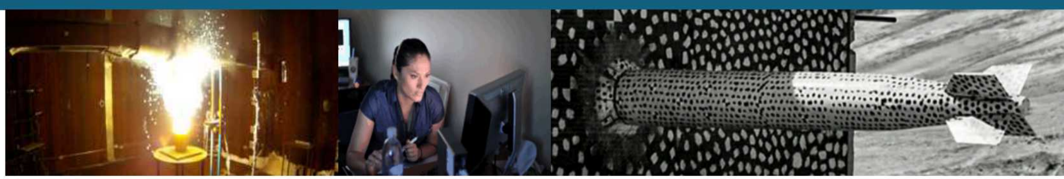
SAND2019-12413C

Electrochemical Sensor of Gas Phase



Carlos R. Perez, Kyle Klavetter,
Jonathan Coleman, Mike Siegal (PI)

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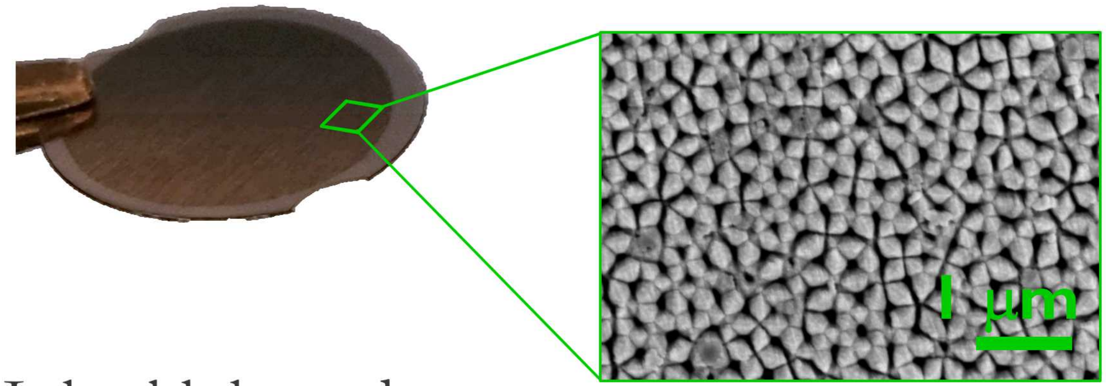
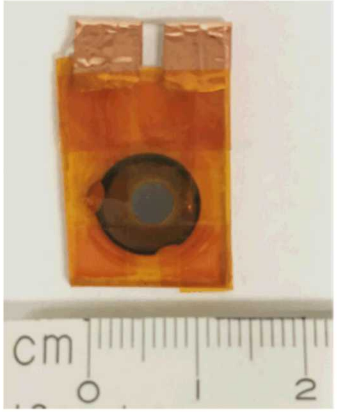
Technology Summary

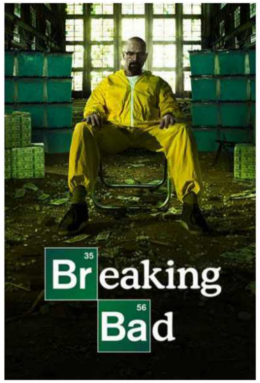
- Electrochemical sensor to monitor low concentrations of I_2 gas
  - Sensing of I_2 by means of hydrolyzing I_2 to ionically detectable species





- I_2 health hazards
  - OSHA 0.1 ppm limit (irritation of skin, respiratory system, thyroid)[1]
  - ^{131}I (fission product) is radioactive and can lead to thyroid cancer[2]

- Trace I_2 detection can indicate hazardous or illicit activity
  - Meth lab activity[3]



http://images.amcnetworks.com

[1]CDC Chem. Safety Card, "Iodine"
[2]Sava et al, JACS, 133, 12398 (2011)
[3]CA Dept. Justice, "Iodine: Inhalation Hazards, Detection and Protection"

Survey of existing technology

- Existing technology isn't sufficient to the task

Ion chromatography

(OHSA protocol): 0.4 ppb / lab-based analysis[1]

Photoionization detectors

1 ppb / negligible selectivity[2]

Electrochemical sensors

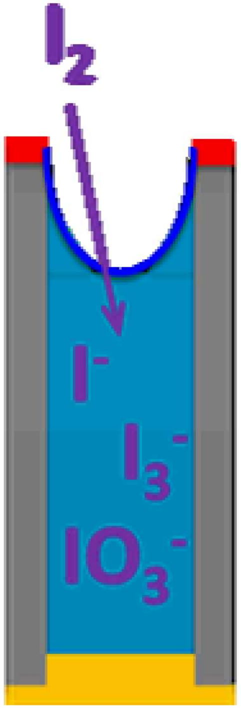
>10 ppb / battery-powered (6 hr use), not selective vs Cl_2, warm-up period needed and ~$2K ea[3]

- Desired properties for our I_2 sensor
  - fieldable
  - low-power/long-life
  - real-time or near real-time detection
    - ppb level detection
  - selective relative to Cl_2

[1]OSHA, "Iodine in Workplace Atmospheres"
[2]CA Dept. Justice, "Iodine: Inhalation Hazards, Detection and Protection"
[3]http://www.gas-sensing.com/c-16-gas-detector.html

Key attributes of our I_2 sensor

- Nanoporous platform is critical
  - Why nanoporous? To retain liquid electrolyte in low relative humidity environments!



Cartoon representation of single nanopore

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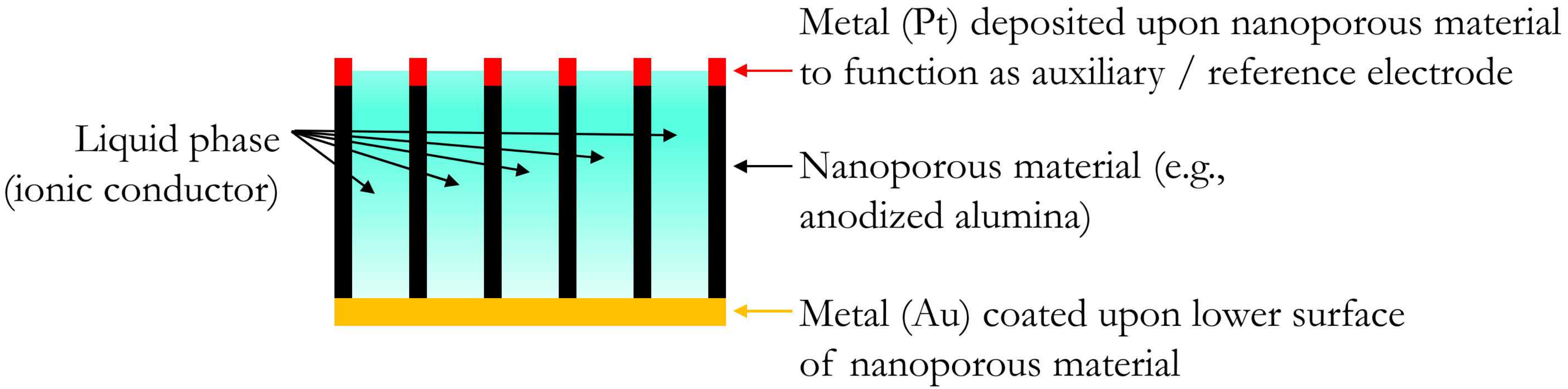
- Properties of selected nanoporous platform
  - Aluminum oxide (anodized aluminum)
  - COTS (commercial off-the-shelf), from InRedox
  - PVD (physical vapor deposition) coated surfaces are the electrodes



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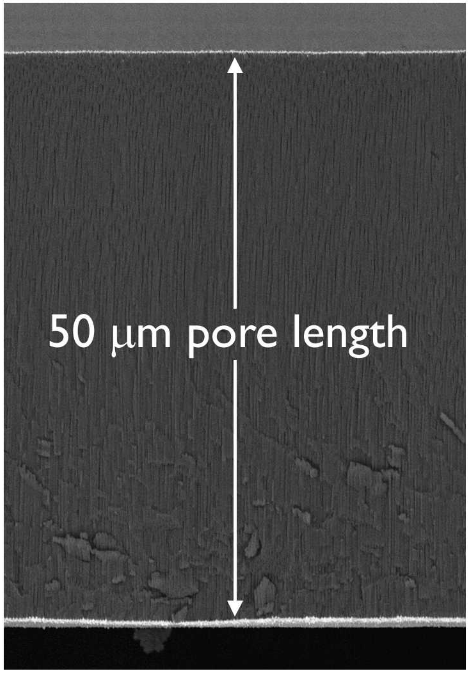
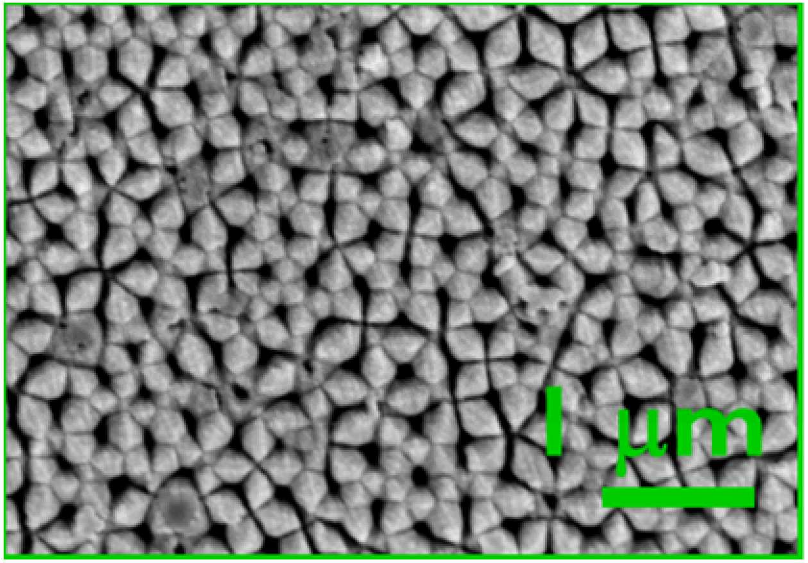


~16% open area



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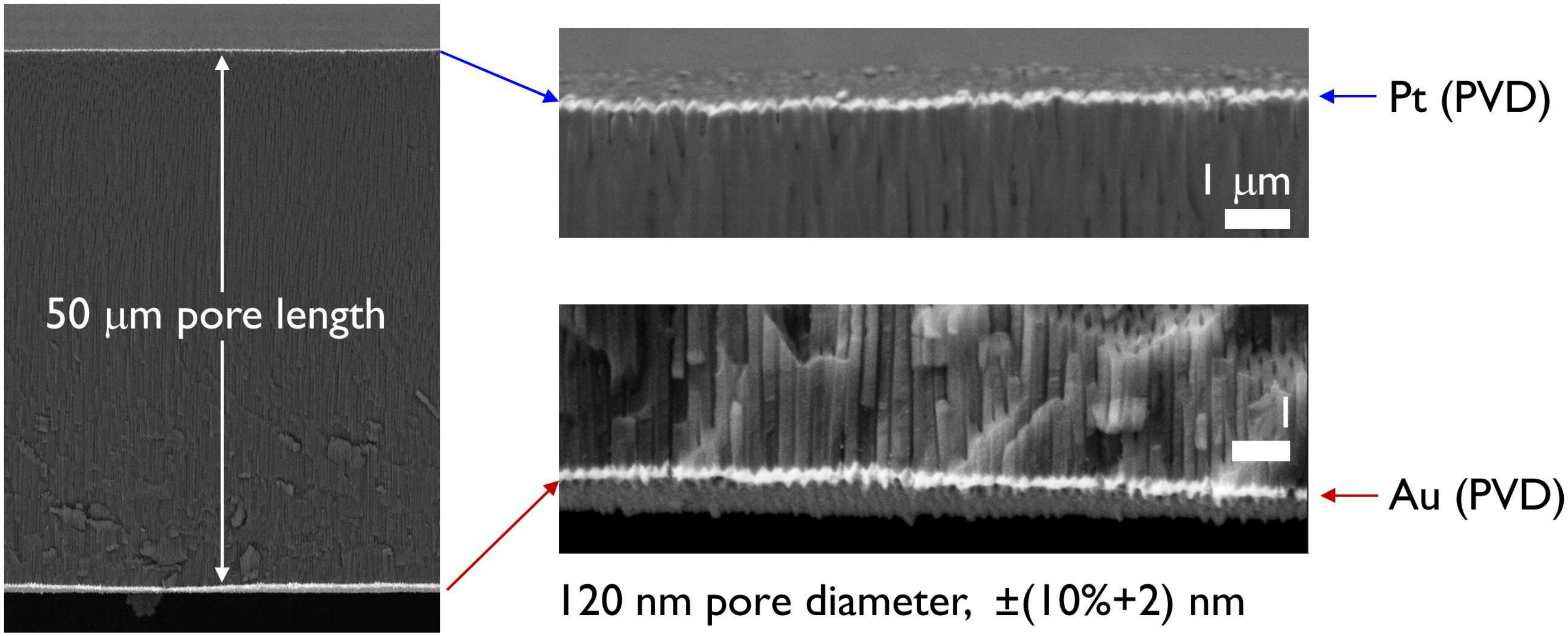
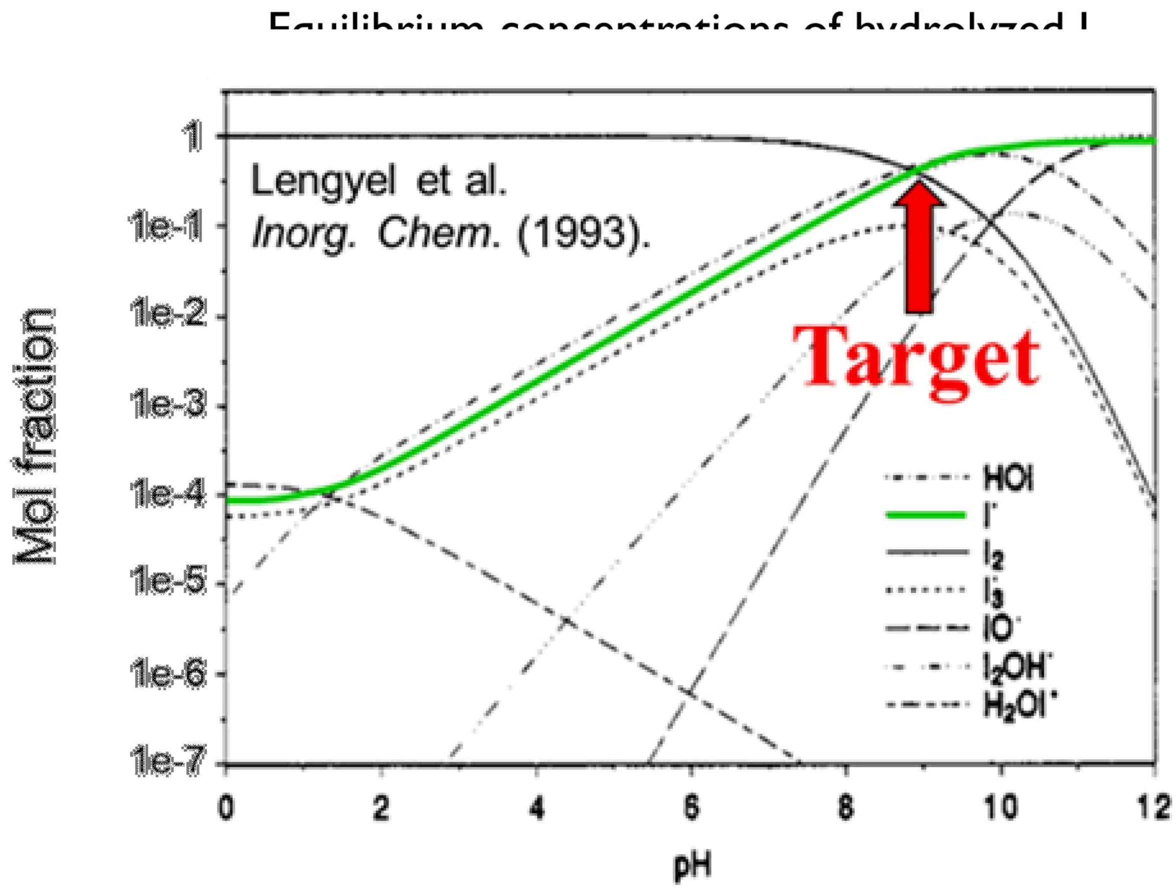


120 nm pore diameter, ±(10%+2) nm

Method for accumulating anionic species of iodine in the sensor nanopores

- The I_2 vapor equilibrates with the aqueous phase in the nanopores of the sensor (Henry's Law)

Critical to maintain pH so that calibration curve is applicable!

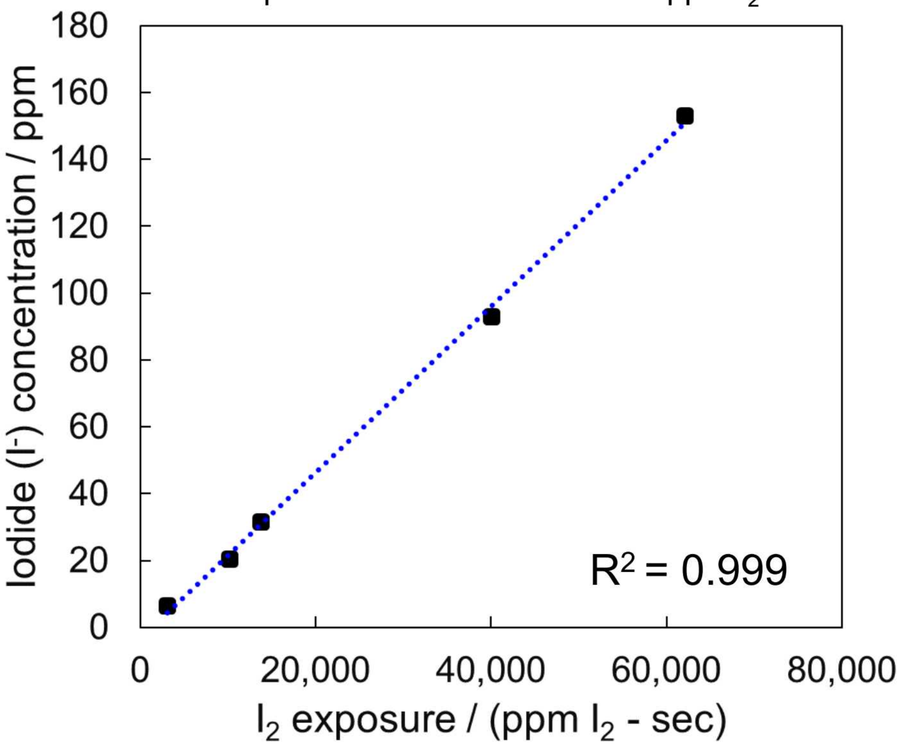


https://chemistryonline.guru/henrys-law/
Lengyel et al, Inorg. Chem., 32, 5880 (1993)

pH 9 buffer accumulates hydrolyzed I_2

Iodide (I^-) accumulation in pH 9 buffer electrolyte from iodine (I_2) exposure

iodine exposure measured in units of ppm-I_2*sec



- Linear relationship between iodine (I_2, gas) exposure and iodide (I^-, aqueous) accumulation up to limit of > 400 ppm I^- *(data point not shown)*
- Thermodynamic limit for iodide accumulation is a function of electrolyte
- Iodide measured by ion selective electrode
- $I_{2(g)}$ measured by commercial sensor

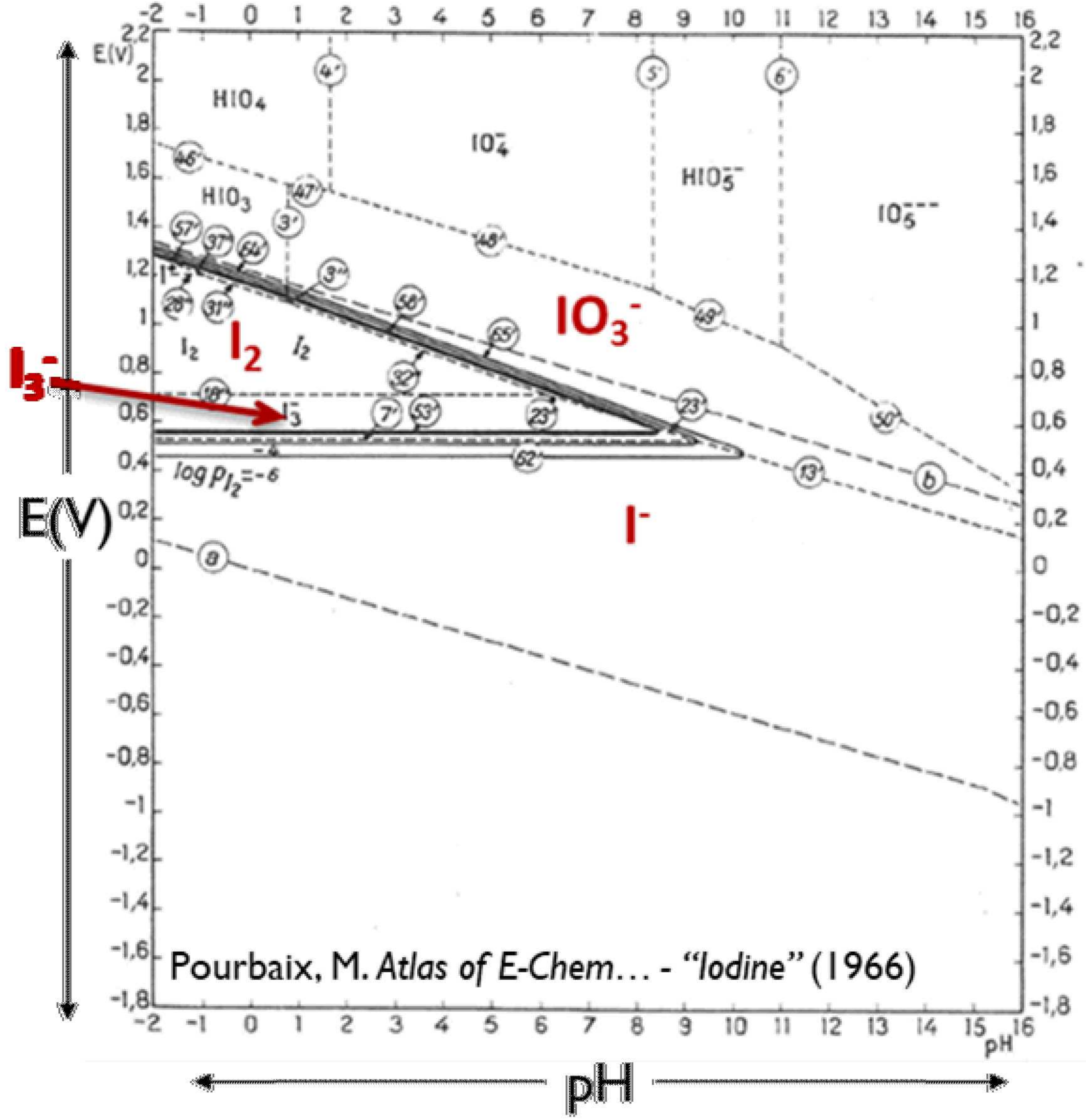
Key point: Ambient iodide can be concentrated in the sensor electrolyte to higher than 400 ppm

Mechanism for I_2 detection

Detection via measured current from the electrochemical oxidation of anionic species of iodine:

$3I^-_{(aq)} = 2e^- + I_3^-{}_{(aq)}$

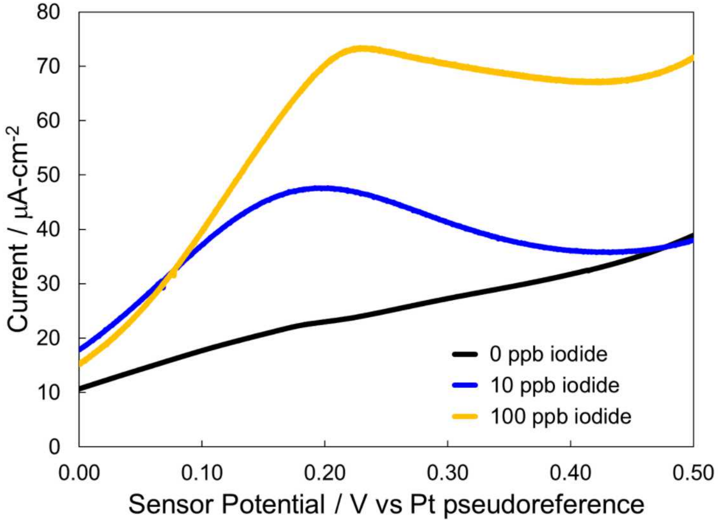
$2I^-_{(aq)} = 2e^- + I_{2(aq)}$



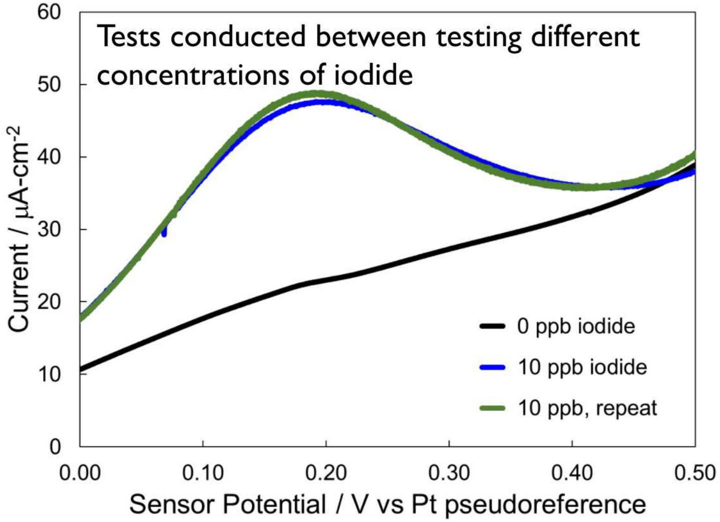
Sensor limit of detection of I^-

- Electrochemical detection of I^- ion in beaker experiment
  - Sensor immersed in solutions of MilliQ water (18.2 MOhm-cm) + 40 mM pH 9 buffer
  - with or without I^- (from 99.995% purity KI salt)

Sensor response vs I^- concentration

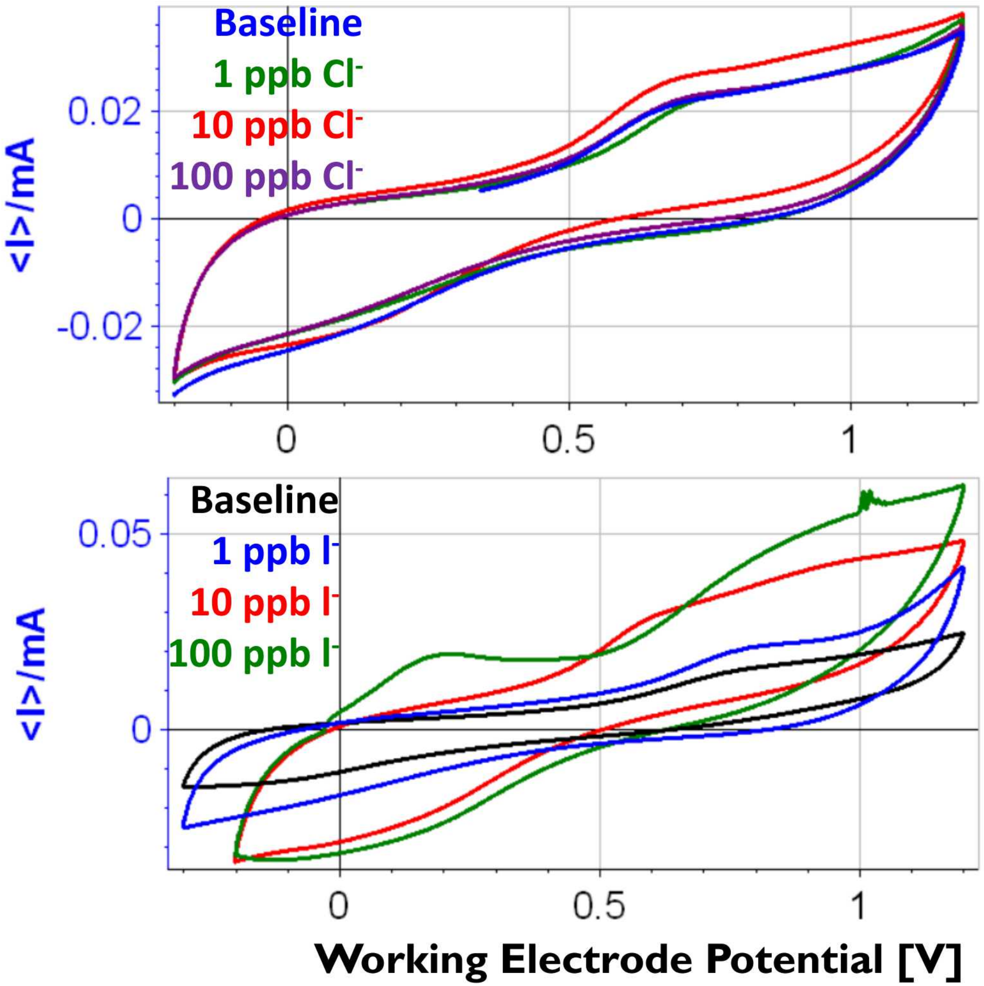


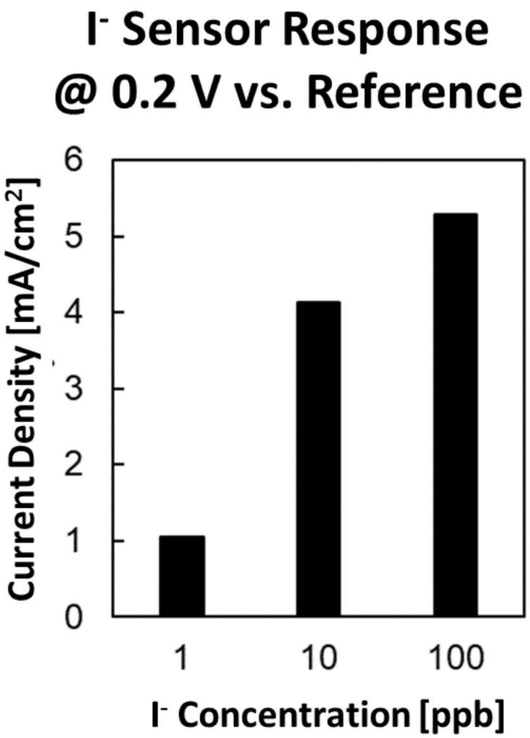
Reproducibility of sensor response



Key result: LOD << 10 ppb
Cyclic voltammetry at 20 mV/s

Cl^- as a confound to I^- detection

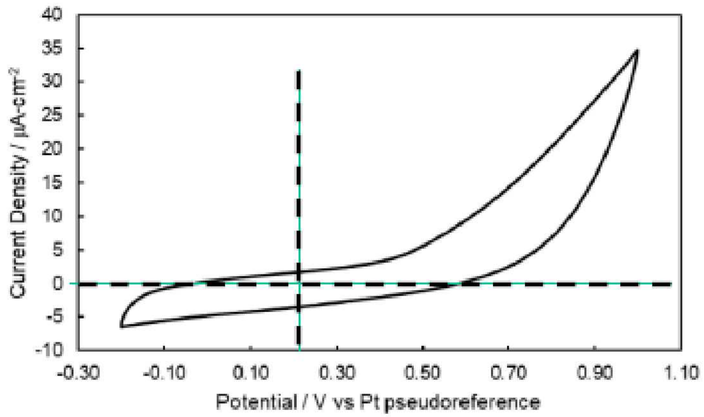


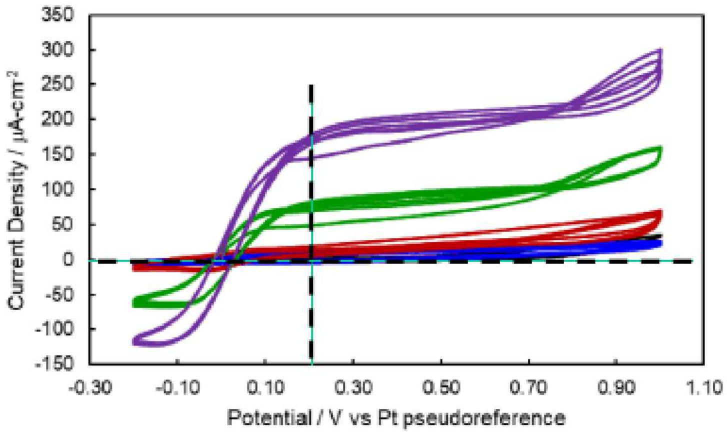


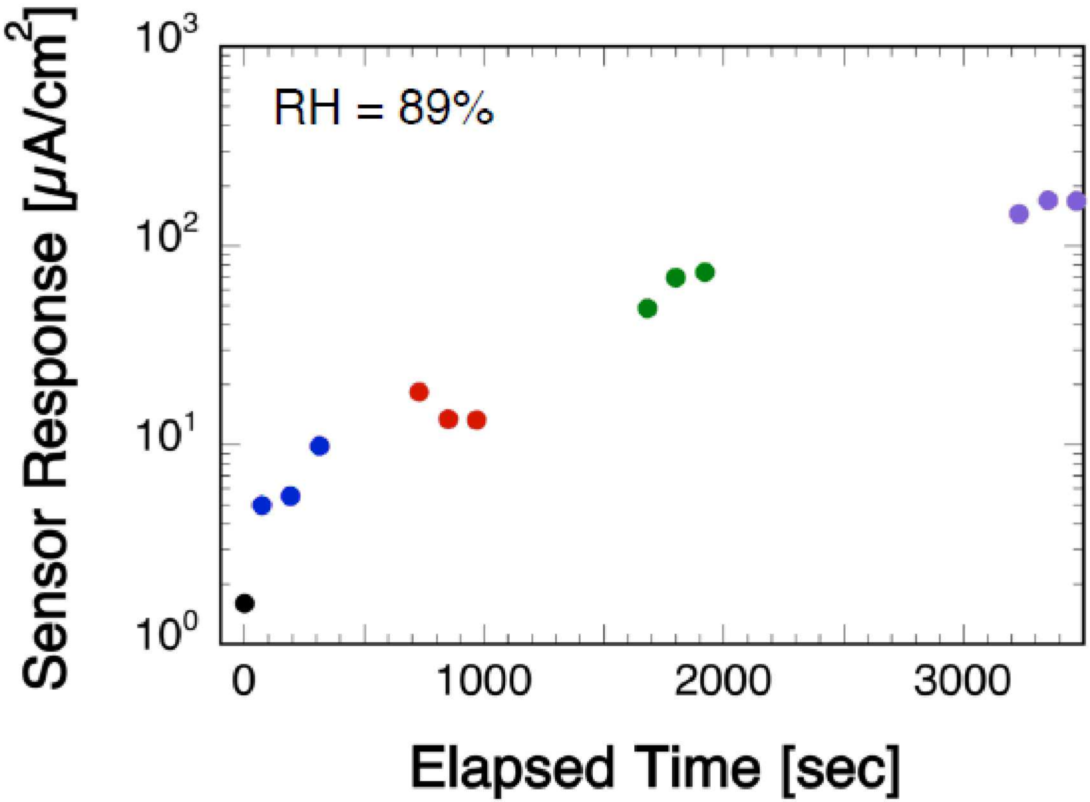
- Device insensitive to Cl^- concentrations up to 100 ppb
- At this same concentrations, I^- is easily detected

Sensor detection of I_2 gas in 89% RH

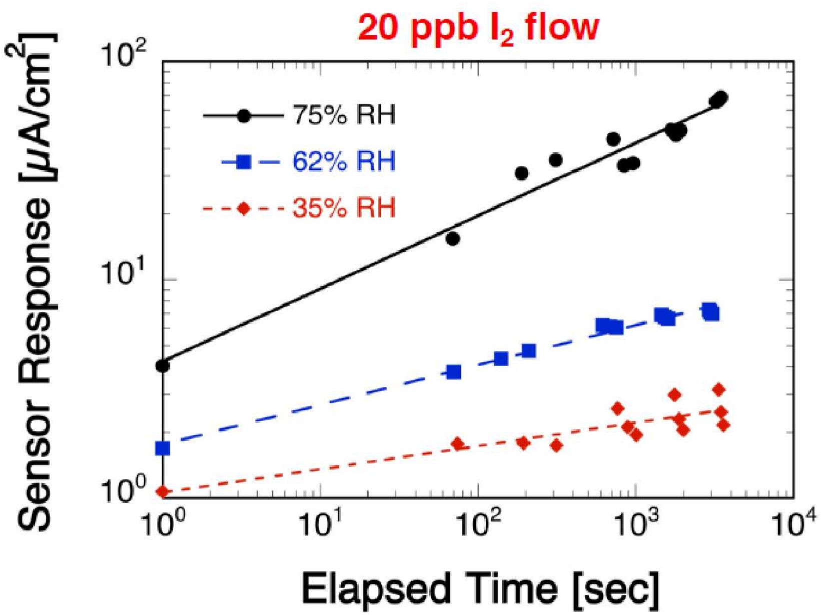
- Pre-wet sensor with pH 9 buffer solution → Establish baseline reading with no I_2 in N_2/H_2O gas flow
- Introduce 20 ppb I_2 flow → Run CV sequence (3x cycles) over time

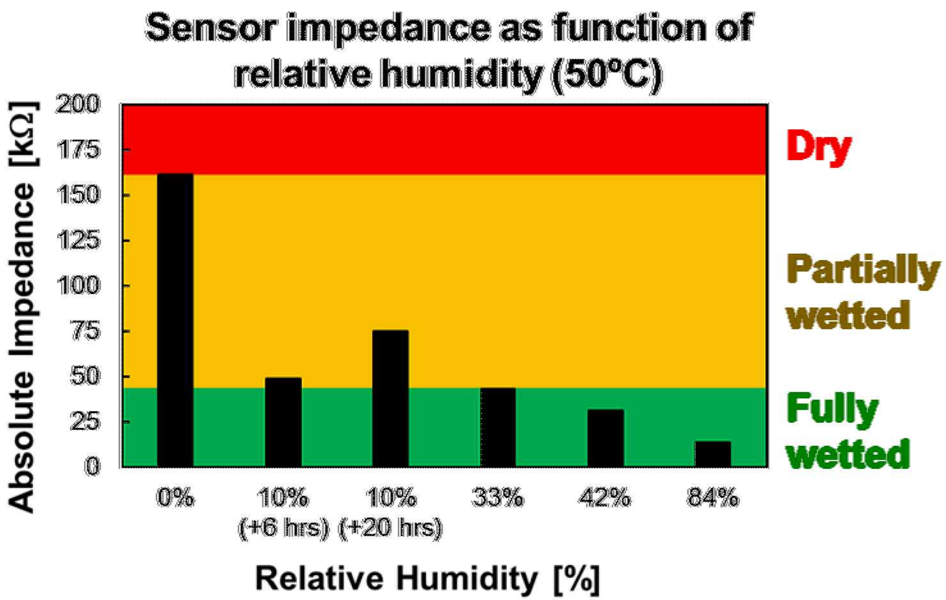






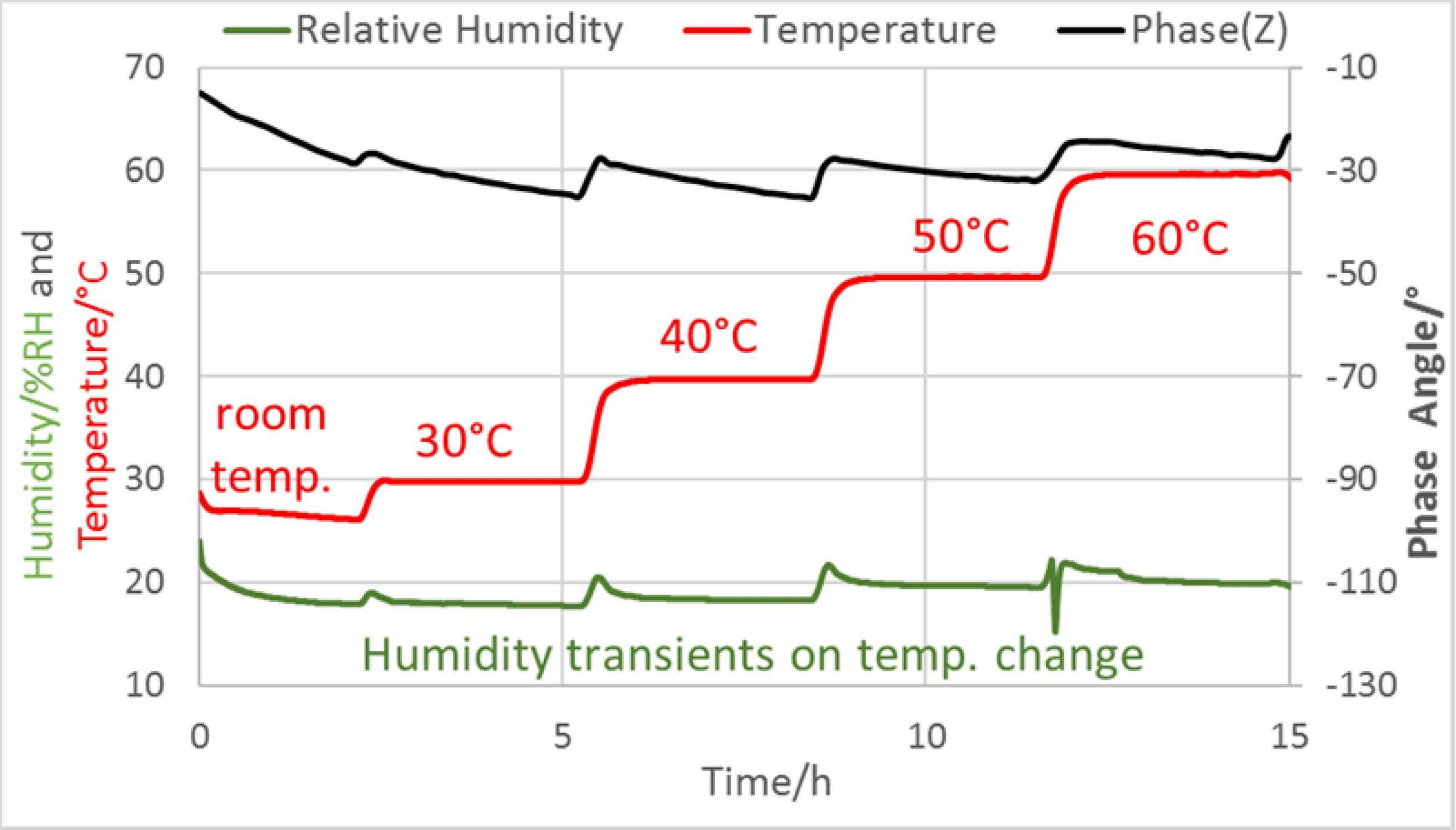
Sensor detection of I_2 gas at variable RH





- Sensor response decreases with decreasing RH
- Sensor response increases with pre-concentration time
- Viable response at RH = 35% for 20 ppb I_2 (gas concentration)

Sensor behavior at low humidity



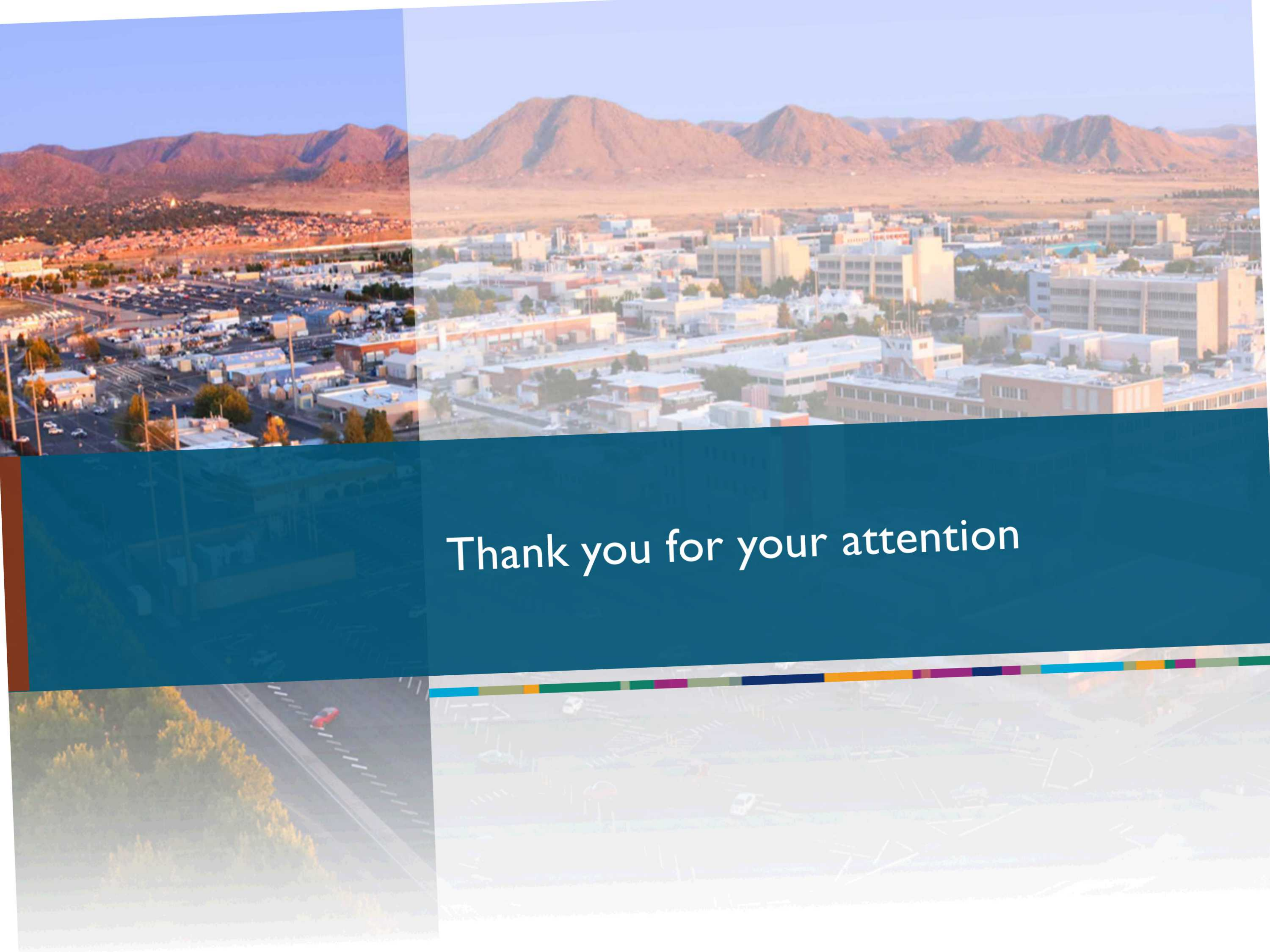
- RH kept within 15-25%, excursions during temperature changes
- Increase in humidity during excursions improves response!
- Device remains wetted up to 60°C

Future work

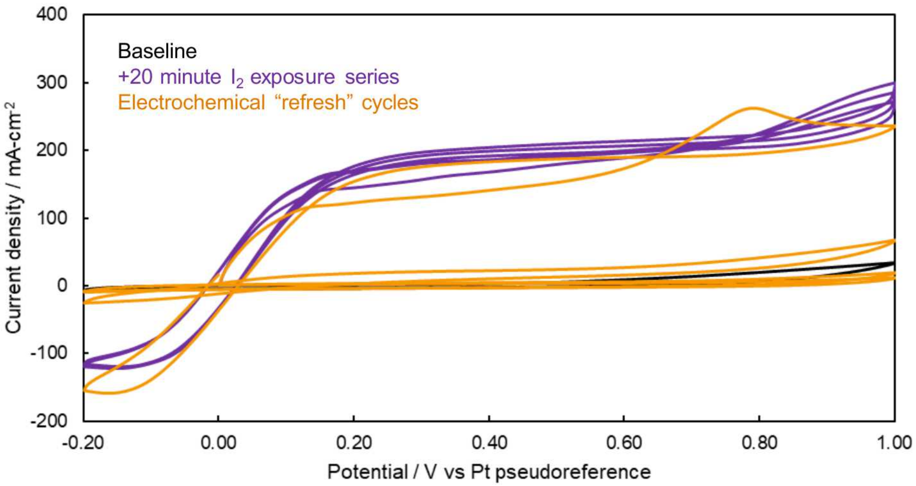
- Demonstrate selectivity of I^- detection over Cl^- for concentration ranges of interest **in the gas phase**

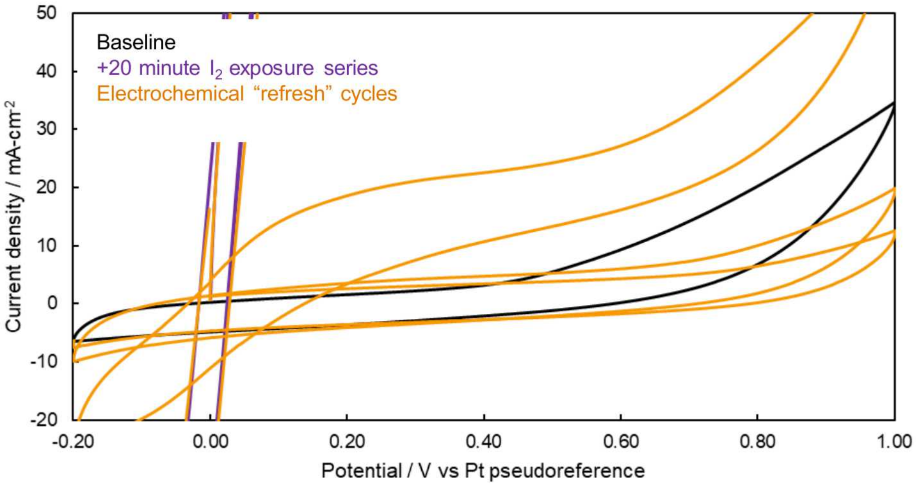
- Detect I_2 with chronoamperometric signal
  - Measured current at fixed voltage
  - Advantage: faster sampling & minimize analyte consumed

- Operate sensor at lower RH by adjusting sensor pore geometry
  - Preliminary results indicate 20 nm pores have slower drying kinetics
  - Take advantage of day/night temperature/RH cycle?


Thank you for your attention

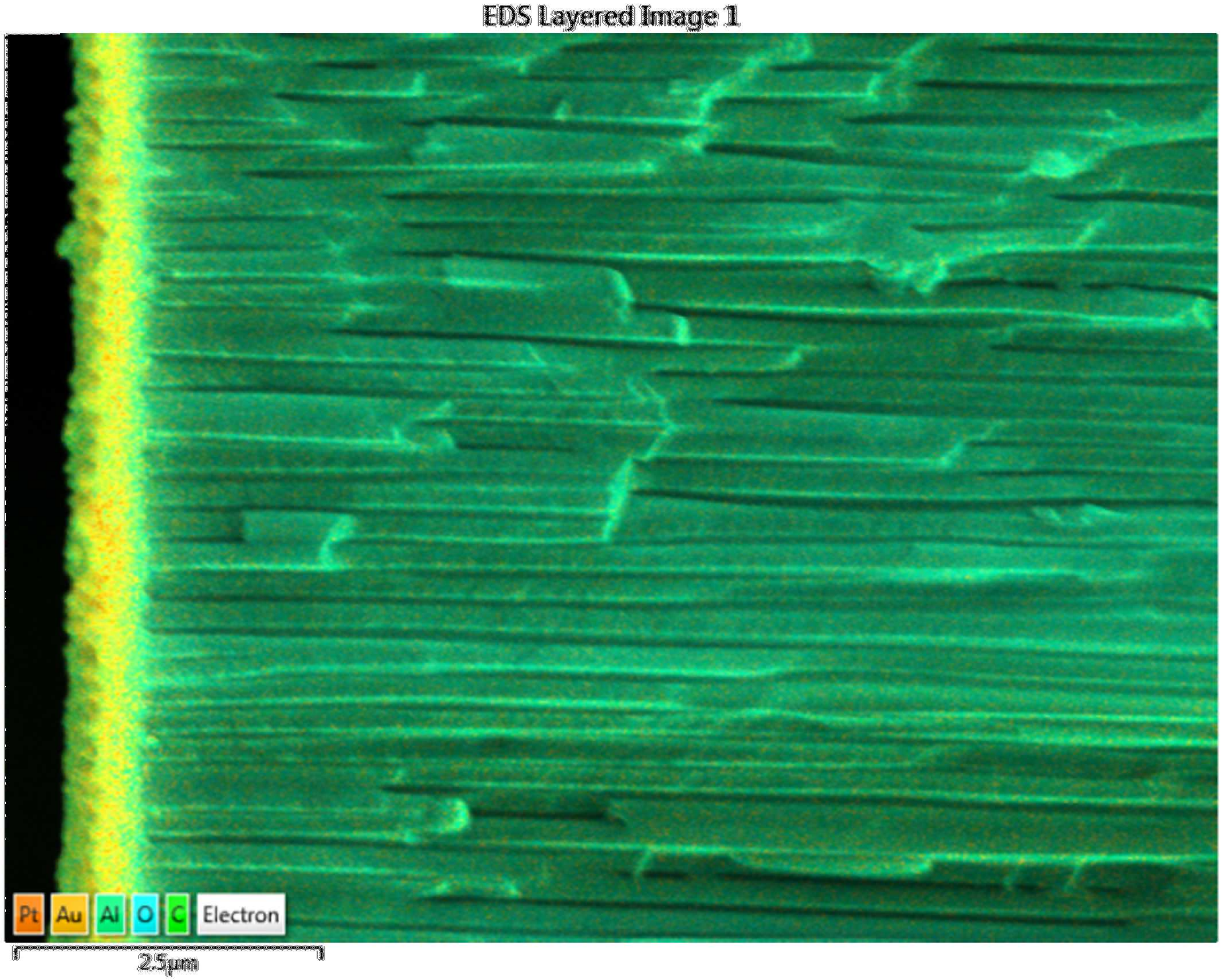
Electrochemical cleaning of sensor





- Electrochemical "refresh" cycles 1, 10, 50 and 100 of 100 cycle CV sequence shown at left in orange
- Purple data shows the sensor when reading after the longest period it was exposed in the I_2 flow chamber
- Black data shows the initial baseline (no I_2)

EDS, Au side



EDS, Pt side