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

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- ² SensorComm Technologies Inc, Albuquerque, NM, USA
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 $1.624 \times 10^8$ Metric Ton CO$_2$ Equivalent.[3]

• Increased regulatory scrutiny of industrial emissions creates a greater need for monitoring technology.

Sources of Methane Emissions (2019)

<table>
<thead>
<tr>
<th>Source</th>
<th>Emissions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nat. Gas Infrastructure</td>
<td>156 mt/yr [1]</td>
</tr>
<tr>
<td>Livestock</td>
<td>62 kt/yr [1]</td>
</tr>
<tr>
<td>Coastal Wetlands</td>
<td>153 kt/yr [1]</td>
</tr>
</tbody>
</table>

A sensing system for CH$_4$ monitoring must differentiate between these sources.

1. EPA Inventory of US GHG Emissions and Sinks: 1990-2019
## Current Methods of CH$_4$ Monitoring

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

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): CH₄
- La₀.₈₇Sr₀.₁₃CrO₃ (LSC): C > 1 Hydrocarbons
- Au: NH₃
- Substrate: YSZ (Gen 1-4) → CSZ; MSZ (Gen 5)
- Electrolyte: Porous YSZ
Video
**Sensor Evolution**

<table>
<thead>
<tr>
<th>Generation 1:</th>
<th>Generation 2:</th>
<th>Generation 3:</th>
<th>Generation 4:</th>
<th>Generation 5:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Razor blade cast substrate. Parts are very brittle.</td>
<td>3D printed substrate. Substantially increased robustness. Used as demonstration for Au/Pt electrode</td>
<td>First 4 electrode design incorporating Pt, LSC, Au, and ITO electrodes on one substrate</td>
<td>Radial configuration to equalize electrode areas.</td>
<td>Robocasted low ionic conductivity ($\text{CeO}_2 - \text{ZrO}_2$) substrates for enhanced sensitivity</td>
</tr>
</tbody>
</table>

**Timeline:**
- Spring 2020
- Fall 2020
- Spring 2021
- Summer 2021
Sensor Test Procedure

Gas Manifold

Data Collection:
- Flow Rate: 150 CCM
- O₂ Content: 21%
- Balance gas: N₂

<table>
<thead>
<tr>
<th>CH₄ Content</th>
<th>BMAT1028</th>
<th>NH₃ Content</th>
<th>Mix CH₄/NH₃</th>
<th>Mix NG/NH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wetlands</td>
<td>Natural Gas</td>
<td>50-250 ppm</td>
<td>1000-4000 ppm CH₄</td>
<td>1500-4000 ppm CH₄</td>
</tr>
<tr>
<td>1000-4000 ppm</td>
<td>1000-4000 ppm CH₄</td>
<td>50-250 ppm</td>
<td>1000-4000 ppm CH₄</td>
<td>1500-4000 ppm CH₄</td>
</tr>
</tbody>
</table>

ITP vs. Pt
LSC vs. Pt
Au vs. Pt

2000 ppm CH₄
100 ppm NH₃
**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
Yttria-Stabilized-Zirconia (YSZ) Substrates

Ceria-Stabilized Zirconia (CSZ) Substrates

Using CSZ produces up to 3.5x enhancement in sensitivity to CH$_4$ and C$_2$H$_6$
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.

![Sensor Signals Diagram]

<table>
<thead>
<tr>
<th>Gas</th>
<th>Sensor Signal</th>
<th>Identification Process</th>
<th>Quantification Process</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Input</th>
<th>Output</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensor Signals</td>
<td>Identification OR Quantification</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CH₄ = 1000 ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>96%</td>
</tr>
</tbody>
</table>
Identification of natural gas from CH\textsubscript{4} and CH\textsubscript{4}/NH\textsubscript{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
600°C < 7% ppm CH$_4$

Quantification Error
450+600°C < 1.5% ppm CH$_4$
PROTOTYPE

Integrated Wireless Sensing Platform

IoT Gateway

Readout Prototype

Integrated Prototype
RESEARCH

Direction for Next BP

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

Compare Sequence

Migration to Integration

sensorcom | Methane Sensing for Natural Gas Infrastructure | Integrated Wireless Sensing Platform
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 transmission.

- 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 \( \text{H}_2/\text{CH}_4 \) (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 CH₄, NH₃, 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 CH₄ (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 H₂ 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

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.
- 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 sufficient sensitivity and selectivity to identify methane emissions from NG infrastructure.

### Task 3 – Artificial 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.
## Gantt Chart – Task 1 / Task 2

### Task 1.0 Project Management and Planning
- **UNM / SCT**
  - **Task 1.1 Project Management Plan**
    - **UNM / SCT**
    - **O**
  - **Task 1.2 Technology Maturation Plan**
    - **UNM / SCT**
    - **O**
  - **Task 1.3 Publication and Presentation of Results**
    - **UNM / SCT**
    - **O**

### Task 2.0 Sensor Fabrication
- **UNM**
  - **Subtask 2.1 Sensor Prototyping**
    - **UNM**
    - **O**
  - **Milestone 2.1 Prototype 2-element sensor**
    - **UNM**
    - **O**
  - **Subtask 2.2 Sensor Element Evaluation**
    - **UNM**
    - **O**
  - **Subtask 2.3 Screen Printed Sensor Fabrication**
    - **UNM**
    - **O**
  - **Milestone 2.3 Multi-Element Sensor**
    - **UNM**
    - **O**

### Current Project Progress

<table>
<thead>
<tr>
<th>Task</th>
<th>Assigned Resources</th>
<th>Year 1</th>
<th>Year 2</th>
<th>Year 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Q1</td>
<td>Q2</td>
<td>Q3</td>
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<td>Task 1.3 Publication and Presentation of Results</td>
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<td><strong>Task 2.0 Sensor Fabrication</strong></td>
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<td>Subtask 2.1 Sensor Prototyping</td>
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<td>Milestone 2.1 Prototype 2-element sensor</td>
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<td>Subtask 2.2 Sensor Element Evaluation</td>
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<td>Subtask 2.3 Screen Printed Sensor Fabrication</td>
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<td>Milestone 2.3 Multi-Element Sensor</td>
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# Gantt Chart – Task 3

## Task 3.0 Artificial Neural Network Development

<table>
<thead>
<tr>
<th>Subtask 3.1 - Laboratory Collection of Training Data</th>
<th>Assigned Resources</th>
<th>Year 1</th>
<th>Year 2</th>
<th>Year 3</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>UNM</td>
<td>Q1</td>
<td>Q3</td>
<td>Q4</td>
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<td>Milestone 3.1 - Initial Training Data Batch</td>
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## Subtask 3.2 - Gas Type Identification Training

<table>
<thead>
<tr>
<th>Milestone 3.2 - Optimized ANN Algorithm for Identification</th>
<th>Assigned Resources</th>
<th>Year 1</th>
<th>Year 2</th>
<th>Year 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UNM</td>
<td>O</td>
<td></td>
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</table>

## Subtask 3.3 - Gas Species Quantification ANN Training

<table>
<thead>
<tr>
<th>Milestone 3.3 - Optimized ANN Algorithm for Quantification</th>
<th>Assigned Resources</th>
<th>Year 1</th>
<th>Year 2</th>
<th>Year 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UNM</td>
<td>O</td>
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</table>

## Subtask 3.4 - Deployment of ANN algorithm on Mobile Hardware

<table>
<thead>
<tr>
<th>Milestone 3.4 - ANN on Development Board</th>
<th>Assigned Resources</th>
<th>Year 1</th>
<th>Year 2</th>
<th>Year 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UNM/SCT</td>
<td>O</td>
<td></td>
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</table>
# Gantt Chart – Task 4

## Current Project Progress

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<thead>
<tr>
<th>Task</th>
<th>Assigned Resources</th>
<th>Year 1</th>
<th>Year 2</th>
<th>Year 3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Task 4.0 - Development of an Integrated Sensing Platform</strong></td>
<td></td>
<td>Q1</td>
<td>Q2</td>
<td>Q3</td>
</tr>
<tr>
<td>Subtask 4.1 - Sensor Interface Development</td>
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<td>O</td>
<td>Δ</td>
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<tr>
<td>Milestone 4.1 - 2-Element Sensor Interface Device Completed</td>
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<td>Subtask 4.2 - Multi-Element Sensor Interface</td>
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<tr>
<td>Milestone 4.2 - Multi-Element Sensor Interface w/ wireless transmission Device Completed</td>
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<td>Subtask 4.3 - Integration of ANN Inference Hardware</td>
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<tr>
<td>Milestone 4.3 - Completed Sensor Package</td>
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</table>
# Gantt Chart – Task 5

## Current Project Progress

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<tr>
<th>Task</th>
<th>Assigned Resources</th>
<th>Year 1</th>
<th>Year 2</th>
<th>Year 3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Task 5.0 - Field Test and Validation</strong></td>
<td></td>
<td>Q1 Q2</td>
<td>Q2 Q3</td>
<td>Q4 Q1</td>
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<tr>
<td>Milestone 5.1 - Field Test Location Selected</td>
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<tr>
<td>Subtask 5.2 - Development of Field Test Plan and Completion of NEPA Documentation</td>
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<td><strong>Comprehensive Field Test Plan (Decision Point I)</strong></td>
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<tr>
<td>Subtask 5.3 - Field Test</td>
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<td>*</td>
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<tr>
<td>Milestone 5.2 - Field Test Results Completed</td>
<td>UNM/SCT</td>
<td></td>
<td></td>
<td>*</td>
</tr>
</tbody>
</table>
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.