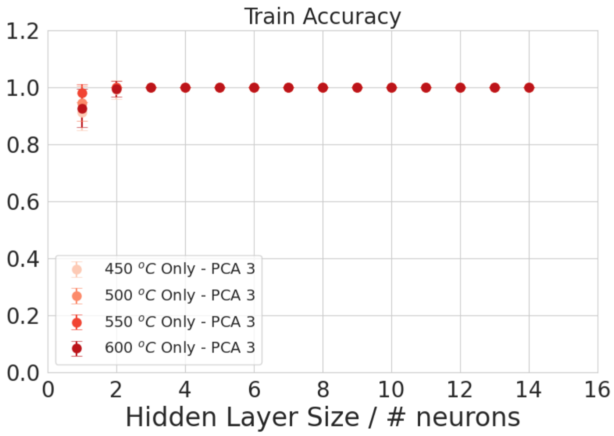
96%

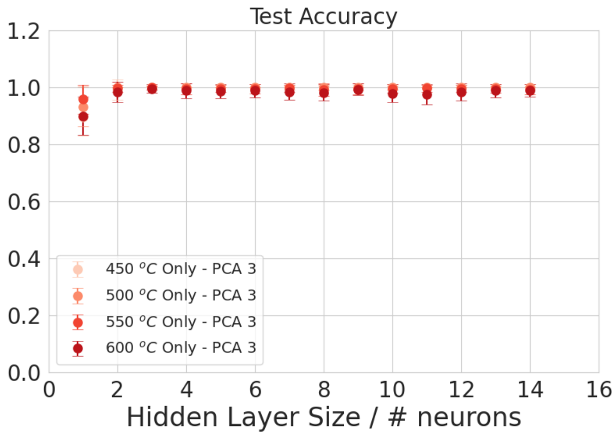
3%

1%

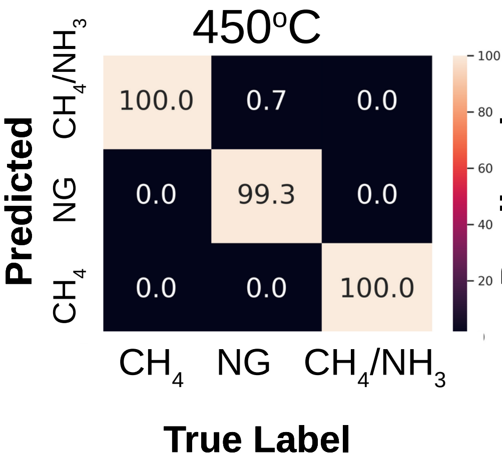
CH_4 = 1000 ppm

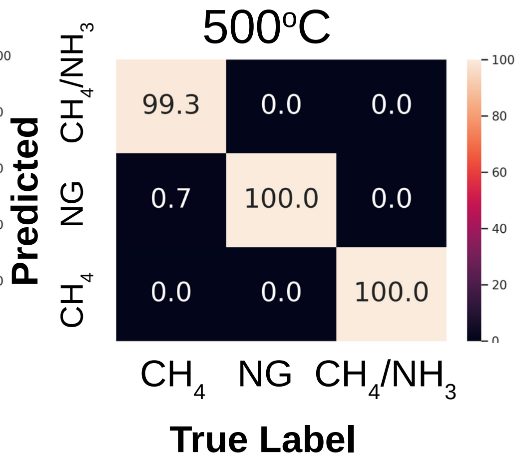
Identification Results: 3 Mixtures

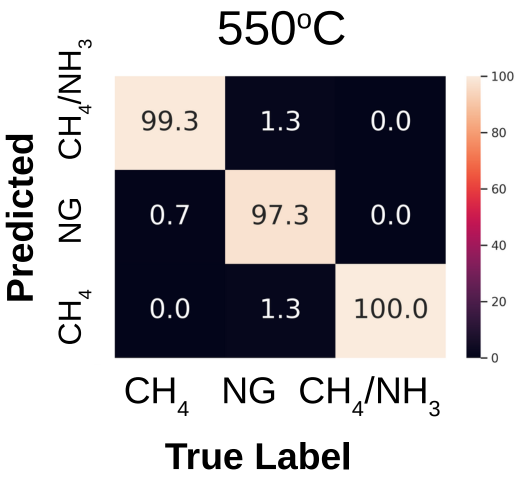


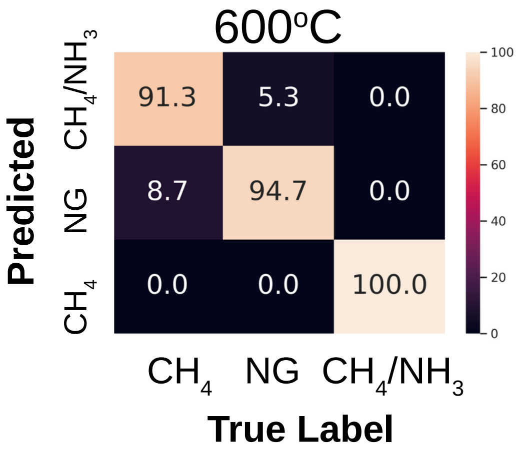


Identification of natural gas from CH_4 and CH_4/NH_3 can be done at one temperature with > 94% accuracy in all cases and > 99% accuracy at 450-500°C.

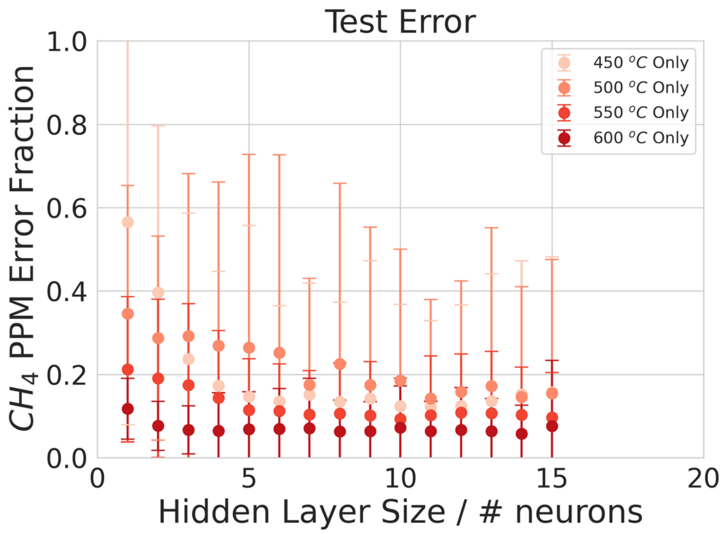


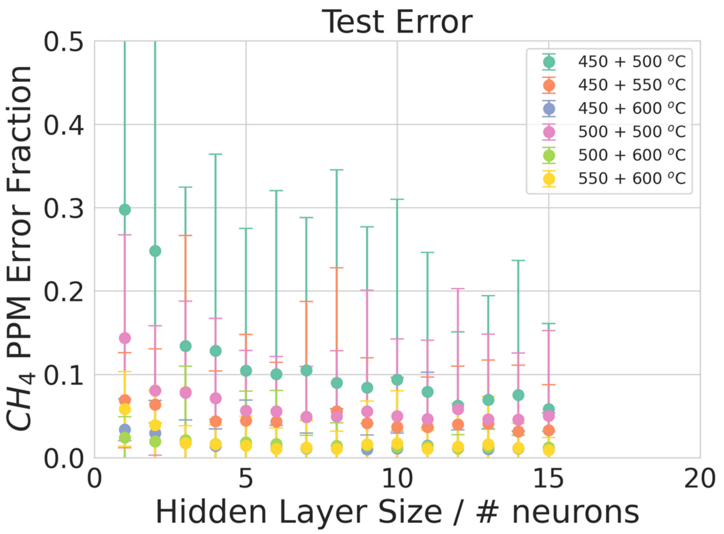






Quantification Test Error Results



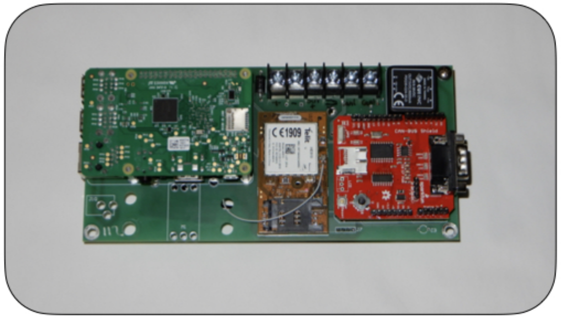


Quantification Error
600C < 7% ppm CH_4

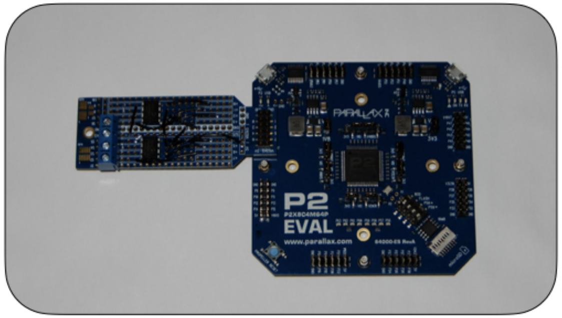
Quantification Error
450+600C < 1.5% ppm CH_4

Integrated Wireless Sensing Platform

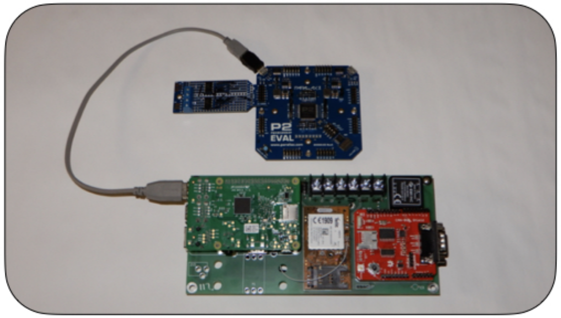
SENSORCOMM TECHNOLOGIES



IoT Gateway



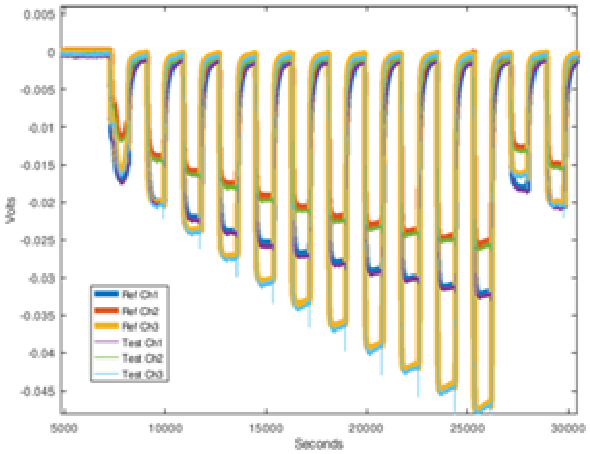
Readout Prototype



Integrated Prototype

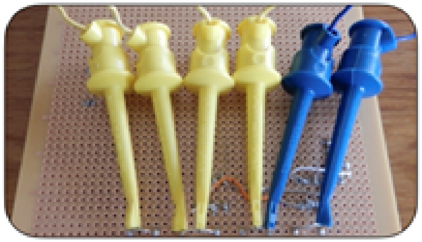
RESEARCH

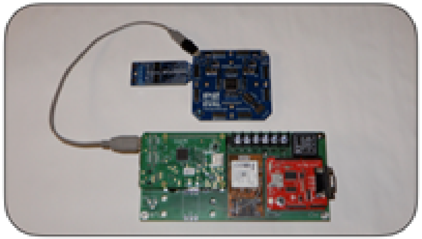
Direction for Next BP



Ref Ch = HP 3478A Multimeter | Test Ch = SCT Prototype

Compare Sequence





Migration to Integration

RESEARCH

- Effects of sampling rate
- DC offset
- Sensitivity to noise
- Aliasing
- Migration to integration

Accomplishments to Date

- Developed additive manufacturing processes for fabrication of multi-electrode MPES devices.

- Developed ANN algorithms that showed >98% accuracy in identification of simulated wetlands, agricultural, and natural gas emissions. Demonstrated < 1.5% ppm error for methane in these three mixture types.

- Developed I-o-T portable electronics packages to perform data acquisition, logging, and wireless data transmision.

- Results were presented at the ECS PRIME 2020, IMCS 2021 conferences. We have submitted a manuscript on the first year’s work to the *Journal of the Electrochemical Society* which has been accepted with revisions.

Lessons Learned – Research Challenges

- **Unanticipated Research Difficulties**
  - Safety protocols to stop spread of COVID in our lab were implemented early in the project and were successful in preventing disruptions of research work throughout the last year.
  - Significant delays due to COVID in sourcing materials and equipment from vendors including custom gas mixtures and furnace components. Delays in international shipping are causing some vendors to have lead times in excess of 10 weeks.
  - Future: If possible, have multiple vendors available to source from. Plan to purchase well in advance of when parts or supplies are needed.

Synergy Opportunities

- Our sensing application is of interest to multiple energy technology areas where the ability to identify and quantify gas mixtures is helpful:
  - Monitoring of hydrogen leaks from hydrogen energy infrastructure and combined H_2/CH_4 (hy-thane) infrastructure.
  - Characterization of bio-methane composition.
  - Emissions monitoring of energy production systems.

Project Summary

- **Key Findings**:
  - We have demonstrated that we can both perform identification and quantification with artificial neural networks for mixtures of CH_4, NH_3, and Natural Gas
  - Temperature can be used as an additional sensitivity tuning parameter for the gases of interest.
  - Identification network: 100% test accuracy (5 mixture, 2 temperature)
  - Quantification network: Error < 2% ppm CH_4 (1000-4000 ppm, 2 temperature)
- **Future Work**
  - Decreasing Sensitivity Limits Tested: We would like to push sensitivity to below 1000 ppm. Preconcentration can also enhance sensitivity.
  - Expand research into developing sensors for H_2 detection which may be of interest as environmental monitoring for industry and the renewable energy future.
  - Quantify other sub-components of natural gas mixture: Ethane and heavy HC content

U.S. DEPARTMENT OF ENERGY
Fossil Energy

Funding:
US Department of Energy
Office of Fossil Energy
Award DE-FE0031864

Appendix

Benefit to the Program

“Advanced Technologies to Mitigate Methane Emissions and Increase Efficiency of the Natural Gas Transport Infrastructure” program seeks technologies to monitor for methane emissions from pipeline infrastructure.

Our technology benefits the program by developing:

- Low cost, robust electrochemical sensors that can be field deployed for emissions monitoring.
- Machine learning technologies for quantification and identification of natural gas emissions.
- I-o-T technology for portable data recording and transmission.

If successful, these technologies can be used to screen pipeline infrastructure for leaks and after repairs are made, reduce both loss of valuable product and lower GHG emissions. This work also supports other efforts at emissions monitoring for the energy industry.

Project Overview – Goals and Objectives

Task 1 – Project Management and Reporting

Compile and update PMP/TMP documents. Publication of papers and presentation of results at professional conferences.

Task 2 – Sensor Fabrication

Fabricate by additive manufacturing techniques sensors capable of detecting methane, ethane, and other constituent gases with sufficent sensitivity and selectivity to identify methane emissions from NG infrastructure.

Task 3 – Artifical Neural Network Development

Develop artificial neural networks to quantify and identify natural gas mixtures. We seek accuracy of 98% for identification and < 2.5% ppm for quantification.

Task 4 – Development of an Integrated Sensing Platform

Develop a portable electronics package capable of performing sensor reading measurements and mobile data transmission. Integrate into a single package the sensors developed in Task 2.

Task 5 – Limited Field Test

Develop Field Test Plan in collaboration with UNM NSF-CISTAR industrial partners. Perform a limited field test to evaluate sensor capability under real conditions and compile results into a report.

Organization Chart

CENTER FOR MICRO-ENGINEERED MATERIALS

Subcontract

SENSORCOMM TECHNOLOGIES

Lok-kun Tsui (Research Asst. Professor, PI)
Fernando Garzon (Professor, Co-PI)

Kannan Ramaiyan (Research Asst. Professor)

Sleight Halley (Graduate Student)

Ceramic Additive Manufacturing
Machine Learning

Kamil Agi (CEO)

James Smith (Electrical Engineer)

Portable Data Acquisition
Data Transmission
Internet of Things

Gantt Chart – Task 1 / Task 2

Current Project Progress

Task	Assigned Resources	Year 1				Year 2				Year 3			
		Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Task 1.0 Project Management and Planning	UNM / SCT												
Task 1.1 Project Management Plan	UNM / SCT	O											Δ
Task 1.2 – Technology Maturation Plan	UNM / SCT	O											Δ
Task 1.3 – Publication and Presentation of Results	UNM / SCT			O									Δ

Task	Assigned Resources	Year 1				Year 2				Year 3			
		Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Task 2.0 Sensor Fabrication	UNM												
Subtask 2.1 – Sensor Prototyping	UNM	O			Δ								
Milestone 2.1 – Prototype 2-element sensor	UNM			*									
Subtask 2.2 – Sensor Element Evaluation	UNM		O			Δ							
Subtask 2.3 – Screen Printed Sensor Fabrication	UNM					O						Δ	
Milestone 2.3 – Multi-Element Sensor	UNM							*					

Gantt Chart – Task 3

Current Project Progress

Task	Assigned Resources	Year 1				Year 2				Year 3			
		Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Task 3.0 Artificial Neural Network Development	UNM/SCT												
Subtask 3.1 – Laboratory Collection of Training Data	UNM	O									Δ		
Milestone 3.1 – Initial Training Data Batch				*									
Subtask 3.2 – Gas Type Identification Training	UNM			O			Δ						
Milestone 3.2 – – Optimized ANN Algorithm for Identification	UNM					*							
Subtask 3.3 – Gas Species Quantification ANN Training	UNM			O					Δ				
Milestone 3.3 – Optimized ANN Algorithm for Quantification	UNM							*					
Subtask 3.4 – Deployment of ANN algorithm on Mobile Hardware	UNM/SCT					O							Δ
Milestone 3.4 – ANN on Development Board	UNM/SCT									*			

Gantt Chart – Task 4

Current Project Progress

Task	Assigned Resources	Year 1				Year 2				Year 3			
Task 4.0 – Development of an Integrated Sensing Platform		Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Subtask 4.1 – Sensor Interface Development	SCT	O			Δ								
Milestone 4.1 – 2-Element Sensor Interface Device Completed	SCT				*								
Subtask 4.2 – Multi-Element Sensor Interface	SCT			O				Δ					
Milestone 4.2 – Multi-Element Sensor Interface w/ wireless transmission Device Completed	SCT							*					
Subtask 4.3 – Integration of ANN Inference Hardware	SCT						O						Δ
Milestone 4.3 – Completed Sensor Package	UNM/SCT										*		

Gantt Chart – Task 5

Current Project Progress

Task	Assigned Resources	Year 1				Year 2				Year 3			
Task 5.0 – Field Test and Validation		Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Subtask 5.1 – Arrange for Access to Field Test Facility	UNM						O	Δ					
Milestone 5.1 – Field Test Location Selected	UNM							*					
Subtask 5.2 – Development of Field Test Plan and Completion of NEPA Documentation	UNM/SCT						O		Δ				
Comprehensive Field Test Plan (Decision Point I)	UNM/SCT								*				
Subtask 5.3 – Field Test	UNM/SCT									O			Δ
Milestone 5.2 – Field Test Results Completed	UNM/SCT												*

Bibliography

IoT-Based Sensor Systems for Intelligence in Transportation, Healthcare and Natural Gas Detection. K. Agi, R. Ian (SCT), L. K. Tsui, F. H. Garzon (UNM), and R. Jordan (UNM/SCT)

Additively Manufactured Mixed Potential Electrochemical Sensors for Natural Gas Detection. L. K. Tsui (UNM), K. Agi (SCT), and F. H. Garzon (UNM)

18th Int. Meeting on Chemical Sensors (May 2021, Online)

Machine Learning for the Quantification and Identification of Natural Gas from Mixed Potential Electrochemical Sensors. L. K. Tsui,* S. Halley (UNM), K. Agi (SCT), and F. H. Garzon (UNM) [**Symposium Organizer*]

Additive Manufacturing for Rapid Prototyping of Mixed Potential Electrochemical Sensors. S. Halley, L. K. Tsui (UNM), K. Agi (SCT), and F. H. Garzon (UNM)

Analytics in Extracting Intelligence from Iot-Based Sensors in Transportation, Healthcare, and Natural Gas Detection. K. Agi, R. Ian, J. Smith (SCT), L. K. Tsui, F. H. Garzon (UNM), and R. Jordan (UNM/SCT)

Publications:

"Combined Mixed Potential Electrochemical Sensors and Artificial Neural Networks for the Quantification and Identification of Methane in Natural Gas Emissions Monitoring" by Sleight Halley, Lok-kun Tsui, and Fernando Garzon.

Submitted to *Journal of the Electrochemical Society*.

2 more papers in progress to be submitted before end of the year.