Chapter 6

Graphite-Polyimide Sensor

Abstract This chapter explains the fabrication and implementation of sensor patches developed from laser-induced polymer films. Photo-thermal induction of commercial films was done to form graphene that was subsequently used as electrodes in sensor patches via transferring them on sticky tapes. The sensor patches were used for different environmental and industrial applications like salinity sensing, taste sensing, and nitrate sensing.

6.1 Introduction

A novel sensor prototype fabricated from the laser induction of commercial polymer films is showcased in this chapter. This type of sensor patch is different from most of the sensors that are developed for different applications. The fabrication technique used for this sensor can generate conductive material from low cost processing material. The manufacturing cost for each sensor is one of the issues that are currently faced by researchers. One of the reasons for this is due to the high value of the equipment or the raw materials that are used to fabricate the sensors. For example, techniques like photolithography (Herzer et al. 2010) is one of the standard methods that is used for fabricating flexible sensors, has a high equipment cost and requires many steps to prepare the sample and form the electrodes on the substrate. It requires expertise to handle the processing materials to operate them. Thus, it is a state-of-the-art to develop a technique for developing quick and cheap sensors. Recently, the idea of developing conductive materials from polymers (Lin et al. 2014) has been proposed by researchers. This is interesting as it helps to fabricate sensors at a low cost on a larger scale. Graphene is one of the popular conductive materials that is used for fabricating sensors due to its certain advantages over other elements like high electrical conductivity, corrosion resistance (Graphene paints a corrosion-free future), which would reduce the oxidation effect on the electrodes.

This chapter showcases the design and development of the laser-induced sensor patches that simultaneously uses the formed graphene as electrodes on commercial tapes to develop the sensor patches. The fabricated sensor patches were then operated on solutions of different saline concentrations to determine their ability to be used salinity sensors in a range of large and small water bodies. Analysis was also done with these sensor patches for taste sensing by experimenting them with different concentrations formed with five chemicals. The sensors were also tested for determining the nitrate concentration in water bodies. Some of the advantages of these sensor patches lie in their easy fabrication process, and excellent electrical and mechanical properties.

6.2 Fabrication of the Sensor Patches

A schematic diagram for the steps of fabrication of the sensor patches is shown in Figure 6.1. Commercial PI films (Zibo Zhongnan Plastics Co., Ltd.) were considered as the raw materials to fabricate the sensor patches. A CO₂ laser system (Model: OLS 6.75 CO₂ laser system, laser spot diameter: 150 microns) was used for the operation on the thermal induction of graphene on the PI films.

Figure 0.1 Schematic diagram of the steps of fabrication of the graphene sensor. (a) The polyimide film, with a thickness of around 120 microns, is taken as the substrate material for the laser writing process. (b) The laser writing was done on the film. (c) The thermally induced material is shifted manually to the Kapton tape by compressing it against the generated graphene. (d) The final product.

The illustrations of the fabrication steps are shown in Figure 6.2. Initially, the polymer film was attached to a glass substrate as a template for its support as shown in Figure 6.2 (a). CorelDraw designing software was utilized for designing the electrodes in an interdigital pattern. Six pairs of electrode fingers were designed with each one having a length of 500 microns and a width of 100 microns. Figure 6.2 (b) depicts the laser induction process done on the attached polymer film. The sp^3 hybridized carbon atoms of the PI film was photo-thermally converted to sp^2 hybridized atoms of graphene. Power, speed and z-axis were some of the laser parameters that were optimized for the laser-induction process. Power (W) is defined as the amount of energy that the laser nozzle operates on. Speed (m/min) defines the agility of the nozzle to determine the movement of the nozzle over the sample in the x-y direction. Z-axis (mm) defines the position of the focal point of the laser over the sample. This was achieved by operating on the height of the laser platform in the z-direction.

Figure 0.2 Fabrication steps of the sensor.

The optimized values considered for fabricating the sensor patches were: Power: 9 watts, speed: 70 m/min, z-axis: 1 mm. The photo-thermally induced graphene was manually transferred to a commercial Kapton tape having a thickness of 1000 microns. Although both the processing material and Kapton tape are made of PI, the commercial polymer films were considered as the processing material instead of Kapton tapes for laser writing is due to two reasons. Firstly, due to the higher thickness of Kapton tapes, photo-thermal induction was not possible to disintegrate the sp^3 hybridized carbon atoms of the PI films to sp^2 hybridized carbon atoms of graphene. This could have been done only possible with thinner films. Secondly, the sticky nature of the Kapton tape would lead to the subsequent coagulation of the thermally-induced graphene, damaging the design of the electrodes. The positioning of the Kapton tape over the induced graphene is shown in Figure 6.2 (c). The transfer of graphene was done via the application of manual pressure over the tape.

Figure 0.3 Front and rear views of the sensor patch.

The pressure was initially applied first in the region of the electrodes of the sensor and consequently moving towards the sensing area of the sensor patches to ensure proper adherence of the induced

graphene on the Kapton tapes. The tape was then carefully pulled off from the PI film to avoid the damage on the design of the transferred graphene. Figure 6.2 (d) depicts the final step of the process where the sensor patch consisted of transferred conductive material on the Kapton tape. A difference in electrical conductivities of less than 20 mS/m was obtained between the induced and transferred graphene. The front and rear views of the final product are shown in Figure 6.3. The SEM images depicting the top and cross-sectional views are shown in Figures 6.4 (a) and 6.4 (b). It is seen from the SEM images that the edges and electrode lines of the transferred induced material came off cleanly on the Kapton tapes.

Figure 0.4 SEM image of (a) Top view of an electrode finger of the sensor patch (b) Zoomed top view showing the electrode lines.

6.3 Complex Nonlinear Least Squares Curve Fitting

The characterization of the developed sensor patches was done to analyze their responses to the dielectric materials operating on different permittivity values. The equivalent circuit was determined to obtain the electrical parameters using the complex nonlinear least square curve fitting (CNLS) technique. It operates on the electrochemical spectrum analyzer algorithm by obtaining a comparative study between the experimental values with the predictive responses. This was done to obtain the system kinetics

explaining the diffusion process occurring at the electrode-electrolyte interfaces. The Nyquist (Cole-Cole) plot for each chemical was analyzed by plotting a curve between the real part (resistance) and imaginary part (reactance) of the impedance as the x-axis and y-axis respectively. Statistical analysis was done using a specific algorithm to determine the amplitude of the residual mean-square value using equation 6.1 (Zia et al. 2015):

$$r_{amplitude}^2 = \sum_{i=1}^N \frac{(Z'_{iobs} - Z'_{icalc})^2 + (Z''_{iobs} - Z''_{icalc})^2}{Z'^2_{iobs} + Z''^2_{iobs}} \quad (6.1)$$

where

$r_{amplitude}^2$ determines the quantitative values for the differences between the simulated and experimentally obtained values.

Z'_{iobs} and Z'_{icalc} determines the observed and calculated values for the real part of the impedance.

Z''_{iobs} and Z''_{icalc} determines the observed and calculated values for the imaginary part of the impedance.

Figure 0.5 Least squares curve fitting plot regarding Nyquist plot for the profiling of the sensor done in air. The red dots indicate the experimental data with the green line being the fitted curve.

The characterization of the sensor patches was done by analyzing their profiles in the air to obtain their equivalent circuits as shown in Figure 6.5. The change in the responses of the sensor patches was studied concerning the real (R) and imaginary (X) parts of the impedance (Z). An average of three values was considered for each sensor to ensure repeatability of their responses. These impedance values were set in the electrochemical spectrum analyzer to obtain the equivalent circuit concerning the responses of the sensor patch in the air. The least square curve was fitted in the Nyquist plot of the experimental values to obtain the equivalent circuit as shown in the inset of the figure. The impedimetric components of the equivalent circuit consisted of different components (C_{int} , C_{sol} , and R_{sol}). Each of these individual parameters influences the resultant kinetic response of the sensor patches. C_{sol} and R_{sol} define the solution capacitance and resistance values respectively which relies on the properties of the experimental medium. When there is a change in the solution medium, the conductive properties related to the sensor and also the relative permittivity (ϵ_r) changes. This subsequently changes the solution resistance and capacitance values. C_{int} defines the internal capacitance which occurs due to the electrode design.

Table 0.1 Equivalent circuit parameters (as shown in the inset of Fig. 7(b)).

Equivalent circuit electrical parameters	Curve fitted value	Error%
C_{int} (pF)	71.22	1.95
C_{sol} (pF)	8.99	0.82
R_{sol} (k Ω)	343	4.05

The internal capacitance also alters when the experimental medium changes, but the quantity of this change is negligible in comparison to the changes in the values of solution capacitance and resistance. The internal capacitance mainly depends on the surface area (A) and interdigital distance (d) of the electrodes. The electrode resistance can be considered very small in this case. The simulation

was done with the electrochemical spectrum analyzer for the same range of frequency sweep done between 1 Hz and 10 kHz to obtain a comparison between the experimental results with the theoretical results. Table 6.1 shows the values of the electrical parameters that includes the corresponding errors obtained by determining the differences between the experimental values and curve fitted values for the passive electrical parameters in the equivalent circuit. It is seen that the error values obtained for each parameter were within 5%, which suggests that mean square values is within the range of 10^{-2} (EIS Spectrum Analyzer).

6.4 Salinity Sensing

Water bodies contain different elements that sustain plant and animal life. Each of the constituents has a certain effect on the life-sustaining in the water bodies. The effect of salinity on marine flora and fauna is one of the main factors (Changes in Marine Salinity Levels ; Natural environment). Salinity in the water bodies like sea and rivers can be defined as the quantity of salt present there. The unit of salinity is defined by the electrical conductivity per unit distance ($\mu\text{S}/\text{cm}$) at a temperature. There are ongoing research works to calculate the effects of changes in the salinity level in different water bodies. Some of the common factors affecting the levels are the rise in temperature, oil spills in the water bodies, discharging of waste materials and climatic changes. A rise of the saline levels in the water bodies is detrimental to the plants living in it. The growth of plants and seed germination is adversely affected by even slight increase or decrease in the salt concentrations. Higher levels of salinity can lead to difficulty for the plants in extracting water from the soil and can be toxic for their sustainability. A small increase in salinity level increases the density of certain water bodies like rivers, thus sinking it to the bottom and floating it across the river basins. A lot of research work (Rahman et al. 2012; Robinson and Nakkeeran 2012; Wang et al. 2012; Wu et al. 2011) is going on currently to determine the optimal concentrations of salt in the water bodies. The available techniques are expensive to remove the excess salt present in the water bodies as a result of the high-quality equipment required to extract the salt. The Murray-Darling Basin report 2015-16 (Murray-

Darling Basin Authority annual report 2015-16) showcased the removal of around 524,728 tons of salt water from the River Murray, Australia in one a single year. The presence of this much amount of salt water is alarming considering its presence in just one water body.

The research work done (Bhat 2005; Gadani et al. 2012; Huber et al. 2000; Jonsson et al. 2013; Le Vine et al. 2010; Men et al. 2008; Rahman et al. 2011; Reul et al. 2014; Scudiero et al. 2012) based on the monitoring and evaluation of salinity involves certain demerits that deters them to be used on an industrial scale. Some sensors like that optical ones are used to measure the salinity (Huber et al. 2000) for a concentration from 200 mM to 2M. Apart from the high cost of fabrication of the fabricated sensor formed with the chloride-quenchable fluorescent probe, the prototypes do not measure the small changes having small sensitivity. Other techniques involve the utilization of SMOS satellites developed by NASA (Reul et al. 2014) for measuring moisture in soil and salinity in the ocean. Even though this approach would be much more convenient than the previous one, the cost of the system is high and would be difficult to implement in smaller water bodies. Grating sensors used for salinity and temperature measurements are made up of acrylate and polyimide-coated fibers via determining Bragg's wavelength (Men et al. 2008). The biggest demerit of employing a coating layer on the fibres is their difficulty to be reused. Thus, it is state of the art to fabricate a low-cost, efficient sensing system that can be used to determine the changes in the salinity level to apply immediate remedial measures. Some of the other impedance measurement systems that have been proposed earlier (Jonsson et al. 2013) have certain demerits like low sensitivity and a complicated embedded system that need time and expertise to be operated. The sensors that are being developed with MEMS technology have a high fabrication cost. Another problem is the operation of these sensors in the MHz range which would require high input power. The development of laser-induced graphene sensors shown in this paper was initially tested with a specific range of salt concentrations with the proposal of fabricating a fully functionalized sensing system. The validation of the initial sensing system was followed by fabricating a microcontroller-based sensing system. Figure 6.6 depicts the block diagram of the working principle of the proposed microcontroller-based sensing system. The operation of the

sensor was controlled by the embedded signal-conditioning circuit, which operates on its output to generate an amplified resultant signal. The fabrication and implementation of this system are explained step by step in subsequent sections.

Figure 0.6 Block diagram for the proposed microcontroller-based sensing system for salinity measurement.

6.4.1 Experimental Setup

Sodium Chloride (SA046- 500G) and De-ionised MilliQ[®] water (Resistance: 18.2 MΩ cm and pH: 6.71) were used as the solute and solvent respectively to develop the salt solutions. Serial dilution process was done to develop a series of solutions ranging between 40000 ppm and 4 ppm. Initially, a stock solution of 40000 ppm was formed via the mixture of 4 g of solute to 100 ml of solvent. After the experimentation with this stock solution, the second experimental solution was formed by pipetting 10 ml of the previous solution to 90 ml of de-ionized MilliQ[®] water to prepare 4000 ppm of salt solution. Followed by the experimentation, the third solution was prepared by pipetting 10 ml of the previous solution into 90 ml of deionized MilliQ[®] water to form 400 ppm of salt solution. This procedure was continued till a 4-ppm salt solution was prepared and experimented. The experimental setup depicted in Figure 6.7 shows the use of a

HIOKI IM 3536 LCR Hi precision tester for data acquisition purposes. The LCR meter connected to the sensor patch via Kelvin probes from one end was connected to the computer via a USB - USB cable for data collection using an Excel file via an automated data-acquisition algorithm. The sensor patch was attached to a board using biocompatible tapes (3M Ruban Magique^{MC}) to keep it stable in the water during experimentation. The sensing area of the patch was immersed carefully into the solution to avoid the connect of the bonding pads of the sensor and the Kelvin probes with the solution. After each round of experiment, the sensor patch was washed properly with MilliQ[®] water and dried inside the oven for 10 minutes before reusing it for the next solution. A sinusoidal signal having a voltage of 1 V peak-to-peak was applied as an input from the LCR meter where the frequency was swept between 1 Hz and 10 kHz. The resistance (R) and reactance (X) values were taken from the LCR meter.

Figure 0.7 Experimental setup is showing the attachment of the sensor patch to the LCR meter via Kelvin probes. The sensing area of the patch was immersed in the solution. The LCR meter was connected to the laptop to collect the data.

6.4.2 Results and Discussion

The responses of the sensor patch to the tested samples are depicted in Figures 6.8 and 6.9 for the resistance (R) and reactance (X) values respectively. It is seen that the sensor patch can clearly distinguish the different tested salt concentrations. Although it is seen from Figure 6.8 that the changes in the resistance values are symmetric for the tested solutions, the change in the reactance values as seen from Figure 6.9 is only prominent for a certain range. There is a decrease in the resistance concerning the increase in the salt concentration as a result of the increase in the ionic current passing through the circuit. The operating frequency of had an important role to play for the changes in reactance values in comparison to the changes in the resistance values. For the changes in reactance values, the frequency ranged between 0.4093 kHz – 7.152 kHz showed a strong change for the tested concentrations. The reactance values changed due to the capacitive part of the sensor was due to both the frequency and the concentration of the sample.

Figure 0.8 Response of the sensor patch for different concentrations of salt regarding resistance and frequency.

Figure 0.9 Response of the sensor patch for different concentrations of salt regarding the reactance and frequency.

Figure 0.10 Response of the sensor patch for different concentrations of salt regarding Nyquist plot.

The reactive changes of the sensor patches were due to the changes in the faradic currents going through the tested concentration.

Figure 6.10 shows the Nyquist plotted between the real and imaginary parts of the impedance. The readings depict a show a clear distinction between the different sample concentrations.

Figure 0.11 Standard curve for different experimental concentrations.

A frequency (4.205 kHz) was among the operating range was selected to form the characteristic curve as shown in Figure 6.11. The selected frequency obtained the highest difference in the experimental values among the salt concentrations. The sensitivity of the sensor patches was 0.005 Ω /ppm, as can be obtained from the slope of Figure 6.11. A real sample of unknown concentration was taken from the river was taken for testing to validate the proposed salinity system. After sweeping the frequency between 1 Hz and 10 kHz, the response of the patches towards the selected frequency value was considered to form the standard curve. The experimental values of the tested sample at operating frequency (4.205 kHz) were: Resistance (R): 1828.35 Ω , reactance (X): 1651.7 Ω . Placing the resistance value to the equation acquired from the standard curve,

$$y = 0.005 * (x) + 1651.7 \quad (2)$$

$$1828.35 = 0.005 * (x) + 1651.7 \quad (3)$$

$$x = \frac{1828.35 - 1651.7}{0.005} \quad (4)$$

$$x = 35330 \quad (5)$$

The concentration of the sample obtained from the above calculated was 35330 ppm. This was confirmed with a refractometer which is a standardized device used to calculate the salinity level of real samples in the marine and biological industries (Grosso et al. 2010; Malarde et al. 2008). The actual concentration of the unknown sample was 35000 ppm, which ensures the experimental value to be very close to the actual value with an error % of 0.9. Figure 6.12 depicts the equivalent circuit for the Nyquist plot of the values obtained from the tested samples. It is seen there ca change in the components of the two equivalent circuits in Figures 6.5 and 6.12.

Figure 0.12 Least-square curve is fitting for the Nyquist plot with the experimental data.

A constant-phase element (CPE) has been added in the equivalent circuit in series with the internal capacitor of the sensor. This CPE represents the adsorption capacitance (C_{ad}) that arises as a result of the ionic diffusion process between the sensing surface of the electrodes and the bulk solution (Mamishhev et al. 2004). The solution capacitance (C_{sol}) and resistance (R_{sol}) are two pivotal parameters that

determine the change in response of the patches. Table 6.2 represents the different parameters of the equivalent circuit after the experiments along with their values and error rate. The error rates obtained for each of the elements in the generated equivalent circuit is less than 5% (Rahman et al. 2014). Figure 6.13 depicts the response of the sensor patches towards the changes in temperature regarding resistance values for the measurements taken at five different concentrations at the chosen frequency (4.205 kHz) for five temperature values ranging between 10 °C and 50 °C.

Table 0.2 Equivalent circuit parameters along with their limits, result and error % to determining the fitted curve on the experimental data.

Equivalent circuit electrical parameters	Curve fitted value	Error%
C_{sol} (μF)	1.171	2.46
R_{sol} ($k\Omega$)	18.6	0.49
C_{int} (μF)	6.8	0.95
C_{ad} (μF)	113	2.53

Figure 0.13 Dependence of the sensor response towards the temperature changes for different salt concentrations.

It is seen that the changes in resistance values for each sample is negligible concerning the changes in temperature. Figure 6.14 depicts the repeatability of the sensor responses where experiments with each tested were carried out six times with a gap of two hours between each experimental cycle. Similar to the temperature responses, it is seen from the repeatability of sensor responses for each of each concentration is very high and the deviation from the mean value lies within 2%. To develop a real-time sensing system, the same frequency value (4.205 kHz) was used in the microcontroller-based system to determine if the changes in the concentration of the sample can be determined using the embedded system. A conditioning circuit was formed with the microcontroller before it was used for testing the samples.

Figure 0.14 Repeatability of the sensor response illustrated with six measurements with each salt concentration.

6.4.3 Microcontroller-based Sensing System

Arduino Uno and the Arduino Integrated Development Environment (IDE) were considered as the microcontroller (μC) device and the associated software, respectively, to form the embedded system. Figure 6.15 shows a schematic diagram for the user to connect the sensor to the microcontroller-based system. The

output from the sensor was passed via a buffer and a low-pass filter to the microcontroller. The voltage of 3.3 V with a sinusoidal signal was fed to the microcontroller, and the output was passed through an amplification circuit. This amplifier consisted of a buffer and an active low-pass filter to gain the maximum response from the sensor by reducing the noise and amplifying the signal. Figure 6.16 shows the connection of the sensor with the amplifying circuit. The non-inverting gain of 23 was provided to the output signal of the sensor to have an amplified response of the output voltage from the sensor taking place due to the difference in salt concentrations. The output of the low-pass filter was fed as the analog input to the microcontroller's analog-to-digital (ADC) converter. Figure 6.17 shows the voltage readings for the measured samples. It is seen that the response of the sensor is almost linearly dependent on the concentration. The aim of this proposed idea to obtain a system that gives a full-scale voltage reading during the testing with real-time seawater samples. The microcontroller-based system would be necessary in real-life situations where a selective part of the sensing system can be capsuled inside a waterproof case to determine the changes in saline concentrations of the water.

Figure 0.15 Block diagram depicting the connection of the sensor to the microcontroller. The buffer and low-pass filter were added to the circuitry to improve the output from the sensor.

Figure 0.16 Circuit design for the conditioning circuit used to process the sensor output before feeding it to the microcontroller.

Figure 0.17 Response of the microcontroller for different salt concentrations.

6.4.4 Conclusion

This section describes the fabrication and implementation of a sensing system to detect different salt concentrations in water bodies. The main aim to develop this system was to analyze the current problems faced by flora and fauna existing inside water bodies. Even though the system can detect a range of saline concentrations, there are some issues that need to be addressed before implementing the developed system for real-time applications. Firstly, in addition to sodium chloride, there are other molecular constituents present in the water bodies which can affect the response of the sensor in real-time applications. This can be attained by including the selectivity towards the chosen element. Secondly, the response of the sensor for the saline concentrations can also be influenced by elements having ionic properties like sodium and chloride ions. The similarity in the properties as a result of the similarity in their structures, densities and electron affinities. The issues related to similarity occurs especially with salts having sodium as the cation. This would mislead the monitoring unit leading to erroneous results. These problems if addressed can lead to the development of an enhanced low cost, fully-functionalized salinity measurement system.

6.5 Taste Sensing

Among the five different senses of sight, touch, smell, hearing, and taste, the work is done on the last one is the least. The significance of taste sensing holds its role to determine the condition of a person. A human tongue includes thousands of taste buds, each of which is made up of hundreds of taste cells (Ha et al. 2015). People with taste disorders (Taste disorders) are affected with one of the more significant problems in recent years. More than 200,000 people are effected every year from taste disorders, especially the number of children being one out of every ten (Taste disorder 'prevalent in children') in Australia. This is a very alarming, especially with the view of leading other disorders like obesity and high blood pressure from taste abnormalities. Although the loss of the taste buds for a normal person starts happening after the age of 50, some of the other causes like respiratory infections, radiation therapy and surgeries near

the head or neck region can lead to the loss of taste buds. Although one of the common choices to deal with the people suffering from taste buds problems is otolaryngologists, researchers have been working to deal with it in a scientific manner (Chen et al. 2010; Riul et al. 2003).

An electronic tongue (e-tongue) has recently been a popular choice for taste sensing (Krantz-Rülcker et al. 2001; Tahara and Toko 2013), where a complicated system had been proposed which replicates the functions of a real human tongue. Even though the e-tongue does function similar to a real tongue, there are certain demerits associated with them which makes it compelling for the researchers to find alternative options. Some of the demerits are the high cost of fabrication of the structure (Haddi et al. 2015), increased complexity (Toko et al. 2016) and difficulty of common people to afford it (Etoh et al. 2008). Another major disadvantage related to the e-tongue is the change in its responses based on temperature and humidity (Baldwin et al. 2011). The adsorption of the analyte on the selective sensing surface does limit the reusability of the sensor prototypes (Ciosek and Wróblewski 2011). So, it is desirable to opt for alternative options that could be considered for taste sense. Although some of the groups working in this area have developed sensing systems for taste assessment (Huang et al. 2006), certain limitations associated with their work reduces the potentiality of their uses. For example, the systems that were based on the recognition of just one (Medeiros et al. 2009) or two (Zhao et al. 2003) taste types can be considered for real-time applications. The motive behind our work is to have a sensor prototype which can clearly distinguish the five fundamental taste types. This could help us to fabricate a real-time system that can be used to determine the concentration of a taste in a food material. The succeeding sections report the implementation of the laser-induced graphene sensors for taste sense.

The taste buds of a human being can be categorized into five categories namely sour, salty, bitter, sweet, and umami. Although there are lots of food materials that can be sub-divided into one of these sectors, researchers have classified (The Five Senses of Sensors - Taste) the following chemicals for experimental purposes that can be precisely replicated to these five tastes:

- Sour- Citric acid
- Salty- Sodium chloride
- Bitter- L- tryptophan
- Sweet- Sucrose
- Umami- Guanosine monophosphate (GMP)

After the sensor was fabricated, the chemicals mentioned above were tested at four fixed concentrations. The concentrations were based on the minimum amount (Concentration of chemicals in food samples; Medeiros et al. 2009) of that chemical present in food. Then a comparison was done on each of the four concentrations of the five taste types to verify the differences in their responses.

6.5.1 Experimental Setup

The experiments with the graphene-based sensor patches along with the different chemicals were performed inside the laboratory environment at a fixed temperature (25 °C) and humidity (RH 50%) conditions. Figure 6.18 shows the experimental setup used for testing and data collection. Biocompatible tape (3M 810D Ruban Magique^{MC}) was used to attach the sensor patch to a wiring board to keep it fixed inside the sample during experimentation. The sensing area of the patch was immersed carefully inside the sample in a way such that the bonding pads were not touching the solution. A HIOKI IM 3536 LCR High Precision Tester was attached to the sensor with Kelvin probes from one end during experimentation to analyze the changes occurring in the sensor. An input signal of $1V_{rms}$ was provided as the input from the tester to the sensor. The analyzer was in turn connected to a desktop via a USB-USB cable for collecting the data obtained from the sensor in Microsoft Office Suite using an automatic-data-acquisition algorithm. Three readings per solution were taken as an average having an interval of 5 seconds between each cycle to validate the repeatability of the responses of the sensor patch. The sensor was washed thoroughly after each cycle of experiment with deionized water followed by drying it in an oven for

10 minutes followed by using it for the next experiment. Five different chemicals namely Sodium Chloride (Chem-Supply, SA046-500G), Citric acid (Sigma- Aldrich, 791725-500G), Sucrose (Sigma- Aldrich, S7903-250G), L-Tryptophan (Sigma- Aldrich, T0254-25G) and GMP (Sigma- Aldrich, G8377-5G) were used to analyse the responses of the sensor patches to determine the tastes of salty, sweet, sour, bitter and umami respectively. The solutions were formed by adding the chemicals with deionized MilliQ water[®] (Resistance: 18.2 M Ω cm and pH: 6.71) as solute and solvent respectively. Experiments with four different concentrations namely 1000 ppm, 100 ppm, 10 ppm and 1 ppm for each chemical were carried out using serial dilution mechanism. The first solution of 1000 ppm for each chemical was formed by adding 0.1 gm of the solute to 100 mL of deionized water. After the experiments with the first concentration, 10 mL from this solution was pipetted into 90 mL of deionized water to develop a solution of 100 ppm. Similar steps were performed to form solutions of 10 ppm and 1 ppm for experimental purposes.

Figure 0.18 Experimental setup during the analysis of different chemicals.

6.5.2 Results and Discussion

Figures 6.19–6.28 depict the responses of the sensor patches for different chemicals regarding resistance and reactance for a defined frequency range. Figures 6.19 and 6.20 show a significant change in

the responses for citric acid concerning frequency. The presence of the two distinct operating frequency ranges for the resistance values of citric acid can be ascribed to the presence of four single-bond hydroxyl ions (OH) in its structure (Electrical Conductivity of Aqueous Solutions). The increase in the resistive values at higher frequencies can be ascribed to the presence of solution resistance (R_s) (Kim et al. 2015). The change in the reactance values for citric acid can be ascribed to the adsorption capacitance (C_{ad}) of the solution and the presence of the double-layer capacitance (C_{dl}) at the electrode-electrolyte interface. This leads to an initial increase in reactance values concerning frequency, which after a certain point goes down due to the shorting of the double-layer capacitance. The electrochemical nature of sucrose as seen from Figures 6.21 and 6.22 can be studied by noting the presence of two isomeric forms of this compound. The existence of the glycosidic linkage between the carbon atoms of the glucosyl and fructosyl subunits can be mainly attributed to the change in the impedance behavior of sucrose.

Figure 0.19 Response of the sensor for citric acid (sourness) in terms of resistance vs frequency.

Figure 0.20 Response of the sensor for citric acid (sourness) regarding reactance vs. frequency.

The resistance values increase with an increase in frequency as a result of the increase in ion-solvent interactions at higher frequencies (Juansah and Yulianti 2016). The behavior of the reactance values for sucrose can be ascribed to the same mechanism as that of citric acid. The double-layer capacitance (C_{dl}) plays an important role in the change like the reactance values at lower and higher frequencies. The nature of the response of the sensor towards sodium chloride as seen in Figures 6.23 and 6.24 infers that the conductivity of sodium chloride is highest for the tested chemicals. This is as a result of the ionic properties of its structure. The resistance and reactance values for sodium chloride at lower concentrations can be ascribed to the polarisation of the ions. After a specific concentration, the nature of the resistive and reactive values remains constant for all frequencies, as the sensor output is only due to the solution resistance (R_s) and adsorption capacitance (C_{ad}) respectively. The electrochemical behavior of L-tryptophan and GMP, as seen from Figures 6.25-6.28, are very similar. This is due to their similar chemical structures. The change in the resistance values for both these chemicals can be solely attributed to the solution resistance (R_s).

Figure 0.21 Response of the sensor for sucrose (sweetness) regarding resistance vs. frequency.

Figure 0.22 Response of the sensor for sucrose (sweetness) regarding reactance vs. frequency.

Figure 0.23 Response of the sensor for sodium chloride (saltiness) regarding resistance vs. frequency.

Figure 0.24 Response of the sensor for sodium chloride (saltiness) regarding reactance vs. frequency.

Figure 0.25 Response of the sensor for L-tryptophan (bitterness) regarding resistance vs. frequency.

Figure 0.26 Response of the sensor for L-tryptophan (bitterness) regarding reactance vs. frequency.

Figure 0.27 Response of the sensor for GMP (umami) regarding resistance vs. frequency.

Figure 0.28 Response of the sensor for GMP (umami) regarding reactance vs. frequency.

The nature of the reactance for L-tryptophan can be ascribed to the presence of a carboxylic functional group and a secondary amino

group in its chemical structure. The double bond in the oxygen ion of the carboxylic group leads to an increase in the current at higher frequencies (Zhao et al. 2014), eventually reducing the resultant reactance values. The electrochemical behavior of GMP can only be attributed to the presence of the phosphate group in its structure. At lower frequencies, the sp^3 hybridized bonds between the phosphorus and oxygen atoms deter the change in response of GMP to the applied electric field. The higher frequencies create a polarisation of the oxygen atoms which increases the electronegativity (Properties of the Phosphate Group) and as a result of which, the reactive values slightly changes.

A comparison has been done for the reactive responses of the sensor patches to the five tested chemicals to analyze the differences between their responses. The reactance was selected instead of resistive values as they indicated changes in the relative permittivity (ϵ_r) between the electrode and electrolyte interfaces. Figures 6.29 – 6.32 shows the reactive values for the five chemicals, each of which has four tested concentrations. Prominent differences can be seen between all the values of the chemicals for each of the tested concentration. Even though for bitter and umami, the responses are in proximity to each other, the nature of their changes in the reactance values with the change in concentration is different. The comparative responses of the reactive values can validate that the sensor patches are capable of differentiating each chemical. One of the concentrations (100 ppm) was selected to determine the change in conductivity concerning frequency for these chemicals. The change in the electrical conductivity of the five solutions can be attributed to the relative permittivity of each of the samples. Even though the relative permittivity and electrical conductance are defined to be static and dynamic properties of the sample respectively, an increase in the electrical conductivity will gradually increase the relative permittivity of the sample (Malicki and Walczak 1999; Robinson et al. 2003). Figure 6.33 depicts the differences in conductivities expressed in $\mu S/m$ among the five chemicals. As seen, sucrose has the least conductivity of the five chemicals which is evident from the comparative reactance values shown in Figure 6.22. Similarly, sodium chloride depicted the highest conductivity, as evident from its least impedance shown in Figure 6.24. L-tryptophan and GMP lie in

the second and third least conductive chemicals due to the stability of their structures in comparison to sodium chloride and citric acid.

Figure 0.29 Comparison between the responses of the sensor patch to different chemicals for the concentrations of 1 ppm.

Figure 0.30 Comparison between the responses of the sensor patch to different chemicals for the concentrations of 10 ppm.

Figure 0.31 Comparison between the responses of the sensor patch to different chemicals for the concentrations of 100 ppm.

Figure 0.32 Comparison between the responses of the sensor patch to different chemicals for the concentration of 1000 ppm.

Figure 0.33 Comparison of the conductivity detected by the sensor for different chemicals at a concentration of 100 ppm.

6.5.3 Conclusion

This portion of the chapter elucidated the utilization of the graphene-polyimide sensors as a taste sensor. These patches were tested to test different chemicals that resemble the constituents of a range of food products. The sensor patches were capable of individualizing the chemicals via different sensor responses to the tested chemicals. The sensor patches displayed significant repeatability in their responses to the experimental solutions. There was no hysteresis present in any of responses to the tested concentrations. The response time of these sensor patches was around two seconds that depended on the impedance analyzer, showing their capability to respond to dynamic conditions. The recovery time of the sensor patches obtained during the experimental process was around 10 mins that included the thorough washing of the experimented sensor patch with deionized water and subsequently by drying it.

The experimental results look promising for considering the sensor patches to be a replacement for the commercially available e-tongue for taste sense. These patches can be considered for any person

who is suffering from a taste-disorder disability or can preferably be installed in any food-producing industry to analyze the concentration of the taste of a food product. The sensor patches can also be utilized by the pharmaceutical industries before the injection of drugs in a patient to determine the consequences (Bhattacharyya and Bandhopadhyay 2010). Other than the consumable products, the patches can also be used for testing certain chemicals like dyes (Tahara and Toko 2013), where the precise concentration of any particular synthesized material is pivotal to its performance. Another big merit of these sensor patches is related to the independence of their output on temperature or humidity, as a result of which, it can be used at any operating condition. The simple operating principle and low fabrication cost of the sensor patches are some of the other merits of these patches in comparison to other prototypes that are used in previous research work done on taste sense.

However, there are some glitches that need to be rectified before the real-time application of these sensors. The reactive values of the sensor patches at low frequencies for L-tryptophan and GMP for the four tested concentrations do not differ much from each other. This can provide erroneous results to the monitoring unit about the exact value of a concentration. This makes it mandatory to operate the sensor patches at higher frequencies, thus having a high input power. Secondly, when the sensor patches are considered for real-time applications, the reuse of these patches regarding the optimal sensing area conditions holds a pivotal role in their appropriate responses. One of the proposed ways to achieve this is to install an automated robotic arm fitted with the sensor patches and a water-hose nozzle. The arm could be automated in such a way that the nozzle of the hose would wash the sensing area after each of the experimental rounds, and subsequently allowing it to dry for 10 minutes before they are used for next round. Thirdly, the responses shown above gives us with a platform for a novel sensing system that can be considered as a taste sensor, by the experimentation with individual chemicals individually. The analysis of amalgamation of these chemicals should be done to determine their combined response for as a real-time system. The sensor patches can be tested with a mixture of chemicals to determine the presence of a chemical with a specific concentration. One of the proposed technique would be the introduction of

selectivity to identify a particular analyte. The sensing area can be coated with a layer containing the template of the chosen molecule. This would make the sensor selective to that chemical, as a result of which, the concentration can be determined. Another idea is to introduce the wireless operation of the sensor patches by including RFID tags along with the patches to upgrade their performances for taste-sensing purposes. RFID tags can be integrated on the sensor patches during their fabrication and operated on a specific frequency. Based on the application of taste sensing, low-frequency passive RFID tags can be preferred to be installed in the chips. This would be advantageous for industrial uses, as a reader could be used at the monitoring unit for avoiding any manual intervention during the experimental and data-collection stages. The amendment of the glitches mentioned above with their possible remedies would certainly assist to fabricate and implement a fully-functionalized taste sensing system.

6.6 Nitrate Sensing

Nitrogen is one of the essential nutrients occurring in the nitrogen cycle have to be one of the nitrate nutrient sources for the living beings of the Earth. Excessive nitrate leaching causes a loss from soil into water bodies, treating the aquatic life and human health (Cameron et al. 2013; Hester et al. 1996; Wild and Cameron 1980). The presence of nitrogen can be widely found in the environment as a result of their solubility in water. The surface water in New Zealand is contaminated by the presence of nitrate ions due to excessive agricultural usage of land and cattle farming, which consequently possess a serious threat to the quality of the surface water (Holland and Doole 2014; Monaghan et al. 2007). An excessive quantity of nitrate-N in rivers assist to grow periphyton and macrophytes to very high levels (Davies-Colley and Wilcock 2004). They cause a reduction in the oxygen levels in water, which results in hampering the aquatic life. Contaminated nitrate-N water may lead to serious illnesses like congenital disabilities, spontaneous abortions intrauterine growth restriction and increasing the potential of cancer (Brender et al. 2004; Daniel et al. 2009; Greer and Shannon 2005; Squillace et al. 2002). Also, long-term accumulation of nitrate-N increases the risk of

affecting animal and human health. The blue-baby syndrome is one of the diseases that can be caused by drinking water with elevated nitrate concentrations (Organization 2017).

There has been a considerable amount of work done to determine the concentration of nitrate ion in water. The spectrophotometric method is one of the popular techniques used to determine nitrate-N in water using chemical reagents (Narayana and Sunil 2009). The Griess reaction is considered for the reduction of nitrate ions (Miranda et al. 2001). Ion chromatography (Dudwadkar et al. 2013), optical fibre sensors (Ensafi and Amini 2012; Pellerin et al. 2013), planar electrode sensors (Wang et al. 2015), ion-selective electrodes (Schazmann and Diamond 2007), palladium nanostructures (Pham et al. 2014) are some of the techniques that are used to measure nitrate ions in water. Even though the techniques mentioned above have been successfully validated, most of them are laboratory-based and create a lot of chemical waste, which has detrimental effects on the environment.

Some of the regional communities in countries like New Zealand monitor the water samples from different water bodies like rivers, lakes, and groundwater. The water management collects the samples at regular intervals, usually with an interval of a monthly basis. The laboratory-based methods such as spectrophotometry or ion chromatography were employed to determine nitrate-N concentrations. However, it is difficult to determine the accurate effects of leaching of nitrate-N into rivers or lakes as a result of the fluctuating dynamic water system. Therefore, the monthly sampling measurements would be ineffective to determine the actual nitrate-N profile. The misplacement of information would influence the understanding of the seasonal effects, which would subsequently affect the total nitrate-N estimation. This causes trouble for the policymakers wanting to come to proper conclusions. The work described below employs an Internet of Things (IoT)-enabled smart sensing system to determine the nitrate-N concentration for real-time application. The aim of using the IoT-based system is to create a situation in which the basic information of the developed system is shared in real time. The proposed sensing system will measure the nitrate-N concentration in real time situation and transfer the data to the cloud server pertaining to the system to be considered as a

distributed network. The temperature compensation of the proposed system is also included to increase the efficiency of the measured samples. The nitrate-N and temperature measurement along with their validation are explained in the subsequent sections.

6.6.1 Experimental Setup

Similar to the previous applications explained in this chapter, Electrochemical Impedance Spectroscopy (EIS) has been employed for the measurement of nitrate concentration. Among the different methods available for impedance measurement, Frequency Response Analyser (FRA) can be considered as the de facto standard for EIS measurement. A single input sinusoidal signal with an amplitude ranging between 5 mV and 15 mV is provided as an input in FRA. The frequency is swept in a certain range with a direct current bias voltage, where the signal is applied between the working and sensing electrode. The measurements were done at a certain frequency range to obtain a complete impedance profile. The equation given below can be used to determine the total impedance of an electrochemical system:

$$Z = R + jX \quad (7.2)$$

where Z defines the impedance (Ω); R defines the resistance (Ω) which is the real part of the impedance; X defines the reactance (Ω) which is the imaginary part of the impedance.

The impedance profile data can be depicted graphically as a Bode plot and a Nyquist plot which is also known as Cole-Cole plot. The plot also shows the electrochemical changes taking place at the electrode-electrolyte interfaces. A clamp was used to connect the sensor with the HIOKI IM 3536 LCR meter. The frequency sweep was done between 10 Hz and 100 kHz to determine the profile the sensor in air. A standard temperature and humidity condition were maintained during measurement. Deionized water was considered to be the control solution whereas a standard nitrate-N solution was used to develop a working solution for different concentrated samples. The average pH of all the samples was 6.60. Followed by the characterization of the sensors in the air to determine the experimental

reference curve, they were tested with deionized water and sample water for the experiments. Figure 6.34 depicts the laboratory setup used for EIS measurements.

Figure 0.34 Experimental setup for nitrate measurement.

6.6.2 Comparative Analysis of two Different Sensors

10-ppm Nitrate-N sample water was considered to determine the real part of the impedance of the sensors. The real part of the impedance of the deionized water as the control solution was also measured. The sensor's response was determined from equation 7.3.

$$\text{Sensor's response (\%)} = \frac{R(\text{milliq}) - R(\text{sample})}{R(\text{milliq})} \times 100 \quad (7.3)$$

where R defines the real part of the impedance of the sensors.

6.6.3 Temperature and Nitrate-N Measurement

The sensors were initially used to measure the change in temperature in water. The change in temperature changes the mobility of ions present in water which was determined by the graphene sensors. A GEX MS 7-H550 Digital Hotplate, mercury thermometer, LCR meter, and a desktop were used for data acquisition and

collection. The thermometer was immersed inside the sample water to analyze its temperature. The sensing surface of the sensor was carefully immersed inside the water, and a frequency sweep was done between 10 Hz and 100 kHz to characterize the sensor at different temperatures. 1, 10, 30, 50 and 70-ppm standard nitrate-N solutions were prepared for experiments in five 100 ml beakers. The immersing of the sensor inside the solution was done until the completion of the measurements. Real and imaginary parts impedance were considered by the LCR meter to develop the graphs.

6.6.4 IoT-enabled Smart Sensing System

Internet of Things (IoT- enabled smart sensing system was proposed to monitor and collect the data for nitrate-N measurements. AD5933 (Devices), being the impedance analyzer was used to measure the impedance and the phase shift of the sensor. Before the measurements, the impedance analyzer was be calibrated to obtain its gain. Arduino Uno Wi-Fi (Arduino 2017), consisting of an integrated Wi-Fi module, was considered as the master microcontroller to collect the impedance data from the impedance analyzer. *Thingspeak* (Thingspeak 2017) was used as the web server to gather the measured data and display it in real-time. The Arduino Ciao (Website 2017) library, which is capable of interfacing with system resources and communicating with some of the most common protocols such as (MQTT, XMPP, HTTP, SMTP), was used to transfer the data to the defined private channel in the *Thingspeak* server. HTTP POST was employed to transfer the measured concentration to the *ThingSpeak* cloud server. Security is an important issue in IoT research due to the heterogeneity of the employed sensors. An ADG849 was employed as a switch connected to a calibration resistor and the sensor, where the impedance was calculated using the calibrated gain. The phase shift was also calculated from the connected analyzer. The I²C protocol that was considered to communicate to the impedance analyzer was able to extract the real part of the impedance from the analyzer and gather the information in the main microcontroller. A data processing algorithm was used to convert that resistive part into meaningful temperature and nitrate-N concentration values.

Figure 0.35 Block diagram of the smart sensing system.

The temperature and nitrate-N information were sent to the IoT-based cloud server followed by the measurement of the water sample that was collected from different locations. Figures 6.35 and 6.36 show the block diagram and software flow of the proposed sensing system respectively. Arduino Sketch and Circuit maker (Circuit maker) were used to writing the programming code and draw the circuit diagram of the sensing system respectively. The first step starts with the initialization of the microcontroller with the setup function that is established with the rest connector to provide the cloud-server API (Application Programming Interface) number that is subsequently important to send the measured data to the defined IoT server. The developed calibration curve used to measure the temperature of the deionized water and calculate the nitrate-N concentration along with the compensated temperature — the system communicated with the IoT cloud server to transfer the measured data. The last step is for the microcontroller to go into sleep mode for saving power. Figures 6.37 and 6.38 show a schematic diagram of the signal conditioning circuit and the prototype of the proposed sensing system respectively.

Figure 0.36 Software flow of the individual steps of the operating of the IoT-based system to calculate and transmission of the nitrate concentration to the cloud server.

Figure 0.37 Schematic diagram of the smart sensing system.

Figure 0.38 Prototype of the smart sensing system.

6.6.5 Results and Discussion

Nitrate Measurement

Figure 6.35 depicts the change in the real part of the impedance concerning different concentrations for the swept frequency range. It is seen that there is a prominent change in the real part of the impedance can be distinguished clearly for the different concentrations of nitrate-N in sample water. The presence of nitrate-N ions in the water caused a change in the impedance profile for tested concentrations. It is seen that 1200-1700 Hz is the most sensitive frequency region for tested concentrations where the real part of the impedance showed a higher change in comparison to the imaginary part for the different nitrate-N samples.

Figure 0.39 The change of the real part of the impedance concerning frequency.

Temperature Measurement

The dielectric properties of the deionized water were analyzed via this proposed method. The EIS measurement done on the sample showcased more change in the real part compared to imaginary impedance. The variation of temperature was done between 7 °C and 50 °C to obtain the real part of the impedance shown in Figure 6.36. It is seen from the linear regression analysis that the temperature is correlated with the real impedance ($R^2=0.99$), that can be theoretically calculated from equation 6.4:

$$T (^{\circ}\text{C}) = \frac{(R_T + 29153)}{404.87} \quad (6.4)$$

where R_T defines the measured real part of the impedance for a certain temperature and T defines the calculated temperature.

The slope of the straight line dictates the change of real part of the impedance concerning the change in temperature, which is $\alpha=404.87 \text{ } \Omega/^{\circ}\text{C}$. The operating frequency of the sensor for the

temperature measurement was obtained at 1650 Hz. Figure 6.37 depicts the comparison of the measured and actual temperature.

Figure 0.40 Real part of the impedance as a function of temperature.

Figure 0.41 Comparison of actual and measured temperatures.

It is seen that the experimental and measured temperature are well correlated with each other and $R^2=0.99$ which shows that the sensor can provide measurement of the temperature of sample water can be done quite accurately. 1650 Hz being considered as the operating frequency, was used to develop the calibration standard from a standard nitrate-N sample measurement. All the measured concentrations were taken as the x-axis, and the corresponding real part of the impedance values were taken as the y-axis. Figure 6.38 depicts the final calibration curve for nitrate-N measurements. Linear regression analysis can be done from equation 6.5:

$$C = \frac{R_{cal} - 9196.9}{-667.97} \quad (6.5)$$

where C (ppm) defines the actual concentration, and R_{cal} (Ω) defines real impedance measured by the graphene sensor.

Equation 6.6 shown below, was used to determine any unknown nitrate-N concentration in water. The sensor is sensitive to temperature and change in the mobility of the ions with temperature, the measured resistive values were adjusted by a correction factor α . The R_{actual} defined the modified real part of the impedance due to the change in temperature and was calculated by:

$$R_{actual} = R_{cal} + \alpha \times (T - 25) \quad (6.6)$$

Therefore, the standard formula to calculate the actual concentration after applying a correction factor for the graphene sensor is represented from equation 6.7.

$$C_{actual} = \frac{R_{actual} - 9196.9}{-667.97} \quad (6.7)$$

where C_{actual} is the final corrected concentration due to the temperature change.

The final equation was used to determine the unknown nitrate-N concentration along with including temperature compensation. It is

seen that the sensitivity of the sensor is changed to 667.97 Ω /ppm, which can be used to measure nitrate-N concentrations accurately.

Figure 0.42 Calibration Standard of Nitrate-N concentration (ppm).

Different water samples of unknown concentration were collected from different locations like river, lake, stream and tap water. Since the concentration of nitrate-N level is not very high in the natural water bodies; some nitrate-N samples were spiked with those water samples to increase the level of nitrate-N concentration. The graphene sensors used to measure the temperature of the water samples was followed by the measurement of nitrate-N samples. Among all the other samples, river water was considered to depict the calculation process and measure the nitrate-N concentration. The resistive part of the impedance gave a value of $R_T = -19750 \Omega$. Therefore, from equation 7.4, the calculated temperature was found out to be $T(^{\circ}C) = 23.2^{\circ}C$. The real part of the impedance was found, $R_{cal} = -4568 \Omega$, whereas using equation 7.6, R_{actual} becomes -5288.67Ω . So, finally, the final concentration was 21.69 ppm that is measured from the water sample. This output was verified by a standard UV-spectrometric method. Other sample waters were measured and compared with the laboratory standard method as shown in Table 7.3. It is seen that the sensor showed a very reliable performance in comparison to the

laboratory method. The error rate was found out to be less than 5%, which can be considered to be acceptable performance for the sensing system. The error can be assumed to be due to measurements and presence of other ions in water. But still, the accuracy of the sensor and sensing system was seen to be more than 95% and fairly consistent. The developed sensor is robust and maintains good repeatability.

Table 0.3 Unknown Sample measurement (in ppm) compared with Laboratory standard method.

Sl. No.	Sampling Number	1st Run	2nd Run	3rd Run	4th Run	5th Run	Laboratory Method
1.	River Water	21.69	21.56	21.54	21.63	21.35	21.5
2.	Tap Water	5.25	5.1	5.35	5.15	5.75	5.5
3.	Canal Water	56.75	56.7	56.6	56.65	56.55	56.5
4.	Stream Water	65	65.2	65.1	65.3	65.15	65
5.	River Water	32.35	32.65	32.55	32.45	32.62	32.5

Figure 6.43 displays the reusability performance of the sensor and the sensing system. The sensor can obtain an almost identical result with each experimental run. Graphene as electrodes is corrosion free (Cochlin 2014) and can protect the sensing area from oxidation during the experimentation, thus increasing its repeatability. Mechanically, it is very robust (Geim 2009) and can perform very well during measurements. Figure 6.40 depicts the transfer of data to the IoT-based cloud server showing the concentration of nitrate-N and temperature to be 25.5 ppm and 22 °C respectively. The measurement was done for nearly three hours to determine the actual data in real time. It was found out that the developed system was fairly consistent for monitoring continuous data at defined intervals. The transfer of data has been done simultaneously which helped to monitor the experimental data in real time. There was a delay of 30 seconds in *ThingSpeak* cloud server. The developed sensing system will also be

useful to considering a distributed monitoring system to determine the temperature and nitrate-N concentration in real-time conditions.

Figure 0.43 Repeated unknown sample measurements by smart sensing system.

Figure 0.44 Data transferred to the IoT based web server.

6.6.6 Conclusion

This section of the chapter describes the IoT-enabled sensing system for the detection of nitrate-N concentrations in water samples. Temperature compensation was done to enhance the performance of the developed sensing system. The sensor performance was analyzed regarding its capability to determine the different concentrations of the nitrate-N in the water samples. Due to the low fabrication cost and simple operating principle of the sensor patches, it was easier to develop a low-cost and efficient sensing system to monitor the water samples resembling real-time situations. Another advantage of the sensor was its robustness to assist in their repeatability of the measurements. The developed smart sensing system can be considered for monitoring the real-time nitrate-N concentrations and fabricating a low-cost distributed network with effective performances.

6.7 Chapter Summary

This chapter explains the fabrication and employment of laser-induced graphene sensors from commercial polymer films. The induced graphene was transferred to sticky tapes for using them as electrodes on sensor patches. A few of the major advantages of the developed patches were their quick fabrication process, low cost, simple operating principle, high conductivity and the corrosion-resistant nature of the conductive material. The sensor patches were employed for environmental monitoring purposes where laboratory-made samples to determine the capability of the developed patches to differentiate the nitrate and saline solutions at different concentrations. They were also utilized for industrial applications via experimenting with different solutions formed with five fundamental chemicals which are considered for taste-sensing purposes. The ability of the developed patches to distinguish the five chemicals depended on the differences of their responses. Apart from employing these patches for industrial and environmental purposes, they can also be used for health monitoring via embedding them with a conditioning circuit in conjugation with wearable sensors. The corrosion resistance of graphene makes them preferable to be used to

develop the electrodes for sensor patches that can be used for ubiquitous monitoring of sweat, urine (Nag et al. 2017a; Nag et al. 2017b), etc. The inclusion of selectivity to the sensor patches would further increase their potentiality for different applications.

6.8 References

- Arduino (2017) Arduino Uno WiFi. <https://store.arduino.cc/usa/arduino-uno-wifi>. Accessed 4/09/2017 2017
- Baldwin EA, Bai J, Plotto A, Dea S (2011) Electronic noses and tongues: Applications for the food and pharmaceutical industries *Sensors* 11:4744-4766
- Bhat S (2005) Salinity (conductivity) sensor based on parallel plate capacitors
- Bhattacharyya N, Bandhopadhyay R (2010) Electronic nose and electronic tongue. In: *Nondestructive Evaluation of Food Quality*. Springer, pp 73-100
- Brender JD, Olive JM, Felkner M, Suarez L, Marckwardt W, Hendricks KA (2004) Dietary nitrites and nitrates, nitrosatable drugs, and neural tube defects *Epidemiology* 15:330-336
- Cameron K, Di H, Moir J (2013) Nitrogen losses from the soil/plant system: a review *Annals of Applied Biology* 162:145-173
- Changes in Marine Salinity Levels. http://pisaster.genetics.uga.edu/groups/evolution3000/wiki/cb536/Changes_in_Marine_Salinity_Levels.html.
- Chen Q, Zhao J, Guo Z, Wang X (2010) Determination of caffeine content and main catechins contents in green tea (*Camellia sinensis* L.) using taste sensor technique and multivariate calibration *Journal of Food Composition and Analysis* 23:353-358
- Ciosek P, Wróblewski W (2011) Potentiometric electronic tongues for foodstuff and biosample recognition—An overview *Sensors* 11:4688-4701
- Circuit maker. <https://circuitmaker.com/>. Accessed 4/09/2017 2017
- Cochlin D (2014) Graphene paints a corrosion-free future. <http://www.manchester.ac.uk/discover/news/graphene-paints-a-corrosion-free-future/>. Accessed 28/08/2017 2017

- Concentration of chemicals in food samples.
http://www.testmeters.com.au/files/2014/12/Sodium_and_Salt_Content_in_Food_Samples.pdf.
- Daniel WL, Han MS, Lee J-S, Mirkin CA (2009) Colorimetric nitrite and nitrate detection with gold nanoparticle probes and kinetic end points Journal of the American Chemical Society 131:6362-6363
- Davies-Colley R, Wilcock B (2004) Water quality and chemistry in running waters Freshwaters of New Zealand Christchurch: New Zealand Hydrological Society and New Zealand Limnological Society
- Devices A AD5933: Impedance Analyzer. Analog Devices.
<http://www.analog.com/media/en/technical-documentation/data-sheets/AD5933.pdf>. Accessed 04/09/2017 2017
- Dudwadkar A, Shenoy N, Joshi J, Kumar SD, Rao H, Reddy A (2013) Application of ion chromatography for the determination of nitrate in process streams of thermal denitration plant Separation Science and Technology 48:2425-2430
- EIS Spectrum Analyzer.
<http://www.abc.chemistry.bsu.by/vi/analyser/>.
- Electrical Conductivity of Aqueous Solutions.
<http://www.colby.edu/chemistry/CH141/CH141L/CH141Lab4Fall2009.pdf>.
- Ensafi AA, Amini M (2012) Highly selective optical nitrite sensor for food analysis based on Lauth's violet-triacetyl cellulose membrane film Food Chemistry 132:1600-1606
- Etoh S, Feng L, Nakashi K, Hayashi K, Ishii A, Toko K (2008) Taste sensor chip for portable taste sensor system Sens Mater 20:151-160
- The Five Senses of Sensors - Taste
<https://www.digikey.com/en/articles/techzone/2011/jul/the-five-senses-of-sensors---taste>.
- Gadani D, Rana V, Bhatnagar S, Prajapati A, Vyas A (2012) Effect of salinity on the dielectric properties of water
- Geim AK (2009) Graphene: Status and Prospects Science 324:1530-1534 doi:10.1126/science.1158877

- Graphene paints a corrosion-free future.
<http://www.manchester.ac.uk/discover/news/graphene-paints-a-corrosion-free-future>.
- Greer FR, Shannon M (2005) Infant methemoglobinemia: the role of dietary nitrate in food and water *Pediatrics* 116:784-786
- Grosso P, Le Menn M, De La J-LDB, Wu ZY, Malardé D (2010) Practical versus absolute salinity measurements: New advances in high performance seawater salinity sensors *Deep Sea Research Part I: Oceanographic Research Papers* 57:151-156
- Ha D et al. (2015) Recent achievements in electronic tongue and bioelectronic tongue as taste sensors *Sensors and Actuators B: Chemical* 207:1136-1146
- Haddi Z, El Barbri N, Tahri K, Bougrini M, El Bari N, Llobet E, Bouchikhi B (2015) Instrumental assessment of red meat origins and their storage time using electronic sensing systems *Analytical Methods* 7:5193-5203
- Herzer N, Hoepfener S, Schubert US (2010) Fabrication of patterned silane based self-assembled monolayers by photolithography and surface reactions on silicon-oxide substrates *Chemical Communications* 46:5634-5652
- Hester R, Harrison R, Addiscott TM (1996) Fertilizers and nitrate leaching. In: *Agricultural chemicals and the environment*. pp 1-26
- Holland LM, Doole GJ (2014) Implications of fairness for the design of nitrate leaching policy for heterogeneous New Zealand dairy farms *Agricultural water management* 132:79-88
- Huang AL et al. (2006) The cells and logic for mammalian sour taste detection *Nature* 442:934
- Huber C, Klimant I, Krause C, Werner T, Mayr T, Wolfbeis OS (2000) Optical sensor for seawater salinity *Fresenius' journal of analytical chemistry* 368:196-202
- Jonsson J, Smedfors K, Nyholm L, Thornell G (2013) Towards chip-based salinity measurements for small submersibles and biologists *International Journal of Oceanography* 2013
- Juansah J, Yulianti W Studies on Electrical Behavior of Glucose Using Impedance Spectroscopy. In: *IOP Conference Series*:

- Earth and Environmental Science, 2016. IOP Publishing, p 012039
- Kim MJ, Choe S, Kim HC, Cho SK, Kim S-K, Kim JJ (2015) Electrochemical behavior of citric acid and its influence on Cu electrodeposition for damascene metallization *Journal of The Electrochemical Society* 162:D354-D359
- Krantz-Rülcker C, Stenberg M, Winqvist F, Lundström I (2001) Electronic tongues for environmental monitoring based on sensor arrays and pattern recognition: a review *Analytica chimica acta* 426:217-226
- Le Vine DM, Lagerloef GS, Torrusio SE (2010) Aquarius and remote sensing of sea surface salinity from space *Proceedings of the IEEE* 98:688-703
- Lin J et al. (2014) Laser-induced porous graphene films from commercial polymers *Nature communications* 5
- Malarde D, Wu ZY, Grosso P, de la Tocraye JdB, Le Menn M (2008) High-resolution and compact refractometer for salinity measurements *Measurement Science and Technology* 20:015204
- Malicki M, Walczak R (1999) Evaluating soil salinity status from bulk electrical conductivity and permittivity *European Journal of Soil Science* 50:505-514
- Mamishhev AV, Sundara-Rajan K, Yang F, Du Y, Zahn M (2004) Interdigital sensors and transducers *Proceedings of the IEEE* 92:808-845
- Medeiros ES, Gregório R, Martinez RA, Mattoso LH (2009) A taste sensor array based on polyaniline nanofibers for orange juice quality assessment *Sensor Letters* 7:24-30
- Men L, Lu P, Chen Q (2008) A multiplexed fiber Bragg grating sensor for simultaneous salinity and temperature measurement *Journal of Applied Physics* 103:053107
- Miranda KM, Espey MG, Wink DA (2001) A rapid, simple spectrophotometric method for simultaneous detection of nitrate and nitrite *Nitric oxide* 5:62-71
- Monaghan R, Hedley M, Di H, McDowell R, Cameron K, Ledgard S (2007) Nutrient management in New Zealand pastures—recent developments and future issues *New Zealand journal of agricultural research* 50:181-201

- Murray-Darling Basin Authority annual report 2015-16.
- Nag A, Mitra A, Mukhopadhyay SC (2017a) Graphene and its sensor-based applications: A review Sensors and Actuators A: Physical
- Nag A, Mukhopadhyay S, Kosel J Urinary incontinence monitoring system using laser-induced graphene sensors. In: SENSORS, 2017 IEEE, 2017b. IEEE, pp 1-3
- Narayana B, Sunil K (2009) A spectrophotometric method for the determination of nitrite and nitrate Eurasian Journal of Analytical Chemistry 4:204-214
- Natural environment.
<http://www.environment.nsw.gov.au/salinity/basics/naturalenvironment.htm>.
- Organization WH (2017) Water-related diseases.
http://www.who.int/water_sanitation_health/diseases-risks/diseases/methaemoglobin/en/. Accessed 27/02/2017
- Pellerin BA, Bergamaschi BA, Downing BD, Saraceno JF, Garrett JD, Olsen LD (2013) Optical techniques for the determination of nitrate in environmental waters: Guidelines for instrument selection, operation, deployment, maintenance, quality assurance, and data reporting Quality Assurance, and Data Reporting In: Techniques and Methods:1-D5
- Pham X-H et al. (2014) Electrochemical detection of nitrite using urchin-like palladium nanostructures on carbon nanotube thin film electrodes Sensors and Actuators B: Chemical 193:815-822
- Properties of the Phosphate Group.
<http://www.tud.ttu.ee/im/Tonu.Reintamm/shabarova/4.4.html>.
- Rahman H, Harun S, Yasin M, Phang S, Damanhuri S, Arof H, Ahmad H (2011) Tapered plastic multimode fiber sensor for salinity detection Sensors and Actuators A: Physical 171:219-222
- Rahman HA, Harun SW, Yasin M, Ahmad H (2012) Fiber-optic salinity sensor using fiber-optic displacement measurement with flat and concave mirror IEEE Journal of selected topics in quantum electronics 18:1529-1533

- Rahman MSA, Mukhopadhyay SC, Yu P-L (2014) Experimental Investigation: Impedance Characterization. In: Novel Sensors for Food Inspection: Modelling, Fabrication and Experimentation. Springer, pp 37-71
- Reul N et al. (2014) Sea surface salinity observations from space with the SMOS satellite: A new means to monitor the marine branch of the water cycle *Surveys in Geophysics* 35:681-722
- Riul A, Malmegrim R, Fonseca F, Mattoso L (2003) An artificial taste sensor based on conducting polymers *Biosensors and Bioelectronics* 18:1365-1369
- Robinson D, Jones SB, Wraith J, Or D, Friedman S (2003) A review of advances in dielectric and electrical conductivity measurement in soils using time domain reflectometry *Vadose Zone Journal* 2:444-475
- Robinson S, Nakkeeran R Photonic crystal based sensor for sensing the salinity of seawater. In: *Advances in Engineering, Science and Management (ICAESM)*, 2012 International Conference on, 2012. IEEE, pp 495-499
- Schazmann B, Diamond D (2007) Improved nitrate sensing using ion selective electrodes based on urea-calixarene ionophores *New Journal of Chemistry* 31:587-592 doi:10.1039/B702841P
- Scudiero E, Berti A, Teatini P, Morari F (2012) Simultaneous monitoring of soil water content and salinity with a low-cost capacitance-resistance probe *Sensors* 12:17588-17607
- Squillace PJ, Scott JC, Moran MJ, Nolan B, Kolpin DW (2002) VOCs, pesticides, nitrate, and their mixtures in groundwater used for drinking water in the United States *Environmental Science & Technology* 36:1923-1930
- Tahara Y, Toko K (2013) Electronic tongues—a review *IEEE Sensors Journal* 13:3001-3011
- Taste disorder 'prevalent in children'. <http://www.sbs.com.au/news/article/2011/04/26/taste-disorder-prevalent-children>.
- Taste disorders. <https://www.nidcd.nih.gov/health/taste-disorders>.
- Thingspeak (2017) Thingspeak. <https://thingspeak.com/>. Accessed 26/08/2017 2017

- Toko K, Tahara Y, Habara M, Kobayashi Y, Ikezaki H (2016) Taste sensor: Electronic tongue with global selectivity *Essentials of Machine Olfaction and Taste*:87-174
- Wang S, Wang J, Li G, Tong L (2012) Modeling optical microfiber loops for seawater sensing *Applied optics* 51:3017-3023
- Wang X, Wang Y, Leung H, Mukhopadhyay SC, Tian M, Zhou J (2015) Mechanism and experiment of planar electrode sensors in water pollutant measurement *IEEE Transactions on Instrumentation and Measurement* 64:516-523
- Website A (2017) Ciao. <https://www.arduino.cc/en/Reference/Ciao>. Accessed 26/08/2017 2017
- Wild A, Cameron K (1980) Nitrate leaching through soils and environmental considerations with special reference to recent work in the United Kingdom. In: *Soil nitrogen as fertilizer or pollutant*.
- Wu C, Guan B-O, Lu C, Tam H-Y (2011) Salinity sensor based on polyimide-coated photonic crystal fiber *Optics express* 19:20003-20008
- Zhao F, Li X, Xu W, Zhang W, Ying X (2014) An Electrochemical Sensor for L-Tryptophan Using a Molecularly Imprinted Polymer Film Produced by Copolymerization of o-Phenylenediamine and Hydroquinone *Analytical Letters* 47:1712-1725
- Zhao GQ, Zhang Y, Hoon MA, Chandrashekar J, Erlenbach I, Ryba NJ, Zuker CS (2003) The receptors for mammalian sweet and umami taste *Cell* 115:255-266
- Zia AI, Mukhopadhyay SC, Yu P-L, Al-Bahadly IH, Gooneratne CP, Kosel J (2015) Rapid and molecular selective electrochemical sensing of phthalates in aqueous solution *Biosensors and Bioelectronics* 67:342-349