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Direct Write 3D Printing of Functional Ceramics

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DIRECT WRITE 3D PRINTING OF FUNCTIONAL CERAMICS

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Master's Program in Mechanical Engineering

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Dedication

To my supporting parents, and my future wife and kids.

DIRECT WRITE 3D PRINTING OF FUNCTIONAL CERAMICS

by

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THESIS

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Table of Contents

List of Tables

List of Figures

List of Illustrations

Chapter 1: Introduction & Background

1.1 Introduction

In recent years improvements in 3D-Printing technologies have aided rapid prototyping and complex geometry manufacturing of functional ceramics. Functional ceramics such as dielectrics, piezoelectrics, ferroelectric are used as energy harvesters, sensors, actuators, among other purposes.[1] Ceramic sensors are highly desired for their longevity, resistance to chemical degradation and its high-temperature operation range. Humidity sensing is an important issue in many industries to include instrumentation, automated systems, agriculture, climatology, and industrial chemical processes.[2], [3]For example you may find humidity sensors in airplanes this provides the instrumentation crucial information about the flying conditions. Many chemical processes also may require low moisture levels to maintain quality control, and In the food industry monitoring humidity levels may prevent food from going bad in an industrial setting. Alumina (Al_2O_3) is a ceramic commonly functionalized for Relative Humidity sensing.[4]There are a few methods of manufacturing of ceramic censors using additive manufacturing and one method is direct write 3D-Printing using paste extrusion. when (Al_2O_3) nanoparticle powder is combined with a water-based binder a paste can be created which can then be used in a 3D-Printer to create complex geometries to then be used as a sensor. 3D-Printed (Al_2O_3) Relative Humidity sensors are evaluated in this investigation to help understand the influence of geometry and different binder wt% in the paste mixture. These results are then compared to a commercially available RH sensor. [5]

1.2 Background

Humidity is defined as the amount of water vapor in an atmosphere; Humidity is measured as the ratio or percentage of the amount of moisture content in the air to the maximum

moisture level that the air can hold.[2], [3].When Humidity reaches 100% humidity, due point occurs, this is the point at which the air can no longer hold water. Since the amount of water that the air can hold changes with pressure and temperature, it is essential that Relative Humidity is measured.[2]–[4] The way we measure Relative Humidity is with instruments called hygrometers. One type of hygrometer is a sling psychrometer the way it works is you have two thermometers side by side, one of them has a cloth attached to it at the tip this cloth is dipped in water, now you have your wet bulb and dry bulb, to measure relative humidity you must spin the thermometers to dry the wet bulb. As water evaporates from the wet bulb the temperature drops in that thermometer since an evaporative process is a cooling process. This process gives a difference in temperature between the thermometers; these measurements are then used with a wet-bulb dry bulb chart to determine the Relative Humidity.[6] This is a reasonably simple way to measure Relative Humidity, it can even be measured with a human hair because its length will change with humidity, when placed in tension it is easy to calibrate the change in length to the Relative Humidity percentage using another hygrometer.

Table 1.1: Wet-bulb Dry-bulb Chart for Relative Humidity Measurement

Relative Humidity (%)

Dry-Bulb Tempera-ture (°C)	Difference Between Wet-Bulb and Dry-Bulb Temperatures (C°)															
	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
−20	100	28														
−18	100	40														
−16	100	48														
−14	100	55	11													
−12	100	61	23													
−10	100	66	33													
−8	100	71	41	13												
−6	100	73	48	20												
−4	100	77	54	32	11											
−2	100	79	58	37	20	1										
0	100	81	63	45	28	11										
2	100	83	67	51	36	20	6									
4	100	85	70	56	42	27	14									
6	100	86	72	59	46	35	22	10								
8	100	87	74	62	51	39	28	17	6							
10	100	88	76	65	54	43	33	24	13	4						
12	100	88	78	67	57	48	38	28	19	10	2					
14	100	89	79	69	60	50	41	33	25	16	8	1				
16	100	90	80	71	62	54	45	37	29	21	14	7	1			
18	100	91	81	72	64	56	48	40	33	26	19	12	6			
20	100	91	82	74	66	58	51	44	36	30	23	17	11	5		
22	100	92	83	75	68	60	53	46	40	33	27	21	15	10	4	
24	100	92	84	76	69	62	55	49	42	36	30	25	20	14	9	4
26	100	92	85	77	70	64	57	51	45	39	34	28	23	18	13	9
28	100	93	86	78	71	65	59	53	47	42	36	31	26	21	17	12
30	100	93	86	79	72	66	61	55	49	44	39	34	29	25	20	16

Illustration 2.1: Psychrometer

There is an obvious flaw with this instrument and that is that by the time you measure the relative humidity it may no longer be at that percentage and just to find out whether the RH is increasing or decreasing we need to take many measurements and that is not ideal in an industrial setting or system controls instrumentation. We need a real-time measurement to be able to use this information for systems that are humidity sensitive or humidity dependent processes. For this reason, we must look at a more modern RH sensor and the answer for this seems to be a capacitive sensor. A capacitive sensor can measure humidity in real time, the mechanics behind this type of sensors are not complicated and are usually made with ceramic materials which give these sensors the edge when operating in harsh environments and with a non-toxic ceramic like (Al_2O_3) acting as a dielectric material it is safe to be used in many industries.[2], [7], [8]

1.3 Capacitive RH Sensor

A capacitive RH sensor works just like a normal capacitor, you need two parallel conductive plates and a dielectric material between them to make a capacitor. The dielectric of the sensor is porous (Al_2O_3) and the sensitivity of the sensor depends on the pore size and distribution. (Al_2O_3) is a commonly used ceramic in humidity sensors due to its high-temperature operation and good chemical and mechanical stability. (Al_2O_3) also has excellent water absorbing and desorbing qualities which makes it an ideal material for a highly responsive RH sensor.[8] The capacitance of the sensor changes with the absorption of water and capillary

condensation at the surface, water has a polar structure, making it a good dielectric. As the air in the pores of the ceramic is replaced with water vapor the overall capacitance will increase. This change is directly related to the increase in relative humidity and can be calibrated to make a Relative Humidity sensor.[8], [9][10][11]

$$C = \frac{\varepsilon A}{d}$$

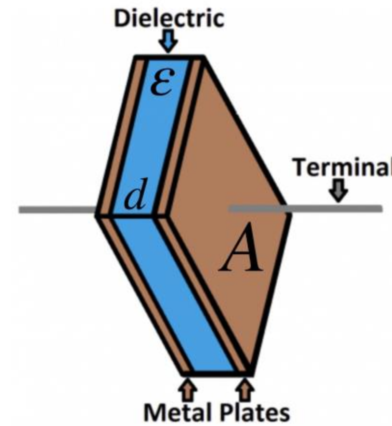

Figure 1.1: Capacitor Formula

1.4 Systematic Errors

A humidity sensor data output is non-linear which makes it more complicated to read that a temperature sensor, also the results are affected by things like temperature and bulk capacitance. Bult capacitance is the capacitance that is already there even when the moisture level is zero and can change with your set up and even the cables you use. Bulk capacitance is easy to deal with because the results can be normalized. Changes in temperature will cause displacements in the graph witch again if the software used to interpret the results can compensate for this displacements there's no problem when the results are normalized. Since the results are not-linear there is an error formula used to make up for this error which can result in a highly reliable humidity sensor. The non-linear behavior can be attributed to lateral diffusion of water into the pores aside from capillary condensation effects. Another theory that can explain the non-linearity if BET theory which can be used to attempt to describe the absorption of gas in the solid surface of the sensor [2], [3], [10][11]

1.5 3D-Printing

Additive manufacturing is also known as 3D-Printed is a form of manufacturing that produces minimal material waste by synthesizing a part layer by layer. This process allows for complex geometry. The type of 3D-Printing used in this project is direct write 3D-Printing. Ceramic powder is mixed with a water-based binder to create a paste that is then used with a machine that has been modified for paste extrusion. These machines work by placing the material in a syringe and inside a piston cylinder in the machine to be extruded out.[12] One option for a binder is Poly-(vinyl Alcohol) it is a clean non-toxic material and aids the rheology of the paste as is easy to control by changing the water content. The rheology of the paste plays an important role in the printability and shape retention of the material. According to the literature review, there are three drivers that control the printability of the paste "(i) reversible shear-thinning behavior to viscosity around 10–100 Pa s at high shear rate to facilitate material extrusion and to retain the shape afterward, (ii) free of particle agglomerates that may clog the printing nozzle, and (iii) possessing relatively high modulus (G′) with $\tau y > 200$ Pa to allow structural self-support and fabrication of high aspect ratio structures."[5][13][12]

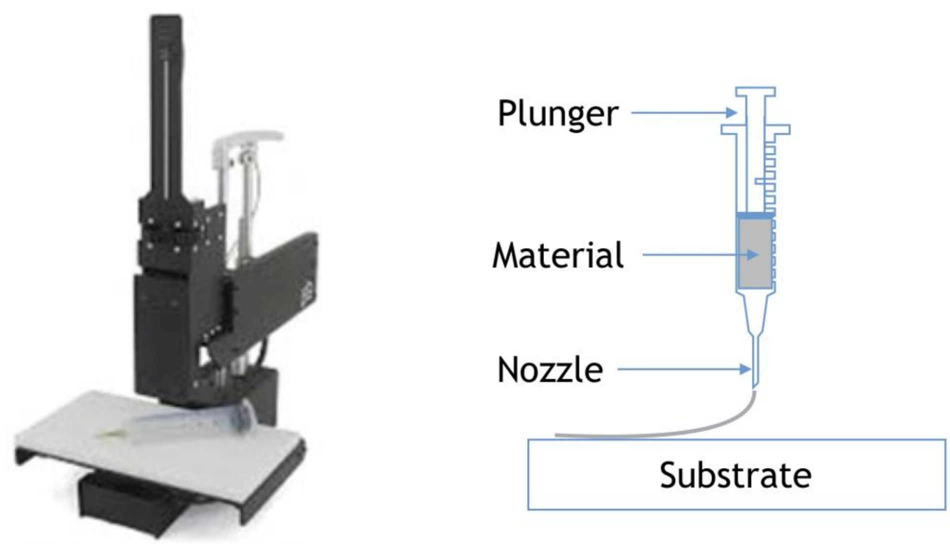

Illustration 1.2: PrintrBot 3d Printer

Chapter 2: Experimental method

A Humidity sensor's ability to measure the moisture in the air depends on its contact with the atmosphere that it wants to measure. Commercially available sensors use complex 2D designs in an attempt to increase the surface of the sensor and maintain a small profile. A 3D printed lattice structure will have a larger surface area than a commercially available sensor and this lattice sensor is evaluated in this experiment to determine if there is an advantage to the maximizing surface are through modern manufacturing technics. A 3D lattice structure sensor will be compared to a solid 3D-Printed sensor to see the influence of the lattice structure then these results are then compared to the commercially available RH sensor. A Total of 18 sensors were made for control of quality and repeatability of the results. Another parameter that will is evaluated is the binder concentration to determine the influence of the binder in the ability to measure moisture in the air. Three different concentrations of the binder are used 4%, 5%, and 6% and 6 samples were printed per concentration.

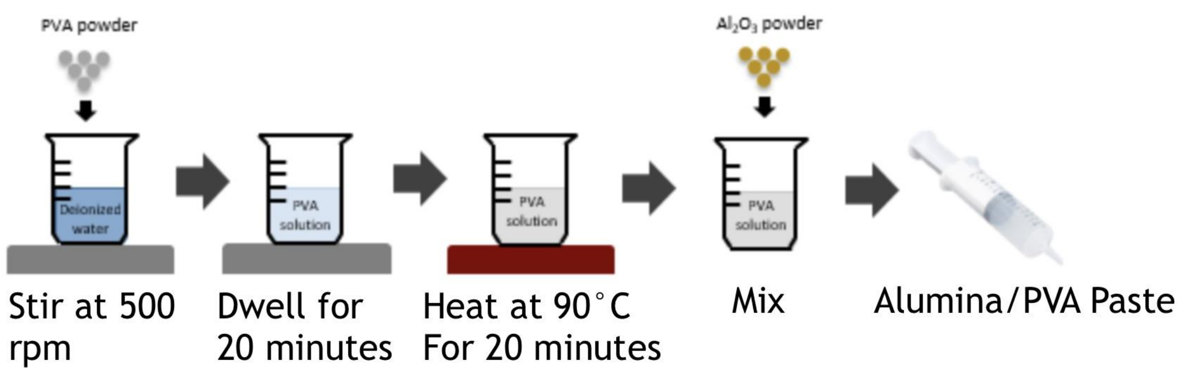

Illustration 2.1: Process for Making Ceramic Paste

2.1 Ceramic Paste

To make the ceramic paste first we begin by preparing the binder solution for these two ingredients are needed deionized water and poly(vinyl-Alcohol) also known as (PVA) powder. First, the water is placed under heavy stirring at 500 rpm and the powder is added one gram at a

time to ensure that it mixes well and no solids are formed from the powder. Here is where the wt% of PVA powder will change depending on the concentration 8%,10%,12%. The mix is then allowed to dwell for 20 minutes furthermore, the mixture is placed in a hot plate at 90°C under heavy stirring at 500 rpm. After 20 minutes in the hot plate, the mix will become transparent and it must be under stirring until a homogeneous mixture is achieved. The PVA binder is often used because of its binding strength making the final part strong. The PVA solution is then allowed to cool down to room temperature to then be mixed with the ceramic powder and make the paste. The ceramic powder used is (Al_2O_3) alpha stage nano-particle powder sized at 100nm. A 50/50 wt% was used in all three combinations to remain a fixed parameter in this experiment. The (Al_2O_3) nanoparticle powder is mixed with the newly made binder one gram at a time to help obtain a homogenous paste, once the paste is ready it is placed inside a syringe. Three different paste where made, one per PVA concentration. The final content of PVA binder in the paste was 4, 5 and 6 wt%.

Table 2.1: List of PVA Concentrations and Final Paste PVA Concentration.

PVA Binder

	PVA wt% In water solution
Binder 1	8
Binder 2	10
Binder 3	12

Alumina/Pva

	Alumina/PVA wt%	PVA wt%
Paste 1	50/50	4
Paste 2	50/50	5
Paste 3	50/50	6

2.2 Computer Code

For this experiment, a custom computer code to run the 3d printer was needed. The Machine used is a PrintrBot Simple 3D-printer modified for paste extrusion. The code used is G-Code and it was modified using a free online software Slic3r the code is then exported and

imported into Cura another free available software that communicates with the 3D-printer. The code includes custom extruder and printing speeds that were optimized by experimenting to determine the best extrusion speed to ensure continues flow of material.

2.3 Design of RH Sensor

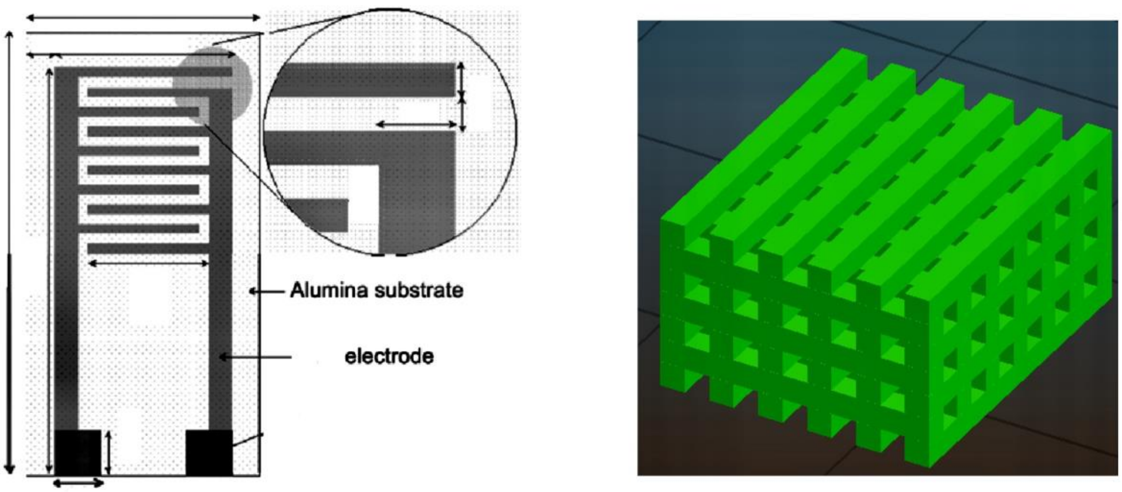

Illustration 2.2: Sensor geometry 2-D and 3-D.

The design for the sensor chosen was a simple lattice structure in an effort to increase the sensor surface area to allow and evaluate how more contact with the environment affects the RH sensor. In a 2-D sensor, illustrated in Figure 2.2 shows how the sensors are is optimized then optimised even more with the lattice design in 3-D. To compare the results of the lattice a second design is printed to compare a solid cube with the same dimensions of the lattice structure to evaluate how the extra exposure to the environment helps the RH sensor. In Illustration 2.1 both designs evaluated are clearly shown. The quality of the prints was satisfying as well as the shape retention of the sensors. The quality of the manufacturing of the sensors is largely attributed to the excellent rheology of the paste as mentioned in the literature review it is responsible for the printability of the paste.

Illustration 2.3: Process of Manufacturing

Illustration 2.3 shows the process of manufacturing an RH sensor from beginning to end. After 3-D Printing a sample it is dried in the fridge to help the sample retain its shape for 12 hours then is placed in an oven at 40 degrees Celcius for another 12 hours to finish drying. The dried sample is then painted top and bottom with silver paint which will act as the electrodes of the capacitor. The painted samples are then placed in the oven for 20 minutes at 120 degrees Celcius to help the paint cure. When the samples are ready they are tested for continuity using a multimeter to ensure that the electrodes are functional and if they are the RH sensor is complete.

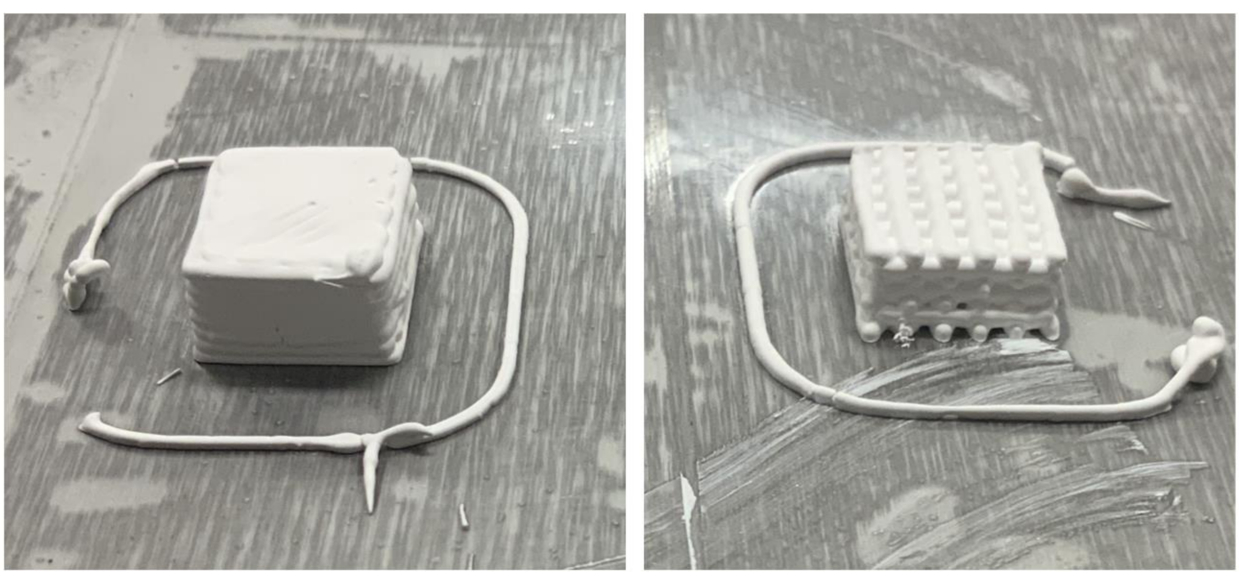

Illustration 2.4: Solid vs. Lattice

2.4 Rehology

The rheology of the paste revealed the printability of the paste, and from the results, it is determined that all three paste are good options at low shear rates and highly printable. It is also revealed that the wt% of the PVA binder controls the rheology of the paste. The graphs reveal a non-newtonian shear thinning behavior. These characteristics are considered to be ideal for 3D-Printing ceramics with paste extrusion according to the literature review.

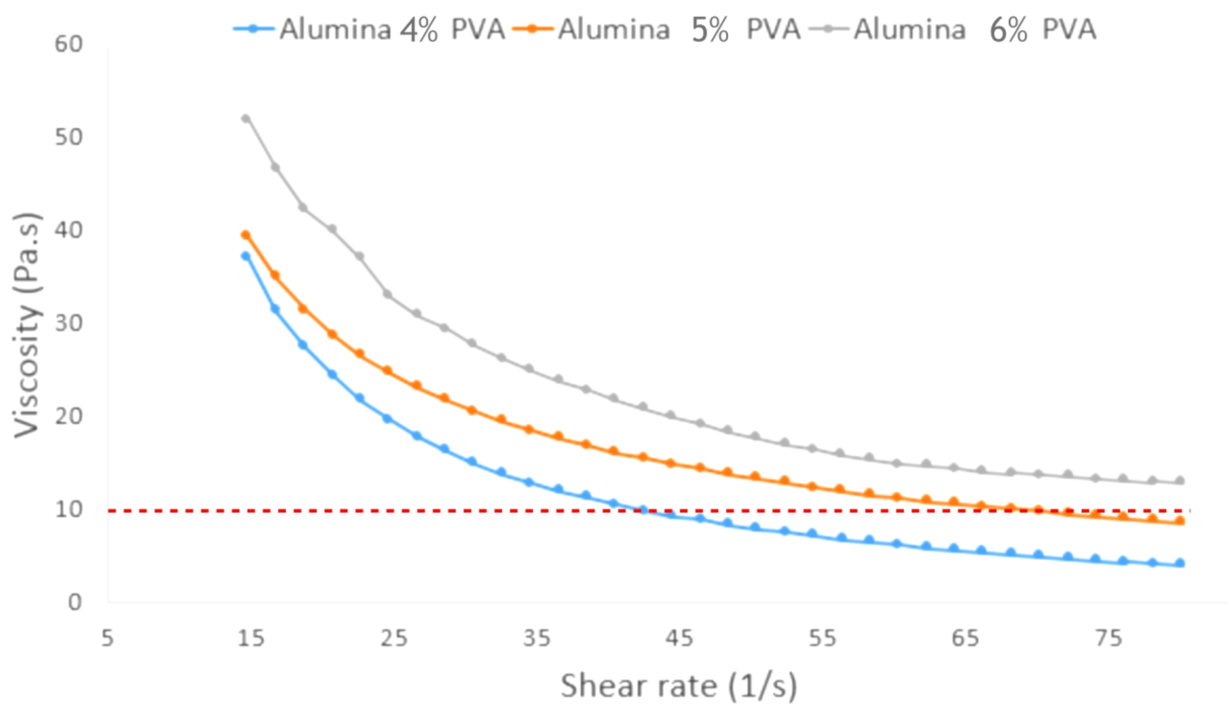

Figure 2.1: Rehology of Ceramic Paste.

The red line in the graph above shows the lower limit of the viscosity of 3D-printing. As it can be observed every paste has a region where the paste is printable at lower shear rates. It is important to notice that the paste with 6 wt% PVA remains above the limit even at higher shear rates making it the best combination, but of course this will not be the only parameter affecting the final performance of the sensor so it is important to use all three paste to determine its effect on the sensors ability to measure moisture. The viscosity changes from one concentration to the next for two different things one the binder content in addition to the PVA concentration the

binder also drives the water content in the final paste. The less binder in the original mix the more water there will be.

2.5 Experimental Procedure

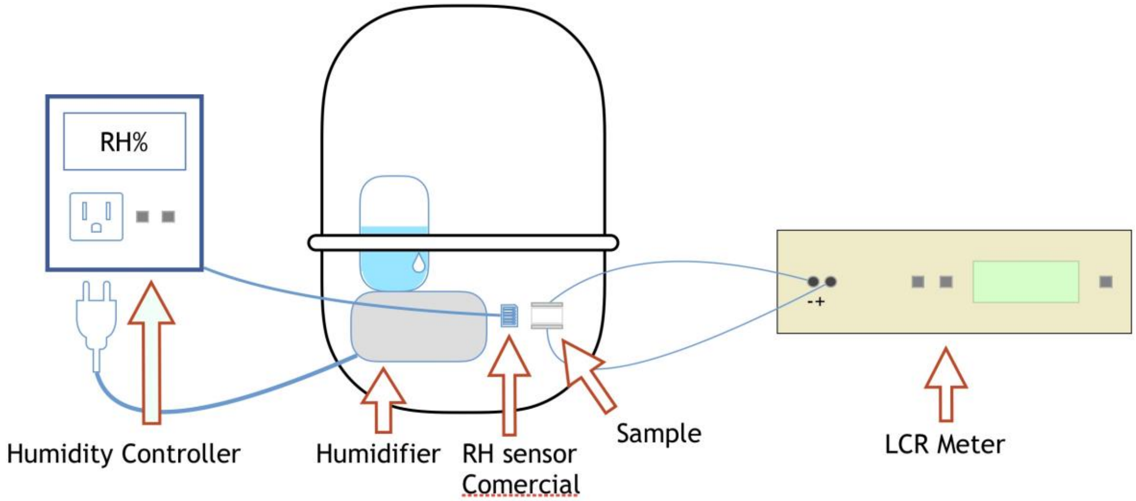

Illustration 2.5: Experimental Set Up

For the experiment, an LCR Meter was used to measure the capacitance along with a humidifier and a humidity controller and a commercially available RH sensor. The humidifier Printed sensor and commercial censor are placed in a closed environment to help keep humidity levels steady and easier to control. The humidifier is connected to the controller which controls the humidity in the enclosure. Each sensor was tested one by one. There was a total of 5 lattice structures per paste concentration and an additional solid sensor per paste concentration tested. The LCR Meter was used to determine what the capacitance of our sensor was at every moisture level evaluated.

Chapter 3: Results, Discussion and Conclusions

3.1 Results Of LCR Meter

The results from the LCR were measured from 30% to 80% humidity to remain 10% higher than the average humidity in the room and the upper limit is due to the ability of the humidity controller to maintain the humidity properly above 80%. This is still considered a large range and gives us a picture of how the sensor will operate. The capacitance is measured in Farads and in this case the results are displayed in Pico Farads (pF). The following graphs show the sensor response of the three PVA concentrations.

Paste #1	Sample 1 (pF)	Sample 2 (pF)	Sample 3 (pF)	Sample 4 (pF)	Sample 5 (pF)
30%	2.31	2.21	2.22	2.08	2.21
40%	2.33	2.22	2.25	2.09	2.24
50%	2.38	2.32	2.28	2.10	2.31
60%	2.50	2.48	2.42	2.24	2.56
70%	2.88	2.88	2.71	2.46	2.73
80%	3.79	3.68	3.20	3.08	3.18

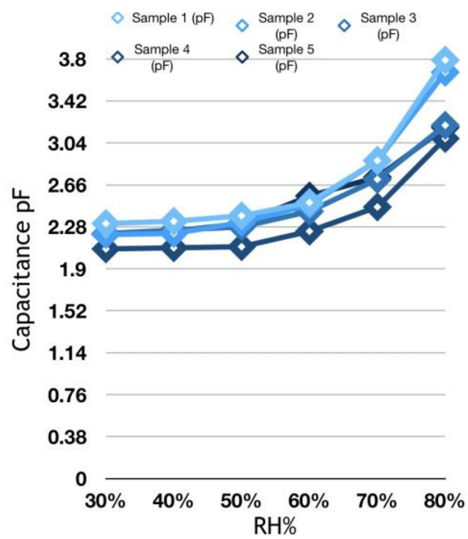

Figure 3.1: Results for the 4 wt% PVA Samples

The date in the image above was collected using the LCR Meter and it represents the lattice samples using the three wt% PVA concentration. From the Table, it is clear that there is a response as an increase in capacitance in relation to the increase in humidity. All five samples react similarly and within the same range with slight differences in step increments and initial capacitance, which may be due to small changes in the geometry of the samples. In addition to a clear trend in response, the bulk capacitance can be seen in the graphs as it is clear that they are not reaching zero. This results will be normalized to be compared to one another and the

different concentrations of PVA samples. From the literature normalizing the results is common practice and it is done by the software that collects data from the sensor.

Paste #2	Sample 1 (pF)	Sample 2 (pF)	Sample 3 (pF)	Sample 4 (pF)	Sample 5 (pF)
30%	2.26	2.45	3.96	4.11	4.01
40%	2.28	2.48	4.01	4.13	4.02
50%	2.29	2.53	4.03	4.14	4.03
60%	2.45	2.65	4.18	4.28	4.21
70%	2.71	2.97	4.47	4.72	4.59
80%	3.20	3.50	5.18	5.10	5.00

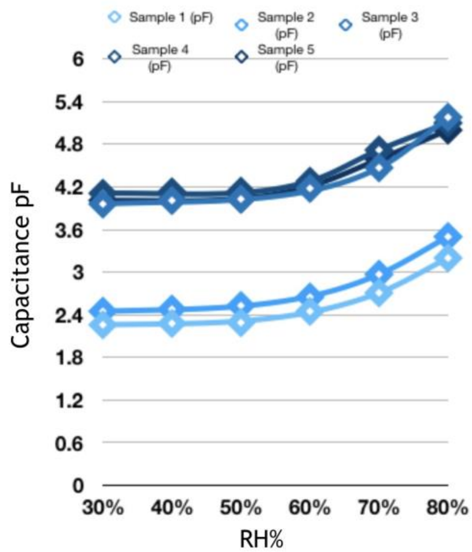

Figure 3.2: Results for the 5 wt% PVA Samples

The 5 wt% results show two of the results starting at a lower point, the bulk capacitance seems to be different but from the literature review this can be explained as a dislocation of the results due to a temperature change in this case the temperature changed about six degrees from one set of measurements to the next. This does not affect the results of the response of the sensor it simply shifts the results and this would be taken care of by the software in a commercial sensor. In this case, the results are normalized to be able to compare the response of the sensors.

Paste #3	Sample 1 (pF)	Sample 2 (pF)	Sample 3 (pF)	Sample 4 (pF)	Sample 5 (pF)
30%	2.45	4.26	4.41	4.42	4.34
40%	2.46	4.27	4.42	4.43	4.35
50%	2.50	4.28	4.45	4.50	4.36
60%	2.7	4.49	4.52	4.60	4.51
70%	3.15	4.82	4.80	4.99	4.81
80%	3.54	5.41	5.41	5.60	5.35

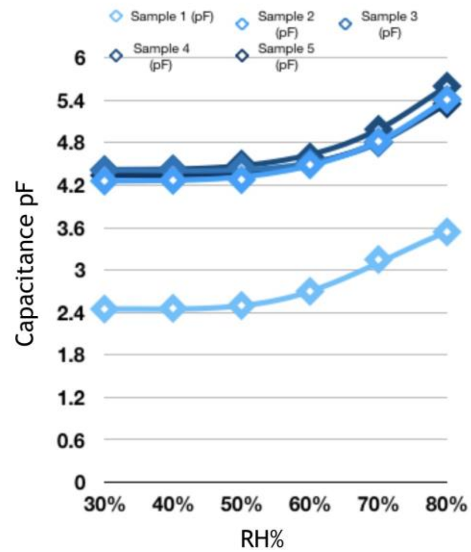

Figure 3.3: Results for the 6 wt% PVA Samples

Here the results show a similar trend to the previews samples. Next, to be able to see the effect of the concentrations of PVA content the results are normalized, the averages are taken and compared between different concentrations.

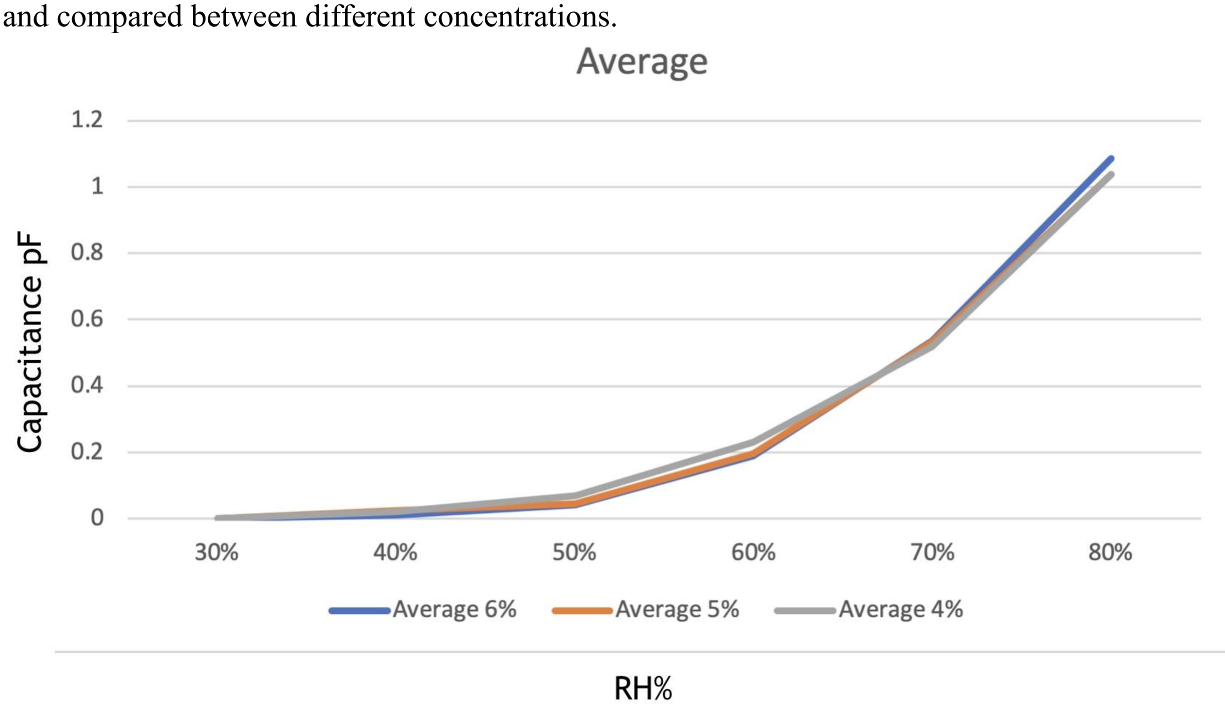

Figure 3.4: Averages of Sensor Response of 4, 5 and 6 wt% PVA Samples

The results show that the PVA content does not have a significant impact on the sensor response since this is the only parameter being considered so far. All samples have the same geometry and we can see that the only difference is a small wt% in the PVA concentration. These results are good because now it is proven that the binder content does not affect the response and it is possible to 3D print a strong RH sensor using this binder without affecting the sensitivity of the sensor. To further study the response of the sensor another test must be considered, a good sensor doesn't only have a good response it also has good time response and this must be evaluated to understand more about the 3-D Printed sensor.

3.2 Time Response

For the time response, the experimental set up was the same but a timer was added to compare the response time between the 3-D Printed sensors and the commercially available sensor. The commercial sensor was evaluated at the same time as the printed sensor and every time so the results of the commercial sensor vary with changes in temperature and base humidity in the room it was done this way to keep the results fair and under the same conditions between the printed and commercial sensors. The results of the time response difference are represented as a percentage and the graph represents time vs the three different concentrations.

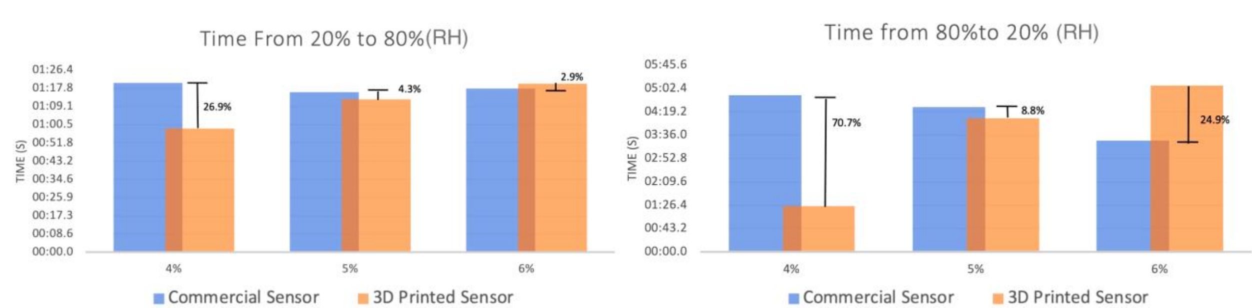

Figure 3.5: Time Response Results (Lattice)

The results show the time response from 20% to 80% on the left and 80% to 20% on the right. The 4 wt% samples were on average 26% faster on the way up than the commercial sensor and 70% faster in the way down. This shows a large advantage on the 3-D Printed sensor when it comes to dissipating water. The sample with 5 wt% is similar to the commercial sensor but still faster and the 6 wt% was slower than the commercially available sensor revealing the maximum PVA percentage that can be used to outperform a normally available RH sensor. The results show a trend, the lower the concentration of PVA, the quicker the sensor reacts. To understand the results and the inner mechanics of the sensor and the influence of the PVA content a closer look is needed. With the help of a Scanning Electron Microscope (SEM), we can see the microstructure of the surface in contact with the environment.

3.3 SEM Results

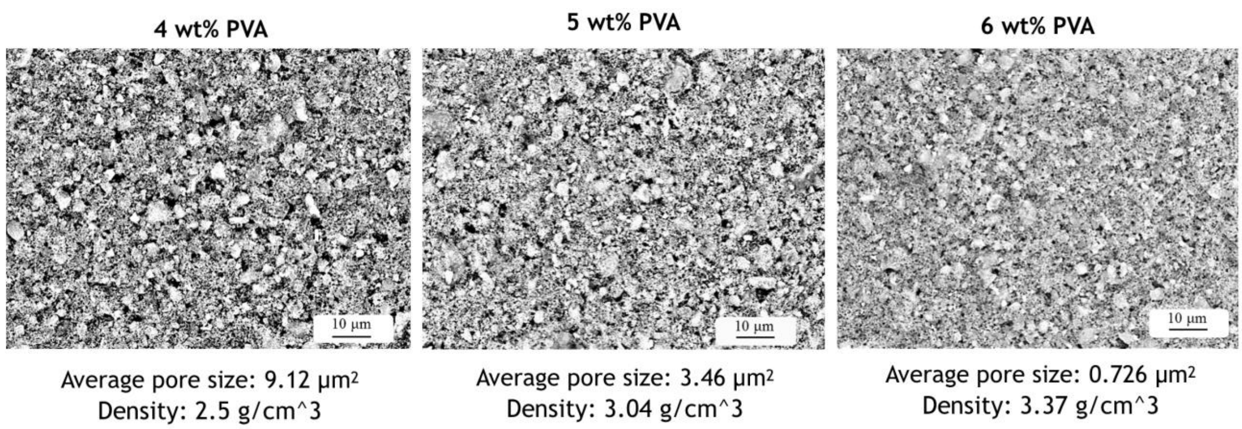

Illustration 3.1: SEM Results

The SEM reveals a difference in pore size average size between the three samples, and the difference in density supports the porosity. The less PVA, the more water there is in the sample this water evaporates during the manufacturing process explaining the difference in porosity. The water content is the driver in the porosity. The more pores create a complex microstructure that

results in a higher surface area. In addition to the different pore sizes, the pore distribution also seems to increase with water content as shown in.

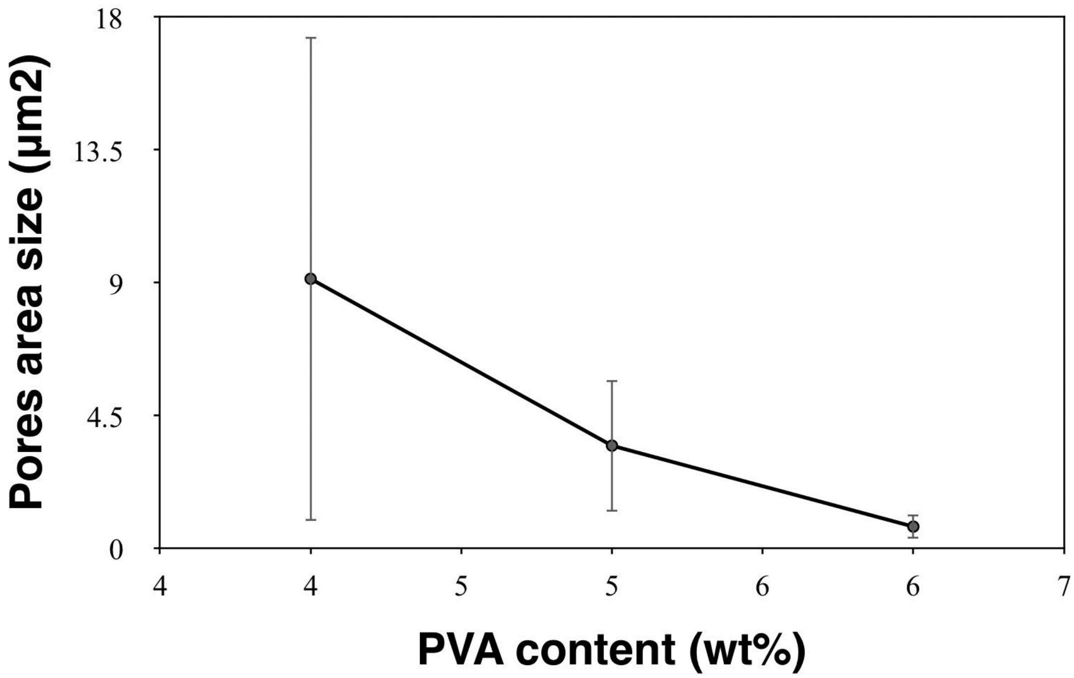

Figure 3.6: Pore Size Distribution.

Now the only thing left to evaluate is the influence of the geometry by comparing the time response of the solid samples to the lattice results.

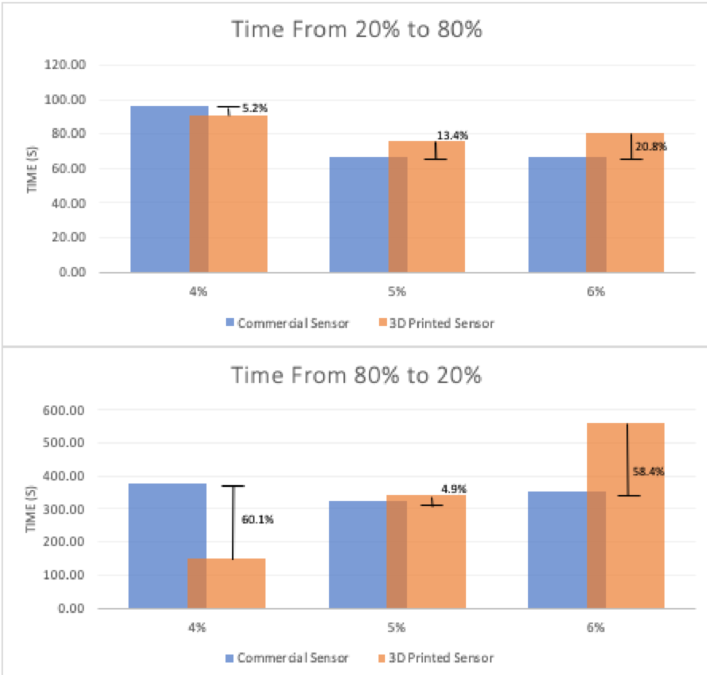

Figure 3.7: Time Response Results (Solid)

The results in Table 3.2 show that the solid is much slower than the lattice but still following the same trend as expected. These results are due to the difference in surface area. The lattice structure advantage in being a lattice structure is that the thickness remains minimal and water cannot penetrate deep allowing it to dissipate water faster by maintaining a high volume to surface area ratio.

3.4 Conclusion

In conclusion, a suitable RH sensor can be 3D-Printed using PVA as a binder and it can be optimized through geometry and binder content. In addition, the PVA content influences the rheology and printability of the paste. The water content influences the porosity and the porosity influences the time response. Further optimization of the geometry will help the response of the sensor and the reduction of PVA content will increase the water content to increase the porosity and increase the time response of the sensor. Future research may even increase the density of the paste to the point that is impermeable to then post-process the sensor and add surface porosity through a chemical process. This sensor would be ideal because water would not be able

to travel deep in the layers increasing the time response and a chemical process may help control the pore size more accurately.

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Vita

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