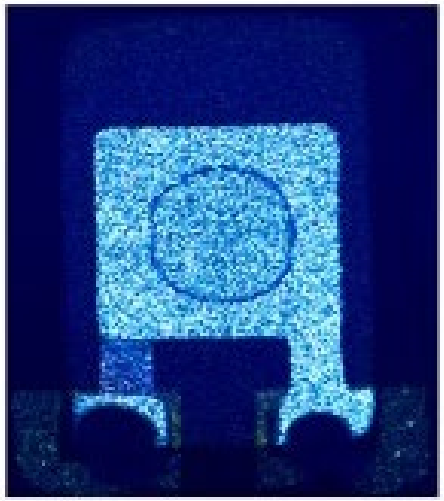
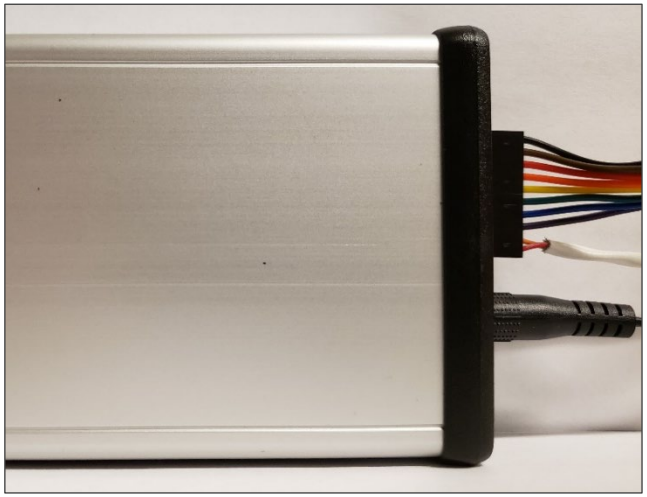
Low-Power, Low-Cost Gas Sensors: From Molecules to Modules





Bryan W. Boudouris

Davidson School of Chemical Engineering and Department of Chemistry

Purdue University

2022 Spring P2SAC Virtual Conference

General Process Safety Session

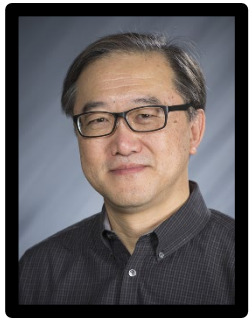
Wednesday, May 11, 2022

Email: boudouris@purdue.edu; Twitter: @Boudouris_Group

Multi-disciplinary Team with Complementary Expertise

- Jim Braun
  Building Systems

- Jeff Rhoads
  Sensor Development



- George Chiu
  Mechatronics and Hardware Integration

- Bryan Boudouris
  Functional Chemistries

- Will Buchanan
  T2M Support and Business Development











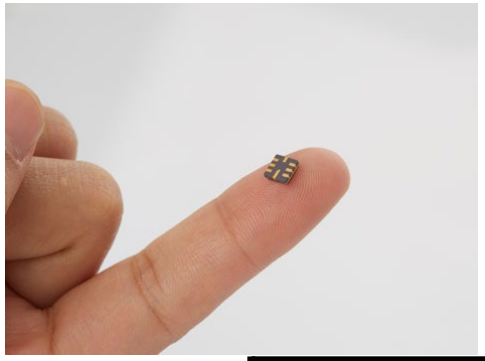
Post-Doctoral Research Associate: Xikang (Po) Zhao (ChemE); Nikhil Bajaj (ME); *Allison Murray (ME)*
Graduate Students: **Zachary Siefker (ME)**; *Allison Murray (ME)*; **John Hodul (Chem); Joe Meseke (ME); Nikhil Carneiro (ME)**
Undergraduate Research Assistant: **Abhi Boyina (ME)**; **Eugenio Frias Miranda (ME)**; Nikhil Carneiro (ME); Katie Mao (ME); Joshua Jenkins (ME)

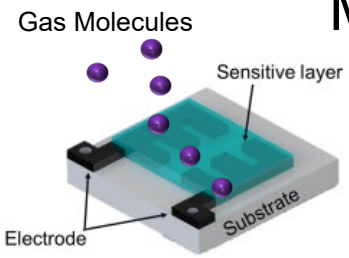
The Focus of Our Work is on Performance and Price

Mass Spectrometry

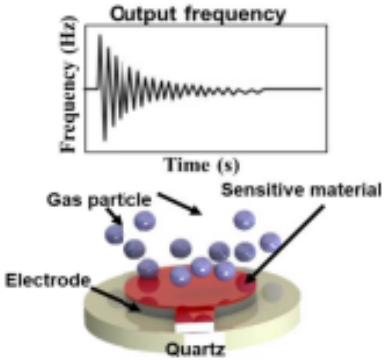
Gas Chromatography

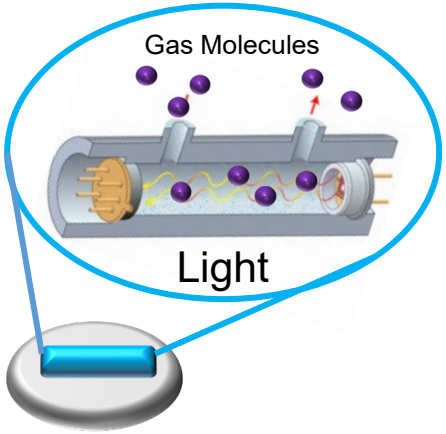
MEMS Offer Low-Cost, Low-Energy Solutions





MEMs



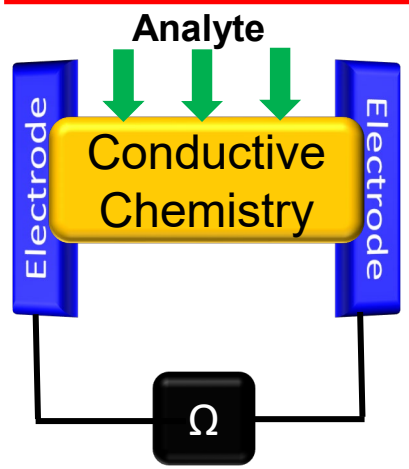


Electrochemical | Electromechanical | Optical

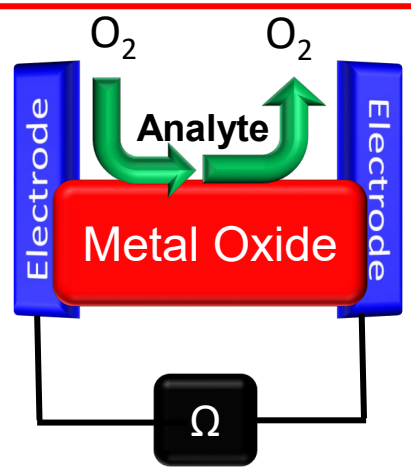
Ahmad Asri, M. I.; et al. *IEEE Sens. J.* **2021**, *21*, 18381–18397.

Gravimetric MEMS Sensors Have Potential Advantages

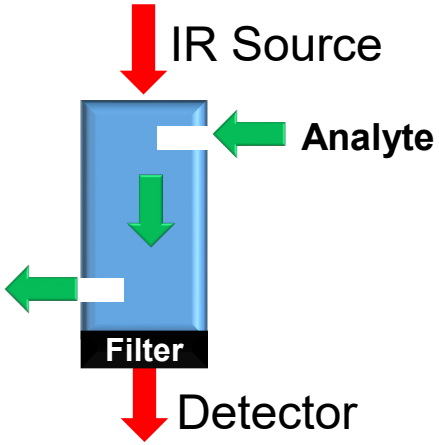
Sensor Type	Measurement Range	Size Footprint	Cost	Power Usage	Drawback
Chemiresistive (Electrochemical)	< 0.1 ppm - 10,000 ppm	< 25 mm^2	< $50	100 μW	Requires conductive materials to operate
Metal Oxide (Electrochemical)	2,000 ppm - 50,000 ppm	< 25 mm^2	$50 - $75	200 mW	Requires elevated temperatures or extensive chemistry fabrication to operate
Non-Dispersive IR (Optical)	< 0.1 ppm - 10,000 ppm	3 cm^2	$100 - $200	300 mW	Difficulty distinguishing and quantifying target analytes in the presence of other gas analytes (i.e., selectivity)
Gravimetric (Electromechanical)	< 0.1 ppm - 10,000 ppm	< 25 mm^2	< $50	60-100 mW	Can experience drift issues, need to be accounted for through software algorithm and references



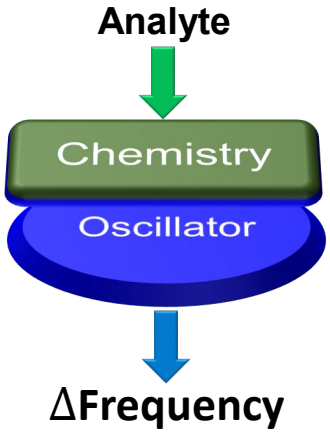
Chemiresistive



Metal Oxide



Non-Dispersive IR

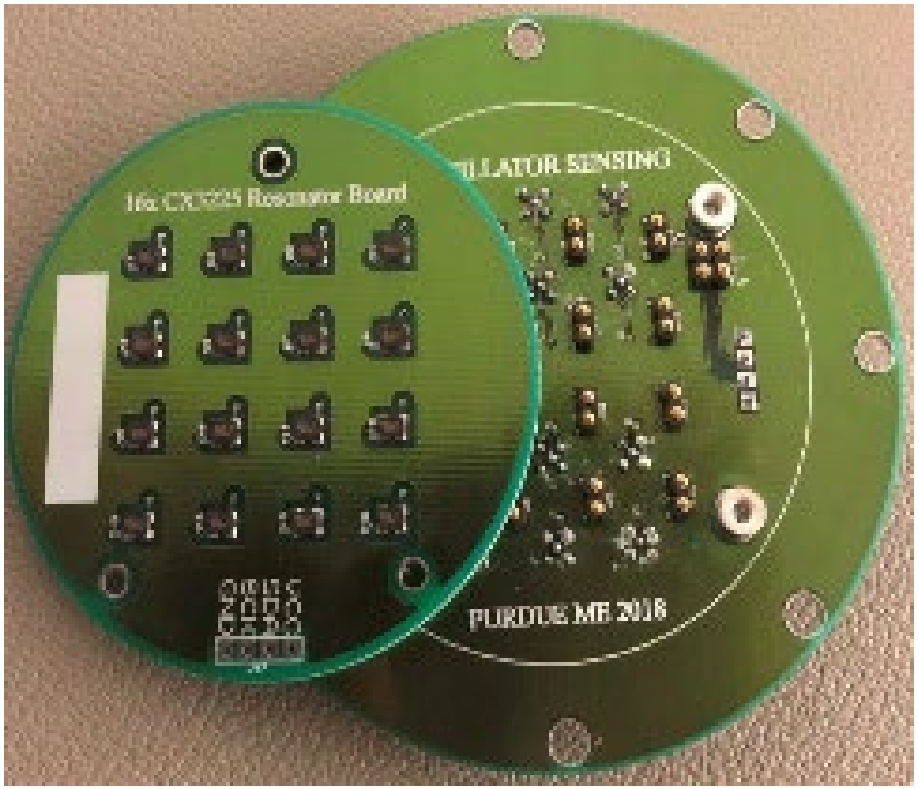


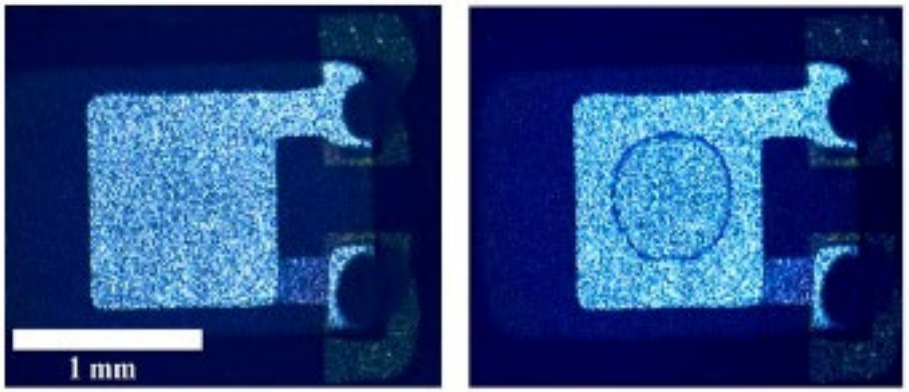
Gravimetric

- No one sensor class that can effectively detect every target gas analyte
- Minus NDIR, selectivity on device is driven through the surface chemistry
- Materials cost and processability are just as critical as performance!

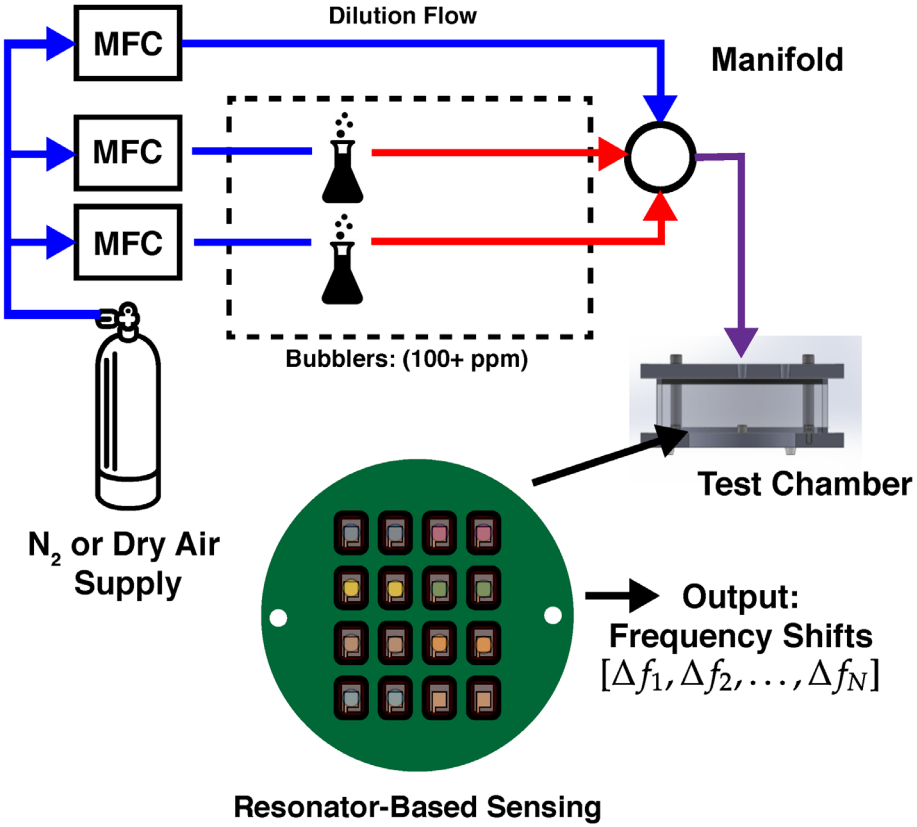
16 Sensors Are Easily Printed on a Handheld Board

High-Resolution MEMS Sensor



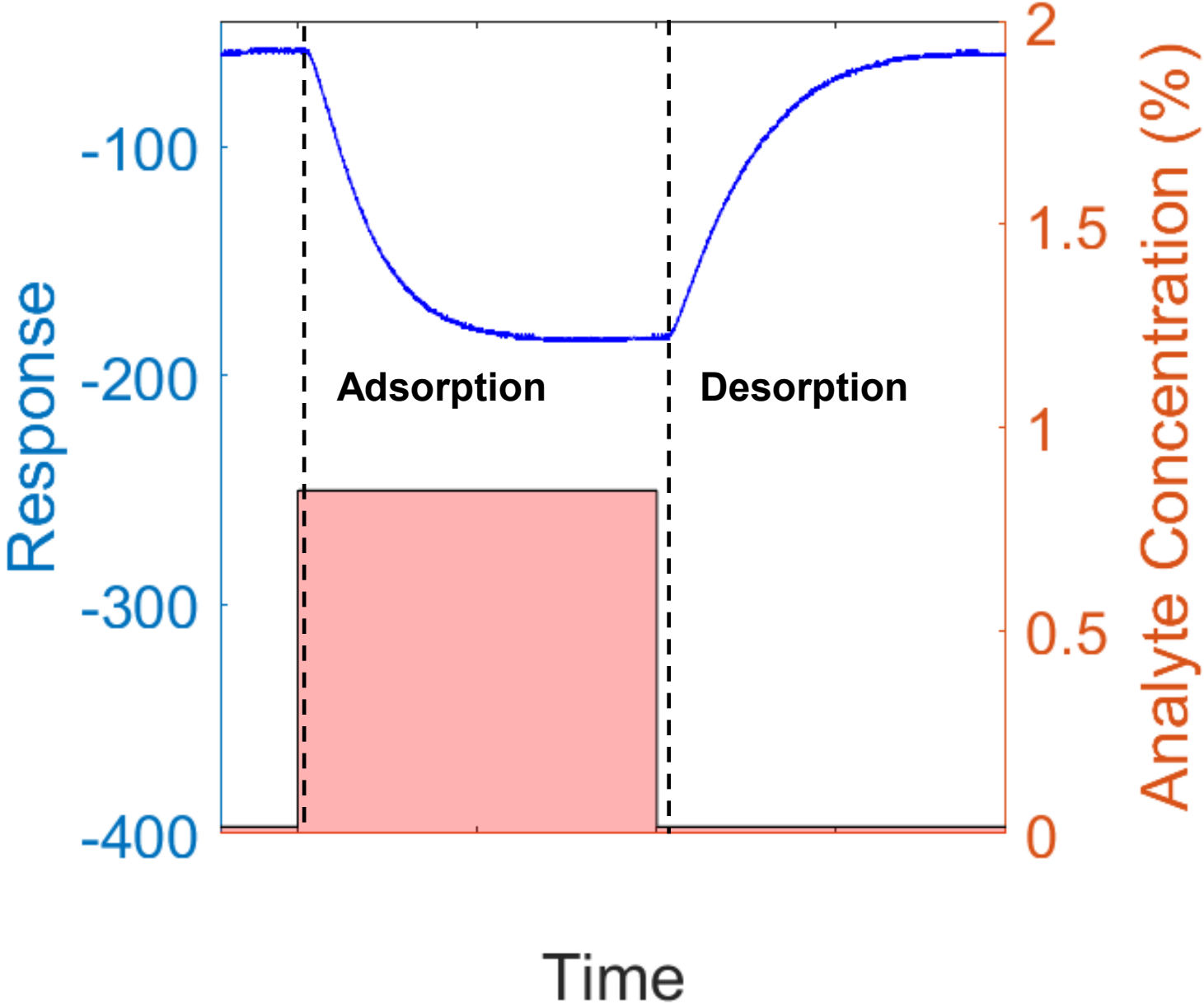


Benchtop Testing Setup

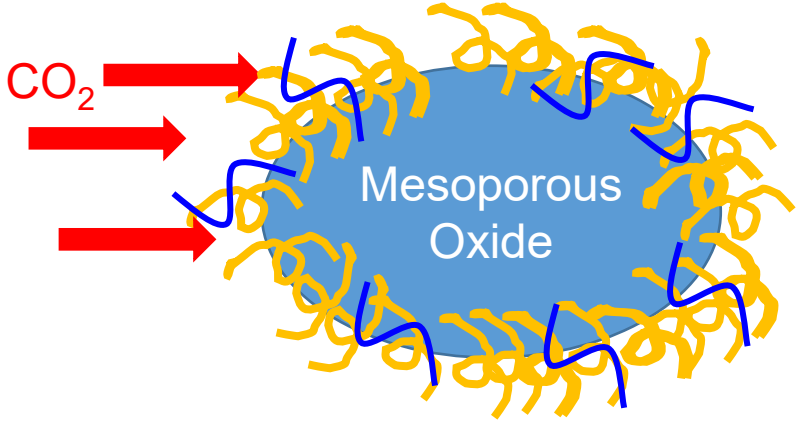


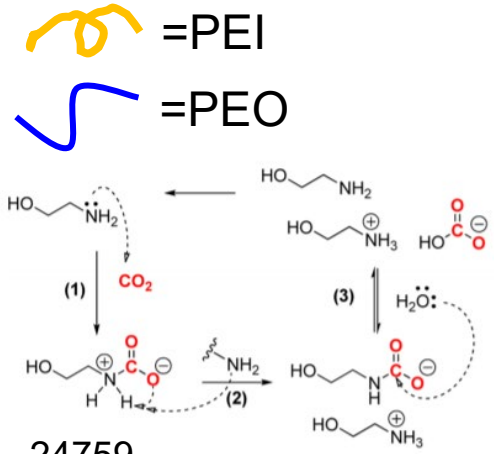
- Multiple analytes available and can be fed as gas or as vapors by bubbling a carrier gas through a liquid analyte.
- Multiple resonators on a single board allow for internal standards for each test.

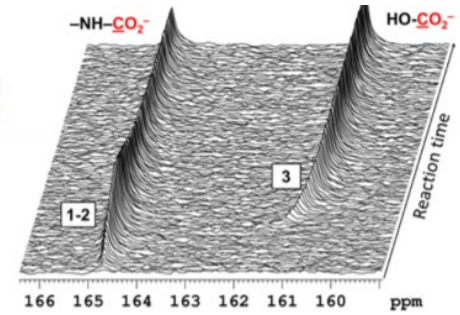
Sorption-based Detection Yields Common Sensing Signals



Designing a Chemistry to Detect Carbon Dioxide



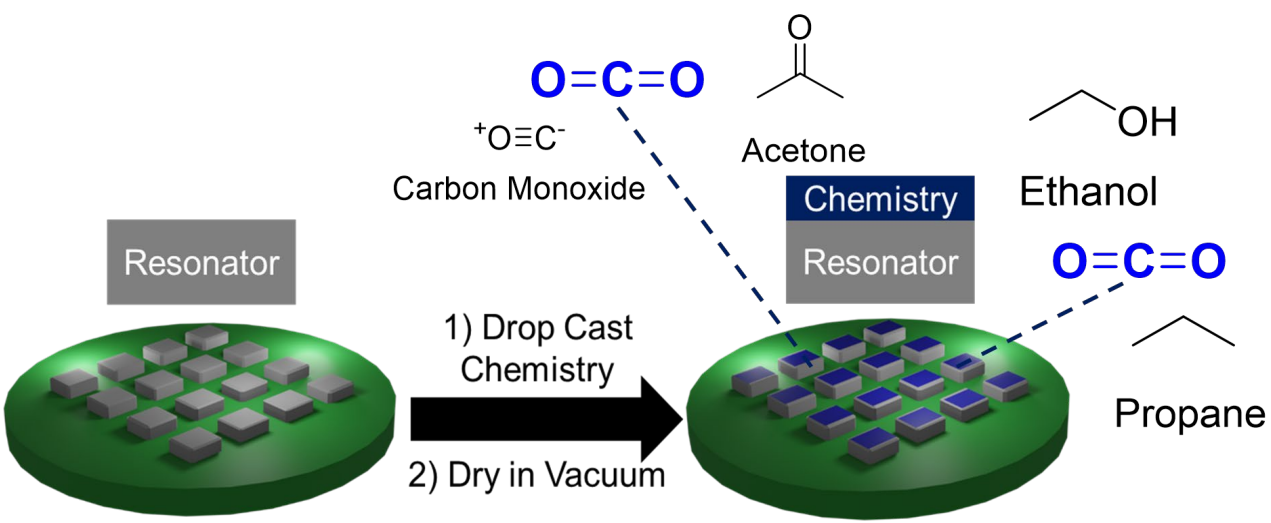


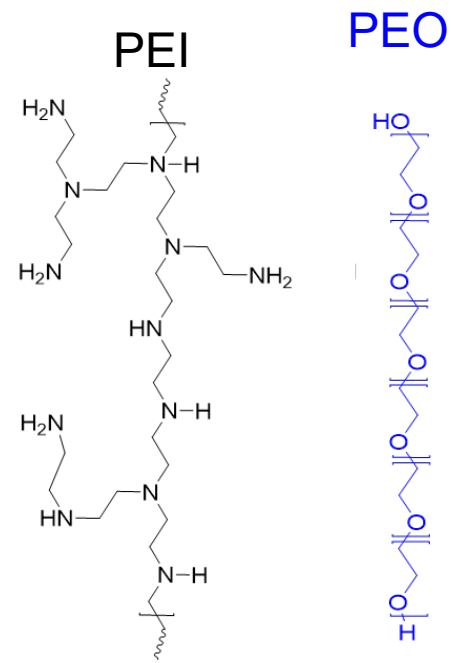


ACS Applied Materials & Interfaces **2015,** *7*, 24748 – 24759.

Energy & Fuels **2016**, *30*, 1223 – 1236.

Polymers offer Processability and Commercial Availability

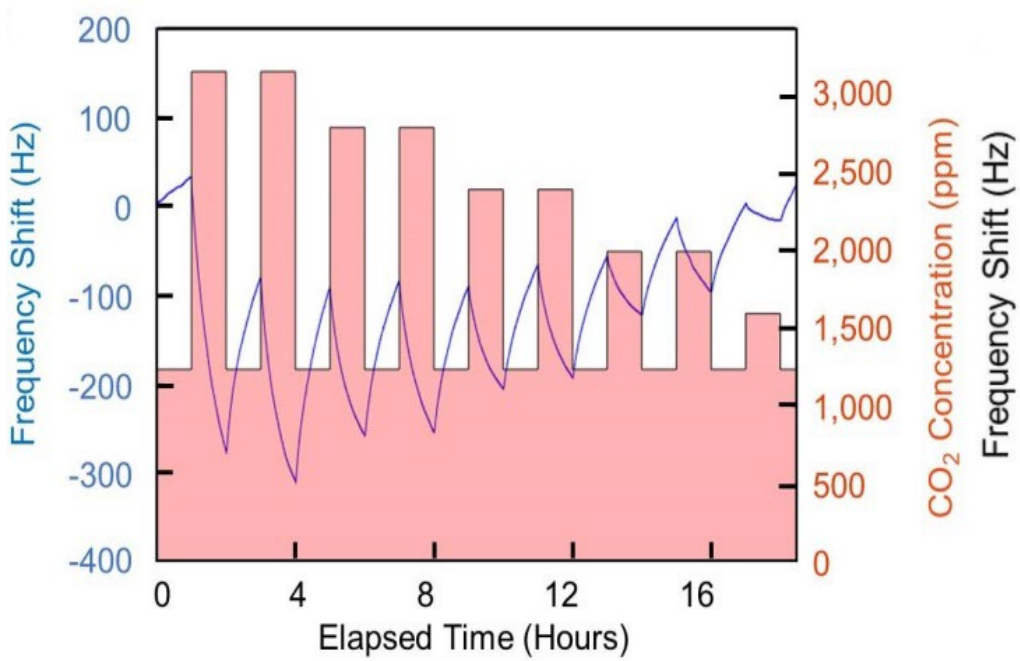




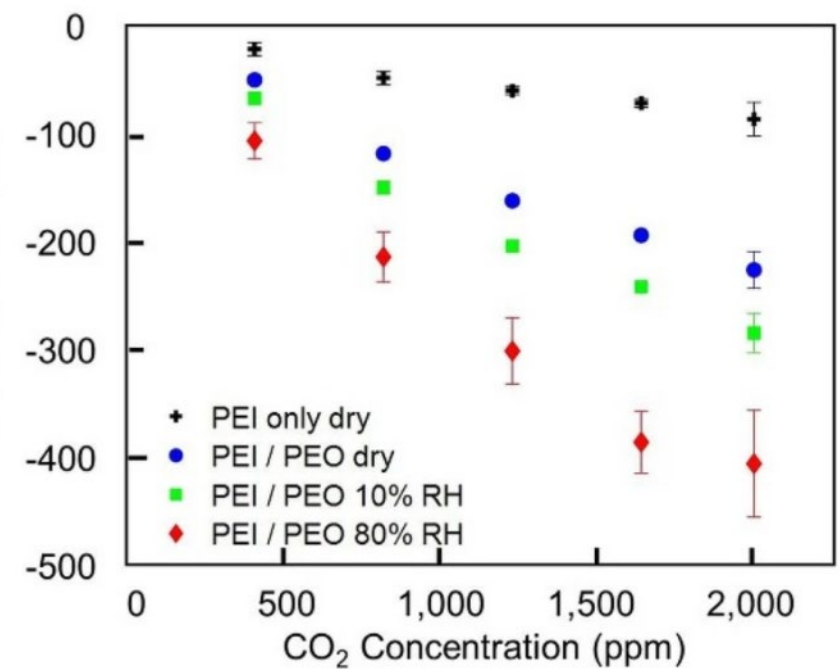
Siefker, Z.A.; Hodul, J.N.; et. al. *Sci. Rep.* **2021**, *11*, 13237.

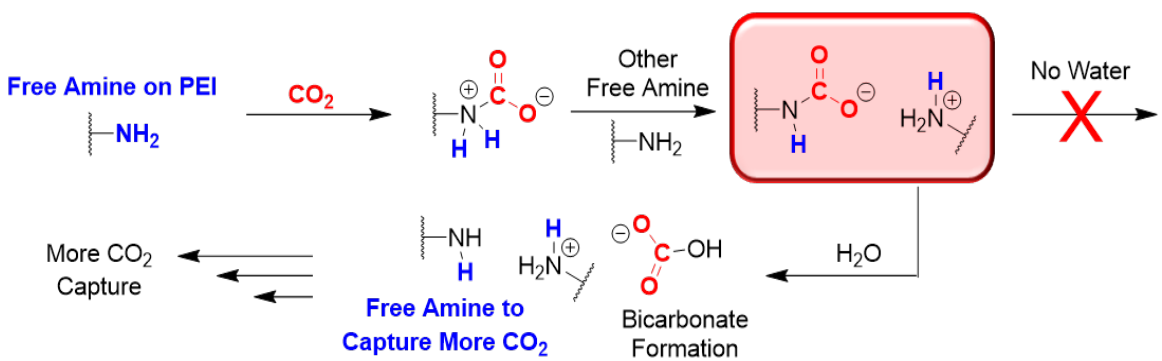
CO_2 Sensor Responds Quickly under a Range of Conditions

PEO-PEI Provides a Real-time Response to CO_2



PEO-PEI Responds in Dry and Humid Environments



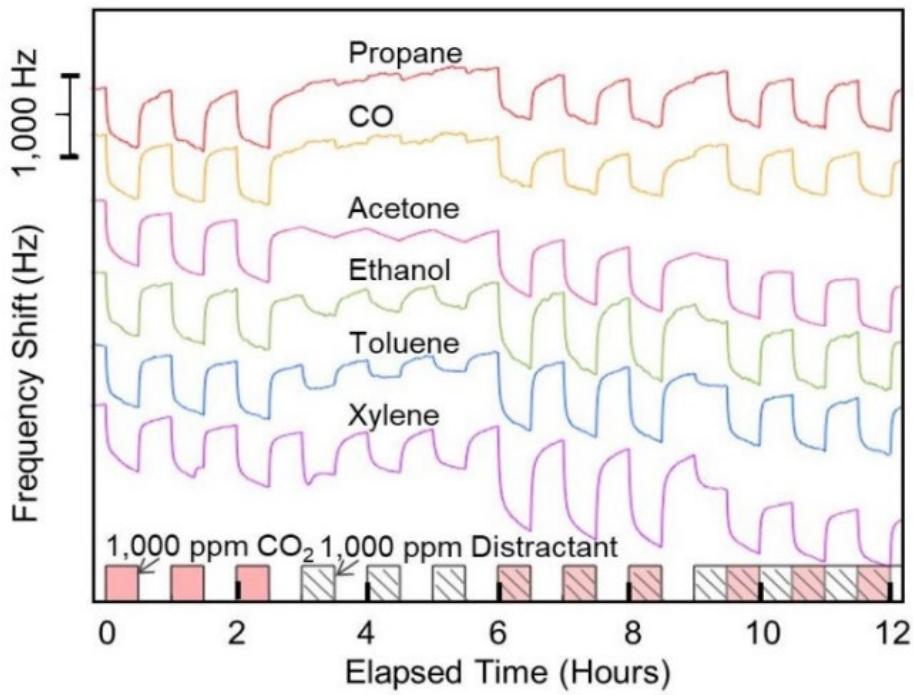


- Sensor detects CO_2
- Performs in both ambient air and nitrogen environments
- Performs in practical environments (i.e., humidity)

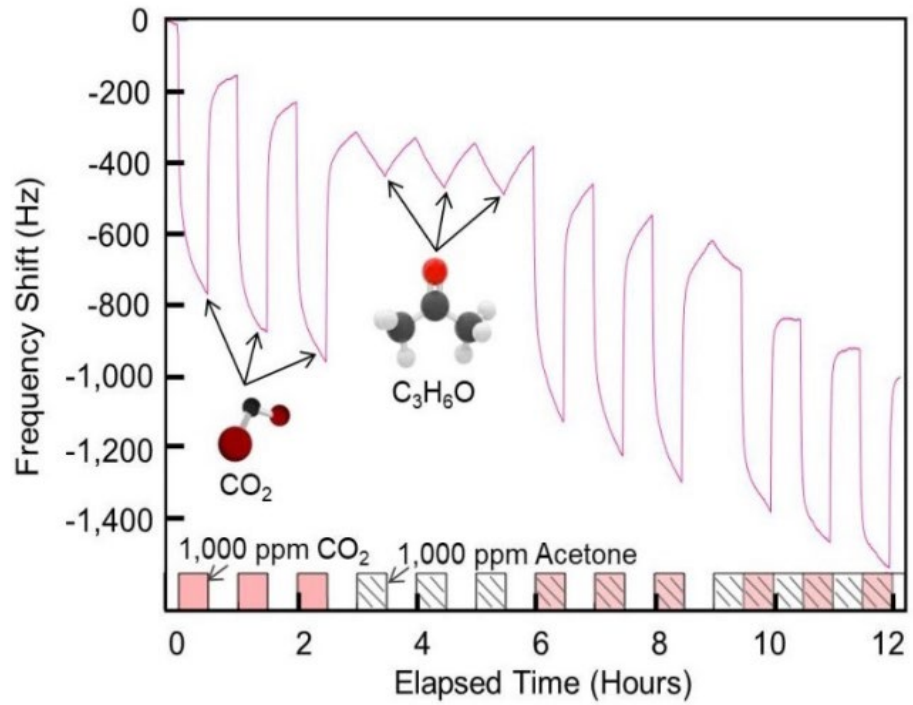
Siefker, Z.A.; Hodul, J.N.; et. al. *Sci. Rep.* **2021**, *11*, 13237.

Selective Towards CO_2 Relative to Common Distractants

PEO/PEI Chemistry is Unaltered By Potential Interfering Gases



Zoomed-in View of Response to Acetone Vapors

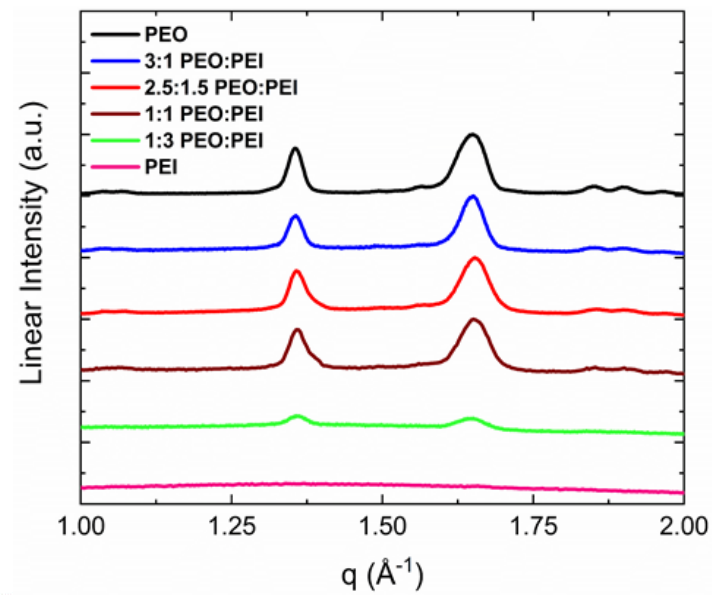


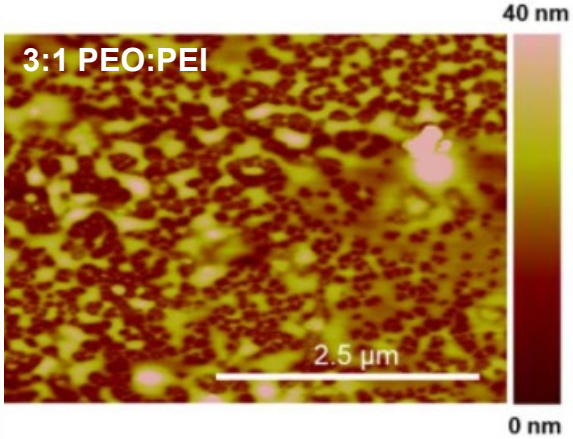
- The distractant gases (i.e., interfering analytes) spanned broad chemical composition and are potentially present in current practical Indoor Air Quality (IAQ) monitoring scenarios.

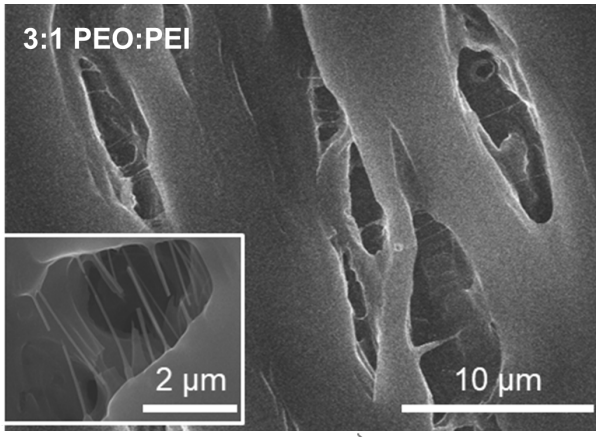
- <u>The distractant gases are at significantly higher concentrations than what would realistically be present when performing real indoor monitoring tests.</u>

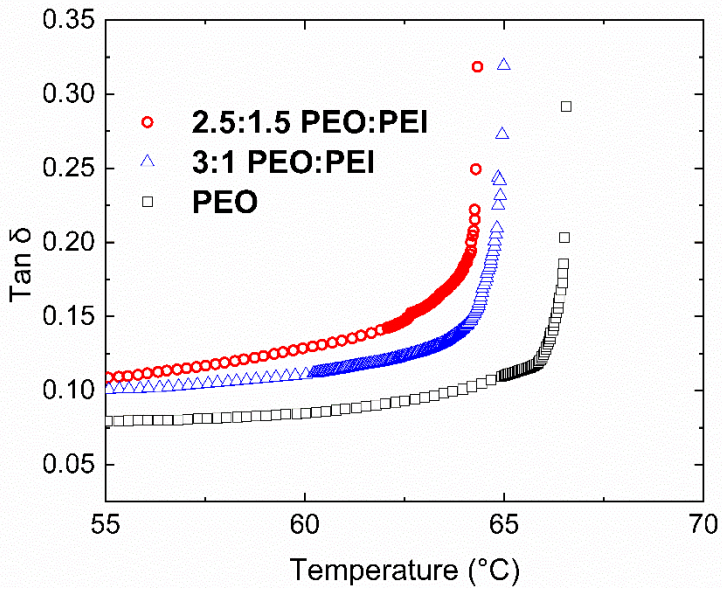
Siefker, Z.A.; Hodul, J.N.; et. al. *Sci. Rep.* **2021**, *11*, 13237.

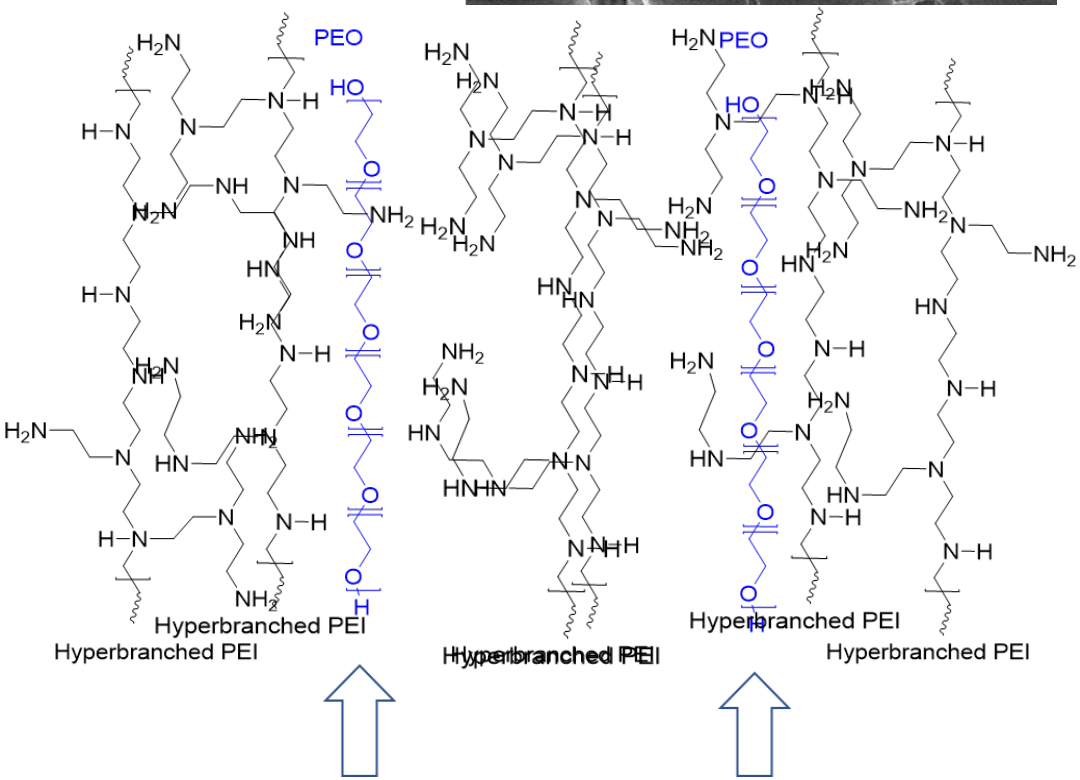
PEO Imparts Nano- and Microstructure to the PEI





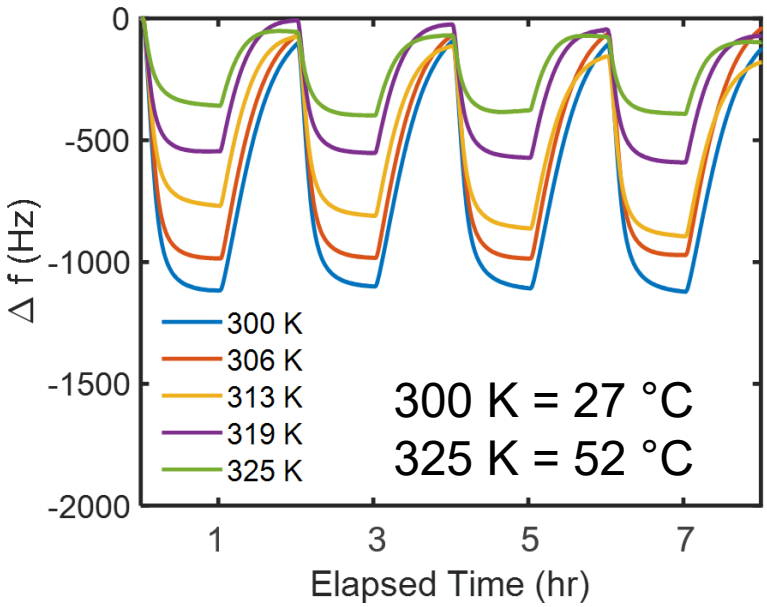


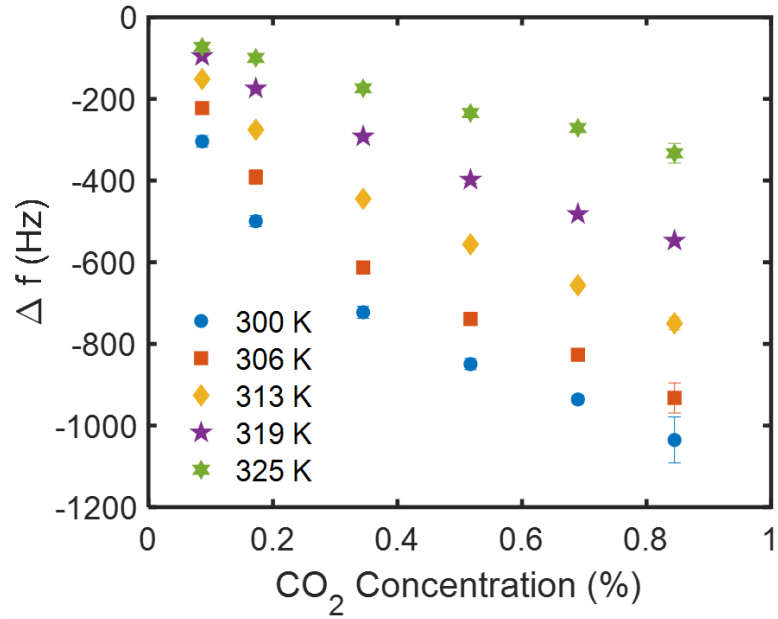


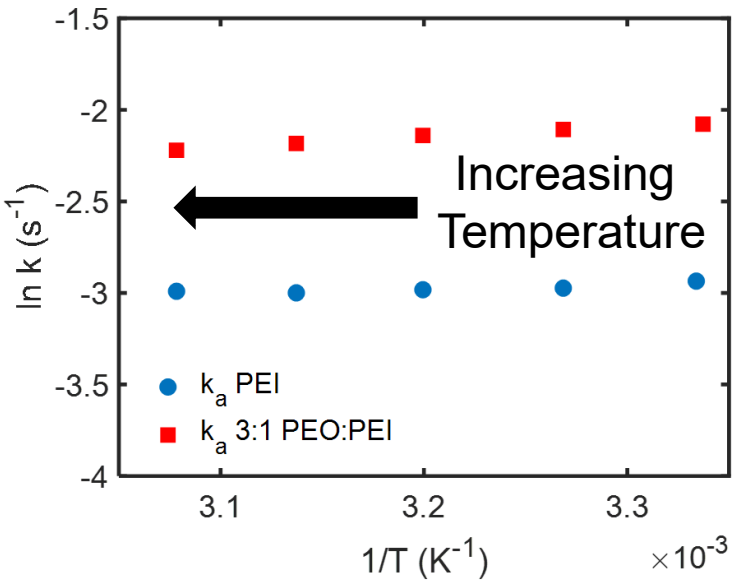


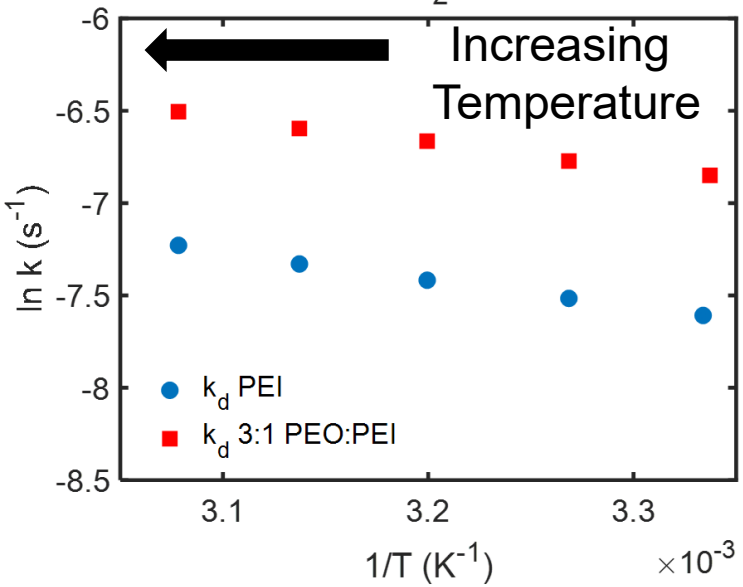
Siefker, Z.A.; Hodul, J.N.; et. al. *Sci. Rep.* **2021**, *11*, 13237.

T Impacts Performance but can be Taken into Account



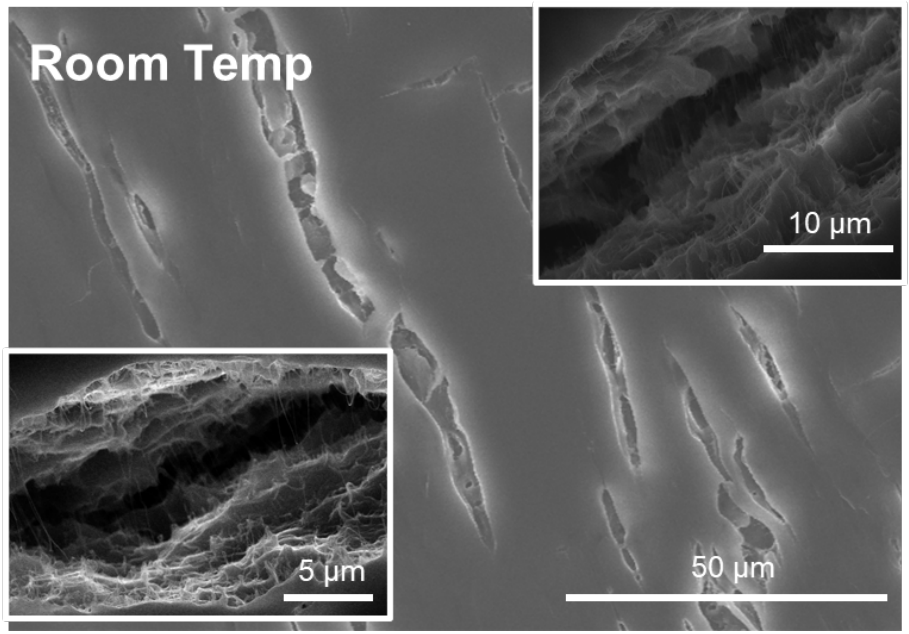


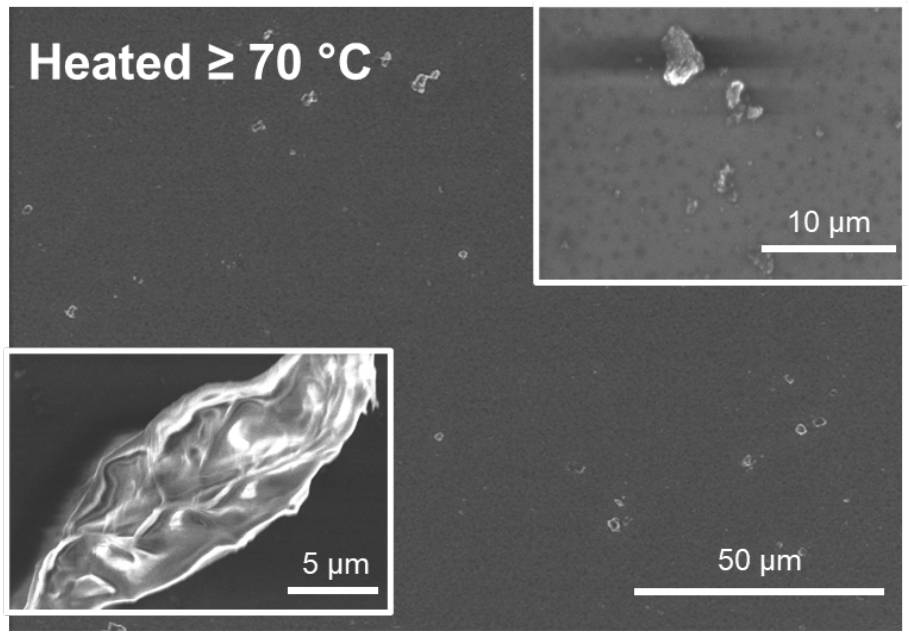


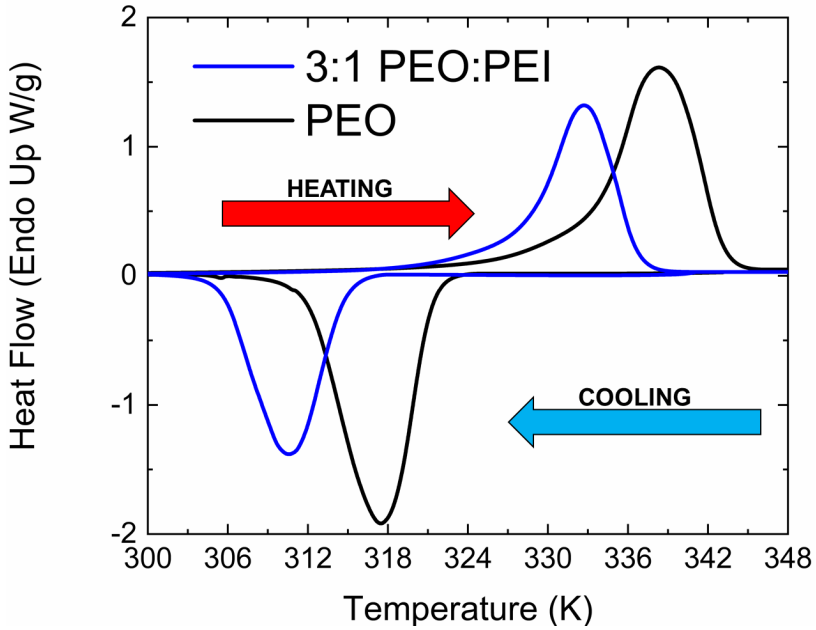


Siefker, Z.A.; Hodul, J.N.; et. al. *ACS Appl. Polym. Mater.* **2022**, *in press*.

There is an Upper Temperature Limit





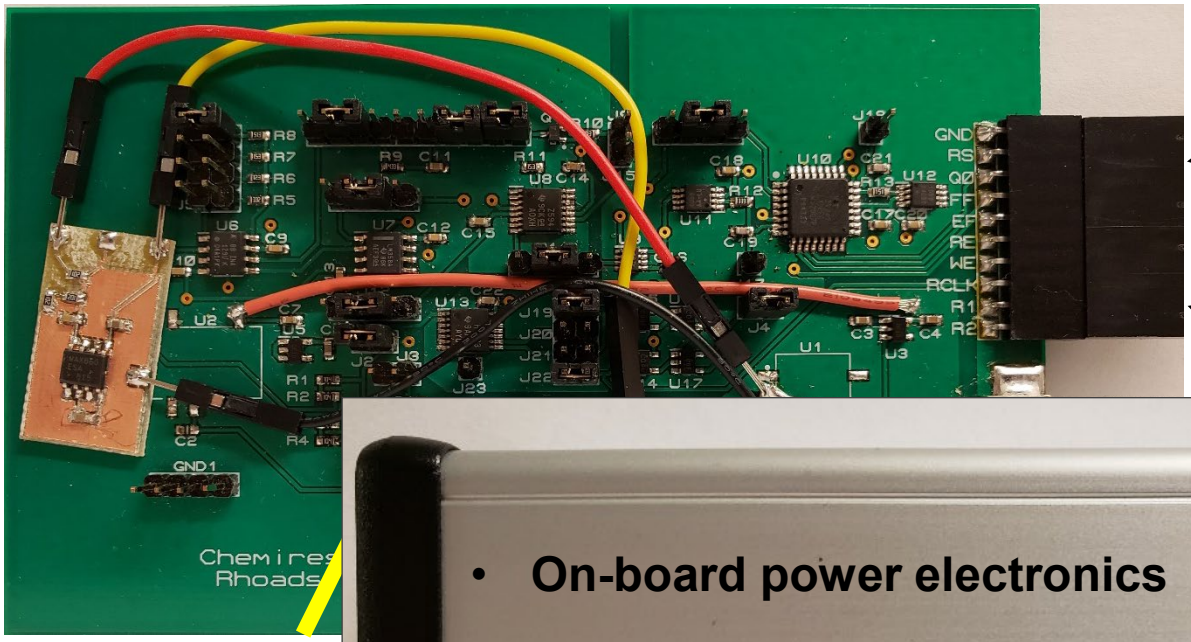


As polymers melt, porous structure disappears, and amines are no longer accessible to interact with CO_2.

In turn, performance decreases.

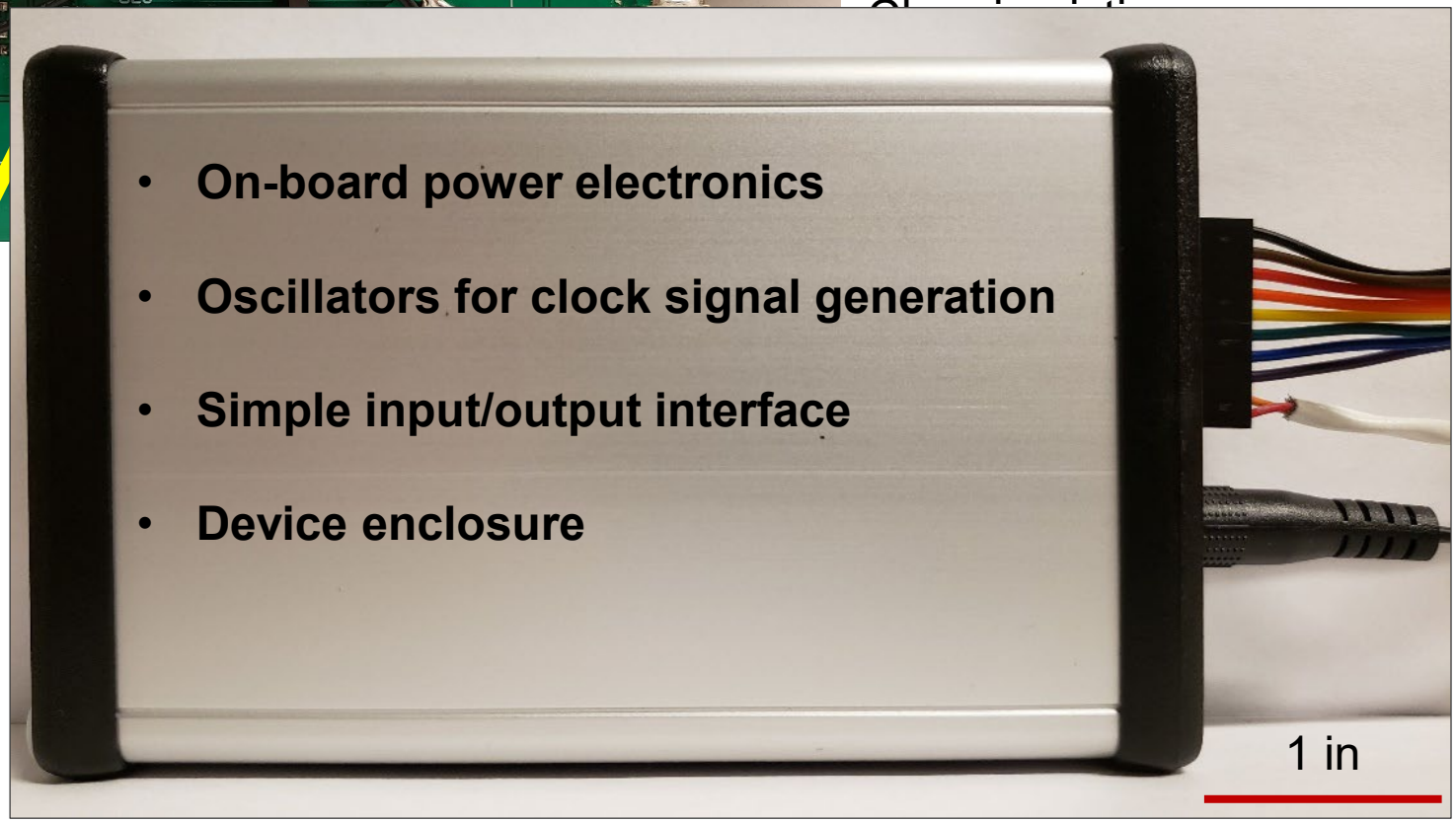
Siefker, Z.A.; Hodul, J.N.; et. al. *ACS Appl. Polym. Mater.* **2022**, *in press*.

Integrated Sensors and the Final, Compact Product



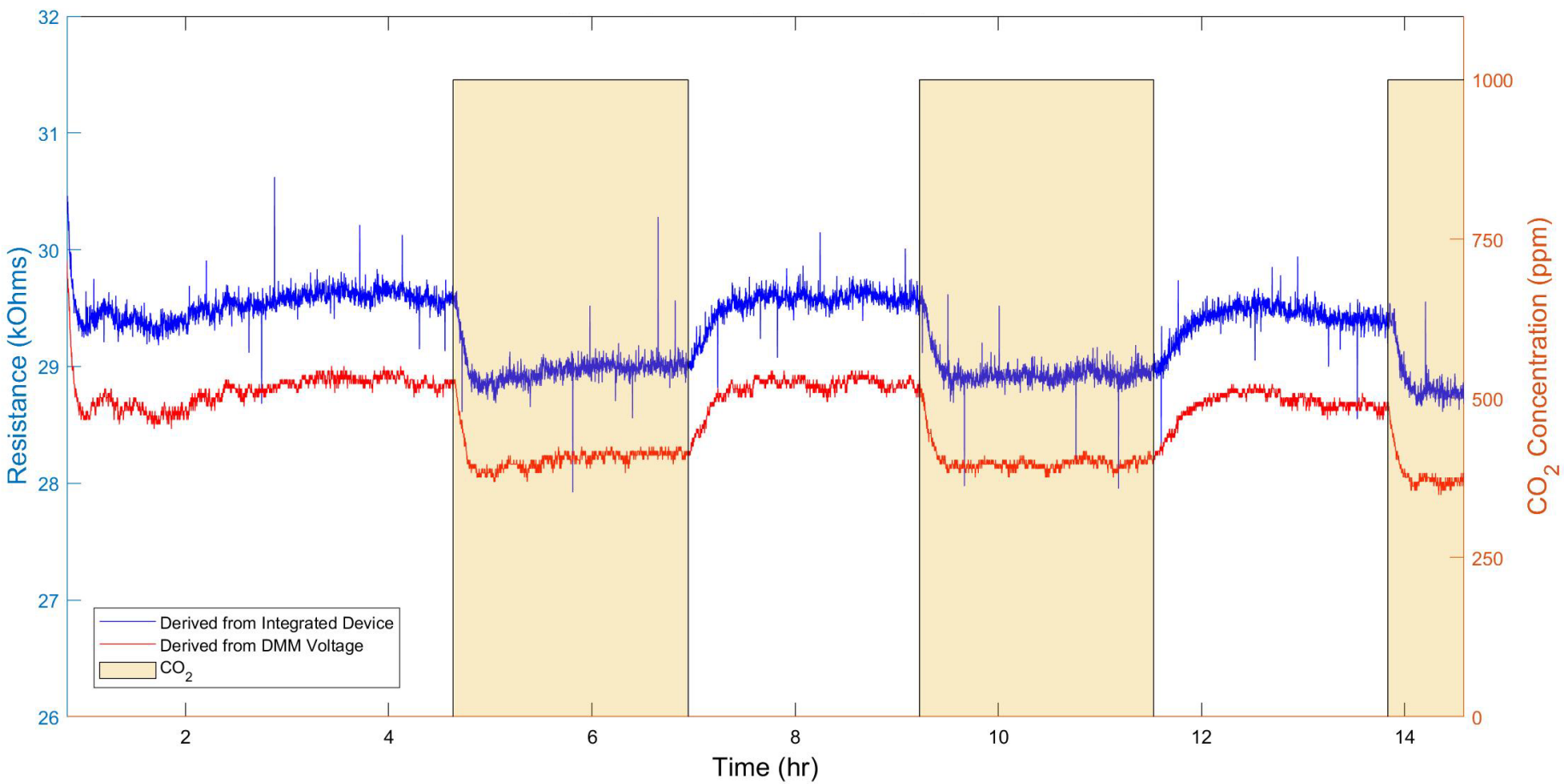
Integrated device output

Wheatstone bridge voltage output



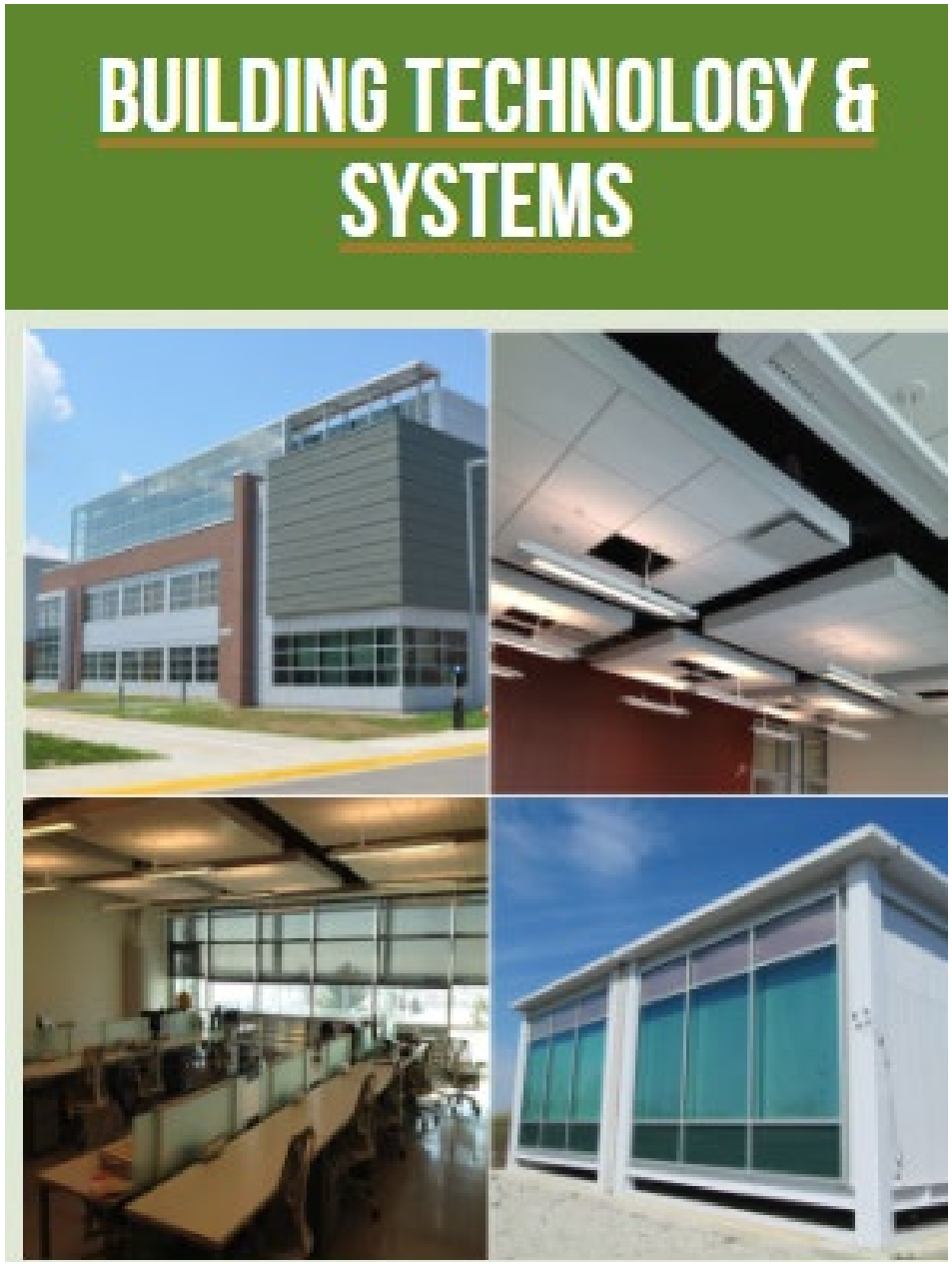
- **On-board power electronics**
- **Oscillators for clock signal generation**
- **Simple input/output interface**
- **Device enclosure**

Integrated Device Performs as Well as Standalone System



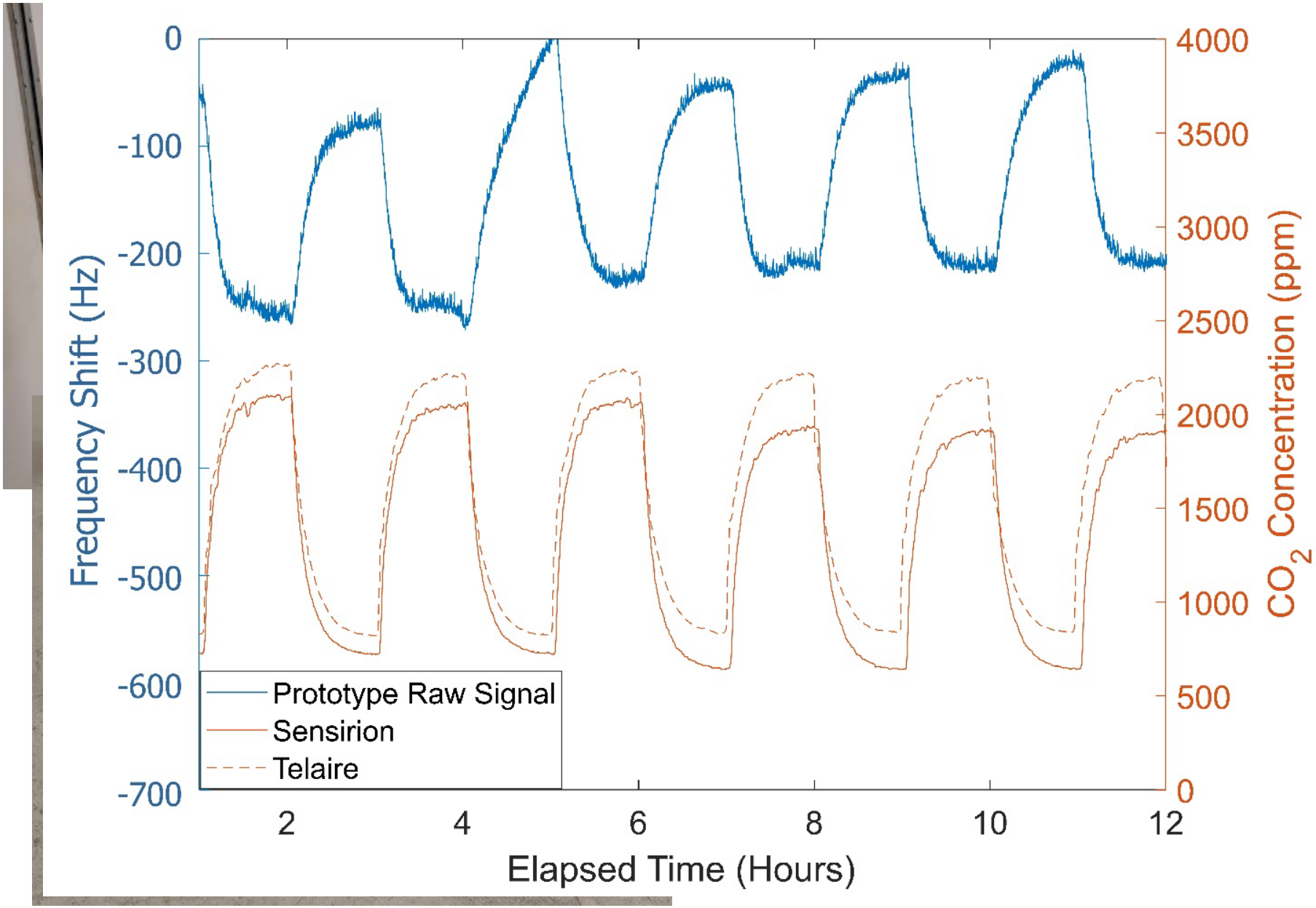
- External validation occurring currently at Michigan State University
- Commercial partners have the capability to scale to production level

Testing at the Center for High Performance Buildings



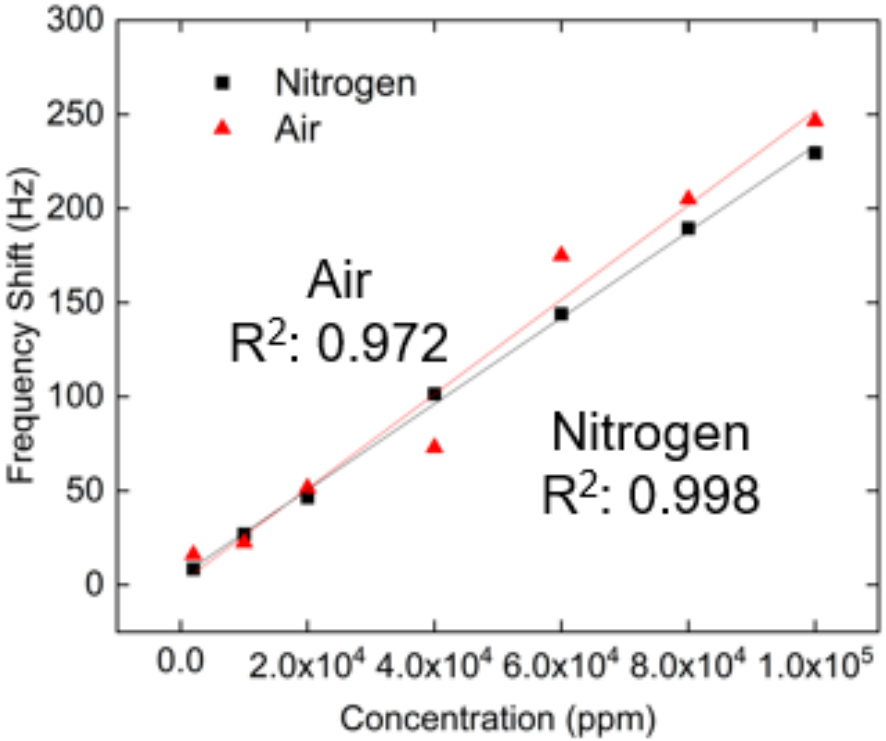
Indoor Air Quality Testing Room

Prototype Sensor Works as Well as COTS Sensor

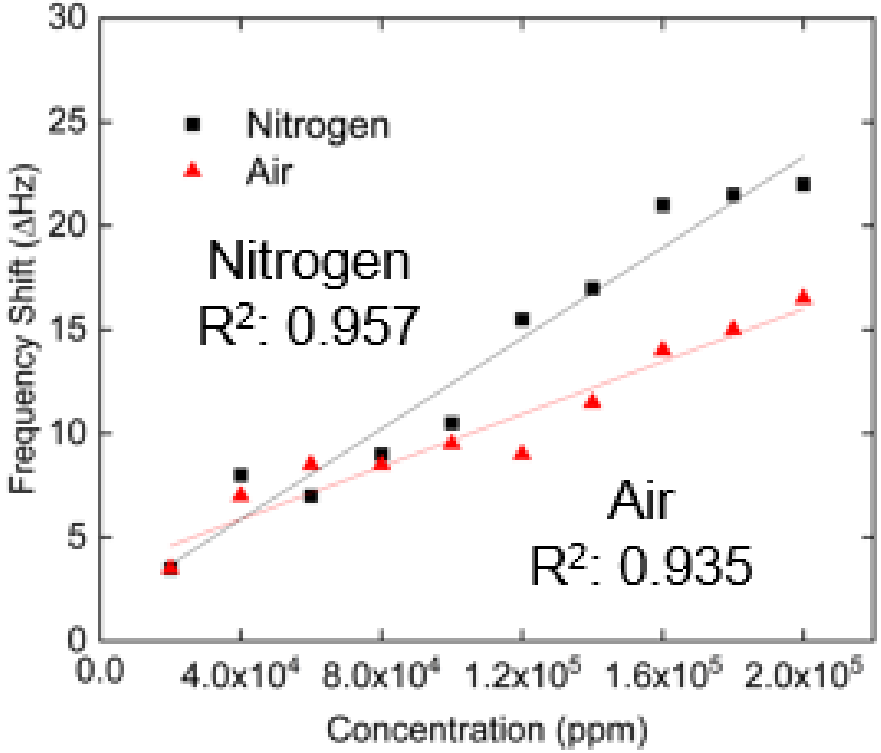


Different Chemistry Detects Flammable Refrigerants

Isobutane (R-600a) Detection



Difluoromethane (R-32) Detection

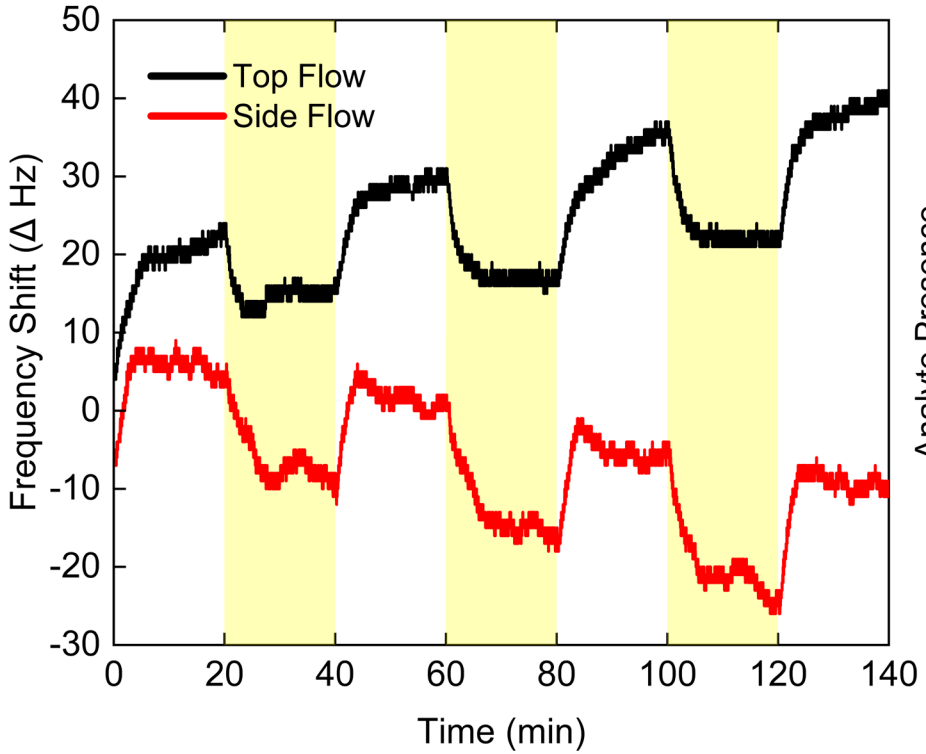


- This detection required the simple printing of a polyaniline (PANI) ink to the top of the mass resonators.

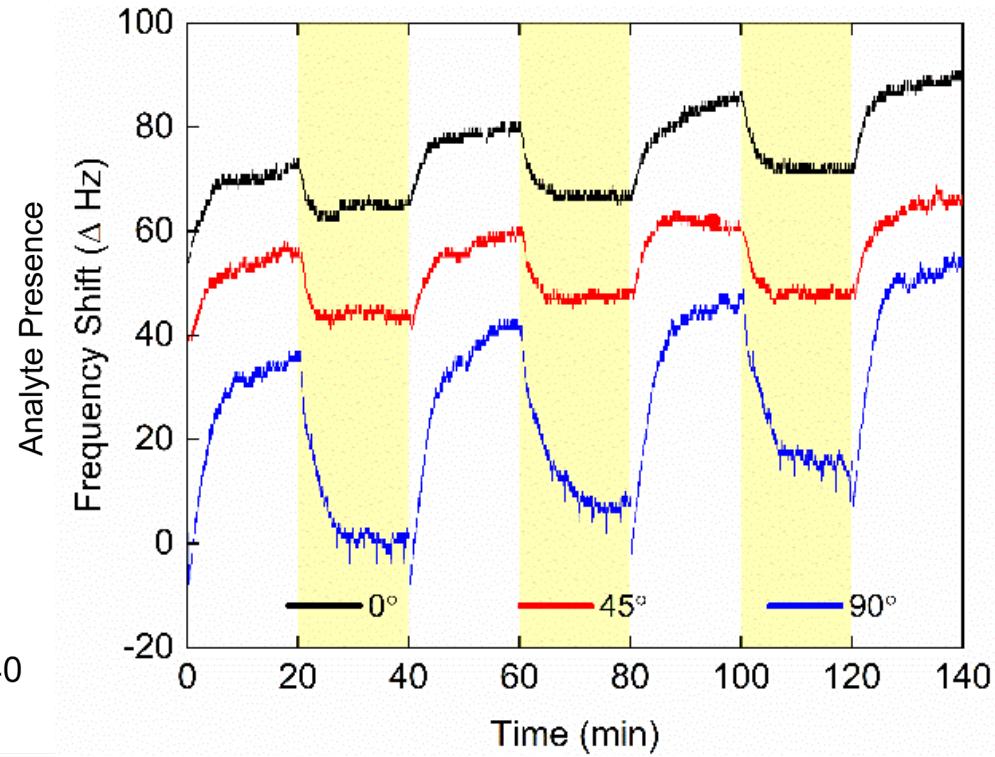
- The customers were interested in detecting at higher concentrations (i.e., near the LFL of the refrigerant gases) based on safety standards.

Sensors Provide Robust Behavior to Different Conditions

Response as a Function of Flow Input



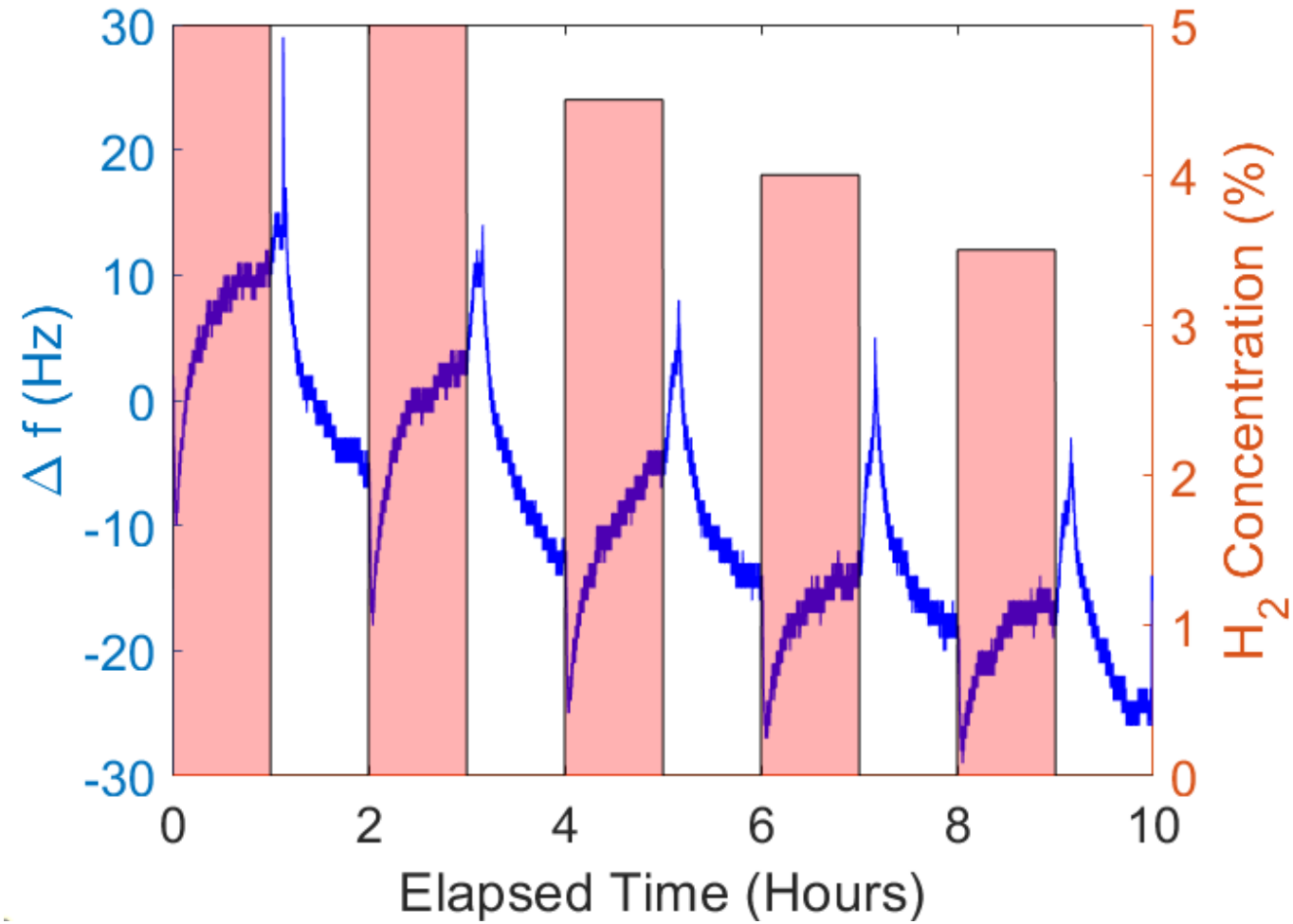
Response as a Function of Orientation



- The examples shown are for R-32 detection, but they are applicable to a range of different gas chemistries.

- While there are slight changes to the response function for these different scenarios, they are consistent. Thus, simple calibrations can be used to correct when converting from frequency shift to concentration.

Room Temperature H_2 Sensing using Pd Nanosheets



- Chemistry involves simple Pd precursor materials and common ligands that are reacted at 80 °C to yield Pd nanosheets (PdNS), which are suspending in hexanes for printing.

- **< 1 µg of PdNS (i.e., < $0.01 per precursor materials) is used per device.**

Acknowledgements

Boudouris Research Group

- Lizbeth Rostro (Dow); Aditya Baradwaj (Intel); Sanjoy Mukherjee (University of California, Santa Barbara); Seung Hyun Sung (LG); Varad Agarkar (Louisiana State University) Ned Tomlinson (Bostik); Martha Hay (Intel); Jaeyub Chung (University of Minnesota); Daniel Wilcox
- Ryan Mulvenna (Dow); Darby Hoss (Intel); Jennifer Laster (Intel); Teng Chi (University of Notre Dame); Xikang Zhao (Chinese National Petroleum Corporation); Teng Chi (University of Notre Dame)

Collaborators

- Jeff Rhoads (ME Purdue)
- Hari Subramani (Chevron)

- Jim Braun
- George Chiu
- David Corti
- Letian Dou
- Arsineh Hecobian
- Jianguo Mei
- Brett Savoie

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