Passive Wireless Sensors Fabricated by Direct-Writing for Temperature and Health Monitoring of Energy Systems in Harsh-Environments

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West Virginia University (WVU)

Background- Harsh Environment Sensing Needs

- Online monitoring of energy systems in extreme conditions is required for mining/drilling, transportation, aviation, energy, chemical synthesis, and manufacturing applications.
- Harsh-environments include:
  - High temperature (1000°C-2000°C).
  - High pressure (up to 1000 psi).
  - Various pO_2 levels.
  - Corrosive conditions (molten inorganics or reactive gasses) .
- Ability to monitor:
  - Temperature
  - Stress/strain within energy or reactor components
  - Failure events
  - Overall health

Processing Vision – Peel and Stick Sensor

Item A represents the organic carrier film.

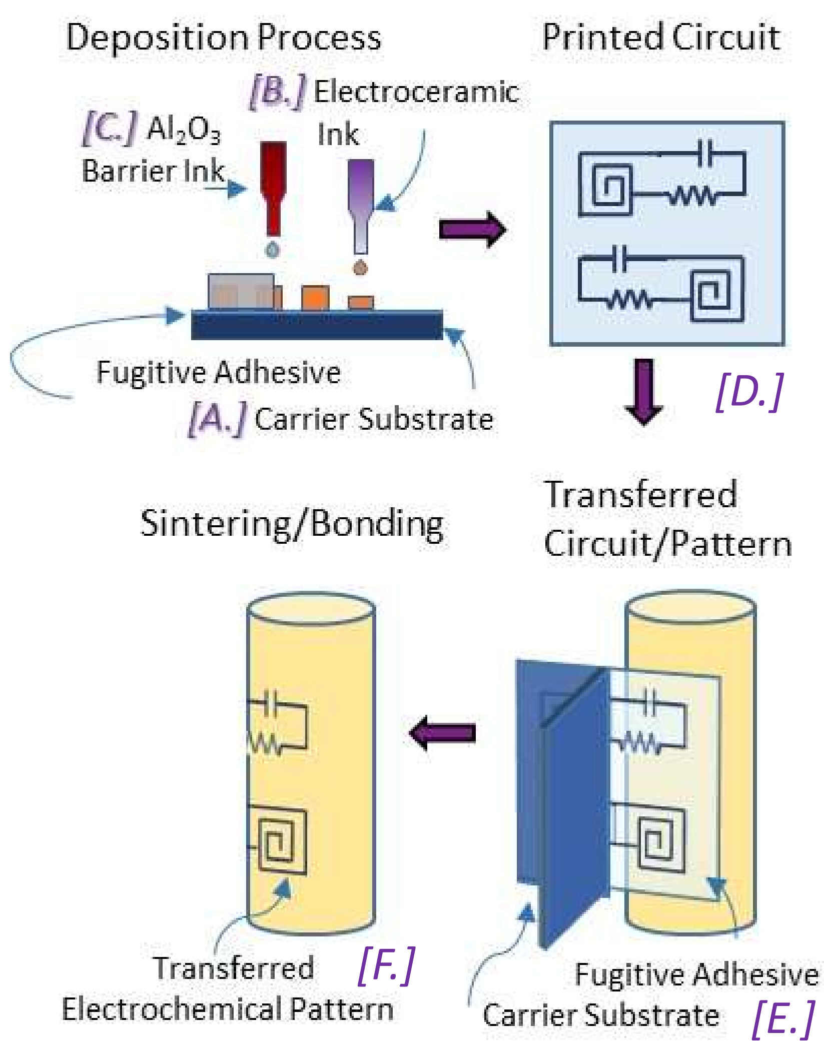
Item B represents the polymer-precursor ink (converts to an electroceramic after heat treatment).

Item C represents a possible barrier layer.

Item D represents RF circuit sensor circuit printed on the transfer paper.

Item E shows the RF circuit pattern being placed upon the energy-system component.

Item F represents the pyrolysis of the organic carrier and bonding.



Program Objectives

Task 2:

- Investigate phase formation, sintering/grain growth, and electrical properties of polymer-derived electroceramic composites between 500-1700 °C.

Task 3:

- Define processes to fabricate sensor through direct-writing (or micro-casting) electroceramic composites.
- Develop methods to form monolithic “peel-and-stick” technology.

Task 4:

- Design of RF passive wireless LCR circuits and receiver (reader) antennas for testing at temperature up to 1700°C.

Task 5:

- Demonstrate the passive wireless sensor system on a SOFC repeat unit and a singular gas turbine blade prototype as example applications.

R&D Team (Co-PIs)

Dr. Edward M. Sabolsky (WVU Mechanical and Aerospace Engineering) will act as PI of the program (both technical and administrative), and will be responsible for ceramics processing and sensor testing.

Dr. Kostas Sierros (WVU Mechanical and Aerospace Engineering) will lead development of micro-patterning and robo-casting of ceramic materials, and will be the co-developer of the printing inks and direct-writing tasks.

Dr. Daryl Reynolds (WVU Computer Engineering) will lead the electronics design, interfacing and circuitry, in addition to the development of the passive wireless communication and testing.

Dr. Matthew Seabaugh and Mr. Gene Arkenburg (Nexceris LLC) are Director of Product Development and SOFC Group Leader, respectively. Assist in testing technology on SOFC platform.

Dr. Kristen Brosnan (GE Global Research) is the Manager of Ceramic Structures and Processing Laboratory. Consult and mentor team for turbine blade application and demonstration.

Major Milestones:

Materials/Sensor Fabrication

M1- (Task 2)$\Rightarrow$ Down-select composite composition for Task 3. (June 2016→June 2018).
M2- (Task 3)$\Rightarrow$ Define basic ink/paste formulation for printing. (June 2016→Aug. 2018).
M3- (Task 3)$\Rightarrow$ Completed baseline sensor printing on oxide substrates. (August 2017).
M4- (Task 3)$\Rightarrow$ First demo of pattern transfer. (March 2017 →Oct. 2018).
M5- (Task 3)$\Rightarrow$ First demo of circuit pattern transfer. (March 2017 →Nov. 2018).

Passive Wireless Circuit Modeling and Testing

M6- (Task 4)$\Rightarrow$ Completed design and testing of sensor circuit. (Sept. 2016).
M7- (Task 4)$\Rightarrow$ Completed wireless coupling modeling for applications. (March 2017).
M8- (Task 4) $\Rightarrow$ Establish high-temp testing setup. (Nov. 2017).

*Roughly 9-12 months behind on Materials/Sensor work (two students left program in one year).

- Michael Comparetto (M.S. student)- sensor testing (**Graduated** Dec. 2018)
- Kavin Sivaneri Varadharajan Idhaiam (Ph.D. student)- materials/sensor research (started Jan. 2018).
- Harish Palakurthi (Ph.D. student)- electronics/wireless research (started Jan. 2018).

Task 2.0: Fabrication and Characterization of Polymer-Derived Electroceramic Composites. (Sabolsky, Sivaneri)

Task 2.0 Objective:

1) Investigate phase formation, sintering/grain growth, and electrical properties of electroceramic composites for applications at 500-1500 °C.

   - **System 1:** Silicide/carbide/oxide system (Mo/W-silicide and polymer-derived versions).

   - **System 2:** Oxide system (La_2NiO_4).

Task 2.0 Approach:

- **Subtask 2.1 Analysis of Multifunctional Electroceramic Composites through Polymer-Derived Precursors:**

Silicon-containing polymers such as polysilane, polycarbosilanes, and polycarbosiloxanes will be investigated as precursors to fabricate various electroceramic compositions. This will include the addition of fillers.

- **Subtask 2.2 Thermal Processing of Composite Compositions:**

Samples will be pressed into bars, and also screen-printed onto Al_2O_3 or ZrO_2 dense substrates (for initial observation on shrinkage effects). Thermal processing the materials in various atmospheres (air, inert, reducing atmosphere) will be completed up to 1700^{o}C.

- **Subtask 2.3 Composite Material Testing and Characterization**

Electrical testing (at high-temperature) and phase/chemistry characterization will be completed on the polymer-derived electroceramic composites.

Task 2.0 Current status:

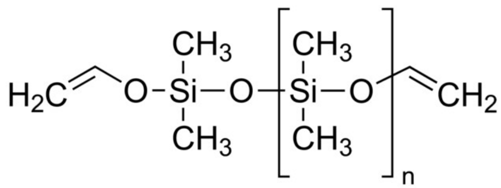
- **Subtask 2.1 Synthesis of Multifunctional Electroceramic Composites through Polymer-Derived Precursors:**
  - ✓ Commercially available silicon-containing polymer Poly di- methyl siloxane (PDMS) is investigated as precursor.
  - ✓ Fabricated various electroceramic compositions.
  - ✓ ***System 1:*** (a) Metallic molybdenum (Mo) and (b) ceramic molybdenum disilicide ($MoSi_2$) were used as particle fillers.
  - ✓ ***System 2:*** La_2NiO_4 conductive composite (Risk Mitigation composition).

- **Subtask 2.2 Thermal Processing of Composite Compositions:**
  - ✓ Effect of thermal processing of the PDC materials in inert atmosphere is investigated on the phase formation of different composites.
  - ✓ Investigated the thermal processing of oxide system (La_2NiO_4) on Al_2O_3 and Y_2O_3-ZrO_2 substrates.

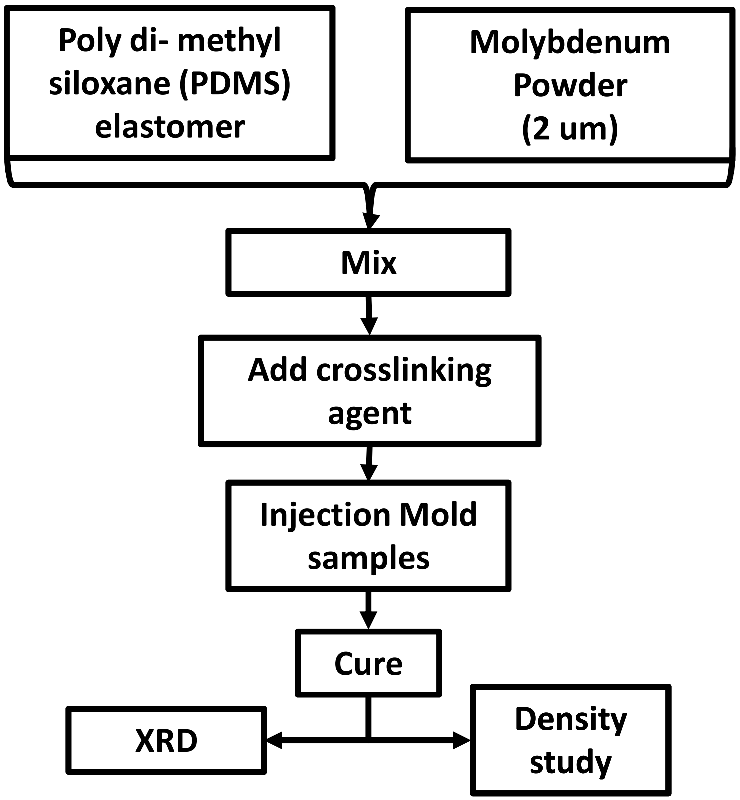
- **Subtask 2.3 Composite Material Testing and Characterization:**
  - ✓ Phase/chemistry characterization is completed on the polymer-derived and oxide electroceramic composites.

System 1-a: Mo:PDMS Polymer Derived Composite (PDCs)

- Molar ratios of Si in PDMS and molybdenum are varied to synthesize PDCs of different compositions.



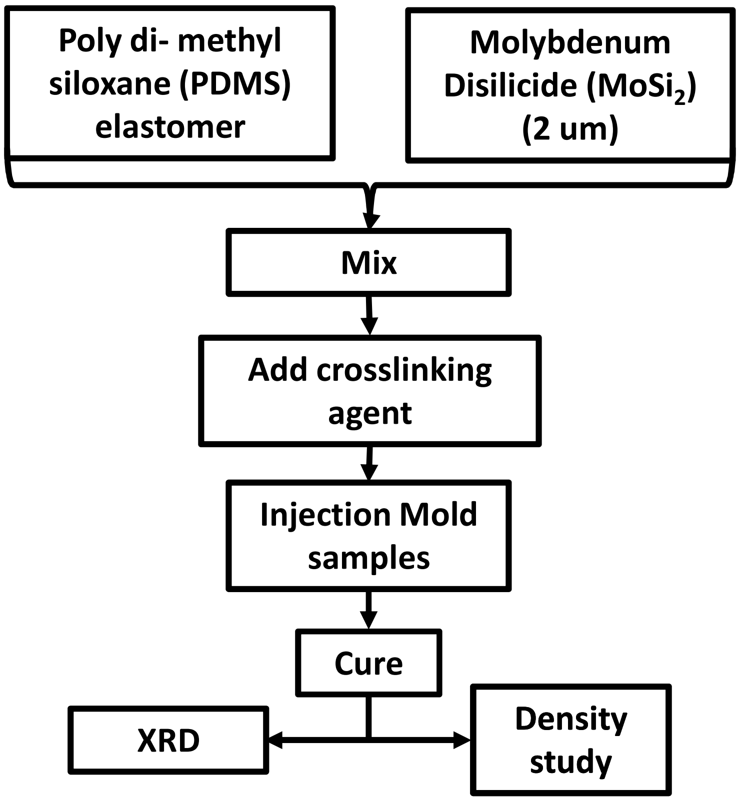
- Molybdenum to Silicon molar ratios 1:1, 2:1, 3:1 and 4:1 are synthesized and characterized.
- PDCs are fired at a constant temperature of 1400˚C in Argon atmosphere.



System 1-b: $MoSi_2$:PDMS Polymer Derived Composite (PDCs)

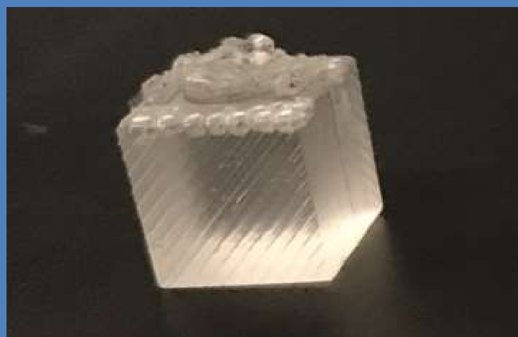
- Molybdenum disilicide ($MoSi_2$) weight ratios of 30%, 40%, 50% and 60% are synthesized and characterized.

- PDCs are fired at a constant temperature of 1400˚C in Argon atmosphere.



Thermolysis of PDMS/Mo

0.25-0.5 ^{o}C/min until 500^{o}C
1 ^{o}C/min until 1400^{o}C, 2 h



Pure PDMS

PDMS, 500^{o}C

PDMS, 1400^{o}C

2:1 Mo:Si

3:1 Mo:Si

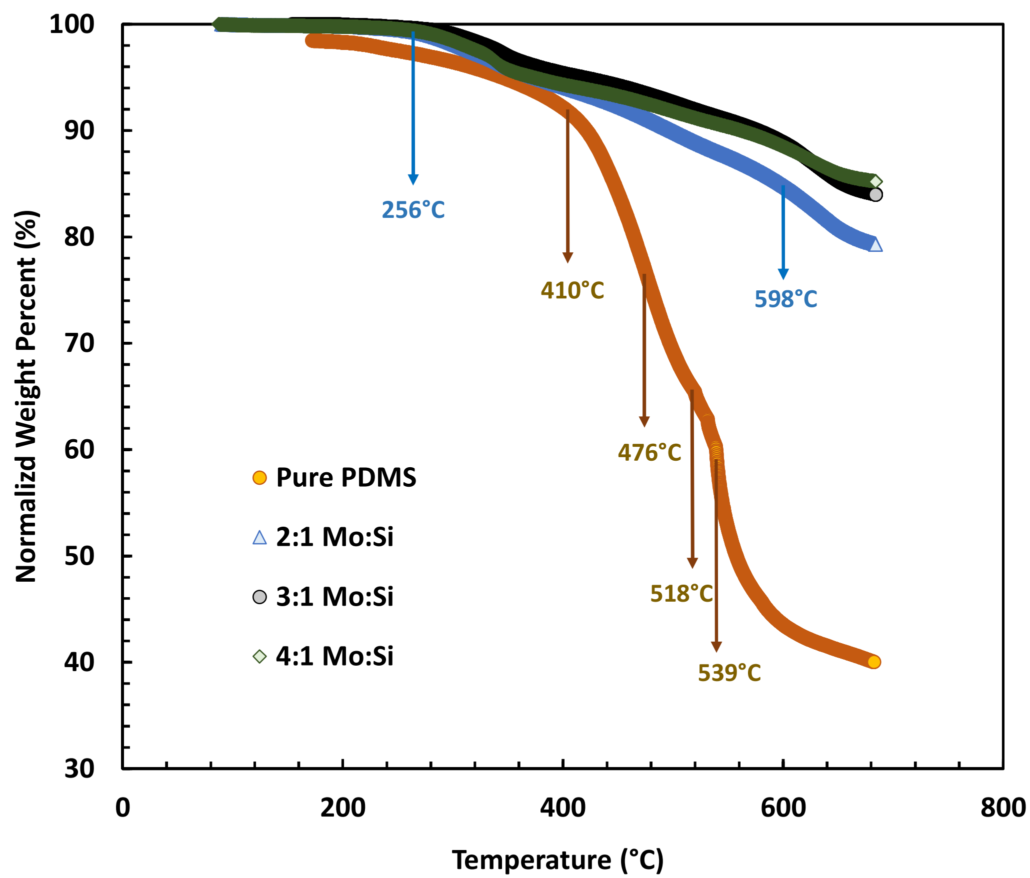
4:1 Mo:Si

- PDMS fractures by 500^{o}C, and complete micro-cracking by 1400 ^{o}C.
- 2:1 Mo:Si showed large volume change and fractured completely.
- 3:1 and 4:1 remained complete during the slow thermolysis (surface oxidation).

Thermogravimetric (TGA) Analysis of PDMS/Mo

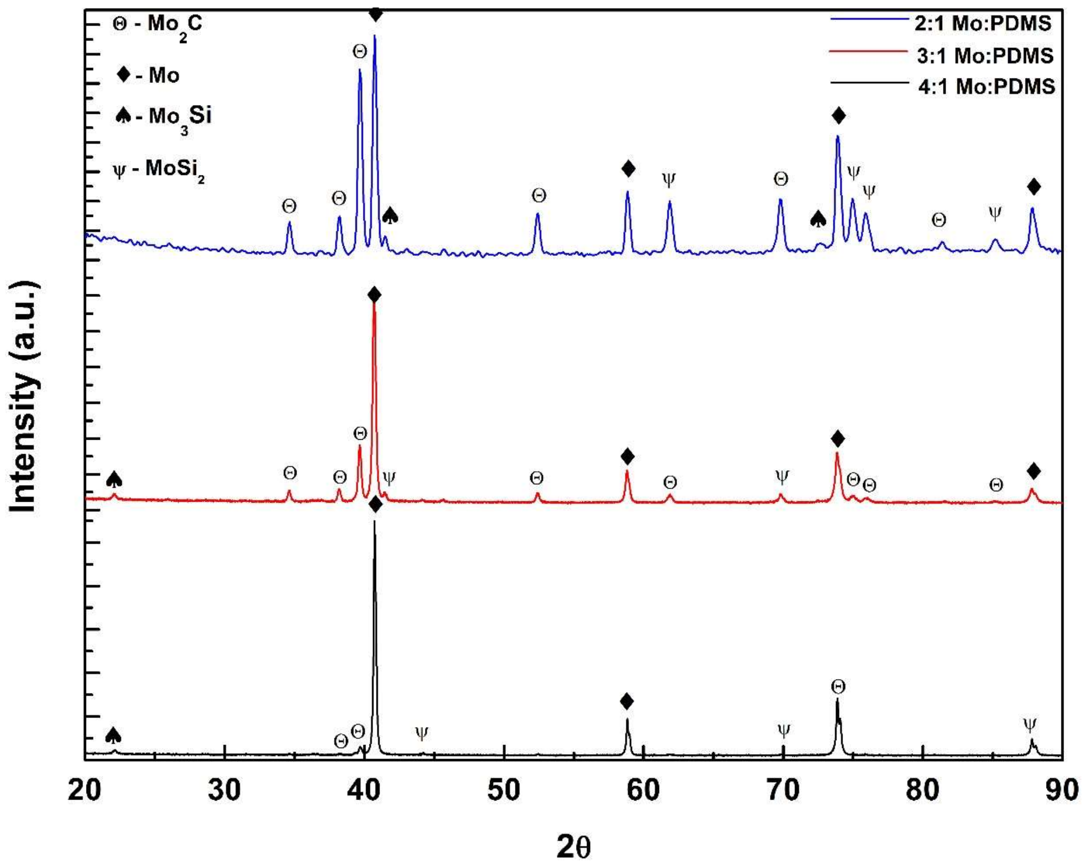
- PDMS initiates major decomposition at 410^oC, with highest rates between 518-539 ^oC.

- Mo addition results in a earlier onset of decomposition, and rather constant loss until near 600 ^oC. (higher content pushed 10-20 ^oC earlier).



$$(C_2H_6OSi)_n \xrightarrow{550^oC} Si - O - C - H_{amorphous} + CH_4 \uparrow + H_2 \uparrow$$

XRD Analysis of PDMS/Mo After Thermolysis

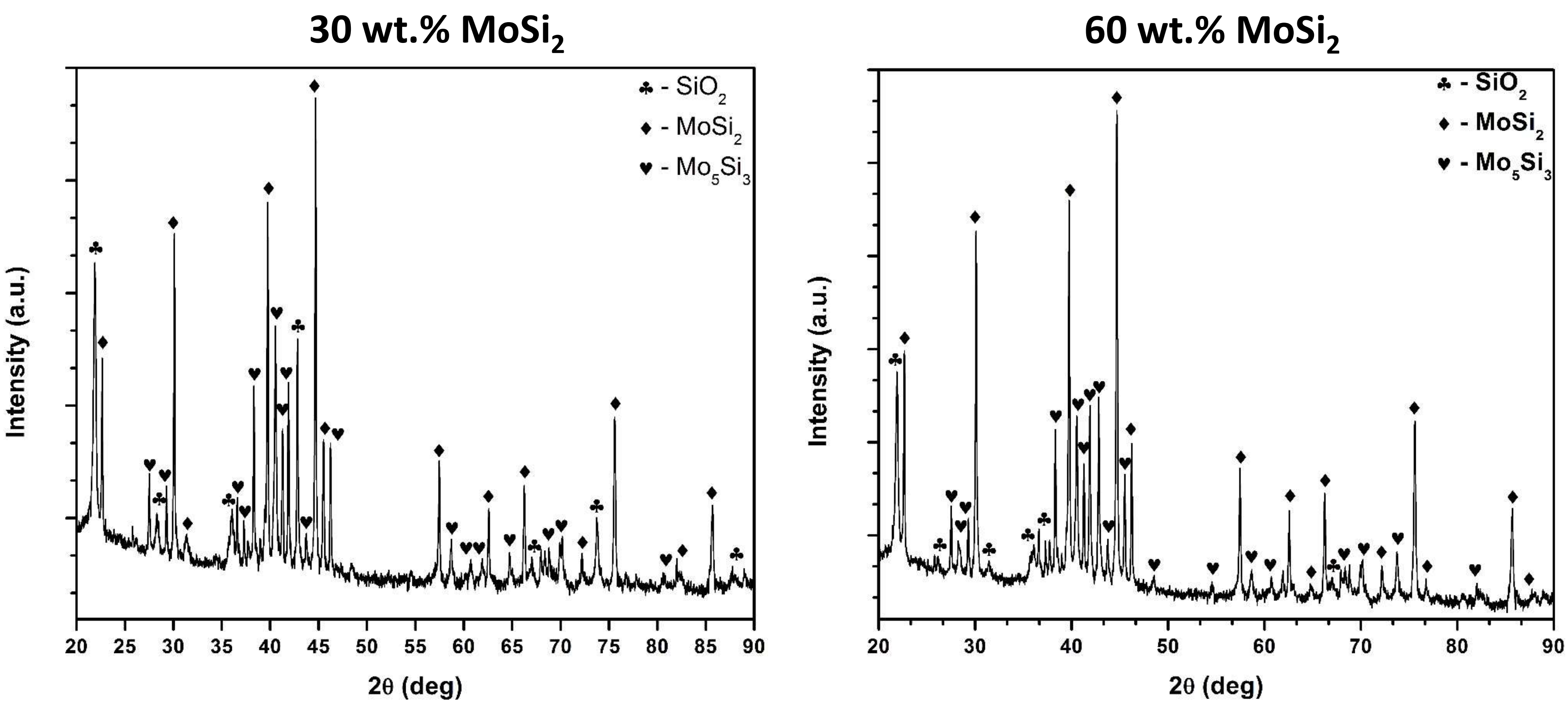


Argon
1 °C/min heating
1400 °C, 2 h

$$Si - O - C - H_{amorphous} + Mo \xrightarrow{1400^{o}C} MoSi_2 + Mo_3Si + Mo_2C + Mo_{unreacted}$$

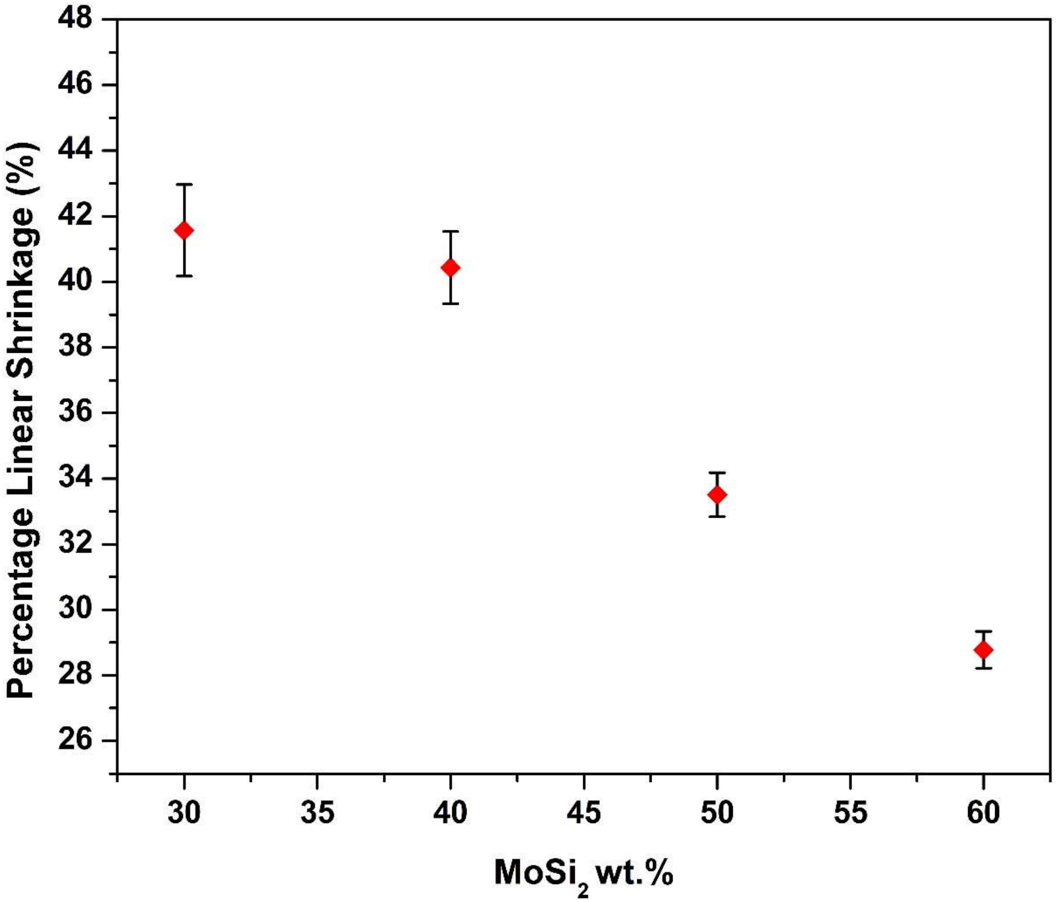
- Heated polymerization (90 °C, 30 min) was required due to Mo settling.
- Primarily Mo and Mo_2C, with some $MoSi_2$.

XRD analysis of PDMS/$MoSi_2$ PDCs



- Heated polymerization (90 ^{o}C, 30 min) was required due to $MoSi_2$ settling.
- Primary phase is $MoSi_2$ as expected, the formation of 5-3 silicide is due to the reaction with the silicon in the polymer.
- The formation of SiO_2 is observed.

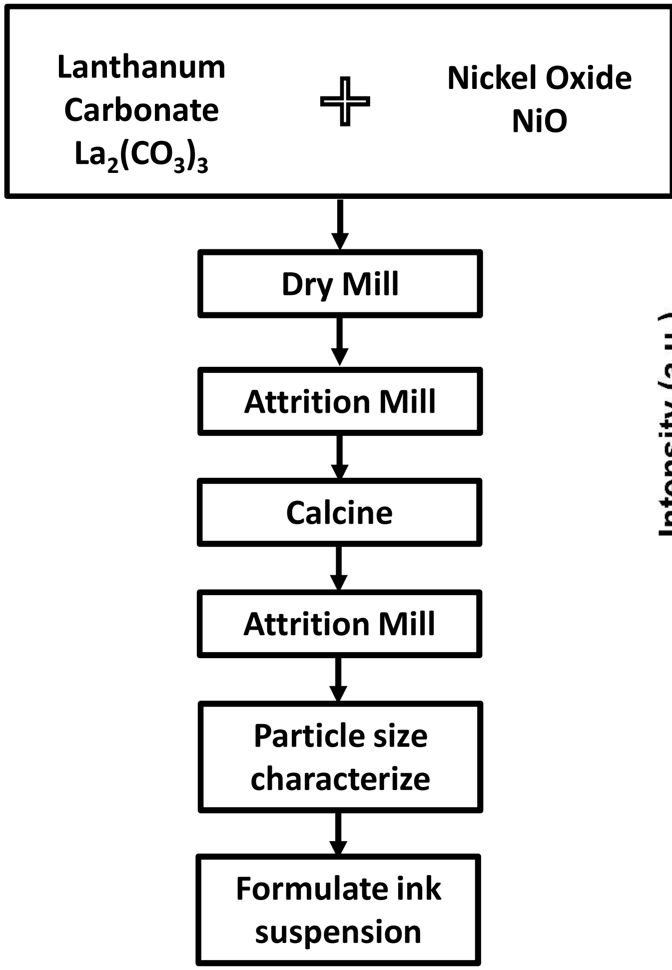
PDMS/MoSi$_2$: Linear and Volumetric Shrinkage



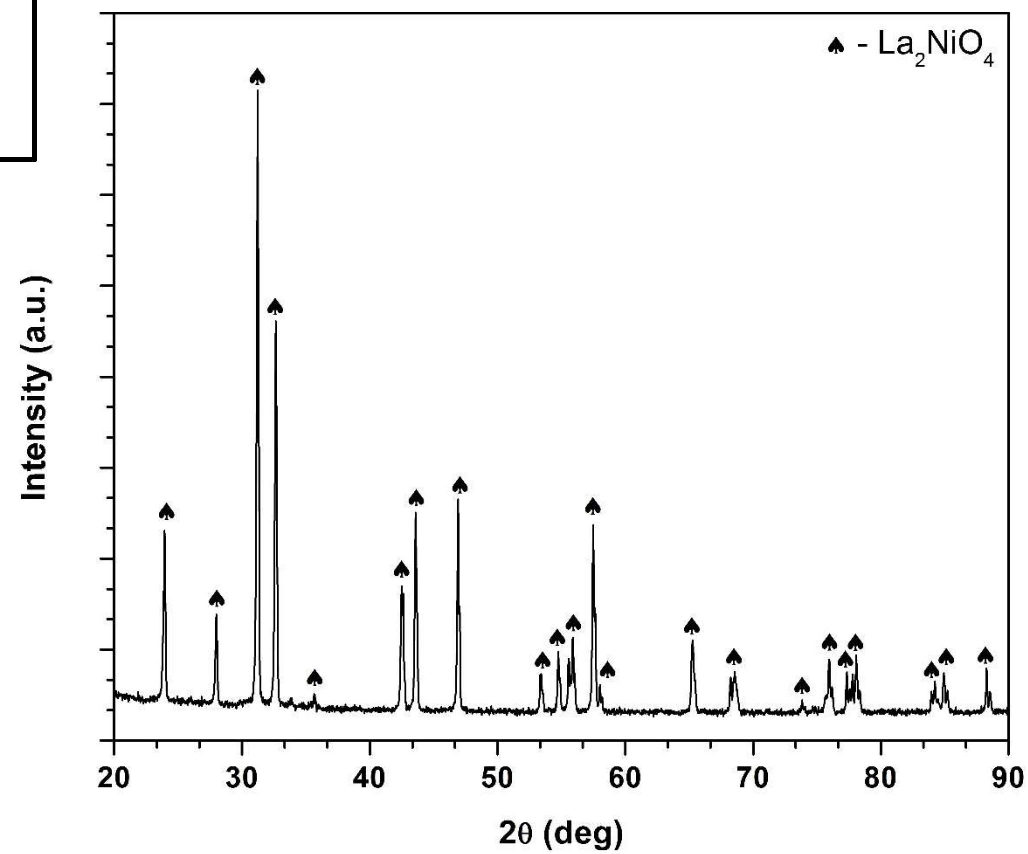
Argon
1 ^{0}C/min heating
1400 ^{0}C, 2 h

- 25-40 % linear shrinkage (with decrease in linear shrinkage with increased weight percentage of MoSi$_2$).
- Larger shrinkage variation at 50 wt.% MoSi$_2$

System 2: Conductive oxide- Lanthanum Nickelate



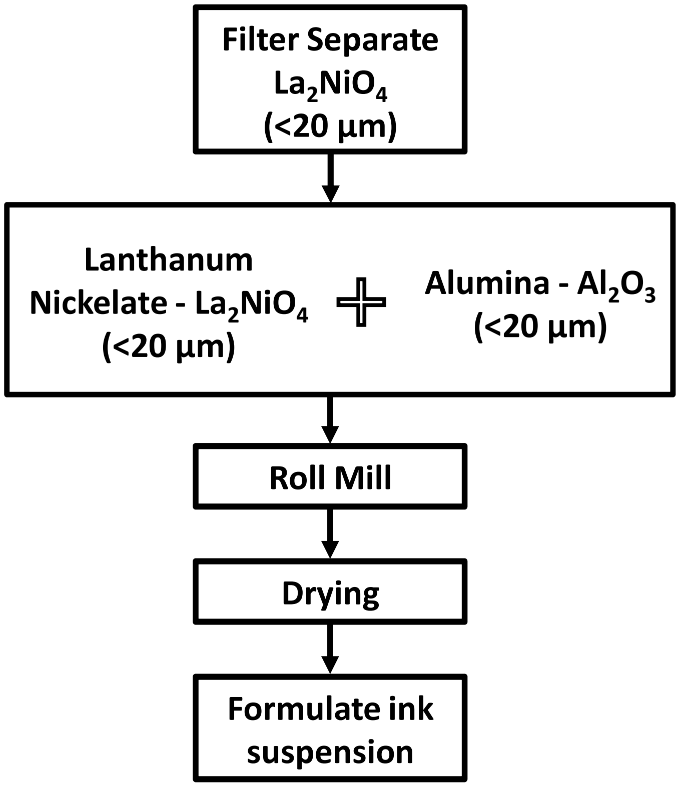
X-Ray Diffraction of Lanthanum Nickelate



- P-type semiconductor (some mixed-conduction).
- CTE~ 13×10^{-6} /K (with K_2NiF_4 structure).
- σ = 60-100 S/cm (200-1400°C)*.

Ceramics International 34 (2008) 651–655

System 2: LNO – Al_2O_3 Composite

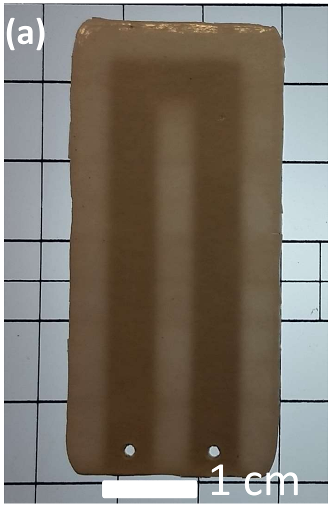


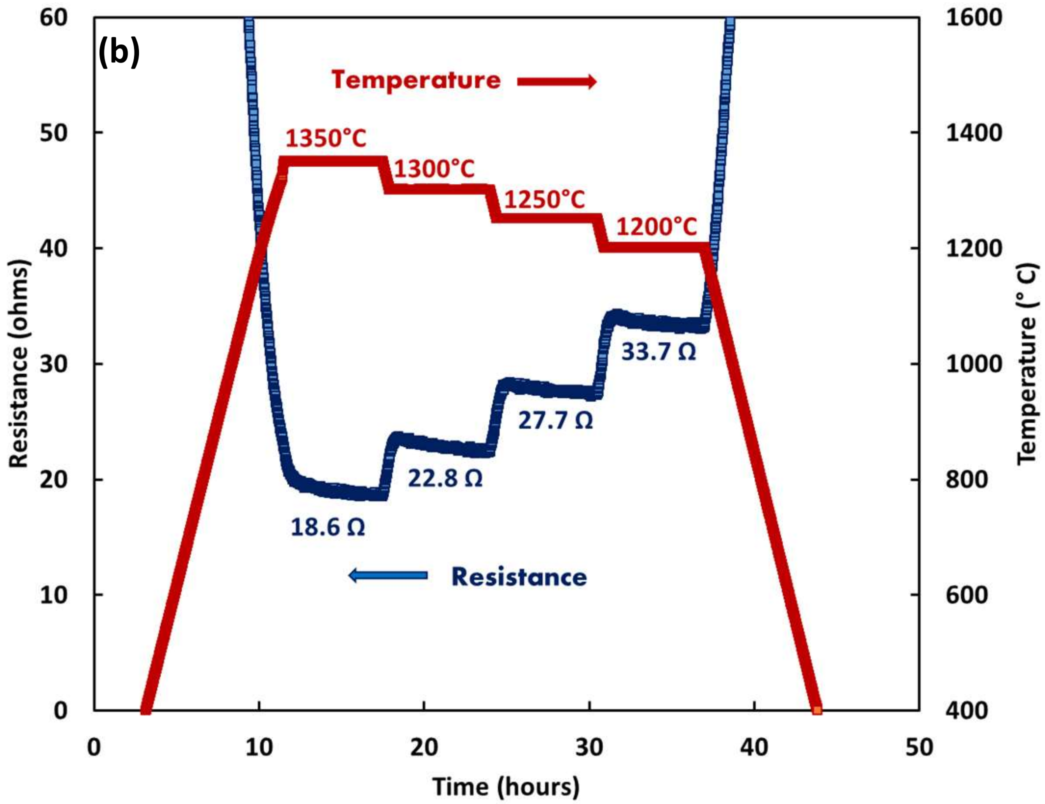
- La_2NiO_4 – Al_2O_3 composites were synthesized to overcome the coarsening and delamination of La_2NiO_4 during sintering.

- Three different composites were synthesized to analyze the bonding to the substrate.

Composite	La_2NiO_4 (vol.%)	Al_2O_3(vol.%)
La_2NiO_4 - Al_2O_3	50	50
La_2NiO_4 - Al_2O_3	60	40
La_2NiO_4 - Al_2O_3	70	30

System 2: La_2NiO_4 Thermistor Evaluation





- ~8 cm long printed thermistor.
- Tested within a refractory brick at 1350°C, 1300°C, 1250°C, and 1200°C (6 h hold) with a cold end kept at a temperature <200°C.
- Resistance decreases during the hold due to thermal diffusion (and coarsening).

Task 2.0 Summary:

- Two PDC systems were studied: Mo:PDMS and $MoSi_2$:PDMS,
  - Characterized phase formation during pyrolysis .
  - Characterized thermal processing.
  - Quantified shrinkage and densification.
- Synthesized and characterized composites of Lanthanum Nickelate.

Task 2.0 Near-term Future Work:

- Synthesize:
  - Silicide-carbide systems with active (Si, W) and inactive (Al_2O_3, ZrO_2) fillers.
  - Other conductive oxide based composites.
- Effects of thermal processing.
- Study phase formation.

Task 3.0:
Direct-Writing, Patterning, and Transfer of the Sensor System.
(Sierros/Sabolsky/Sivaneri)

Task 3.0 Objectives:

- To define processes to direct-write through ink-jet and robo-casting the polymer-derived electroceramic composites onto oxide and polymer surfaces.

- To develop a method to transfer the pattern from an organic film to a ceramic surface and bond after thermal treatment.

- To develop a process based on photolithography to fabricate smaller sensor architectures to overcome the geometrical limitation of the direct-writing process.

Task 3.0 Approach:

Subtask 3.1 & 3.2 Direct-Writing and Micro-Casting Process Development:

- Develop and characterize inks within a permissible surface tension and viscosity level. Direct-writing with Nordson EFD Performus VI robo-printer.
- General process for droplet deposition, drying, and thermolysis will be defined.
- Develop a process to pattern micro sensor design directly on a ceramic and oxide substrate.
- Determine parameters for micro-casting including the viscosity, aspect ratio, particle size distribution and thermolysis.

Subtask 3.3 Baseline Sensor Testing and Design Optimization:

- Initial sensor configurations will be designed, with focus on temperature and strain measurements. The electrical performance testing will be completed at high-temperature (500-1700 ^{o}C).

Subtask 3.4 "Peel and Stick" Development:

- Investigate methods to transfer the sensor circuit/system to the active energy system component, which will be represented by alumina and zirconia substrates.

Task 3.0 Current Status:

Subtask 3.1 Direct-Writing Process Development:

- ✓ Developed inks within a permissible surface tension and viscosity level.
- ✓ Direct-writing with Nordson EFD Performus VI robo-printer.

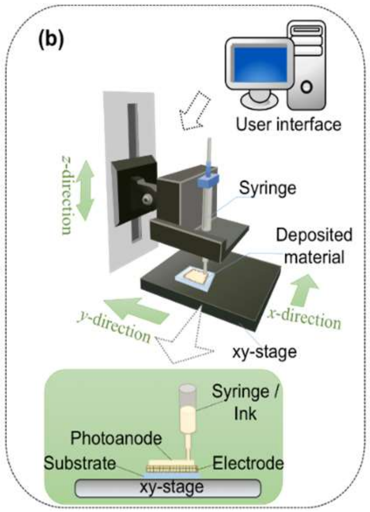
Subtask 3.2 Micro-Casting Process Development:

- ✓ Developed a micro-casting process based on photolithography to pattern reduced geometry sensor structures.
- ✓ Including methods to alter the wetting and drying characteristics of the deposited composite solutions.

Subtask 3.3 Baseline Sensor Testing and Design Optimization:

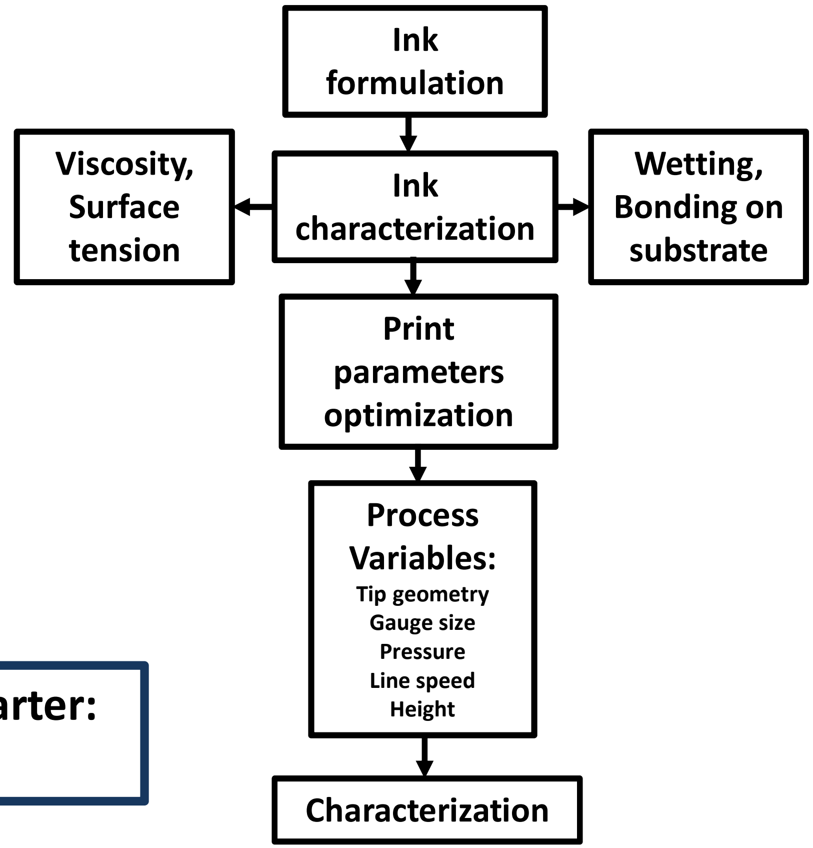
- ✓ Ink deposited directly on oxide surfaces undergo thermal treatment defined by thermal schedules in Task 2 as a starting point.

Initial Robo-Casting Evaluation:



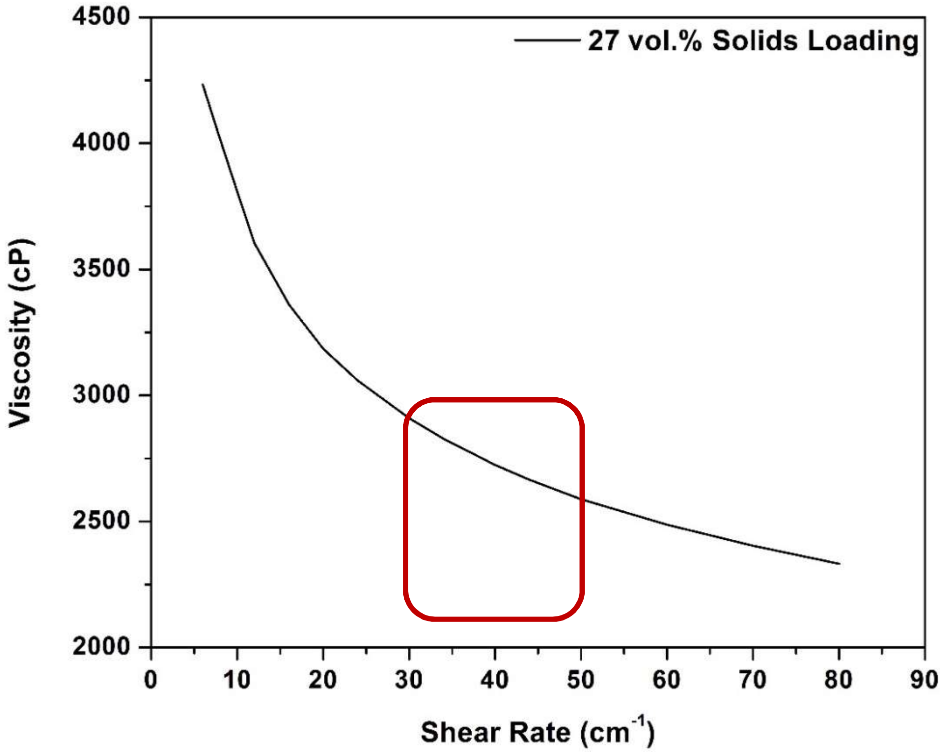
(a) Direct writing Ag ink for flexible electrodes

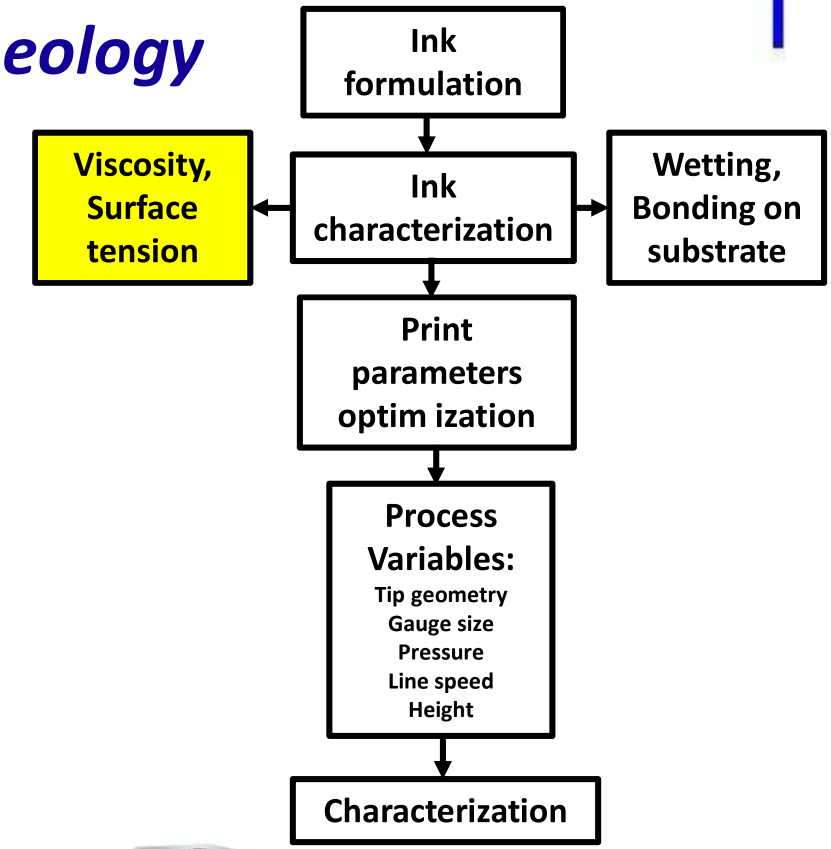
(b) Nozzle-based robotic deposition (NBRD) system and ink printing.



One System Initially Evaluated Last Quarter:
LNO Suspension Ink (Terpineol vehicle)

System 1: La_2NiO_4 – Al_2O_3 Ink Rheology





Key Rheology Parameters:

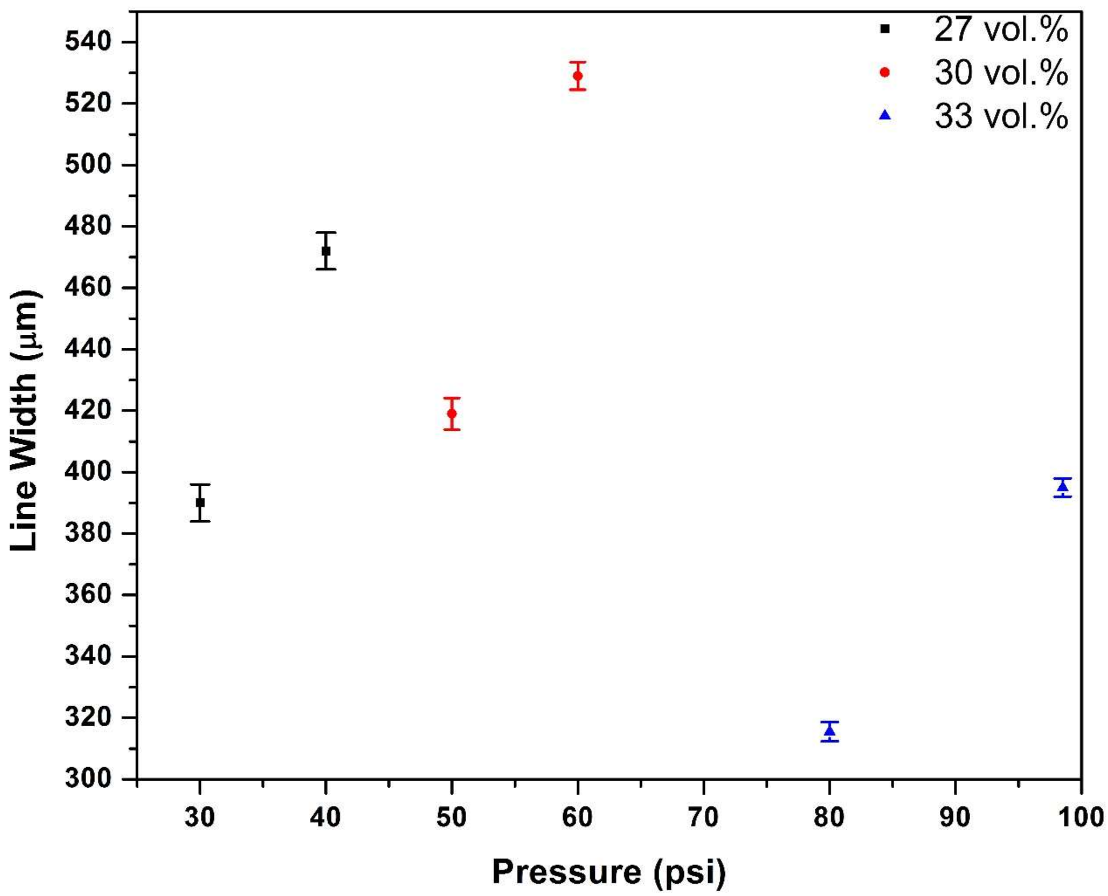
1) Shear thinning (in order to lock pattern).
2) Viscosity between 2000 – 3000 cP.
3) Limited wetting to retain dimensions.

Brookfield DV-II+ Pro
(plate-on-plate)

Initial Robo-Casting Evaluation:

Evaluated Parameters:

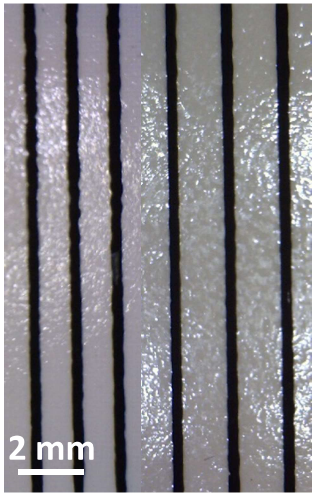
- **Average Particle Size: <10 µm**
- **Substrate: Transfer Paper**
- **Print Rate: 15 mm/sec**
- **Pressure: 10 – 100 psi**
- **Ink: 27, 30, and 33 vol.% of (50-50) La_2NiO_4- Al_2O_3 composite in terpinol/methylcellulose organic ink vehicle.**



Initial Robo-Casting Evaluation:

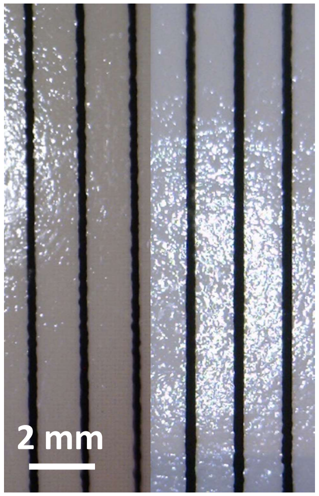
Line Analysis:

30 psi 40 psi



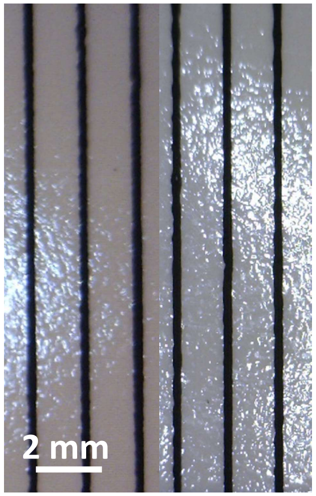
27 vol.%

50 psi 60 psi



30 vol.%

80 psi 90 psi



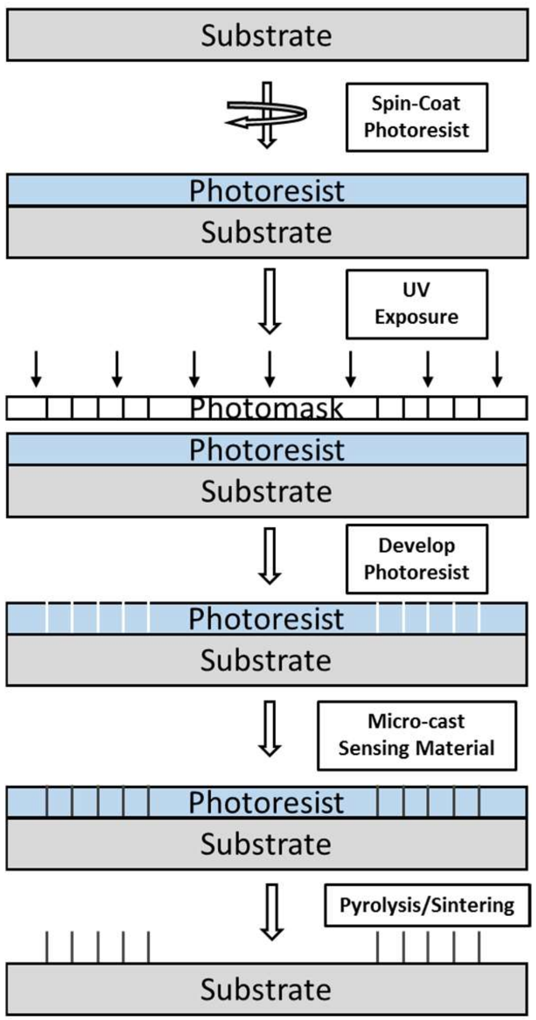
33 vol.%

Travel Speed - 15 mm/sec

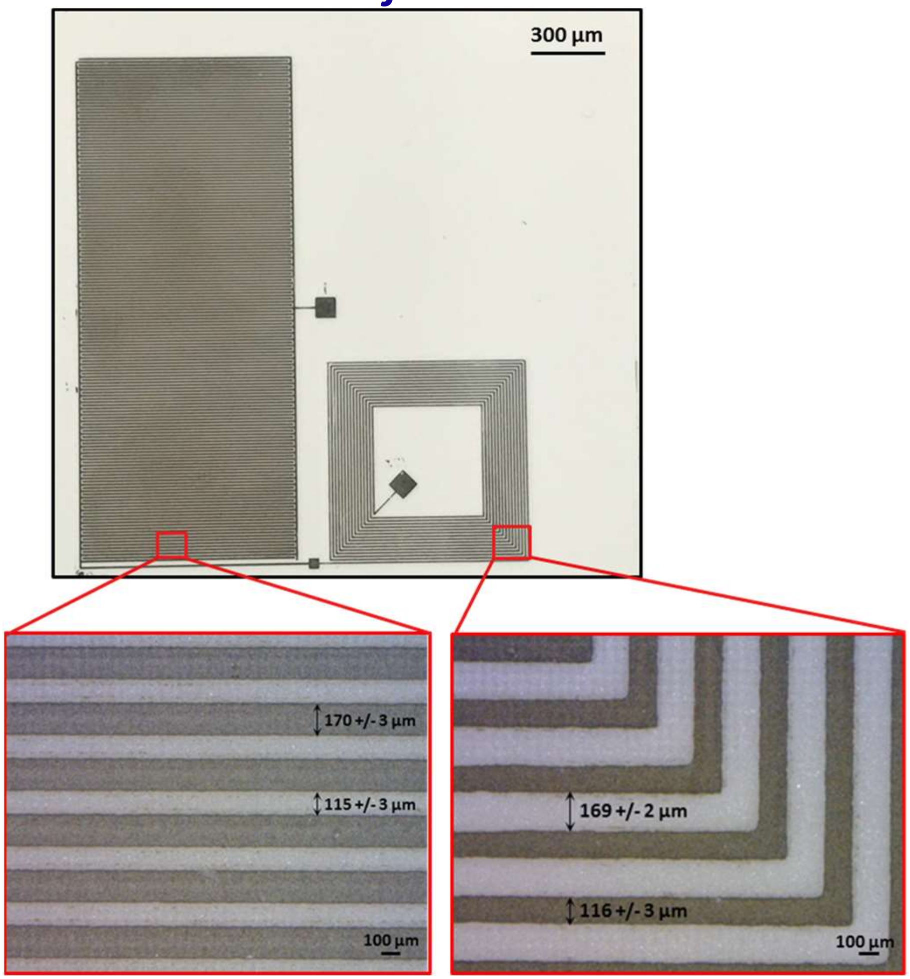
- Faster head speed → thinner consistent lines.
- Faster head speed → good surface tension to printed line.
- Faster head speed → lowers particulate buildup (increased shear at tip reduces effect).

Task 3.2 Micro-Casting Process:

Micro-Casting Process



50.8 x 50.8 mm sensor design on Al_2O_3 substrate after sintering at 1200 ^oC for 2h.



Task 3.0 Summary:

- Direct-write preceramic precursor onto oxide substrates and bond.
- Print/micro-cast (to initiate task 4) conductive oxide suspension and bond to the surface.

Task 3.0 Near-term Future Work:

- Robo- cast preceramic ink precursor onto oxide substrates and optimize firing temperature for optimum density.
- Achieve print resolution <100 um to print next generation LCR circuits.
- Perform "peel and stick" demonstration using micro-casting process.
- Test 50.8 x 50.8 and 25.4 x 25.4 mm design.

Task 4.0: Passive Wireless Communication Circuit Design and Testing. (Reynolds/Palakurthi)

Task 4.0 Objectives:

- To design and model a passive wireless LCR circuit and receiver (reader) antennas for communication.
- To fabricate and test the sensor design and circuit at room temperature and up to 1700^{o}C.

Task 4.0 Approach:

- **Subtask 4.1: Passive Wireless Communication Circuit Design and Testing. (Q1-4)-** This task will focus on the design of electroceramic print geometries, including width/length and spacing for the planar inductance coil, that will affect circuit component behavior in predictable and measurable ways.

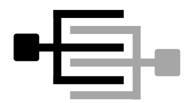
- **Subtask 4.2: Circuit Fabrication and Testing at Lower Temperatures. (Q3-9)**- Ink-jet and/or robo-casting will be used to create the sensor systems using both Ag inks and the electroceramic inks developed as part of this project, and they will be tested at low temperature (<100°C).

Task 4.0 Current Status:

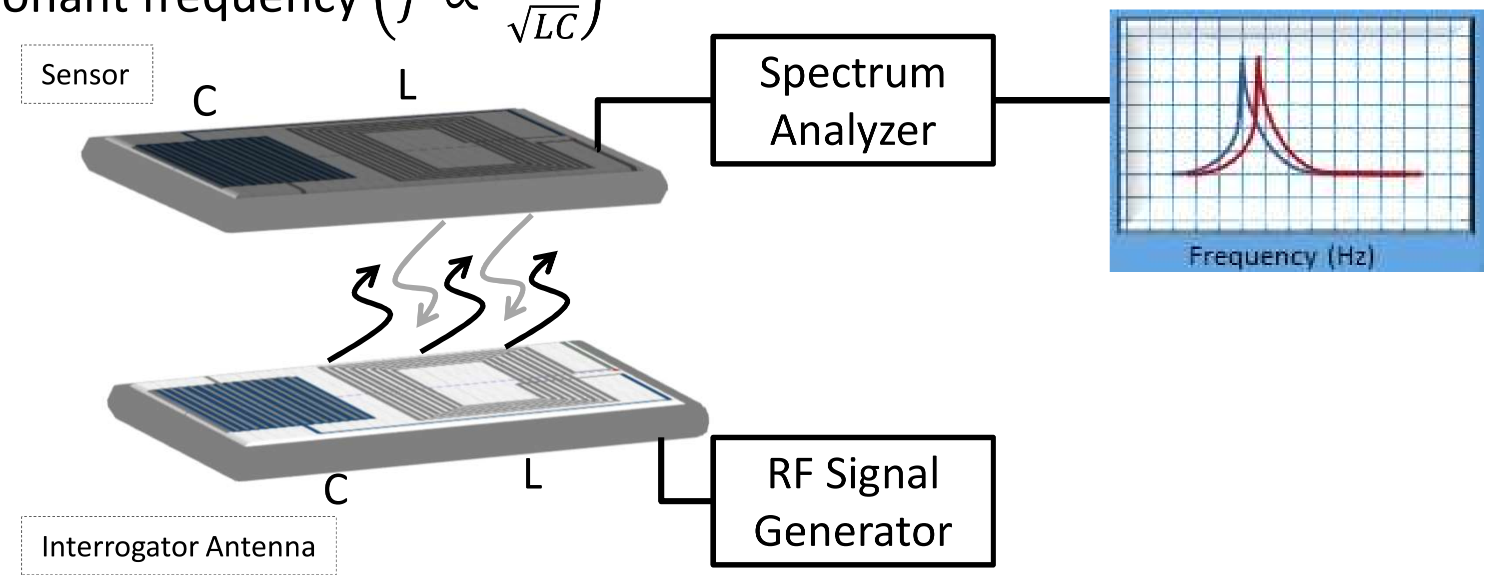
- Built a high temperature testbed
  - ✓ Performed passive wireless high temperature sensing tests.
  - ✓ Successfully demonstrated that the sensor can serve as a single-use high temperature passive wireless sensor.
- Built the ANSYS designs for smaller form factor sensors
  - ✓ Sensor designs now fit inside of 50.8 x 50.8 and 25.4 x 25.4 mm squares.

LC Passive Wireless Temperature Sensors

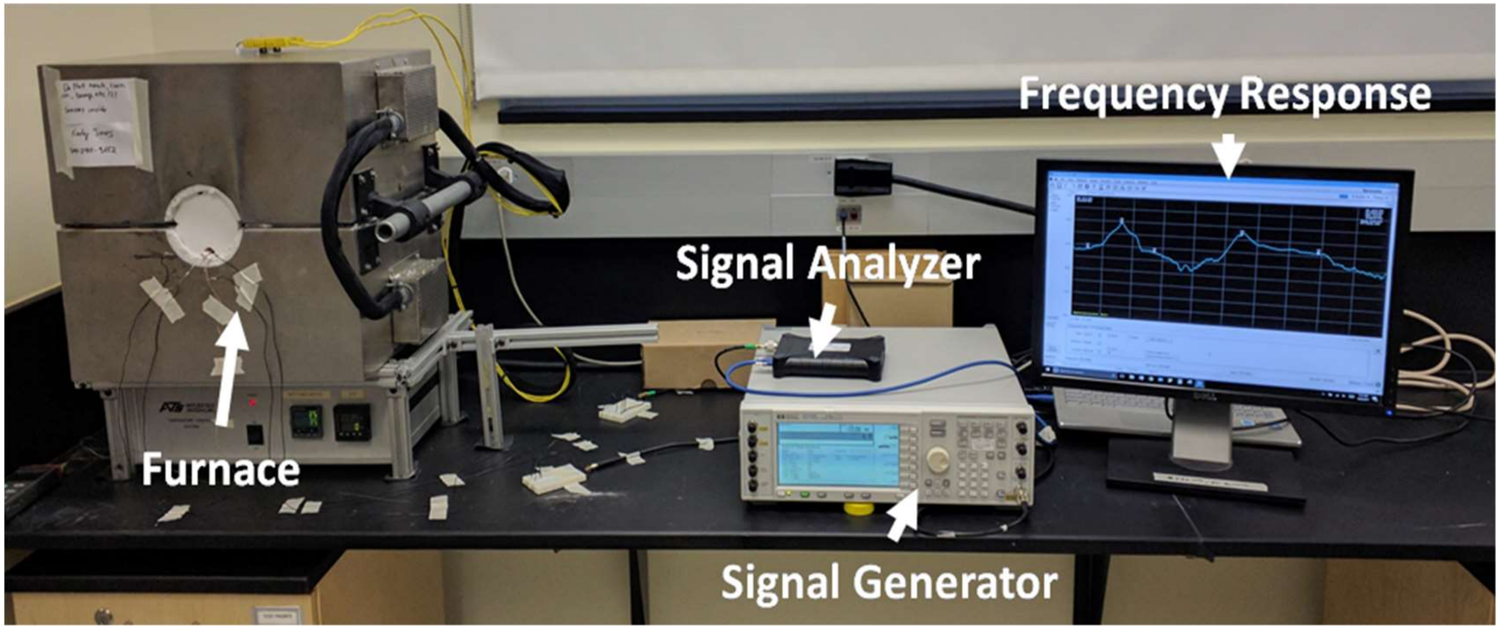
- An inductance coil (L) and a capacitor (C) form the LC circuit and are placed on the surface of the sensor / interrogator.

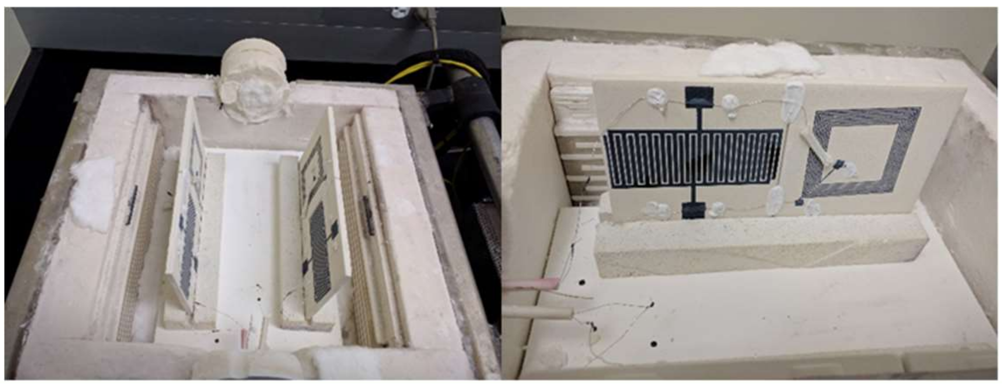
InterDigitated Capacitor (IDC) ⟶ 

- The Capacitor is temperature dependent which causes shifts in the sensor's resonant frequency $\left(f \propto \frac{1}{\sqrt{LC}}\right)$



High Temperature Testbed





Sensor placement
in the furnace

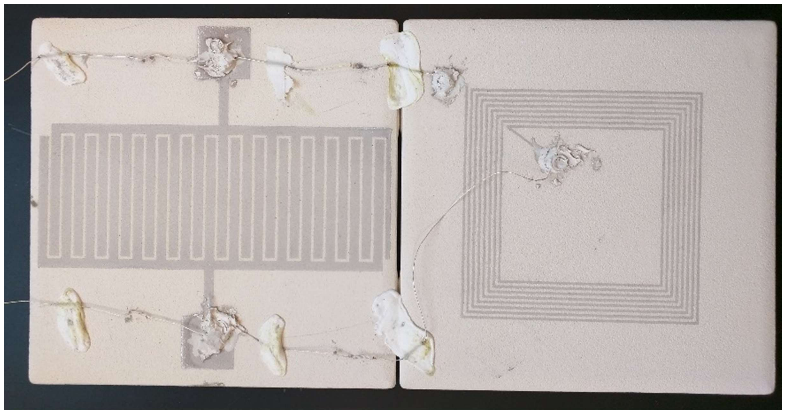
ANSYS Modeling and Simulation Results

- Comparing the accuracy of the M&S results to actual measurements of fabricated sensors

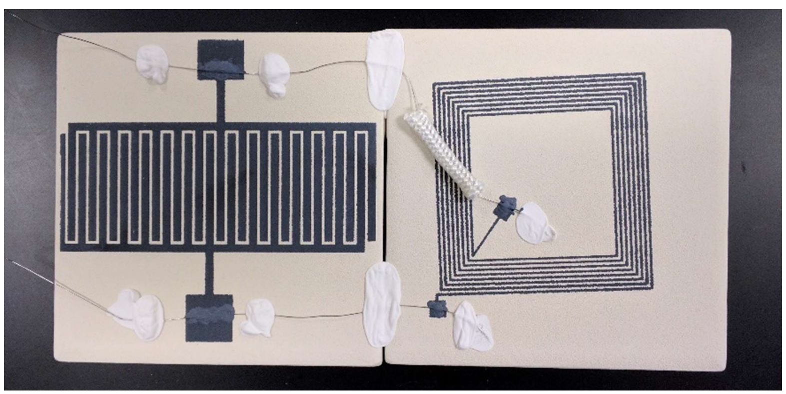
Sensor Type	**Inductance** (μH)	**Capacitance** (ρF)	$\boldsymbol{F_{res}}$ (MHz)
Simulated	6.942	19.815	13.569
Fabricated	5.82	19.9	14.789

Fabricated Sensors

- Sensor Design 1 with silver ink

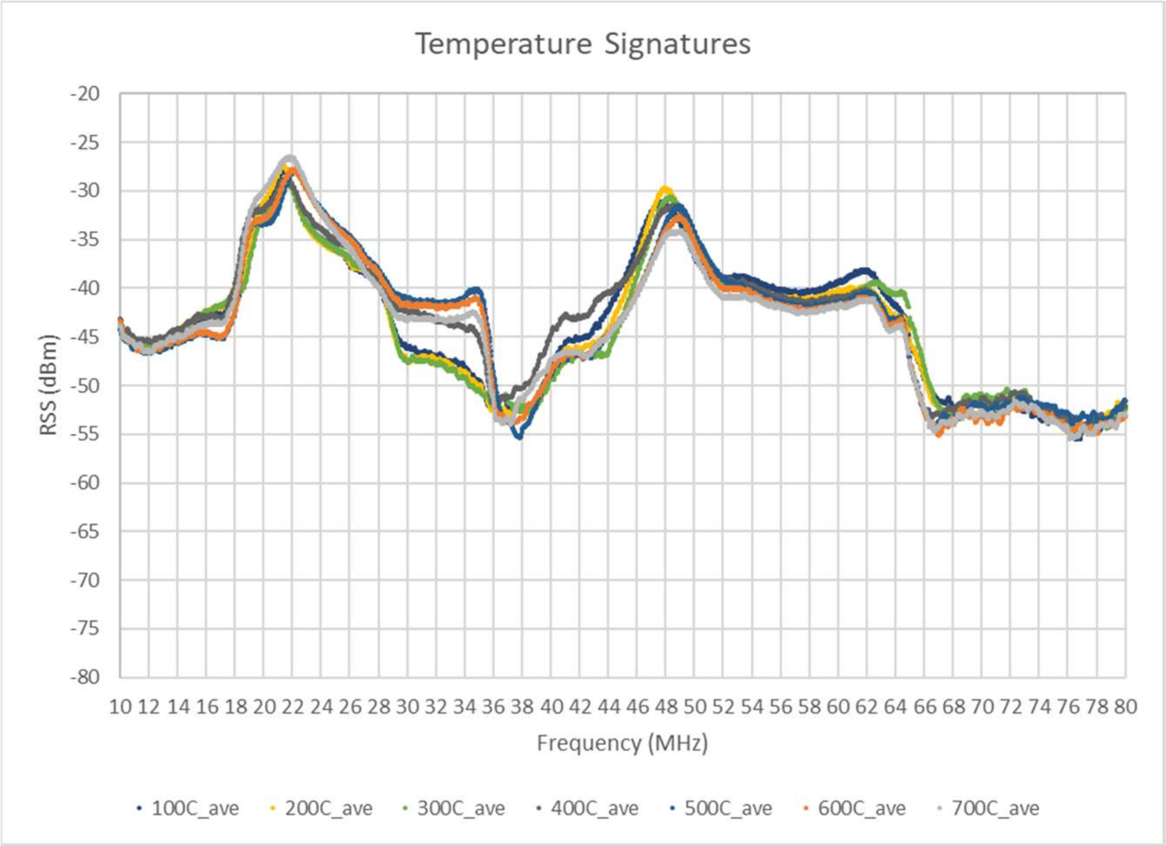


- Sensor Design 1 with Lanthanum Nickelate (LN) based ink



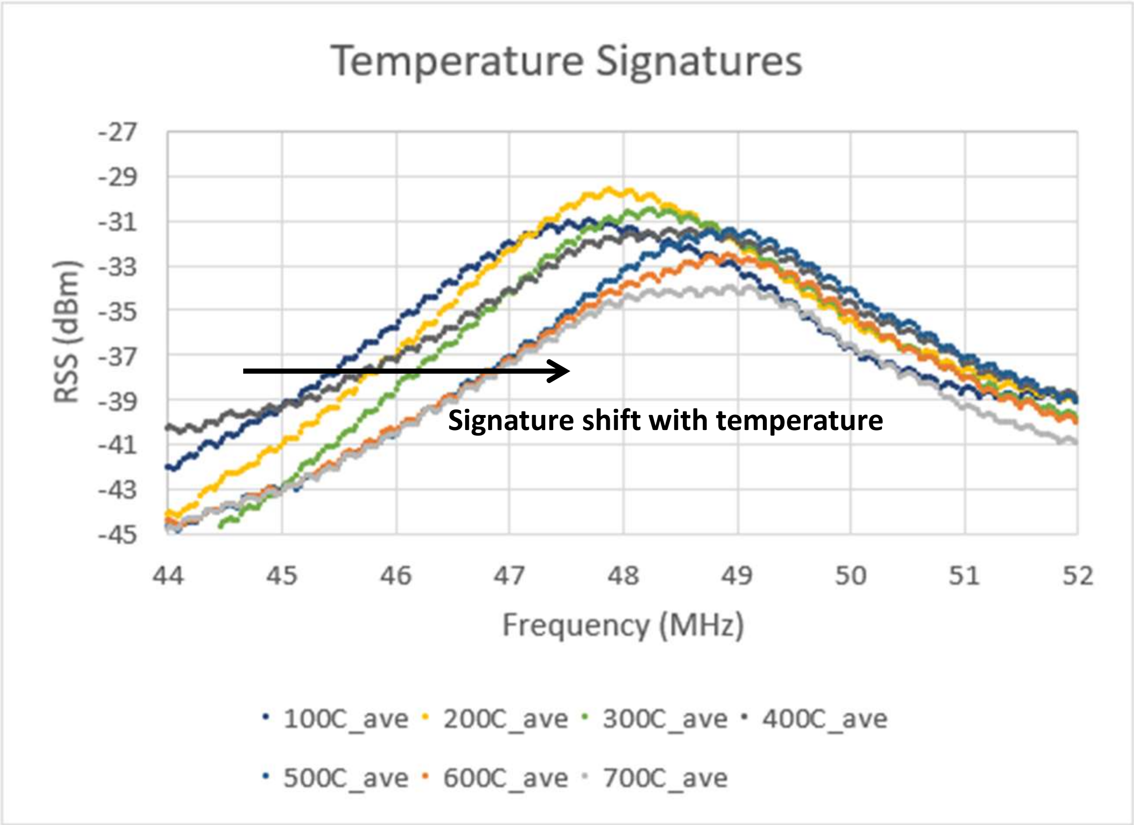
Single-Use High Temperature Passive Wireless Temperature Sensor

- Sensor Design 1 (LN based ink)
  - Temperature signatures of the sensor at temperature from 100 – 700°C



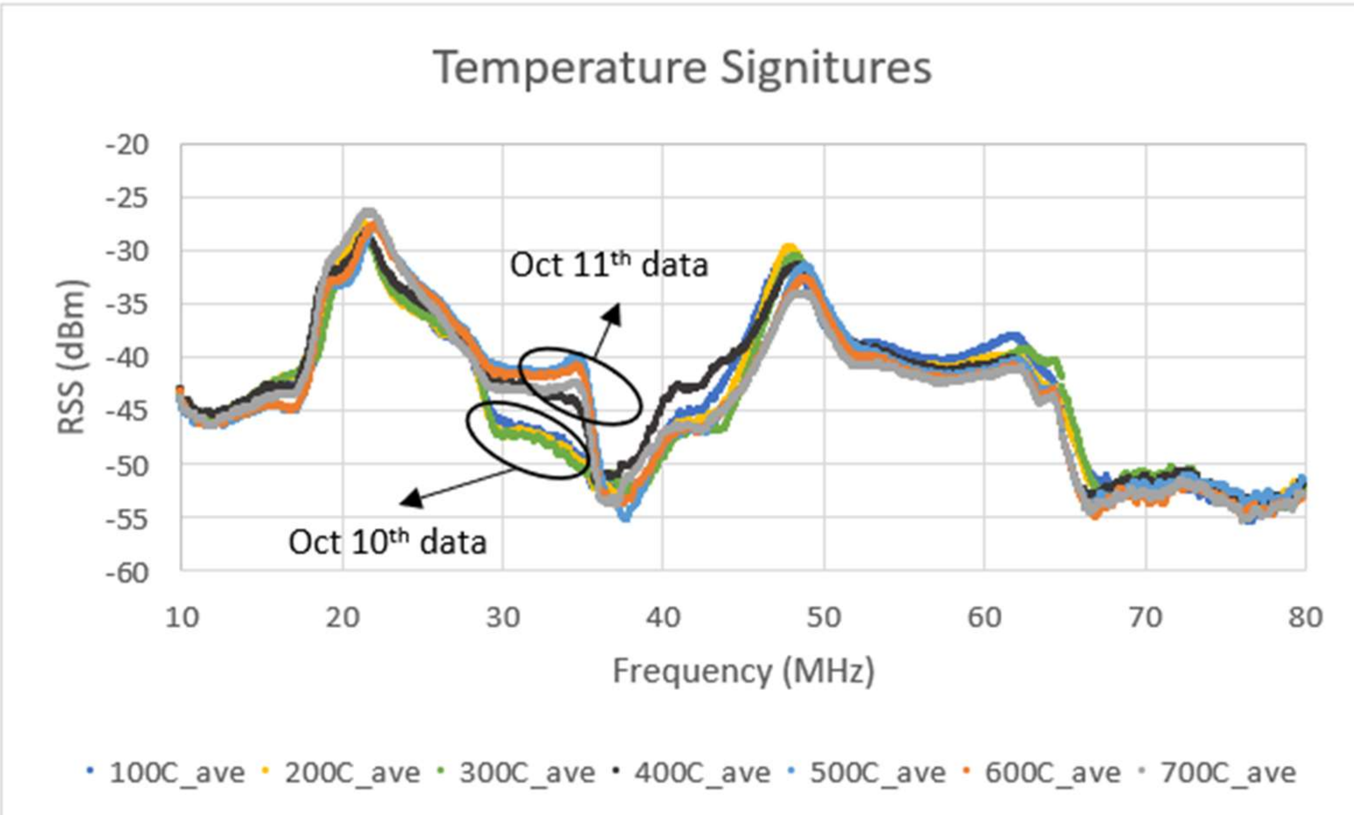
Single-Use High Temperature Passive Wireless Temperature Sensor

- Sensor Design 1 (LN based ink) Zoomed into 44 MHz – 52 MHz
  - Temperature signatures are unique and distinguishable
  - Sensors had a sensitivity of 1.88 kHz/^{o}C.



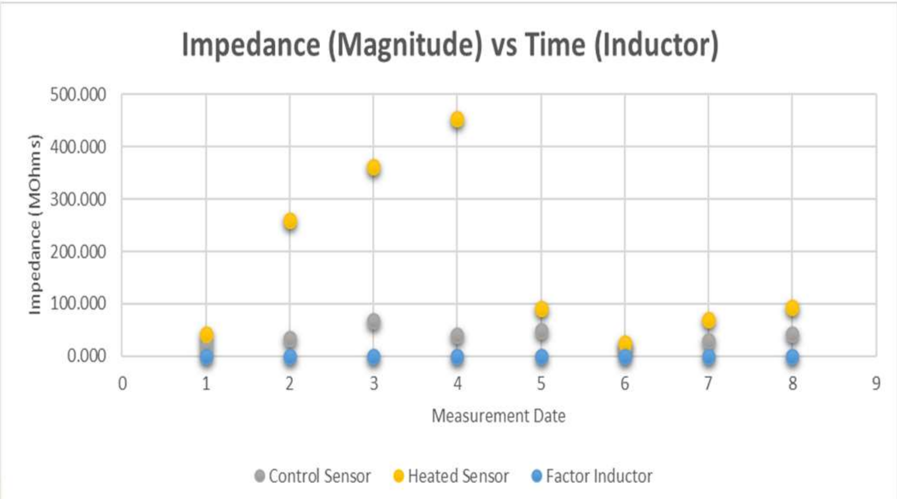
Single-Use High Temperature Passive Wireless Temperature Sensor

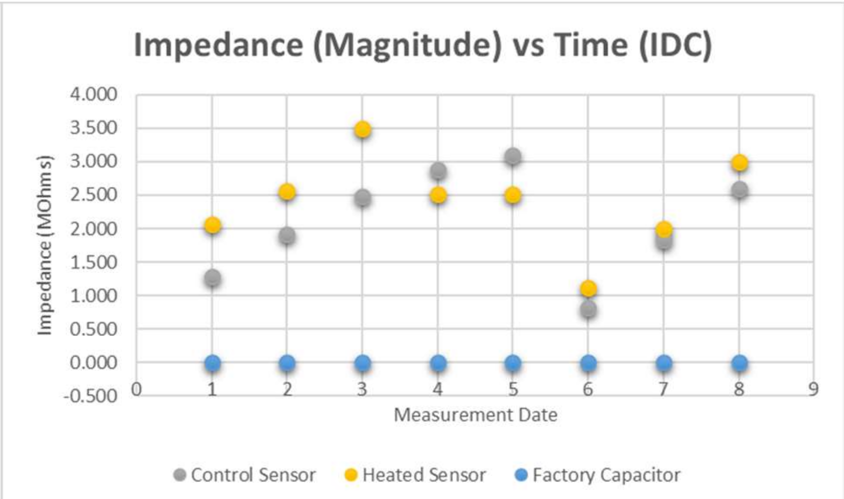
- There is a difference in the temperature signatures recorded over 2 days (Oct 10th and Oct 11th)
  - Sensor's frequency response data might not be repeatable



Single-Use High Temperature Passive Wireless Temperature Sensor

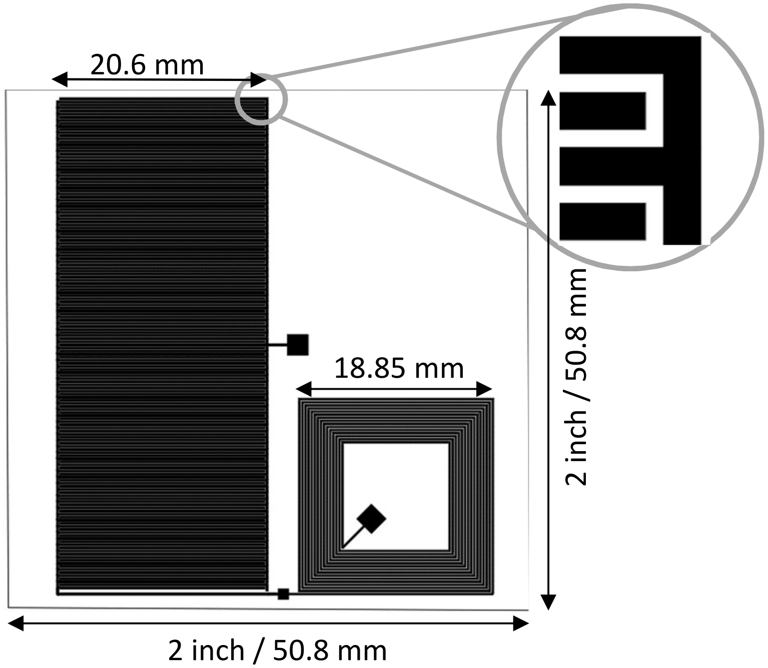
- Over several days, heated one sensor to 700°C and then cooled it down to room temperature while keeping another sensor at room temperature the whole time
  - Measured their capacitance, inductance, and impedance
  - The heated sensor's impedance changed significantly with each heating / cooling cycle



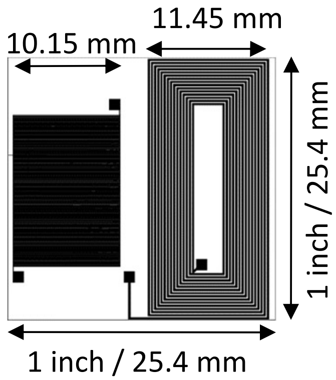


Smaller Form-Factor Sensor Designs

- 2 inch sensor
  - IDC
    - Number of fingers : 80
    - Width of each finger : 0.2 mm
    - Gap between fingers : 0.1 mm
  - Inductor
    - Number of turns : 15
    - Width : 0.15 mm
    - Gap : 0.15 mm



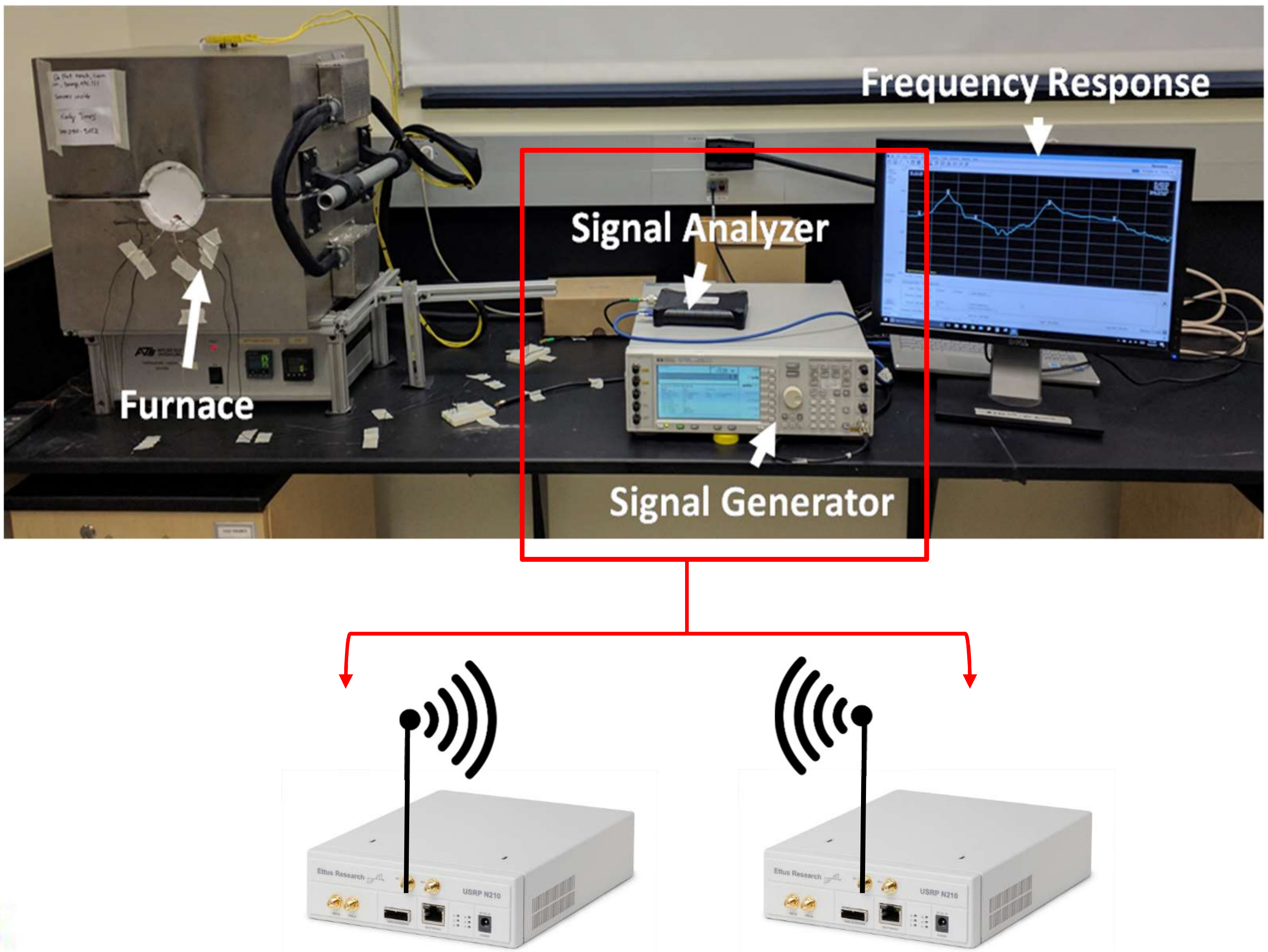
- 1 inch sensor
  - IDC
    - Number of fingers : 96
    - Width of each finger : 0.05 mm
    - Gap between fingers : 0.025 mm
  - Inductor
    - Number of turns : 15
    - Width : 0.15 mm
    - Gap : 0.15 mm



Software Defined Radio

- Universal Software Radio Peripheral (USRP) is a software defined radio designed by Ettus research
  - Comparatively less bulkier and cheaper alternative hardware platform
  - Use a host computer to generate/receive signals for the USRP hardware
  - Could be used with an open source software - GNU Radio

USRP Usage in current setup



Task 4.0 Summary:

- Completed preliminary high temperature passive wireless temperature sensing
  - Created a high temperature sensing testbed
  - Successfully demonstrated that the sensor can serve as a single-use high temperature passive wireless sensor
  - Built smaller form-factor 3D models and simulations of sensor designs

Task 4.0 Near-term Future Work:

- Work with newer sensor designs to investigate the high temperature performance of the sensors
- Build a USRP powered wireless sensing platform

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