FLEXIBLE PH SENSOR WITH POLYANILINE LAYER BASED ON IMPEDANCE MEASUREMENT

Cheng-Hsin Chuang[1]*, Hsun-Pei Wu[1], Cheng-Ho Chen[2], Peng-Rong Wu[2]

[1]Department of Mechanical Engineering,

[2]Department of Chemical and Materials Engineering,

Southern Taiwan University, Tainan, 71005, TAIWAN

*Corresponding author: chchuang@mail.stut.edu.tw

Abstract- A flexible sensor with conducting polyaniline layer for detecting pH value based on the impedance measurement is fabricated and demonstrated in this study. The pH sensor consists of an interdigital electrode array on a flexible printed circuit and a thin-film polyaniline as the sensing layer. As the conductivity of polyaniline depends on the redox state, the impedance change of the polyaniline after it has reacted with different pH value solutions works as the sensing mechanism. In order to obtain a reliable and stable impedance measurement result, a standard procedure for pH value detection is also developed. As the experimental results show, the impedance variation of the pH sensor is less than 1% in an ambient environment, and the measured impedance increases with pH values varying from 2 to 12. In addition, the impedance change between the unreacted sensor and the reacted sensor exhibit 3 orders of difference; thus, the resolution of the pH value detection is very high, making it possible to detect the impedance by means of a simple electronic device. Consequently, the low-cost, disposable, flexible IDT electrode sensor with a polyaniline layer effectively demonstrates the feasibility of pH value detection. Moreover, the sensor can be applied to other applications, such as gas detection, humidity and glucose, etc.

Index terms: Flexible; Polyaniline; pH value; Impedance

I.   INTRODUCTION

The direct benefit of water quality monitoring is that it provides accurate and reliable data on the amount of dissolved oxygen in the water, pH value, temperature and turbidity. Many aquatic animals and plants can only survive within specific pH values and are not suited to live in more acidic or alkaline environments; thus, the measuring of pH is of utmost importance. Recently, there has been considerable interest in water quality monitoring and environmental protection. In 2005, Federico Hahn [1] proposed a novel valve for the automatic calibration of a chloride sensor for river water monitoring and, in 1996, Kazunori Ikebukuro [2] proposed a microbial cyanide sensor for the same purpose. Both Hahn and Ikebukuro found that Cl^+ and pH values both affected the habitat of aquatic animals and plants; however, the devices they used were too complicated and time-consuming. Between 2000 and 2010, Zhe Jin, Pilar T. Sotomayor, Cyrine Slim, and M.M. Ayad [3-6] presented an improved optical pH sensor using polyaniline. Because the color of polyaniline changes with the pH value, they used a spectroscope to observe the color change after the sensor reacted. However, the drawback of this method was that the spectroscope was too bulky, which limited its usage in fieldwork. In 2006, polyaniline film was utilized to detect humidity and temperature based on the electrical impedance sensing method [7]. In this study, instead of the optical quality, we employed the electric property of polyaniline in the pH sensor; thus, it was possible to integrate it in a handheld electronic device. Furthermore, in order to enhance the sensitivity of the pH sensor and reduce the cost of fabrication, an interdigital (IDT) electrode array was designed and fabricated on a flexible printed circuit (FPC) by standard MEMS technology. In the experiments, a rapid and reliable measurement procedure was also determined based on sensor characterization for different pH value solutions. The sensing mechanism of polyaniline, the sensor fabrication and the experimental results demonstrating the feasibility of pH detection using the impedance measurement are discussed in the following sections.

II.   CHARACTERISTICS OF POLYANILINE

A.   Conductive Polyaniline (PANI)

Polyaniline (PANI) is an important member of the family of intrinsically conducting polymers (ICP). Due to its unique electrochemical property and environmental stability, PANI has been studied extensively by scientists and applied in many fields, such as secondary batteries, biosensors, corrosion protection, anti-static packaging materials, and light-emitting diodes (LEDs), etc.

Chemical oxidization and electrochemical synthesis are two major routes for preparing PANI. As MacDiarmid et al. [8] demonstrated, the chemical structure of PANI can be schematically represented, as shown in Figure 1. The completely reduced form (Figure 1-a) and oxidized state (Figure 1-d) are named the leucoemeraldine base (LEB) form and the pernigraniline base (PNB) form, respectively. If the PANI contains 50% reduction and 50% oxidation states, the structure is referred to as the emeraldine base (EB) form (Figure 1-c). Moreover, the EB form of PANI can be doped by a protonic acid, such as HCl, HNO3 or H2SO4, to produce the emeraldine salt (ES) form of PANI, which has moderately high conductivity. Compared with other conducting polymers, PANI has certain advantages, such as easy synthesis, low cost, high environmental stability, and a special doping/dedoping mechanism, as well as physical properties controlled by both oxidation and protonation states. As the conductivity of PANI depends on the redox state, the resistance of PANI can be sensitive to the pH value.
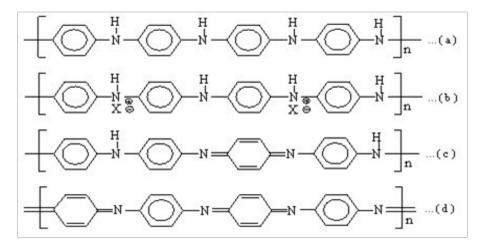

Figure 1: Four different forms of PANI: (a) leucoemeraldine base (LEB); (b) metallic emeraldine salt (ES); (c) emeraldine base (EB); and (d) pernigraniline base (PNB)

B. PANI-DBSA (PANDB)

As noted above, chemical oxidation and electrochemical polymerization are the two major methods used to synthesize PANI. For chemical oxidation polymerization, it is possible to produce PANI suspension with a controllable morphology on a mass scale. The process usually needs a strong protonic acid as the dopant to produce the ES form of PANI which has a moderately high conductivity of up to 10-100S/cm. However, the residue of the strong proton acid in the PANI can corrode the metal electrodes of the sensor which are covered by the ES form of PANI. Therefore, a weak proton acid, dodecyl benzene sulfonic acid (DBSA), was utilized as the dopant in the synthesis of polyaniline in this study. The chemical formula of PANI doped by DBSA, so-called PANDB, is illustrated in Fig. 2 [9]. PANDB has better compatibility with common organic solvents which makes thin-film formation by simple spin coating an easy task; however, its conductivity is lower than that of PANI doped by strong proton acid. In our pH value sensor, the sensing mechanism was the impedance change for different pH conditions, rather than the impedance value. Hence, PANDB was a suitable sensing material for the pH sensor and provided a reliable impedance measurement without corrosion of the metal electrodes by the residual acid.
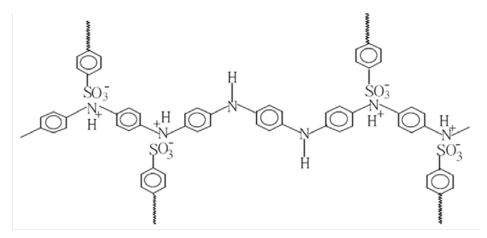

Figure 2: Scheme of the molecular formula of PANDB

III.   DESIGN AND FABRICATION OF FLEXIBLE PH SENSOR

A.   *Synthesis of PANDB*

In this study, DBSA was used as the dopant. The procedure, as shown in Fig. 3, involved 9.3g of aniline monomer, 26.12g of DBSA, and 22.82g of ammonium persulfate (APS), dissolved in RO water by constant magnetic stirring. First, the DBSA solution was introduced into the aniline solution and stirred for 10 min; then the APS solution was introduced and allowed to react for 6 hrs. During the procedure, the color of the solution changed twice. When color changes occurred, the solution temperature simultaneously increased due to an exothermic reaction. As observed in the synthesization process, the color changed from white to brown and from brown to dark green at 34 and 43 min of reaction time, respectively. Therefore, the state conversion could be distinguished by the color change. After polymerization for 6 hrs, the dark green PANDB suspension was filtered and washed with acetone and de-ionized water until the filtrate became colorless and the pH value of the filtrate was the same as that of the de-ionized water. Finally, 20c.c. of DI water was mixed with PANDB to obtain a PANDB suspension for dip coating on the sensor surface.
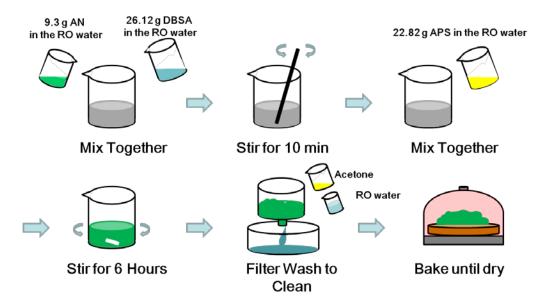

Figure 3: Scheme of the synthesis process of PANDB

B.   Fabrication of Flexible pH Sensor

In the fabrication process, as illustrated in Fig. 4, an interdigital (IDT) electrode array was first patterned on a 3.5 × 2.5 cm2 flexible printed circuit (FPC) by standard photolithography and wet etching, as shown in Fig. 4(a). The total pair number of IDT electrodes was 28, and the total area of IDT electrodes was about 5mm square, defined as the sensing area. The width, spacing and thickness of each electrode were 30μm, 60μm and 10μm, respectively, as shown in the optical micrograph in Fig. 5(a). After stripping the residual photoresist and cleaning the sensor with acetone and methanol in the ultrasonic cleaner in sequence, 0.05 ml of PANDB solution was dropped on the sensing area by micro pipette. The flexible sensor was then baked with PANDB at 500°C for 30 min; the thickness of the PANDB layer was about 9~10μm, as measured by a white light interferometer. Finally, the finished flexible pH sensor was ready for the impedance measurement of an undetermined sample within the sensing area, as shown in Fig. 5(c). Consequently, a low-cost, light-weight and disposable pH sensor was fabricated, with only a small amount of sample required for the reaction with PANDB.

a. Bottom Electrode Layer   **b. Impedance Sensing**

FPC Substrate

Coat PR S1813 Layer

Expose and Develop

Etching and Remove PR

Impedance Analyzer

H   L

PI   Bottom Electrode
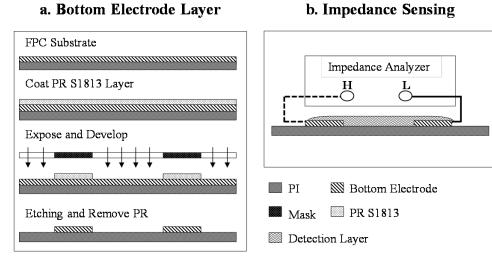
Mask   PR S1813

Detection Layer

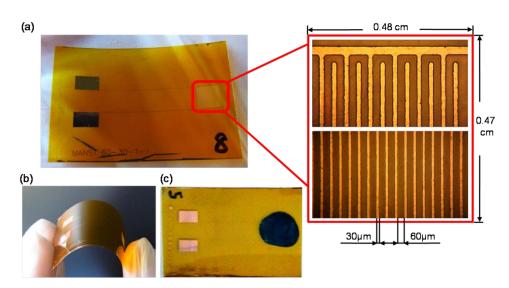Figure 4: Microfabrication process of PANDB sensor

Figure 5: (a) IDT electrode array on FPC, and optical micrograph of IDT electrodes; (b) bendable sensor; (c) finished flexible pH value sensor with PANDB layer within IDT electrode array

IV.   EXPERIMENTAL METHOD

The experimental setup for the impedance measurement of the different pH value solutions is shown in Fig. 6. The two wires connected to the pH sensor were calibrated first by an LCR meter (WK6420, Wayne Kerr Electronics, UK), with the data acquisition controlled by the computer-based LabView program for scanning the impedance spectrum in a frequency range of 1k to 100k Hz at 2V. In order to test the sensor's capability to differentiate pH values, testing solutions with pH values from 2 to 12 were prepared with sodium hydroxide (NaOH) and acetic acid (CH3COOH) for alkaline and acid solutions, respectively. As the water content can significantly affect the resulting impedance; each sensor was baked at 40°C for 30 min after being doped with a test sample on the sensing area. The baking process was necessary for there to be stable measurement results; therefore, a built-in heater or a two-step measurement could be utilized for hand-held devices in the future. Factors which could have had an influence on the resulting impedance were the reaction time for the test samples reacting with PANDB after being dropped on the sensor but before baking, and the standing time for the impedance measurement after baking due to the humidity in the ambient environment. Therefore, not only the impedance variation between solutions with different pH values must be characterized, but the concerned factors should also be standardized in order for the sensing results to be reliable and repeatable.

In the experimental results, the different reaction times, varying from 1 to 70 min, were evaluated for the purpose of rapid detection. In addition, the impedance change for standing times within 90 min was also monitored to get rid of the humidity effect.
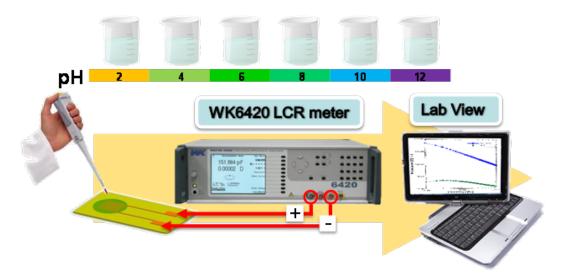

Figure 6: Experimental setup and impedance sensing of different pH solutions

V.   EXPERIMENTAL RESULTS

A.   *Effect of Reaction Time*

In order to determine a sufficient reaction time for rapid detection after the testing solution was dropped on the sensing area, a testing solution with a pH value of 12 was utilized, and 8 pH sensors were used for 8 different reaction times of 1 to 70 min with 10-min spacing. As noted in the experimental method, the sensors were baked after a specified reaction time and their impedance was measured after cooling for 10 minutes at the ambient temperature. The impedance of a pH sensor without the test solution was also measured as the control, Z_0. The impedance change corresponding to the Z_0 for each reaction time, $\Delta Z = Z - Z_0$, can be normalized by being divided with Z_0, i.e., $\Delta Z/Z_0$. The normalized impedance changes for the different reaction times are plotted in Fig. 7. Note that each impedance magnitude was measured at 30 kHz and 2 V. The results showed that the normalized impedance change had a great jump at 10 min of reaction time; however, this increase was no long observed after 30 min reaction time. Compared with the control pH sensor, Z_0, the impedance increased after PANDB reacted with the alkaline

solution because the electron-hole combination occurred as the p-type PANDB reacted with the hydroxide ion OH⁻ and caused the carrier mobility to decrease. However, when the reaction time was longer than 30 min the electron-hole combination could be d due to the thin film effect. Consequently, the flexible pH sensor exhibited good sensitivity and rapid detection, and the normalized impedance change reached 300 ~ 400% within 10 min of reaction time.
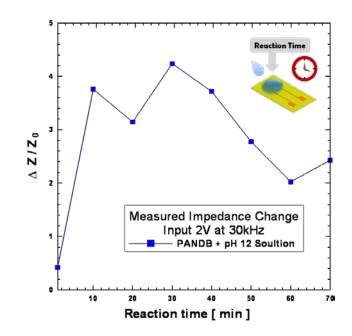
Figure 7: Normalized impedance change for different reaction times.

B. *Impedance Change in Ambiant Environment*

After baking, the pH sensor reacted with the testing solution; thus, the impedance variation as it cooled in an ambient environment needed to be characterized to ensure stable measurement results. A pH sensor was dropped with 0.05 c.c. alkaline solution of pH 12 for 10 min of reaction time, then baked at 40°C for 30 min. The impedance of the pH sensor was recorded by the LabView program every 2 minutes during 1.5 hrs of standing time in an ambient environment at a room temperature of 25°C and humidity of 47% after being removed from the hotplate. Using the impedance measured at 1 min of standing time, Z_1, as the baseline for the remaining impedance data, the variation of impedance change can be derived as $\Delta Z/Z_1$, where $\Delta Z=Z-Z_1$, as shown in Fig. 8. The results showed that the variation of impedance was less than 1%, which meant the impedance results were quite stable for the pH sensor placed in an ambient environment for a period of time. In addition, the impedance increased slightly at the beginning

due to the cooling effect; however, the impedance held steady after 10 minutes standing time. Consequently, 10 min standing time was adequate for a stable impedance measurement. For the different pH value testing solutions, 10 min for either the reaction time or the standing time was determined as the standard procedure.
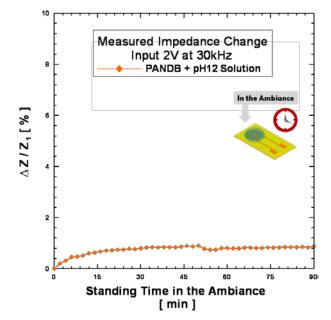

Figure 8: Impedance variation at room temperature within 90 min

C.   Impedance Measurement of Flexible pH Sensor

After baking, the pH sensor reacted with the testing solution; thus, the impedance variation as it cooled in an ambient environment needed to be characterized to ensure stable measurement results. A pH sensor was dropped with 0.05 c.c. alkaline solution of pH 12 for 10 min of reaction time, then baked at 40°C for 30 min. The impedance of the pH sensor was recorded by the LabView program every 2 minutes during 1.5 hrs of standing time in an ambient environment at a room temperature of 25°C and humidity of 47% after being removed from the hotplate. Using the impedance measured at 1 min of standing time, Z_1, as the baseline for the remaining impedance data, the variation of impedance change can be derived as $\Delta Z/Z_1$, where $\Delta Z = Z - Z_1$, as shown in Fig. 8. The results showed that the variation of impedance was less than 1%, which meant the impedance results were quite stable for the pH sensor placed in an ambient environment for a period of time. In addition, the impedance increased slightly at the beginning due to the cooling effect; however, the impedance held steady after 10 minutes standing time.

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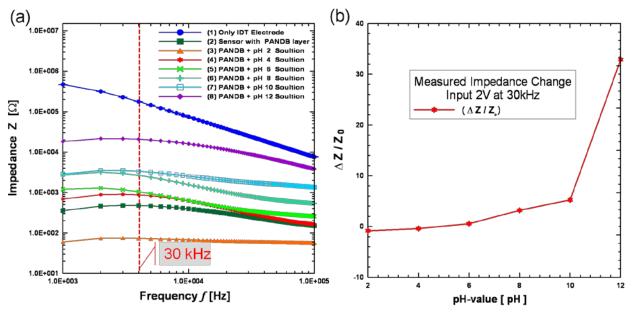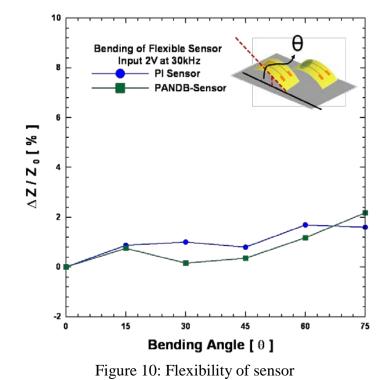

Figure9: Impedance measurement from pH2 to pH12

D.   *Flexibility Properties*

In order to investigate the stability of the sensor output when bending the flexible pH sensor, the impedance change with different bending angles was measured for the flexible sensors either with or without the PANDB layer, as shown in Fig. 10. The bending angle is defined as the angle between the sensor substrate and the horizontal surface at the end. The range of bending angle was from 0° to 75°; i.e. 0° meaning that the substrate was flat without bending. As shown in Fig. 10, the normalized impedance change at 30 kHz slightly increased with the bending angle, but the impedance variation was within 1% when the bending angle was less than 60°C. Therefore, the flexible pH sensor exhibited good stability even when the sensor was bent at a wide angle.

Figure 10: Flexibility of sensor

VI.   CONCLUSIONS

For this study we designed and fabricated a flexible sensor with a conducting PANDB layer for the detection of different pH solutions based on the change in impedance. As the redox state of PANDB changed after reaction with different pH values, the impedance change was several times the original impedance before reaction, which meant not only that the magnitude of impedance change could be easily detected by simple electronic equipment, but also that the resolution of the pH sensor was very high. In addition, the variations of impedance in an ambient environment and at different bending angles were less than 1%. Thus, the pH sensor was able to provide a reliable and stable result and would be suitable even for samples which cannot be measured on site, as is the case in fieldwork. In conclusion, in this study we have demonstrated the feasibility of sensing pH values by means of a low-cost, disposable, flexible IDT-electrode sensor with a PANDB layer. We believe the flexible sensor has great potential for other applications, such as gas detection, humidity and glucose, etc.

ACKNOWLEDGMENTS

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