A Passive Radio-Frequency pH-Sensing Tag for Wireless Food-Quality Monitoring

Wen-Ding Huang, Sanchali Deb, Young-Sik Seo, Smitha Rao, Mu Chiao, and J.C. Chiao

Abstract— **We present a new method, suitable for food quality management by wirelessly monitoring pH level changes in food with a flexible pH sensor embedded in a batteryless radio-frequency (RF) transponder. The wireless sensor tag includes a flexible pH sensor based on miniature iridium oxide (IrO_x) and silver chloride (AgCl) sensing electrodes integrated on a deformable substrate, and batteryless wireless communication circuitry. The sensor tag and reader system is designed to achieve convenient, long-term, and on-demand wireless in situ monitoring of food quality, especially for large-quantity applications and continuous monitoring from place of production to retail stores. Low-cost IrO_x sol-gel fabrication process was applied on polymeric substrates to form the flexible sensing films, and a sensitivity of –49.7 mV/pH was achieved. Inducting coupling provides electromagnetic energy from the reader to drive the transponder circuits that re-transmit the sensor-data modulated signals back to the reader. The electrochemical potential created by the IrO_x/AgCl sensing electrodes is converted to a modulated frequency and the system achieves a sensitivity of 633Hz/pH. The wireless pH sensing system was tested for in situ monitoring of the spoilage processes in fish meats continuously for over 18 hours. The feasibility of wirelessly monitoring pH values in fish meats that could be used to identify spoilage remotely has been demonstrated.**

Index Terms— **Wireless, pH sensor, IrO_x flexible substrate, passive radio-frequency circuit, in situ monitoring, food quality.**

I. INTRODUCTION

Food freshness is a key factor for public safety. Management and monitoring of food quality are important in food storage and transition. Food safety issue is a vital concern as shown in the Hazard and Critical Control Point (HACCP) by the U.S. Food and Drug Administration (FDA). There are up to 81 millions of Americans each year suffering from food-borne illnesses, and 9,100 cases of fatality [1]. The waste of food due to spoilage is also a major concern for not only business owners but also many countries [1].

Three different modalities for food spoilage monitoring have been utilized in research and commercial fields, besides

direct tasting by experts. A common food freshness monitoring method is to use gas sensors which often are made of metal oxide semiconductors (MOS), conducting organic polymers or piezoelectric crystals. These sensors rely on the changes of conductivity in the sensing films induced by the adsorption of gases and subsequent surface reactions [2-3] that are produced by food during spoilage processes. For the MOS sensors, the required operating temperature is between 200°C and 650°C as the organic volatiles transferred to the sensing surface need to be oxidized which causes the changes of electrical resistance. The selectivity and sensitivity of MOS sensors are easily influenced by the operating temperature and microstructures of metal oxide films since the sensing depends on the physical characteristics of MOS. Conducting organic polymer sensors, on the contrary, require a low operating temperature and usually are very sensitive to moisture [3] which may not be suitable for robust applications. For piezoelectric crystal sensors, a good quality of coating process is required during the fabrication to maintain a consistent sensitivity [3], which may not be a cost-effective option. In general, gas sensors are easily affected by environmental conditions such as moisture and temperature due to the sensing principles.

The other two modalities to monitor food freshness are based on the detection of enzymes [4-7] and storage temperature changes [8]. For enzyme sensors, to monitor different types of foods will require differently specific enzymes. For example, detection of total volatile basic nitrogen (TVB-N) [4-5] and Histamin [6-7] enzymes is widely used for seafood freshness sensing. However, Gram [9] reported that spoilage mechanisms vary for different races of fishes. Glutamate dehydrogenase and glucose oxidase [10] detection is widely used for freshness sensing of fruits, vegetables and related food products such as juice or wine. The detection of enzymes often needs to be carried out manually in selected samples as it is impossible to conduct the tests on every product. It is also difficult to integrate specific enzyme sensors in a food package that allows wireless interrogation. The enzyme sensors often utilize enzyme oxidases in the sensing electrodes which may not be appropriate or even safe to be used directly in a food/meat package. Furthermore, the enzyme sensors usually require complicated fabrication processes such as the polymer treatment, temperature control, and chemical compound mixing to achieve the required sensing performance [4]. The expensive chemical agents, specific surface treatment, and complicated fabrication process will increase the costs which

in return is difficult for large-scale applications.

To manage produce quality by monitoring ambient temperatures during transit and storage is an indirect but common means to "estimate" the food quality; often it is not accurate or specific enough. Therefore, a direct, simple, accurate method that can be integrated with low-cost electronics and wireless capability to monitor food quality is needed. .

During the food spoilage processes, the growth of yeasts and microbes plays a notable and major role inside the food. The original chemical compounds such as glucose, lactic acid and certain amino acids are catabolized by microbes or microflora in the meat or food [11]. As the food condition changes, the pH level also changes with the metabolism actions of the bacteria and microbes [7, 11-12]. Therefore, monitoring pH profiles in food provides a means for food quality measurement.

Considering the needs for a direct, simple, accurate, continuous, remote and cost effective food freshness monitoring system, we proposed to implement a flexible pH sensing tag in the produce wrap along with a passive RF telemetry circuit that could be embedded in the product label as a freshness indicator which allows a wireless reader to interrogate the pH level in the food remotely. We have fabricated IrO_x/AgCl electrodes on a deformable bio-compatible polymer by using the IrO_x sol-gel fabrication processes [13]. Compared with other IrO_x fabrication methods including sputtering [14], electro-deposition [15-16], and thermal oxidation [17], the sol-gel process [18-20] provides better cost effectiveness and coating efficiency of IrO_x thin film deposition. In our experiment, an IrO_x thin film formed by the sol-gel process performs a stable sensitivity for pH and quick response time which both represent a high-quality sensing film [21]. Unlike the gas sensors, our pH sensors have better sensitivity and selectivity as it is less temperature and moisture dependence. Our IrO_x pH sensors do not require a high operating temperature thus eliminate the need for electronic heaters under the sensors. Unlike the enzyme sensors, our pH sensors can continuously monitor the pH level of food and can be integrated with wireless telemetry. Furthermore, our IrO_x pH sensor can be easily embedded in a passive RFID (radio-frequency identification) circuit [22] for batteryless wireless communication since the power consumption is very low. The RFID transponder can harvest RF power which transmits from a reader, and then send the modulated data back to the reader.

In this paper, a prototype of a batteryless, wireless pH sensing tag for continuous and real-time fish meat quality monitoring has been demonstrated. We proposed such a method as a cost-effective solution to monitor food quality in large quantity during storage and delivery.

II. METHOD
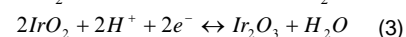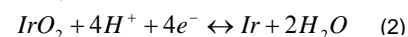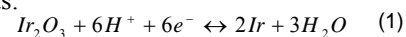
A. Flexible IrO_x Sensor

1) Design and Fabrication

The IrO_x/AgCl pH sensing electrodes were fabricated on a polyimide substrate with steps shown in Figure 1. For the IrO_x working electrode, a layer of chromium was deposited on a piece of polyimide substrate as metal adhesive. Then a 0.1-μm thick layer of gold was deposited with e-beam evaporation. Iridium oxide sensing film was formed by the sol-gel process [13]. One gram of anhydrous iridium chloride ($IrCl_4$) was dissolved in 42 ml of ethanol followed by adding 10 ml of acetic acid in the solution. The solution was stirred continuously by a magnetic rod at the bottom of the beaker for an hour. The bare gold electrode was then dipped and coated with a 10-cm/min withdrawing rate in the sol-gel solution. The electrode was then annealed at 300°C to oxidize the iridium surface. The heating profile started at 25°C and increased to 300°C in a 2-hour period. The temperature then stayed at 300°C for 5 hours, and cooled down back to the room temperature in 10 hours.

Fig. 1. IrO_x electrode fabrication processes: (a) Cr and Au deposition on a polyimide substrate, (b) S1813 photoresist lift-off process, (c) SU-8 deposition for the sacrificial layer, and sol-gel process in $IrCl_4$ solvent, (d) lift-off process and thermal treatment, (e) Cr, Pt and Ag deposition, (f) S1813 photoresist lift-off process, and (g) AgCl electroplating.

For the AgCl reference electrode, 5-nm thick of chromium, 3-nm thick of platinum, and 30-nm thick of silver layers were deposited. A thin film of silver chloride was formed by the electrochemical anodization method. In the electroplating process, an anodic silver electrode and a platinum cathode electrode were immersed in 0.1-M HCl solution with an electrical current of 0.5 mA applied for 5 seconds. The Cl⁻ ions would merge with the silver ions on the surface of electrode which turned the electrode color into gray. The electrode was then immersed in 3-M KCl solution for 24 hours to saturate and stabilize the standard potentials of AgCl [23].

The pH sensing mechanism is based on the three possible redox equilibriums between two oxidation states of iridium oxide [23] as:

$$Ir_2O_3 + 6H^+ + 6e^- \leftrightarrow 2Ir + 3H_2O \quad (1)$$

$$IrO_2 + 4H^+ + 4e^- \leftrightarrow Ir + 2H_2O \quad (2)$$

$$2IrO_2 + 2H^+ + 2e^- \leftrightarrow Ir_2O_3 + H_2O \quad (3)$$

and the electrochemical potential is determined by:

$$E = E^0 - 2.303\frac{RT}{F}pH = E^o - 0.05916pH \quad (4)$$

where E^0 is the standard electrode potential with a value of 577mV for a AgCl reference electrode. F is the Faraday's constant with a value of 96,487 coul/equiv, and R is the gas

constant with a value of 8.314 joules/deg. *RT/F* is equal to 25.688 at 25°C. The pH potential sensitivity will be – 59mV/pH if all of the space charges in the film are formed, which is called the Nernstian response (Eq. 4) [24-25]. It should be noted that since the Nernstian response of IrO$_x$/AgCl sensing film electrodes depends on the surface microstructures and oxidation states of the films [13], the sensitivity of the pH sensor is expected to vary between Nernstian and near-Nernstian responses [24-25] depending on the fabrication parameters.

2) Calibration

Figure 2 shows our fabricated flexible IrO$_x$/AgCl pH electrodes. The size of sensing electrode is 2mm×2mm, the conducting line between the sensing electrode and contact pad is 8mm in length and 1mm in width. The size of contact pad for probing is 8mm in length and 3mm in width. The conducting lines and contact pads are for testing purpose only.

The sensor produces an electrochemical potential responding to the pH level of solution. The electrodes were connected to an Agilent 34401A digital multi-meter with a GPIB interface to a LabView-based program for real-time potential recording. A unit gain amplifier TLC074 (Texas Instrument) served as a buffer for impedance matching. During the calibration procedure, the acid or alkaline buffer solutions were dripped near the sensor in the beaker along with a commercial glass-rod pH meter to verify the pH value. The electrochemical potentials and pH values were displayed and recorded in a computer simultaneously.

Fig. 2. The fabricated IrOx flexible pH sensor.

B. Transponder System Design

The wireless pH sensing system includes a passive transponder (tag) embedded with our flexible iridium oxide pH sensing electrodes, and a reader. The batteryless operation relies on the inducting coupling between reader and tag coil antennas with tuning capacitors at a resonant frequency. The operation principle is similar to the one for RFID. Figure 3 shows the blocks diagram of the wireless pH sensor system.

Fig. 3. Block diagrams of the passive wireless pH sensor system.

The transponder consists of a voltage multiplier or charge pump [26], a relaxation oscillator [27], and a frequency modulator. The antenna inductor (L2) and a capacitor (C2) form a resonant circuit which receives RF powers from the reader. The voltage multiplier consists of diodes and capacitors amplifying the voltage from hundreds of millivolts to volts. A voltage regulator was utilized to limit the output voltage at 2.5V. The relaxation oscillator converts the electrochemical potentials generated by the pH electrodes to frequency-varying signals which are based on the voltage level at the input of the comparator [27], as shown in Figure 4. The sensor signals then drive a frequency modulator to modulate the carrier signals back to the reader antenna. In our design, the modulated frequency decreases from 22 kHz to 15.9 kHz responding to the pH level from 2 to 12.

Fig. 4. The relaxation oscillator design in the transponder.

The reader consists of a class-E amplifier, an envelope detector, band-pass filters and an interface to computer. The class-E amplifier [28-30] driven by a frequency source provides 100-Vpp square waves at 1.34 MHz tuning to the resonant frequency of the LC circuit in the reader antenna. The carrier frequency signals are transmitted to the tag powering up the integrated circuits in the tag. The modulated frequencies in the returned signals at the resonant frequency are detected by an envelope detector [22] while the carrier frequency component is rejected by band-pass filters. Band-pass filters further reduce the noises and harmonics outside the desired band. A comparator is used to convert the low-frequency sinusoidal signals to square waves that then are digitally processed by a LabView-based program in real time to count the frequency. The frequency is converted to the corresponding pH value according to the calibration curve.

C. Food Freshness and pH Level

To demonstrate the wireless pH sensing system for monitoring food freshness, the relationship between the pH level and food spoilage processes needs to be defined. In this work, we used fish meat as an example to demonstrate the concept. Once the meats or fishes are prepared at the produce factories, oxygen stops to deliver into muscles or tissues, which induces biochemical reactions contributing to flavors and spoilage processes. Generally speaking, the processes follow three major steps [31]:

Step 1: Rigor mortis during which the pH value decreases. Due to the lack of oxygen in the dead tissues, the glycogen will be decomposed and become lactic acid. On the other

hand, the Adenosine Tri Phosphate (ATP) is also hydrolyzed to be phosphoric acid. Therefore, the pH level of the muscles/tissues will decrease while they become hardened. The phenomenon is typically called "rigor mortis".

Step 2: Autolysis during which the pH value slightly increases. After the rigor mortis period, the muscles/tissues will start to be dissolved into smaller molecules by enzymes. The muscles will become softer as called "off-rigor". The proteins in the dead muscles also dissolve to be amino acid which includes different types of chemical compound ex. Amine. Thus, the pH level will increase.

Step 3: Spoilage during which the pH value increases again. With amino acid produced, some microbes start to grow and absorb the amino acid and proteins. There are different chemicals such as indole, skatole, ammonia, and sulfide created after the absorption processes in bacteria. The ammonia-based chemicals increase the pH level of the meat/fish and start producing bad odors.

(a)   (b)

Fig. 5. Tilapia fillets stored at (a) 5°C in a refrigerator, and (b) at the 25°C room temperature.

As described above, it is possible to relate pH-level variations in meats to the three transitions in the spoilage processes. In this work, we demonstrated and compared the pH profiles of fish meats stored at two different temperatures. One Tilapia fillet was stored and monitored in a refrigerator at 5°C, (Figure 5(a)) and the other one was stored and monitored at the room temperature of 25°C (Figure 5(b)) for 17 hours. The quality of fish filets could be identified by the smell and color to verify the information recorded by our sensor system, as the different colors shown in Figure 5. A flexible pH sensor was placed at the bottom of each fish meat. The fishes were then wrapped to avoid loss of moisture. During the experiments, the potential changes responding to the pH levels were detected by our IrO_x flexible pH sensor continuously for 17 hours with a sampling rate of 1Hz. Furthermore, the wireless IrO_x pH sensors then were used to repeat the experiments for the demonstration of wirelessly monitoring food spoilage processes.

III. EXPERIMENTAL RESULTS

A. pH Sensor Performance

1) Sensitivity

The sensitivity of our flexible IrO_x pH sensor was measured by testing eight different pH buffer solutions individually from pH=2 to 12 at the room temperature. Each pH buffer solution was dripped on the IrO_x/AgCl electrodes and the potential was recorded for 5–10 seconds until the potential stabilized. The sensor then was washed in DI water and air dried for next test.

Figure 6 shows the potential responses with a sensitivity of – 49.7mV/pH which is a near-Nernstian response along with a high correlation coefficient r^2 of 0.97. The potential was in a linear relationship with pH between pH=2 and 12.

2) Stability

In the previous experiment, the sensitivity of our pH sensor was obtained in less than 10 seconds. However, monitoring food quality requires stable long-term measurements. To demonstrate the stability of our sensors, we used eight different buffer solutions ranging from pH=1.5 to pH=12 to test our pH sensor in a longer period of time. Each pH buffer solution was dripped on the sensor, and the potentials were recorded for 5 minutes with a sampling rate of 1Hz. The sensor then was cleaned in DI water and dried for the next solution. Figure 7 shows that eight different stable potential levels which are 511 mV, 429 mV, 354 mV, 239 mV, 206 mV, 175 mV, 46.9 mV and   23 mV at eight respective pH levels of 1.5, 2.85, 3.9, 6.35, 7.86, 9.15, 10.15 and 12. The sensor was able to obtain stable potentials for five minutes with drifts dV less than 5 mV which is defined as the potential shifting from the peak value to 90% of the equilibrium potential value [21]. Our pH sensor showed stable outputs indicating that it is suitable for long term monitoring.

Fig. 6. The measured sensitivity of the pH sensor.

Fig. 7. Stability test for our IrOx pH sensor.

3) Reversibility

In previous experiments, the sensor was cleaned and air dried between each test in order to obtain distinct responses for calibration. However, in a long-term monitoring, the sensor will be used continuously. We tested the reversibility of our sensor in a pH titration cycle with pH varying from 2.85 to 12, and then back to pH=1.5 continuously without cleaning and drying the electrodes. During the titration process, 0.1-M KOH or HCl were dripped into the base solution in order to increase or decrease the pH level of the base solution. A commercial pH glass-rod pH meter (HANNA, HI98128) was used as the reference for the pH level in the base solution. The potential was recorded by an Agilent 34401A digital multimeter connected to a computer continuously in this experiment. Figure 8 shows a typical measurement result. The responding potentials in the first acid-alkaline cycle with pH=2.85, 3.9, 6.35, 7.86, 9.15, 10, 12 were 42.96, 35.45, 23.97, 22.6 18.93, 4.22, and –2.37mV, respectively. After the base solution reached the pH level of 12, the second titration cycle was performed from alkaline to acid. The potential returned to 51.25mV when the pH level became 1.5. The experiments were repeated three times and the results are similar to that in Figure 8.

Fig. 8. Measured titration results.

B. Wireless pH Sensor

1) Wireless Communication

The carrier frequency was tuned at the resonant frequency of 1.34MHz. The reader and tag coil antennas have dimensions of $9\times12cm^2$ and $23\times8.5mm^2$. Both the reader and tag were fabricated and assembled on printed circuit boards for demonstration purpose. The coil antenna wire in the tag was wrapped around the printed circuit board while the reader coil was wrapped around a plastic frame, connecting to the reader circuit board with wires, as a handheld antenna. A DC power supply of 8V provides a 400-mA current to the reader. With the coil antennas facing each other in parallel, a communication distance of 10cm in air was achieved with a signal-to-noise ratio of 18dB at the modulated frequencies between 16 and 22 kHz. The frequency shifts could be detected clearly and repeatedly in the computer with a 1-Hz

sampling rate. When the distance increased to 12 cm, the signal-to-noise dropped to 14dB and the peak frequency has a frequency jitter less than 50Hz. The reader frequency counter was not able to count the frequency reliably when the distance increased to 16cm as the tag did not receive sufficient energy from the reader to power up the integrated circuits in the tag.

2) Sensitivity

A new flexible pH sensor was connected to the batteryless tag circuit shown in Figure 3. The potential output modulated the frequency of the relaxation oscillator in the range of 16–22 kHz. The demodulated frequency signals at the reader were recorded in computer with a LabView-based program and verified by an Agilent E4403B spectrum analyzer. Buffer solutions with pH= 2, 4, 7, 10, and 12 were used to measure the sensitivity. Both the electrochemical potentials at the sensor electrodes and the wirelessly detected frequencies were measured and recorded simultaneously. The sensor was washed by DI water and dried by compressed air between tests. Figure 9 shows that the potential and frequency responses between pH=2 and pH=12. The result shows a sensitivity of –51.9mV/pH with a correlation coefficient r^2=0.99 for the tested electrodes, which is also a near-Nernstian response. The sensitivity of the wireless pH sensor system in terms of the modulated frequency is –633 Hz/pH with a correlation coefficient r^2 =0.97. The result shows that the system is able to transduce the pH potential wirelessly. The sensitivity in frequency is sufficient since the sampling rate to record the pH value in the computer is 1Hz.

Fig. 9. Measured sensitivity of our wireless pH sensor system in terms of frequency and potential.

3) Stability

Similar stability tests were conducted with our wireless pH sensor system at pH=2, 4, 7, 10 and 12. Each buffer solution was dripped on the sensor electrodes for 8 minutes. The sensor was then cleaned and dried after each test. The responding modulated frequencies were recorded continuously. Figure 10 shows the frequency responses at five different pH levels. The modulated frequencies stay stable at 22, 20.9, 18, 16.9, and 15.9 kHz corresponding to the pH level at 2, 4, 7, 10, and 12, as expected. Our wireless pH sensor system was able to transduce the sensor signals stably.

frequency stabilized, the same process was repeated and the pH level increased to 12. The sensor was used continuously without cleaning between titration steps. The sensor system responded quickly and distinctly to pH value variations indicating the response time for both the sensor electrodes and the wireless transponder system is sufficiently short for real-time monitoring.

C. In situ Monitoring for Fish Meat Spoilage

Two Tilapia filet samples were used to demonstrate the monitoring of spoilage processes in fish meats. One Tilapia filet was stored at the room temperature of 25°C and the other one was stored in a refrigerator at 5°C. A flexible pH sensor was placed at the bottom of each filet sample with wires connecting to the data acquisition card in the computer. A thin plastic wrap was used to wrap the filet tightly. The sensor potentials were recorded for 17 hours continuously at a sampling rate of 1Hz. Figure 12 shows the potential responses of the two fish samples. The sample stored at the room temperature did follow the aforementioned spoilage steps. Within the first 11 hours, the potential increased from 45.8mV to 101.7mV which represented pH level reduction due to the releasing of lactic acid. After 11 hours, the potential started to drop from 101.7mV to 96.4mV in one hour.

Fig. 10. Stability test for our wireless pH sensor system.

For pH=7, 10, and 12, the frequency drifts were negligible. The noises occurred at pH=2 and pH=4 were caused by the shaking of the sensor during test in which the solution drop encountered localized mixing on top of the electrodes. The drift occurred for the pH=4 case was due to the contact of liquid onto the electrodes as the drop was unevenly dripped on the surface. It took about 2 minutes for the drop of liquid to reach equilibrium to provide stable potential between the IrO_x and AgCl electrodes. This event shows that our sensor is sensitive enough to detect the non-uniform ion distributions in a drop of liquid. In the stability test, it was obvious that when the potentials reached their stable values, the modulated frequencies would stay constant without drifts.

4) Titration Performance of the Wireless Sensor System

The pH sensor system was tested in a continuous titration process at three pH levels of 5, 7 and 12. The result is shown in Fig. 11 with a sampling rate of 5 Hz.

Fig. 12. Measured potential with the flexible pH sensors in fish filets stored at 25° and 5°C.

The declined rate was −5.3mV/hr. This is the second step in the spoilage process called autolysis during which the pH level slightly increases due to the releasing of amino groups from dead muscles. From the 12th to 17th hour, the potential detected by our sensor dropped significantly from 96.4mV to 34.8mV with a rate of −12.32mV/hr. The pH level increases due to the growth of microbes and absorption of the amino and protein groups. The microbes further create chemicals such as indole and skatole which are alkaline decreasing the pH level. On the contrary, the fish sample stored at 5°C in a refrigerator had the potentials increase slowly in 17 hours. There is a clearly distinct difference between these two fish samples within the 17 hours of test and in the voltage range of 140mV which is much larger than the drift voltage of 5mV. The potential profile for the pH level in the fish meat without an appropriate

Fig. 11. Responses in the titration test for the wireless pH sensor system.

Test solution of pH=5 was dripped on the sensing electrodes. After 4 seconds, KOH solution was dripped in the pH=5 solution. The alkalinity raised the pH level to 7, verified by the HANNA pH meter. It took about 1s for the ion distribution in the liquid to reach equilibrium during which the HANNA pH meter also gave scattered readings indicating that the pH values were not stable in the liquid. After the

This article has been accepted for publication in a future issue of this journal, but has not been fully edited. Content may change prior to final publication.

> REPLACE THIS LINE WITH YOUR PAPER IDENTIFICATION NUMBER (DOUBLE-CLICK HERE TO EDIT) <　　　7

storage temperature shows the signature features of spoilage and the rotten smell from the fish starting at the 13th hour verified that. This experimental result indicates that we can potentially recognize the signatures of spoilage by detecting the pH variations to monitor the freshness of fish.

D. Wireless In situ Food Spoilage Monitoring

The wireless pH sensor system consists of both the flexible pH sensor connecting to the printed circuit board of tag and the reader. Two Tilapia fillets were prepared and tested at 25° and 5°C as mentioned before. The sensor was placed under the fish filet with wires connected to the tag. The tag was placed on the side of the fillet and the filet sample was wrapped tightly in a plastic wrap. Readers were placed at a distance of 10cm from the fishes with coil antennas in the same orientation.

Fig. 13. The modulated frequencies transduced from the fish filets with the wireless pH sensor tag wrapped in the package.

Figure 13 shows the modulated frequency profiles during the 17-hour period for the two Tilapia samples at 25°C and 5°C. Similar to the measured potentials in the previous experiment, there are two distinct frequency profiles showing the difference. The frequency profile for the fish sample stored at 25°C for 17 hours showed the 3-step signature in a spoilage process. The frequency increased in the first 6.39 hours from 17 kHz to 17.35 kHz corresponding to the rigor mortis step. From the 6.39th to 11.57th hour, the frequency dropped from 17.35 to 16.99 kHz with a –69.49 Hz/hr decrease rate which represented the second step of spoilage. After the 11.57th hour, the frequency dropped from 16.99 to 16.39 kHz with a rate of –123 Hz/hr indicating the increase of pH in the last step of spoilage. On the contrary, the frequency profile for the fish stored at 5°C in the refrigerator showed a stable increase from 17.1 kHz to 17.5 kHz within the 17-hour period. With the sensitivity curve, the pH level variations during the spoilage processes were indentified in Figure 13. The pH level of the spoiled fish started at around 10 and decreased to pH=9.3 in the first 6.39 hours. Then the pH level increased back to 10.5 in 5.18 hours, and 11.5 in another 5 hours. It should be noted that the transitions between the three steps of spoilage vary in time, comparing Figure 12 and 13. This is due to the original

quality of fish samples obtained from the supermarket. The variations, however, do not affect us from observing the main features of the food spoilage. In this experiment, the spoilage steps of a fish filet could be identified remotely. The quality of fish filets under different storage conditions therefore can be monitored continuously and wirelessly.

IV. CONCLUSION

Our batteryless wireless pH sensor system provides a direct and convenient means to monitor produce/food quality to address food safety and waste issues. The IrO_x pH sensing electrodes are fabricated on flexible substrates that can be deformed on food surfaces to detect pH values. Experimental results show a good correlation between pH and electrochemical potential. The sensor sensitivity, stability and reversibility of the flexible pH sensors were tested with good performance. The electrochemical sensor device architecture allows integration with a batteryless transducer which has a similar operating principle with radio-frequency identification (RFID). This enables the applications of sensor-embedded RFID which not only can be used for large-scale product inventory but also real-time quality monitoring of individual products.

The flexible pH sensor was integrated with a batteryless wireless transducer made on a printed circuit board. For future applications, a RFID chip can be bonded directly on the flexible substrate where the flexible sensor and a planar coil antenna are fabricated in the same batch processes. The sensor system was tested in terms of sensitivity and stability as well as in titration showing good performance in transduction of pH levels in solution. Both the flexible pH sensor and the batteryless wireless pH sensor system were used in the monitoring of fish meats. The results of pH profiles and measured frequency profiles for the fishes stored at the room temperature matched with the major signature steps in spoilage processes. There were distinct differences between the frequency/pH profiles for the fishes stored properly in the refrigerator and those stored improperly at the room temperature. Comparing with the traditional methods to monitor food freshness such as using gas sensors to detect certain volatile from foods, sensors to detect specific enzymes in foods, or simply monitoring the storage temperature, the wireless pH sensors provide an attractive alternative to monitor food quality as the flexible pH sensor could directly detect the chemical reactions in foods and the batteryless wireless transducer system architecture allows integration of inventory capability and real-time on-demand or continuous sensing functionality.

This article has been accepted for publication in a future issue of this journal, but has not been fully edited. Content may change prior to final publication.

> REPLACE THIS LINE WITH YOUR PAPER IDENTIFICATION NUMBER (DOUBLE-CLICK HERE TO EDIT) <   8

REFERENCES

[1] J. C. Buzby and T. Roberts, "Economic costs and trade impacts of microbial foodborne illness," World Health Statistics Quarterly, Vol. 50, pp. 57–66, 1997.

[2] G. Sberveglieri, "Gas Sensors, Principles, Operation and Developments," Springer, New York, 1992.

[3] S. Mannino, S. Benedetti, S. Buratti, M.S. Cosio and M. Scampichio, "Electrochemical sensors for food authentication," Wilson and Wilson's comprehensive analytical chemistry, Vol. 49, pp. 755–770, 2007.

[4] Alexis Pacquit, June Frusby, Danny Diamond, King Tong Lau, Alan Fqrrell, Brid Quilty, and Dermot Diamond, "Development of a smart packaging for the monitoring of fish spoilage," Food Chemistry, Vol. 102, pp. 466–470, 2007.

[5] J. Oehlenschlager, "Volatile amines as freshness/spoilage indicators: a literature review," 25th WEFTA international seafood conference, Vol. 38, pp. 571–586, 1997.

[6] Ivo Frebort, Lenka Skoupa, and Pavel Pec, "Amine oxidase-based flow biosensor for the assessment of fish freshness," Food Control, Vol. 11, pp. 13–18, 2000.

[7] Ching Mail Keow, Fatimah Abu Bakar, Abu Bakar Salleh, Lee Yook Heng, Rahman Wagiran, and Low Sim Bean, "A amperometric biosensor for the rapid assessment of histamine level in tiger prawn spoilage," Food Chemistry, Vol. 105, pp.1636–1641, 2007.

[8] June Frisby, Declan Raftery, Joe P. Kerry, and Dermot Diamond, "Development of an autonomous, wireless pH and temperature sensing system for monitoring pig meat quality," Meat Science, Vol. 70, pp.329–336, 2005.

[9] Lone Gram, and Hans Herik Huss, "Microbiological spoilage of fish and fish products," Food Microbiology, Vol. 33, pp. 121–137, 1996.

[10] Beatriz Serra, Angel Julio Reviejo, and Jose Mannuel Pingarron, "Application of electrochemical enzyme biosensors for food quality control," Electrochemical Sensor Analysis, Vol. 13, pp. 255–298, 2007.

[11] George-John E. Nychas, Panos N. Skandamis, Chrysoula C. Tassou, Konstantinos P. Koutsoumanis, "Meat spoilage during distribution," Meat Science, Vol. 78, pp. 77–89, 2008.

[12] T. F. Brocklehurst, and B. M. Lund, "The effect of pH on the initiation of growth of cottage cheese spoilage bacteria," International Journal of Food Microbiology, Vol. 6, pp. 43–49, 1988.

[13] Wen-Ding Huang, Hung Cao, Sanchali Deb, Mu Chiao and Jung-Chih Chiao, "A flexible pH sensor based on the iridium oxide sensing film," Sensors and Actuators: A, Submitted, 2010.

[14] T. Katsube, I. Lauks and J. N. Zemel, "pH-sensitive sputtered iridium oxide films," Sensors and Actuators, Vol. 2, pp. 399–410, 1981.

[15] Kazusuke Yamanaka, "Anodically electrodeposited iridium oxide films (AEIROF) from alkaline solutions for electrochromic display devices," Japanese Journal of Applied Physics, Vol. 28, pp. 632–637, 1989.

[16] Michel A. Petit, Vincent Plichon, "Anodic electrodeposition of iridium oxide films," Journal of Electroanalytical Chemistry, Vol. 444, pp. 247–252, 1998.

[17] J. V. Dobson, P. R. Snodin and H. R. Thirsk, "EMF measurements of cells employing metal-metal oxide electrodes in aqueous chloride and sulphate electrolytes at temperatures between 25–250°C," Electrochemical Acta, Vol. 21, pp. 527–533, 1976.

[18] K. Nishio, Y. Watanabe, T. Tsuchiya, "Preparation and properties of electrochromic iridium oxide thin film by sol-gel process," Thin Solid Films, Vol. 350, pp. 96–100, 1999.

[19] Akiyoshi Osaka, Toru Takatsuna and Yoshinari Miura, "Iridium oxide films via sol-gel processing," Non-Crystalline Solids, Vol. 178, pp. 313–319, 1994.

[20] Keishi Nishio and Toshio Tsuchiya, "Electrochromic thin films prepared by sol-gel process," Solar Energy Materials& Solar Cells, Vol. 68, pp. 279–293, 2001.

[21] Sheng Yao, Min Wang, and Marc Madou, "A pH electrode based on melt-oxidized iridium oxide," Journal of the Electrochemical Society, Vol. 148, pp. 29–36, 2001.

[22] T. Ativanichayaphong, J. Wang, W. Huang, S. Rao, and J. C. Chiao, "A simple wireless batteryless sensing platform for resistive and capacitive sensor," IEEE Sensors, Vol. 1, pp. 139–142, 2007

[23] A. W. J. Cranny and J. K. Atkinson, "Thick film silver–silver chloride reference electrodes," Meas. Sci Technol, pp. 1557–1565, 1998.

[24] M. Pourbaix, "Atlas of electrochemical equilibria in aqueous solutions," National Association of Corrosion Engineers, pp. 374–377, 1974.

[25] Erno Pungor, "The theory of ion-selective electrodes," Analytical Sciences. Vol. 14, pp. 249–256, 1998.

[26] S. Chen and V. Thomas, "Optimization of inductive RFID technology for product management," IEEE International Symposium on Electronics and the Environment, pp. 82–87, 2001.

[27] E. Haile and J. Lepkowski, "Oscillator Circuits for RTD Temperature Sensors," Application note AN895, Microchip Technology Inc., 2004.

[28] P. R. Troyk and G. A. DeMichele, "Inductively-coupled power and data link for neural prostheses using a class-E oscillator and FSK modulation," IEEE International Conference Engineering in Medicine and Biology Society, Vol. 4, pp. 3376–3379, 2003.

[29] N. Chaimanonart, D. J. Young, "Remote RF powering system for wireless MEMS strain sensors," IEEE Sensors Journal, Vol. 6, pp. 484–489, 2006.

[30] K. Wise, D. Anderson, J. Hetke, D. Kipke, and K. Najafi, "Wireless implantable microsystems: high-density electronic interfaces to the nervous system," Proc. IEEE, Vol. 92, pp.76–97, 2004.

[31] J. J. Rodriguez, M. M. Hernandez, and A. X. Roig, "New methods to determine fish freshness in research and industry," Cahiers Options Mediterraneennes (France), Vol. 51, pp. 63–69, 2000.