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Steven Shapardanis
Matthew Hudspeth
Dr. Tolga Kaya, Sacred Heart University

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Gelatin as a new humidity sensing material: Characterization and limitations

Steven Shapardanis,1 Mathew Hudpeth,2 and Tolga Kaya1,3,a
1School of Engineering and Technology, Central Michigan University, Mt. Pleasant, Michigan, 48859, USA
2Department of Physics, Central Michigan University, Mt. Pleasant, Michigan, 48859, USA
3Science of Advanced Materials Program, Central Michigan University, Mt. Pleasant, Michigan, 48859, USA

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The goal of this work is to assert the utility of collagen and its denatured counterpart gelatin as cost-effective alternatives to existing sensing layers comprised of polymers. Rather than producing a material that will need to be discarded or recycled, collagen, as a by-product of the meat and leather industry, could be repurposed. This work examines the feasibility of using collagen as a sensing layer. Planar electrodes were patterned with lift-off process to work with the natural characteristics of gelatin by utilizing metal vapor deposition, spin coating, and photolithography. Characterization methods have also been optimized through the creation of specialized humidity chambers that isolate specific characteristics such as response time, accuracy, and hysteresis. Collagen-based sensors are found to have a sensitivity to moisture in the range of 0.065 pF/%RH. Diffusion characteristics were also analyzed with the diffusion coefficient found to be 2.5×10^{-5} cm^2/s. Absorption and desorption times were found to be 20 seconds and 8 seconds, respectively. Hysteresis present in the data is attributed to temperature cross-sensitivity. Ultimately, the utility of collagen as a dielectric sensing material is, in part, due to its fibrous macrostructures as well its hydrophilic sites along the peptide chains. Gelatin was patterned between and below interdigitated copper electrodes and tested as a relative humidity sensor. This work shows that gelatin, which is inexpensive, widely available, and easy to process, can be an effective dielectric sensing polymer for capacitive-type relative humidity sensors. © 2014 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4904724]

I. INTRODUCTION

Relative humidity (RH) sensing systems are prevalent in many facets of industry including food processing, semiconductor and electronics manufacturing, and the automotive and medical industries. A high performing sensor will exhibit high sensitivity, repeatability, and linearity as well as low response time and cross-sensitivity with a little hysteresis.1 Micro Electromechanical Systems (MEMS) based sensors offer lightweight, low power, small scale, and low cost alternatives to conventional humidity sensors.2 MEMS humidity sensors can be divided into categories determined by its sensing mechanism, such as capacitive, resistive, mass sensitive, thermal, or optical. Capacitive sensors have been widely used due to their good linearity, fast response time,3 simple processing steps,2 interface circuitry’s simplicity, and low power requirements.1 Different types of materials can be used as the dielectric RH sensing material, but they’re generally either a polymer or a porous metal oxide. A capacitive RH sensor functions due to the dielectric’s affinity for water
sorption. At higher humidity levels, more water is absorbed into the dielclic altering the electric permittivitiy of the material. Electric permittivity changes cause capacitance changes, which can be measured and used to quantify the RH levels.

The most significant sensing polymer qualities are its linearity and hysteresis. These two factors are mostly determined by the hydrophilic nature of the polymer.\(^5\) Linear sorption is related to the concentration of hydrophilic sites along the polymer chain which allow hydrogen bonding between the polymer and water. Water clusters that form on these sites account for hysteresis at higher humidity levels.\(^5\) Therefore, polymers with weak hydrophilic sites are good sensing materials since sorbed water can loosely bond to the polymer while maintaining a lower propensity for water clusters. The most common sensing polymers are polyimides, polymethyl methacrylate, and cellulose derivatives.\(^1,6,7\) Polymers are generally used due to their high linearity, low cost of production, and limited hysteresis when compared with other sensing dielectrics such as porous metal oxides. However, polymer sensing materials cannot withstand high temperatures, can exhibit high hysteresis in constant high humidity environments, and tend to break down faster than their metal oxide counterparts.\(^5\)

Lazarus et al. proposed an RH sensor to detect when a respirator cartridge has been nearly exhausted by utilized inkjet printing to deposit polyimide onto an integrated parallel plate electrode array built using CMOS fabrication processes.\(^7\) Tetelin et al. proposed a polyimide RH sensor based on parallel plate capacitance that achieved a 1.1 second response time for use in diagnosing pulmonary deficiencies.\(^8\) Sen and Darabi proposed a polyimide based RH sensor that employs both interdigitated electrode and parallel plate geometries to improve sensor performance by 18% over traditional parallel plate sensors for use in HVAC applications.\(^9\) Kim et al. determined that thicker polymer layers were important for capturing the effect of fringing electric field lines in interdigitated electrode sensors, and proposed a sensor with both a thicker polymer layer and an etched cavity between the electrodes which had sensitivities of 37.1 \(\text{fF/\%RH}\). Exploring the tradeoff between production costs and performance is the motivation behind developing sensors with new materials and electrode designs for specific applications.

The goal of this work is to investigate the diffusion properties of collagen as an inexpensive alternative for more traditional polymer dielectric materials in the humidity sensing applications. Coming from the bones, tendons, and skin of bovine and pigs, this by-product of the meat and leather industry is plentiful, inexpensive, and simple to process. Almost 30% of the protein found in animals is collagen.\(^11\) This is due collagen’s importance in developing the body’s architecture, such as bones and skin, while also providing mechanical support, such as connective tissues. The physical properties of collagen are derived from its hierarchical structure starting at the molecular level.\(^12\) Beginning with the primary structure, collagen revolves around a repeating Glycine molecule in the form GlyXaaYaa, where Xaa is typically Proline (Pro) and Yaa is typically Hydroxyproline (Hyp). The polypeptide chains form polyproline II (PPII) helices, which are packed together in a tight right handed triple helix known as tropocollagen. Depending on the type of collagen and the source, the packing of tropocollagen into fibers can be widely different.\(^11\) The majority of collagen’s physical properties are due to the formation of these fibers. Collagen is hydrophilic due to the Pro and Hyp residue’s polar side groups, and due to collagen’s fibrous quality it is naturally porous; therefore it has potential as a capacitive humidity sensor’s dielectric material.

II. SENSOR FABRICATION

The capacitive RH sensors were built using coplanar interdigitated electrode geometry with the gelatin dielectric patterned between and below the comb-like electrodes. The process steps are depicted in Figure 1. The substrates were glass microscopy slides diced into 1” × 1” squares. The gelatin thin films were fabricated on site using locally purchased type-A gelatin and deionized water. Previous work has shown that varying the gelatin-to-water concentration over a range of spin speeds from 1000 to 5000 rpm (revolutions per minute) will produce gelatin thin films between 100 and 1200 nm thick.\(^13\) The gelatin sensing film was applied using a Laurell spin coater at 2000 rpm for 20 seconds to create a 300 nm thick film on a 100 nm copper thin film which was deposited onto the gelatin film using metal evaporation. Thicker gelatin film as chosen to eliminate the fringing electric field lines in the dielectric that are not covered by the copper film; this improves the signal-to-noise ratio.

The capacitive RH sensors were evaluated in a high humidity environment to test sensitivity and hysteresis over a controlled period of time. The test setup consisted of a water chamber and an oscillating fan to control the humidity and ensure a uniform environment for the sensors. The RH sensor was placed in the water chamber with a controlled RH of 90% for 20 minutes. The RH sensor was then removed from the chamber and allowed to return to ambient conditions for 20 minutes. This cycle was repeated several times to ensure the data were representative.

The results show that the capacitive RH sensor based on gelatin has a sensitivity of 37.1 \(\text{fF/\%RH}\) and a hysteresis of 3.1 \(\text{fF/\%RH}\) at 90% RH. The sensor showed a fast response time of 1.1 seconds to a change in humidity, which is comparable to other capacitive RH sensors. The sensor was also able to maintain a consistent RH reading over multiple cycles, indicating minimal degradation or hysteresis. The data suggests that gelatin can be a viable alternative to traditional polymer dielectric materials for capacitive RH sensors.
Sensor fabrication was accomplished using photolithography, spin coating, thermal physical vapor evaporation and wet etching techniques. (a) A gel thin film is processed onto the substrate via spin coating then a copper thin film was deposited using thermal PVD. (b) Positive photoresist was patterned onto the copper film. (c) Sodium persulfate was used to etch the copper. (d) A second gelatin film was deposited via spin coating. (e) The photoresist layer was removed with acetone, which lifted off excess gelatin and exposed the copper electrodes. (f) The photo of the device taken with an optical microscope.

Field effects through the air. The copper electrodes were patterned by positive photoresist (Microposit S1813), developed with a solution of 2.3% Tetramethylammonium Hydroxide (TMAH), then etched in a 25% Sodium Persulfate solution for 15 seconds at 50°C. A second 300 nm thick gelatin thin film was applied on top of the patterned electrodes. A lift-off was performed using acetone, which dissolved the photoresist layer, pulling the excess gelatin from the electrodes. The interlocking electrodes were chosen to be large enough (2000 µm long and 100 µm wide, with 100 µm gaps between the electrodes) in order to keep the diffusion one dimensional.

III. SENSOR CHARACTERIZATION

Humidity sensing performance was evaluated using a Blue M Vapor-Temp Controlled Relative Humidity Chamber. The temperature was kept at 36°C while the humidity was ramped up and down between 50% and 90% RH with 10% RH intervals. This was repeated three times, with each interval lasting 10 minutes. The chamber’s relative humidity and temperature was monitored using a Nomad Omega OM-73 Temperature/Humidity Data Logger. The device’s capacitance was monitored with a GLK Model 3000 Digital Capacitance Meter and recorded with a LABVIEW program.

A custom relative humidity chamber was devised to rapidly toggle between high and low relative humidity at fixed temperatures, shown in Figure 2. Compressed air was used to rapidly change the ambient RH within the chamber. Dry air was sent straight from the compressor into the chamber. The wet air was generated using a bubbler system. A sealed container half filled with deionized water was injected with compressed air, the exhaust of which was humid air. The air was heated to 33°C by immersing the tubing leading up to the RH chamber in hot water. Two solenoid valves (WIC Valve 2ACK Series 1/4” NC) were used to control the airflow into the chamber. A Java program was written to control the valves through a controller circuit based on a microcontroller (Arduino UNO Revision 3), two power transistors (Motorola TIP120), and two diodes (1n4004); the program also used the computer’s clock to accurately measure the switching times.

Figure 3(a) depicts both the capacitance and relative humidity as functions of time. This data was processed using a moving average filter in MATLAB to remove environmental noise caused by the test chamber. Changes in relative humidity correspond to precise changes in capacitance. The capacitance tends to lag during desorption, implying hysteresis. Additionally, there is a linear increase in capacitance after the device saturates at a given humidity during adsorption, and a linear decrease in capacitance during desorption. The trend is similarly shown by the commercial reference sensor. Figure 3(b) shows the capacitance as a function of relative humidity and indicates the adsorption and desorption periods. A linear best fit line was produced using MATLAB, the slope
FIG. 2. A custom built humidity chamber was devised to test the response time of the sensors. Compressed air flowed into one of two solenoid valves which were controlled by a circuit based around an Arduino UNO microcontroller. A bubbler chamber was connected to one valve which created humid air by injecting compressed air into deionized water. The second valve controlled the flow of dry compressed air. The output of each solenoid was heated by submerging the line in hot water. The warm air was then sent into the test chamber.

of which was used to determine that the sensitivity of the device is $0.065 \, \text{pF/\% RH}$. The linear fit’s coefficient of determination $R^2$ was found to be 0.9626.

Figure 4 shows the difference between a typical reference sensor response and the capacitive sensor’s response to large, sudden changes in relative humidity. Both sensors respond immediately to increases in RH, though the gelatin device takes longer initially to begin absorbing water. An approximate first order derivative of each measurement with respect to time was used to help determine how the sensors respond to changes in humidity. The gelatin device reaches saturation after 20 seconds, whereas the commercial sensor reaches saturation after 42 seconds. During desorption the gelatin sensor reaches saturation after 8 seconds and the reference sensor reaches saturation after...

FIG. 3. The devices were tested using a commercial RH chamber at a constant $36 \, ^\circ\text{C}$. The devices were tested at $10 \, \%\text{RH}$ intervals for 10 minutes from $50 \, \%\text{RH}$ to $90 \, \%\text{RH}$, then back to $50\%\text{RH}$. (a) The overall data that compares the relative humidity as measured by the commercial data logger to the capacitance of the sensor. (b) The device’s dependence on relative humidity with distinctions between absorption and desorption).
FIG. 4. The typical step response of the humidity chamber to sudden changes in humidity as measured by a commercial RH sensor and the gelatin-based sensor. Vertical dotted lines represent the RH steps (low to high or high to low).

70 seconds (not shown on the plot). Additionally, the commercial sensor lags behind the gelatin sensor in initial response to desorption by 6 seconds. Both sensors exhibit a linear increase during saturation at high humidity which is due to the slow accumulation of humidity within the chamber.

IV. DISCUSSION

In this study we used gelatin rather than collagen to study water sorption. Gelatin is a network of denatured collagen molecules. Hydrated gelatin cast into films will reform collagen-like helical coil macrostructures rather than a statistical coil assumed by most polymers. Gelatin is hydrophilic due to these macrostructures. Water sorption of gelatin has been studied relating it to the mechanical properties it exhibits. Kozlov and Burdygina classify the amount of water bound to gelatin in three forms: water bound inside the collagen-like helices which play a decisive role in structural stability; hydrogen bonded water appearing outside the helices which also provide structural stability; and water loosely bound to the surface. In total, the amount of water bound to gelatin is roughly 40% by weight, and increases relative to the amount of collagen-like structures present.

As water is absorbed into the sensor’s gelatin dielectric, the relative permittivity will change. This is due to the difference in permittivity between water $\varepsilon_2$ and gelatin $\varepsilon_1$, and is modeled by Looyenga’s equation for the dielectric constant of mixtures, as shown in (1):

$$\varepsilon = \left[ (\varepsilon_2^{1/3} - \varepsilon_1^{1/3})v_2 + \varepsilon_1^{1/3} \right]^3$$  \hspace{1cm} (1)

where $\varepsilon$ is the net electric permittivity, $\varepsilon_1$ is the electric permittivity of the polymer, $\varepsilon_2$ is the electric permittivity of water, and $v_2$ is the fractional volume water in the polymer.

Water has a higher electric permittivity than gelatin; therefore as more water is absorbed into the gelatin the net relative electric permittivity of the region between the electrodes will increase. This causes changes in capacitance as predicted by the equation for a parallel plate capacitor:

$$C = \varepsilon_0 \varepsilon \frac{A}{d}$$  \hspace{1cm} (2)

Where $C$ is parallel plate capacitance, $\varepsilon$ is relative electric permittivity, $\varepsilon_0$ is vacuum permittivity, $A$ is the surface area of the capacitor’s overlapping plates, and $d$ is the distance between the plates.

Gelatin becomes less rigid and its shape will change as it absorbs water. The effect of dielectric swelling can be reduced by allowing the material to expand orthogonal to the faces of the capacitor plates. Therefore the sensor design compensates for its expansion by implementing coplanar
interdigitated electrode geometry. The geometry resembles two interlocking combs lying flat on a plane. Gelatin is processed below and between the capacitor’s electrodes. The gelatin that is between the electrodes will engulf the capacitor’s direct electric field lines. The gelatin, and any water absorbed in the gelatin, will then force the electric field to increase or decrease based on the net relative electric permittivity. The effect of the direct electric field between the parallel plates is reduced due to the capacitor’s electrode thickness. As a result the fringing electric field lines have a significant impact on overall capacitance.\(^{17}\) For this reason the device was fabricated on a thin film of gelatin, allowing the capacitor’s fringing electric field will pass through the gelatin film below the electrodes. Additionally, the patterned gelatin is much thicker than the electrodes to allow fringing electric field lines above the device to pass through gelatin rather than air.

Previous work has shown that as the temperature increases, the hydrogen bonded R-groups in the tertiary structure of the collagen-like assemblies are broken, allowing more N-H groups in the gelatin to bond with water molecules.\(^{13}\) The hysteresis due to adsorption and desorption can be accounted for by examining the temperature shifts during the experiment in Figure 3(b). A temperature cross-sensitivity will account for different capacitance levels at the same humidity for different temperatures. An artifact of the humidity chamber is higher temperatures during desorption, which the capacitive sensor cannot distinguish. The temperature dependence of the device produces a significant amount of interference that must be considered while evaluating the viability of gelatin as a realistic dielectric sensing material.

The mechanism behind the movement of water through the gelatin is important for understanding the operation of the sensor, and can be characterized as a diffusion process. After a change in humidity the water concentration within the sensing material will eventually match the concentration of ambient water vapor. This process is dependent on time, the initial and final water vapor concentrations, and the diffusion coefficient and thickness of the sensing material. Fick’s Laws describe the process of diffusion based on these variables:

\[
J = -D \frac{\partial \phi}{\partial x}.
\]

Where \(J\) is the flux, or the number of water molecules moving through a given surface area over time, \(D\) is the diffusion coefficient of the polymer, \(\phi\) is the concentration of water in the volume.

FIG. 5. The experimental response time of a sensor from a low to high humidity change was plotted. Then with known time and water concentration values derived from the experimentally recorded relative humidity and temperature values, a one dimensional model of diffusion was fit to the capacitive response by sweeping \(D\), which is the coefficient of diffusion of the material.
of the polymer, and $x$ is the current depth into the polymer. $\partial \phi / \partial x$ represents the concentration gradient and is a measure of how concentration changes throughout the physical dimensions of the material.

Using known initial and final water vapor concentrations, as well as the response time and geometry of the sensor, one can relate the capacitive response time to a one-dimensional model of diffusion. The final variable, the coefficient of diffusion $D$, can then be swept to fit the model to the experimental results. Finding coefficient of diffusion experimentally like this allows one to further predict the response of sensors with different dimensions. The absolute humidity levels were derived from the temperature and humidity data during initial and steady state condition, finding the initial concentration of water in the material, $\phi_0$, to be $0.8174 \times 10^{-6}$ g/mm$^3$ and the concentration of water at the air boundary, $\phi$, to be $2.792 \times 10^{-6}$ g/mm$^3$. The thickness of the polymer was 600 nm, and the experimental time for the model was set between $0 \leq t \leq 200$ seconds. From this approach Figure 5 was generated and the diffusion coefficient was found to be $2.5 \times 10^{-5}$ cm$^2$/s. The sensor was assumed to have reached the initial and final concentration values when it exhibited a steady state response after a known humidity shift.

V. CONCLUSION

The molecular structure of collagen was evaluated in reference to typical relative humidity sensor dielectrics. Its potential utility as a dielectric sensing material is due to its fibrous macrostructures as well as its hydrophilic sites along the peptide chains. Gelatin, which is denatured collagen, was patterned between and below interdigitated copper electrodes and tested as a relative humidity sensor. The sensor’s sensitivity was found to be 0.065 pF/%RH in a linear range between 50% RH and 90% RH, with hysteresis attributed to temperature cross sensitivity. The absorption response time of the sensor is 20 seconds and the desorption response time is 8 seconds. From the response time tests, the coefficient of diffusion was found experimentally to be $2.5 \times 10^{-5}$ cm$^2$/s, which can be used to predict the behavior of different gelatin-based relative humidity sensor geometries.

Exploring new sensing materials and determining their diffusion constants for humidity sensing are important and timely. We believe gelatin offers a good alternative to more conventional polymers. Our device approach is simple yet effective and provides consistent results. We believe that gelatin is a very promising humidity sensing material and this initial research results will lead to more in-depth studies such as temperature cross-sensitivity and better response times.

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