

Miniature pH Sensor Based on Electropolymerized Polyaniline

Karen S. Santiago and Christina A. Binag

Research Center for the Natural Sciences
University of Santo Tomas
1008 Manila, Philippines

A miniature pH sensor was fabricated by electrochemical polymerization using 0.10 M aniline monomer, 30 mg bovine serum albumin (BSA) dopant, 0.10 M tris(hydroxymethyl)-aminomethane at pH 7, 30-minute polymerization time without stirring, platinum wire support and 9.34 mA cm^{-2} current density as optimum conditions. It showed a sub-Nernstian response of $-42.06 \text{ mV/pH} + 0.5$, a linearity of -0.9985 and favorable response time of $\sim 3 \text{ min}$ for three replicates from pH 3 to pH 10 at room temperature. The sensor exhibited low hysteresis with $\Delta m = 5.83 \text{ mV/pH}$, low drift with an $\text{RSD} = \sim 4\%$, high reproducibility with an $\text{RSD} = \sim 3\%$ and lifetime of > 1.5 months. Furthermore, extensive electrochemical and surface studies was carried out via Cyclic Voltammetry (CV), Scanning Electron Microscopy (SEM) and X-ray Photoelectron Spectroscopy (XPS).

Keywords: polyaniline; conducting polymer; BSA dopant; CV; SEM; XPS

INTRODUCTION

The wide applicability of the glass electrode posted its drawbacks in medical technology due to its fragility and large volume requirement of body fluids that are difficult to obtain. With this problem at hand, the miniaturized polyaniline-based pH sensor can be of great help because it may serve as an alternative. The polyaniline (PAn)/BSA coated on inert metal is robust and could be as little as 0.107 cm^2 , approximately 100 times smaller than the conventional one. Hence, it may be inserted in vivo for real time pH monitoring. Moreover, the preparation of the sensor involves a straightforward procedure, and is inexpensive. The absence of an internal filling solution allows it to be used in any position. Thus, it may be placed vertically, horizontally or even upside down.

Among the array of organic polymers, polyaniline was chosen because of its easy synthesis, inexpensiveness of monomer component and stability in aqueous media. Its monomer consists of a six-membered-ring with amino group, which is linked by head to tail [1] polymerization (Fig. 1).

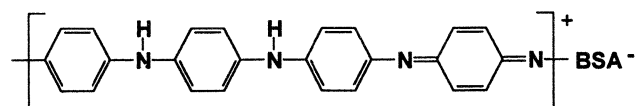


Fig. 1. Molecular structure of polyaniline (doped).

In order to achieve the conducting form of PAn, the electrochemical polymerization and doping, which are oxidative processes, is carried out at a low potential. Doping also involves protonation. The oxidative doping produces a positive charge, which is delocalized over several polymeric units. This necessitates the incorporation of an anionic species as the counterion, in this case BSA (Fig. 1), in order to maintain charge neutrality [2]. The BSA dopant is composed of four unequal sizes of globular units of a carbohydrate-free peptide chain, which is stabilized by disulfide bridges [3].

This paper presents investigations on the optimized parameters for the fabrication of the sensor, and its potentiometric characteristics as well as electrochemical and morphological properties.

EXPERIMENTAL

Reagents and materials. The solutions for polymerization and calibration were prepared using analytical grade reagents and distilled water. In the former, 0.1 M aniline monomer (Fluka), bovine serum albumin dopant (Merck) and 0.1 M of tris(hydroxymethyl)-amino methane (Fluka) were mixed and sonicated (Branson 200 Ultrasonic Cleaner). With the latter, the polyaniline-coated pH sensor was subjected to potentiometric measurements against a silver-silver chloride reference electrode (Orion 900200) immersed in Britton-Robinson Universal buffer solution. The buffer was prepared using 0.040M

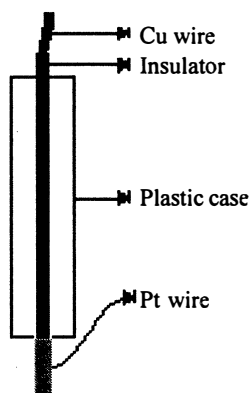


Fig. 2. Sensor configuration consisting of platinum wire, insulated copper wire and plastic case.

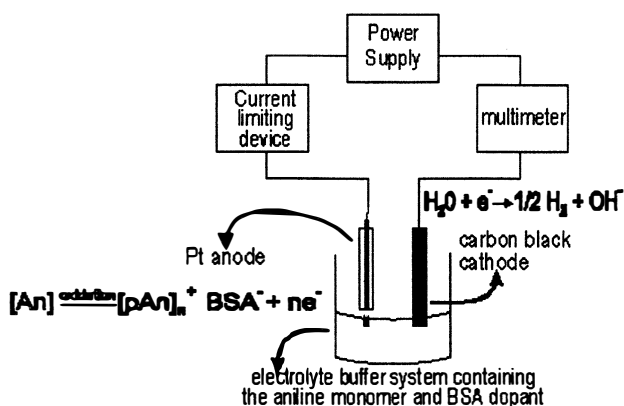


Fig. 3. Set-up for electropolymerization process.

acetic acid (Merck), 0.040M phosphoric acid (Ajax) and 0.040M of boric acid (J. J. Baker) whose pH values were adjusted via the addition of 3.0 M NaOH (Ajax) to the appropriate values.

Aniline monomer was purified by simple distillation. The colorless distillate was stored in a sealed amber bottle to prevent its oxidation [4].

Sensor configuration. The electrode was fabricated using platinum wire (99% Herrington, 0.104 cm²) soldered to an insulated copper wire (5.87 cm). Vulcaseal (Brown Chemical Corporation) was used in covering the electrode with plastic case (lollipop stick which is ~ 4 cm long and ~ 0.5 cm in diameter) (Fig. 2).

Fabrication of the pH sensor. The pH sensor was prepared by electropolymerization of aniline monomer with BSA dopant in tris(hydroxymethyl)-amino methane solution onto a platinum wire (0.104 cm²) under constant current (0.10 mA) against a carbon rod (0.341 cm²). The platinum wire was polished with high grade of sandpaper (1200 grade) and alumina paste (Sigma), and rinsed and sonicated with distilled water for a few minutes prior to use in order to remove impurities [5]. The platinum (anode) and carbon rod (cathode) were faced paral-

lel to each other, which is separated by a distance of 1.0 cm. The current was regulated by adjusting the current limiting device, which was in series with the voltage source (<30 V) and the cell. The set-up is shown in Fig. 3.

Instrumentation and measurement. The sensor signals were monitored using the pH sensor as the indicator electrode and silver/silver chloride as the reference electrode, until a steady state reading of ± 1.0 mV/min was obtained for solutions of different pH values. The cell was hooked-up to a computer using 8-channel, 12-bit ADC card (Innovatronix Inc). The set up for data acquisition, as shown in Fig. 4, allowed monitoring, storage and retrieval of results.

Cyclic Voltammetry. Through cyclic voltammetry (Metrohm), the growth of the polymer onto a platinum disc against Ag/AgCl reference electrode, with platinum auxiliary electrode, was investigated. The following parameters were set as shown in Table 1.

The potentials for the anodic and cathodic peaks were scaled from the obtained voltammogram to be able to detect the voltage by which oxidation and reduction reactions had taken

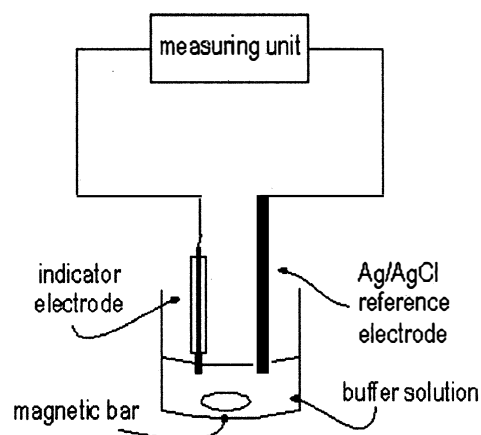


Fig. 4. Set-up for instrumentation and measurement.

Table 1. Parameters used for the polymerization of aniline through Cyclic Voltammetry

Instructions	t/s	Main Parameters		Auxiliary Parameters	
RDE	30.0	Rot speed	0/min	Prep cycles	1
CYCMODE		I range	450 uA	Meas cycles	4
(CS SWEEP	RAMP	U start	(-) 100 mV	U step	5 mV
		U end	(-) 1300 mV	t step	0.50 s
RAMP		U start	(-) 1300 mV	sweep rate	10 mV/s
		U end	(-) 100 mV	U step	5 mV
CSSWEEP)	END			t step	0.50 s
				Sweep rate	10 mV/s

place. More importantly, the potential at which the conducting state of polyaniline is attained, which also occurred during oxidation, was evaluated and determined.

Surface characterization. Surface characterization of the PAN-modified Pt wire was done using XPS and SEM. XPS surface characterization of the membrane films were performed in an ultra-high vacuum (10^{-10} mbar) using VG ESCALAB 2201 XL surface analyzer system with Al K α anode X-ray source. Wide scan surveys as well as high resolution scans were performed at 50 eV and 20 eV pass energies, respectively.

SEM analysis was performed using a JEOL JXA-840 scanning microanalyzer. The SEM filament voltage used was 15kV with a current of 10^{-12} to 10^{-9} A with 3500 – 5000x magnifications.

RESULTS AND DISCUSSION

Galvanostatic electrochemical polymerization of aniline monomer. The pH potentiometric sensor was fabricated via galvanostatic electrodeposition of polyaniline onto the platinum wire using the optimized conditions shown in Table 2. The electrochemical cell, represented in Fig. 3, consisted of platinum, carbon black and electrolyte. The platinum served as the anode wherein oxidation occurs, and for the cathode carbon black was where reduction took place. Hence, the monomers of aniline are repeatedly oxidized and electrodeposited onto the platinum wire electrode. Likewise, it is at the carbon black electrode that reduction of water evolves hydrogen gas while releasing hydroxide ions into the solution.

A constant current of 1.0 mA necessary for amperometric polymerization was maintained using a current limiting device or a galvanostat. The output potential (<30V) that was applied to the cell was in series with a resistor whose resistance was large relative to the resistance of the cell. To ensure and continuously monitor that the adjusted current was being employed, a multimeter was placed in series with the cell.

Sensor response. The pH response of the fabricated sensor was monitored from pH 10 to pH 3 (Fig. 5). The trend of recording was from the highest down to the lowest pH in the

Table 2. Summary of optimized electropolymerization parameters

Optimized Parameters	
polymerization time	30 min
polym'n w/ or w/o stirring	w/o stirring
monomer concentration	0.1 M aniline
amount of BSA dopant	30 mg
type of buffer	0.1 M tris(hydroxymethyl)-amino methane
pH of buffer	pH 7
current (current density)	1.0 mA (9.34 mA/cm ²)
substrate	platinum

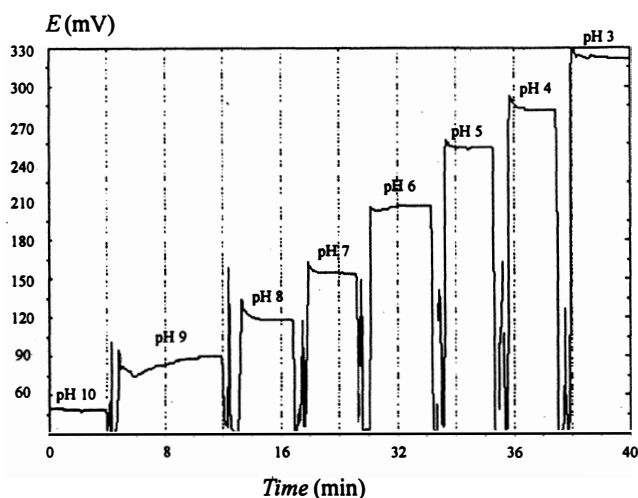


Fig. 5. PAN-based pH sensor's response to different pH of Universal Buffer Solution (pH 10 to pH 3).

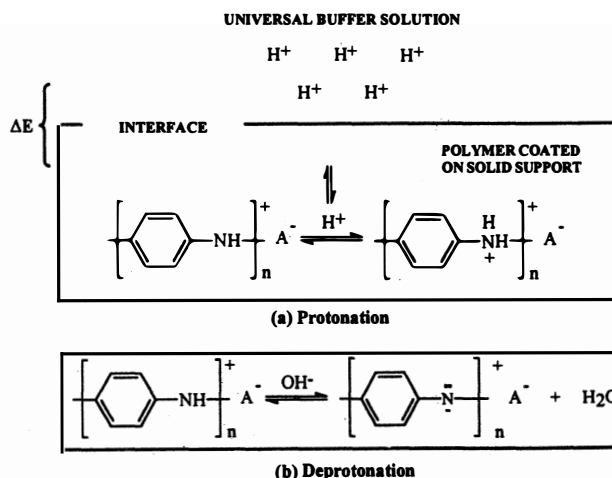


Fig. 6. Diagram of the protonation and deprotonation mechanism of polyaniline as the pH of the solution changes.

range to prevent carry over of hydrogen ions as transferring is done, because such condition will affect the response of the electrode. The steady state value at pH 10 was achieved within 2 to 3 min. On the other hand, as the electrode was immersed to a lower pH, the potential is observed to increase.

This potential response is due to the separation of charges between the bulk of the solution and the surface of the polyaniline membrane, where the exchange of H⁺ takes place. According to the binding theory [7], potential is produced when the H⁺, which was originally electrostatically bound in the sites of the membrane's surface, dissolves in the solution. thus, leaving a compensating charge behind [8].

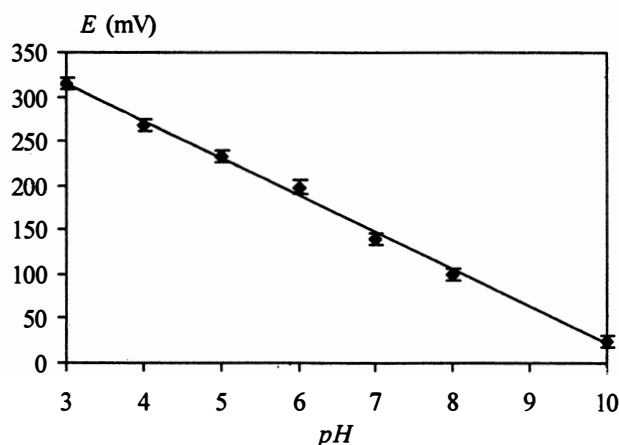


Fig. 7. Calibration curve using the optimized condition with $m = -42.06 \pm 0.6 \text{ mV/pH}$, $r = -0.9985$; and, $t_{\text{ave}} = \sim 3 \text{ min}$.

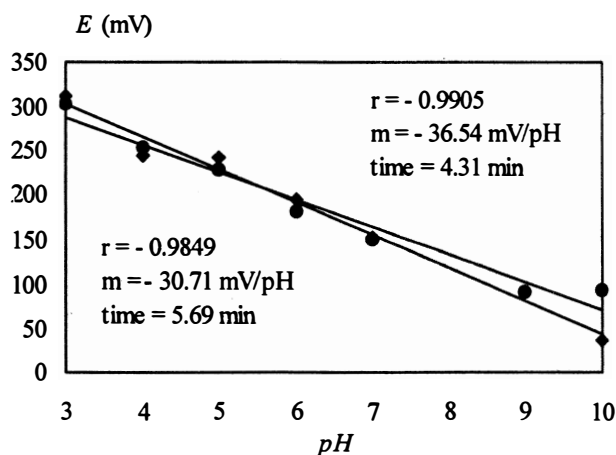


Fig. 8. Potentiometric measurements from pH 10 to 3 ($m = -36.54 \text{ mV/pH}$) and pH 3 to 10 ($m = -30.71 \text{ mV/pH}$).

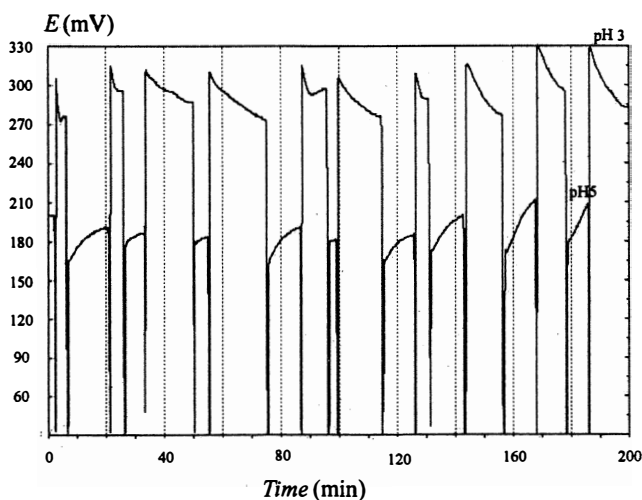


Fig. 9. PAN-based pH sensor's response to two pH values of 5 (RSD = 4.67%) and 3 (RSD = 3.34%).

The protonation/deprotonation mechanism of the nitrogen of the polyaniline as the pH of the solution varies is shown in Fig. 6. At a higher pH, extensive deprotonation occurs which yields a negatively charged nitrogen corresponding to a lower potential. On the contrary, at a lower potential extensive protonation takes place making the nitrogen more positive causing a higher potential.

Calibration. The calibration curve in Fig. 7 shows the measured emf of the sensor against several pH values. It exhibits a linear working range from pH 10 down to pH 3 with a sensitivity of $-42.06 \pm 0.6 \text{ mV/pH}$ and a linearity of -0.9985 at three replicates. This electrode response was sub-Nernstian.

Hysteresis. Hysteresis provides the information regarding the ability of the electrode to give reproducible results regardless of the order of measurements [9]. Here the calibration is performed from pH 10 to 3, then vice versa. For each set, there has been an observed slight variation in potential reading. It is indicated in Fig. 8 that there is a low slope difference of 5.83 mV/pH , which signifies that potentiometric measurements may be done either way.

Reproducibility. Reproducibility presents the precision of the electrode's performance. Figure 9 shows that the electrode is highly reproducible at acidic media. It showed an RSD of 3.34% at pH 3 and RSD of 4.67% at pH 5.

Drift. For a period of 3 h, the response of the electrode was monitored every 30 min. With this, three buffer solutions at its basic, neutral and acidic pH were used respectively. The electrode showed a minimal drift at pH 7 with an RSD of 1.7% and RSD of 2.3% at pH 4, signifying its appropriateness in neutral and acidic media. Due to the instability of polyaniline in basic solutions, there has been a great increase in the RSD at pH 8 (Fig. 10).

The frequent reason that causes electrode drift may be attributed to the reference electrode. A change in the latter's potential may be due to the diffusion of solvent into the reference solution [10].

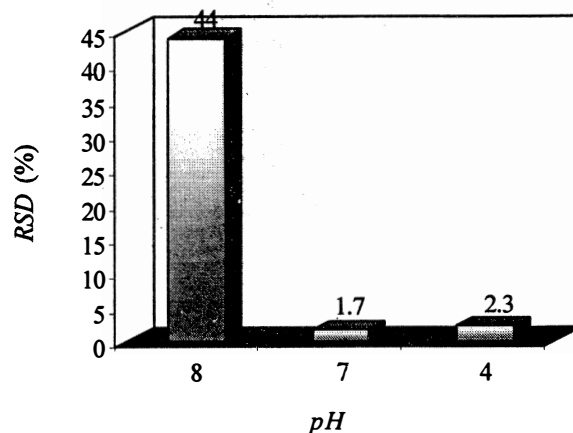


Fig. 10. Performance of the electrode in acidic and alkaline pH.

Lifetime. The stability of the electrode was monitored for >1.5 months with a total of 8 calibration readings. Each of the calibration was done interminantly. No pre-treatment was done before analysis, and electrode was kept inside the dessicator when not in use.

Figure 11 shows the plot of the sensitivity of the electrode as it ages. The first response is nearly Nernstian with a sensitivity of -49.17 mV/pH. After eight calibrations within 48 days, the sensitivity decreased to -32.97 mV/pH.

Cyclic voltammetry. The growth of polyaniline, onto the platinum disc working electrode's surface against silver/silver chloride reference electrode, was monitored using cyclic voltammetry (CV). The voltammogram in Fig. 12 showed the oxidation of aniline monomer, with an anodic peak at around -1.1 V. This peak signifies the conducting state of polyaniline. The terminal peak at the anodic sweep corresponds to overoxidation it underwent, while the initial peak found in the cathodic sweep is its response towards reduction. All these reactions were repeatedly cycled for four times. Continuous cycling conforms to thickening of film, but as seen in the graph there is no shift in potential as this occurs.

The polymer was characterized in a similar solution less the monomer aniline by cycling once. It was scanned from -1500 V to $+1500$ V with a scan rate of 50 mV s $^{-1}$. The voltammogram (Fig. 13) reflects the transitions of polyaniline that took place at different potentials. A cathodic peak occurred at -1.03 V denoting its reduced form. Meanwhile, two characteristic anodic peaks were observed at -1.09 V and $+0.61$ V, indicative of the two oxidation states of polyaniline. However, the conductive form was only acquired at the first oxidation reaction.

Figure 14 shows the mechanism of the three distinct structures of polyaniline: the reduced form, the conducting form and the oxidized form, respectively. In accord with the voltammogram, it experienced two oxidations and one reduction. The voltammogram showed three forms of polyaniline: the reduced (-1.03 V), conducting (-1.069 V), and oxidized ($+0.61$ V) states.

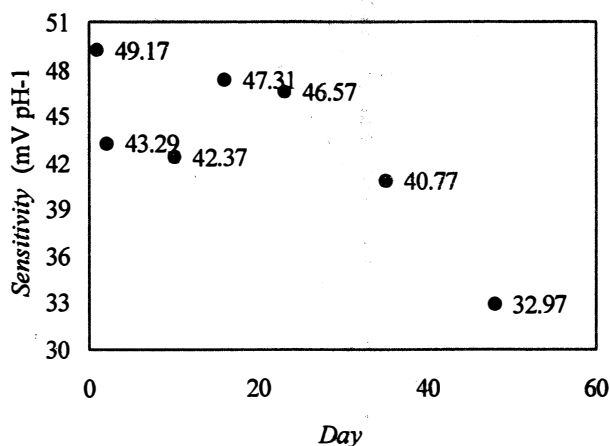


Fig. 11. Stability of the polyaniline-based pH sensor for 48 days.

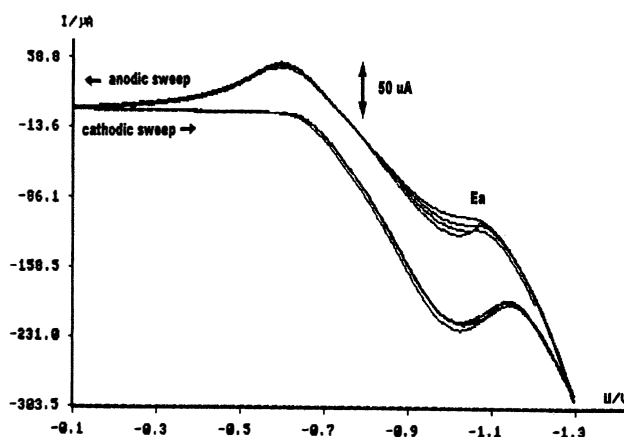


Fig. 12. Voltammogram of PAN grown on platinum disc electrode using 0.1 M aniline monomer, 0.1 M tris(hydroxymethyl)-amino methane buffer solution and BSA dopant with $E_a = -1.1$ V.

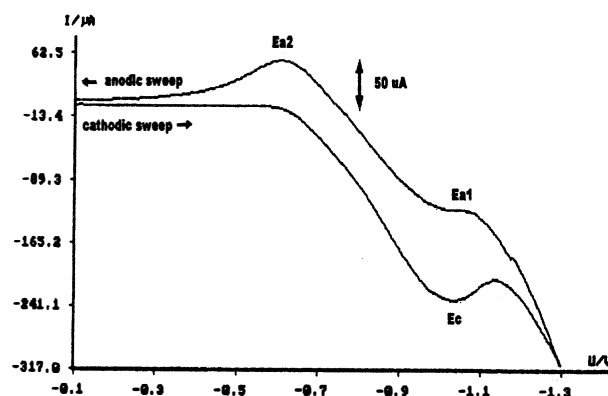


Fig. 13. Characterization of PAN film in 0.1 M tris(hydroxymethyl)-amino methane and BSA dopant with $E_{a1} = -1.09$ V; $E_{a2} = +0.61$ V; and, $E_c = -1.03$ V.

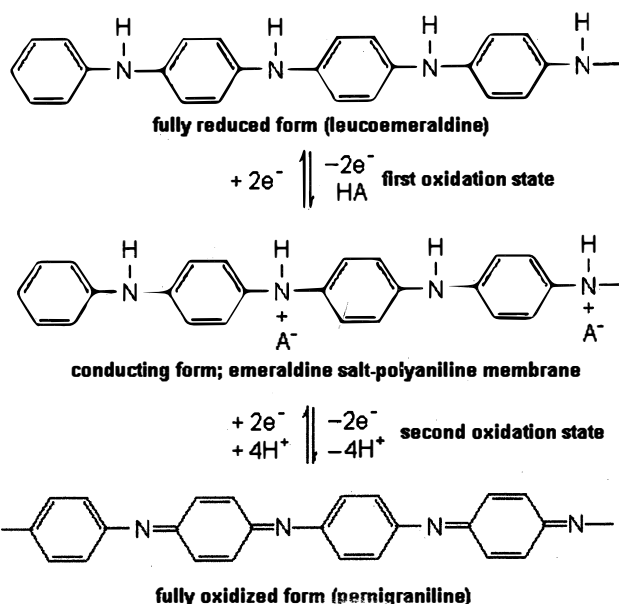


Fig. 14. Schematic diagram of the three forms of polyaniline.

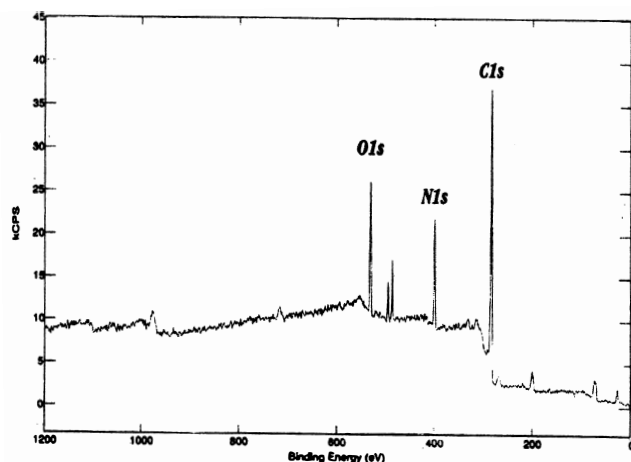


Fig. 15. X-ray photoelectron wide scan spectrum of PAN/BSA membrane.

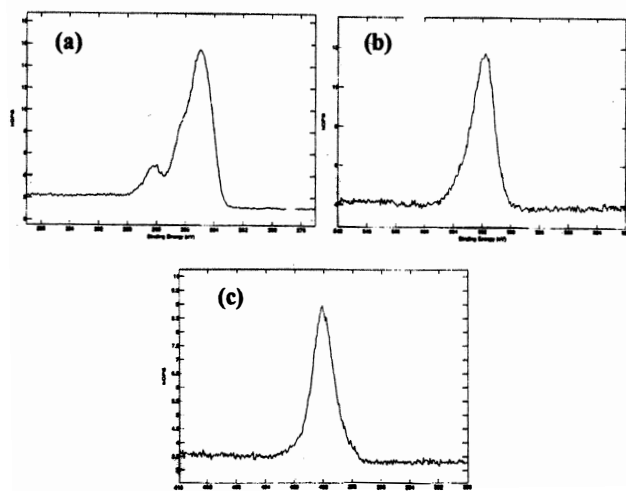


Fig. 16. (a) C1s, (b) O1s, and (c) N1s XPS core level spectra of the PAN/BSA film membrane.

XPS spectra. The XPS survey scan of the PAN/BSA indicated the presence of the elemental components of polyaniline which are C 1s, N 1s and O 1s (Fig. 15). The O 1s component comes from the polymerization process which is an oxidation reaction of aniline monomer, giving rise to C–O and C=O components [12]. This can also be due to the carbonyl oxygen (C=O) present in BSA. However, from the wide scan spectrum, the absence of the doublet S 2p component peak at $E_B \sim 168.5$ eV and ~ 163.7 eV indicates that the O 1s peak is solely due to the oxidation of aniline and not from the BSA. The BSA dopant exists mostly in the bulk of the polymer film and not on the membrane surface.

The C 1s high-resolution elemental spectrum of PAN/BSA (Fig. 16a) centering at $E_B \sim 285$ eV to 286 eV is the contribution from the C–C aromatic and aliphatic carbons. The shoulder at



Fig. 17. Scanning electron micrograph of PAN/BSA membrane (3500x magnification).

higher binding energy from the main C 1s peak is the C–N and C–O carbons, $E_B \sim 287$ - and 288 eV, respectively. The peak at $E_B \sim 289$ eV is basically the C=O carbon.

The O 1s peak centering at $E_B \sim 532$ eV (Fig. 6b) and the N 1s peak at $E_B \sim 399$ eV (Fig. 16c).

SEM. The SEM micrograph showed (Fig. 17) hexagonal-shaped flakes of PAN film coated on Pt wire under 3500x magnification. The high current density (9.34 mA/cm^2) used during the electrodeposition of PAN gave rise to the non-uniform and rough film surface. While a low current density with respect to the anode surface (0.7 mA/cm^2) produced smooth films [11].

CONCLUSION

A small potentiometric pH sensor based on conducting polyaniline was produced using galvanostatic electropolymerization. The pH sensor's potential response is due to the reversible protonation and deprotonation of the nitrogen atoms in the polyaniline arrays as the pH of the solution is varied (pH 10 to pH 3). The non-uniform surface of the membrane still resulted to a sensor of good sensitivity, high linearity and good reproducibility. Furthermore the electrodeposited polyaniline has the advantage ease of miniaturization and fabrication.

ACKNOWLEDGEMENT

The authors would like to thank Prof. E.T. Kang of National University of Singapore for the XPS Analysis and Ms. Ner Rodriguez of Industrial Technology Development Institute of the Department of Science and Technology, Philippines for the SEM analysis.

REFERENCES

- [1] Huang, W. S., Humphrey, B. D., and MacDiarmid, A. G. *J. Chem. Soc., Faraday Trans. 1* (82), (1986).
- [2] Salanec, W. R., Lundstrom, I., and Ranby, B. (Eds.). *Conjugated Polymers and Related Materials: The Interconnection of Chemical and Electronic Structure*, pp. 5-405 (Oxford Science, 1993).
- [3] Binag, C. A., Bartolome, A. J., Tongol, B. J. V., and Santiago, K. S. *Phil. J. of Sci.* 128 (30), 247 (1999).
- [4] Beyer, H. and Walter, W. *Handbook of Organic Chemistry*. (Prentice Hall, 1996).
- [5] Tiemann, R. S., Heineman, W. R., Johnson, J., and Sequin, R. *Sens. Actuators*. 2, 199 (1992).
- [6] Binag, C. A. Ph.D. Thesis. University of New South Wales, Sydney Australia, 1995.
- [7] Bartolome, A. J. M.S. Thesis, University of Santo Tomas, 1997.
- [8] Guilbault, G. G. *Ion-Selective Electrodes Rev.* 1 (139), (1979).
- [9] Smyth, M. R., Vos, J. G. (Eds.). *Analytical Chemistry Symposia Series: Electrochemistry, Sensors and Analysis*, Vol. 25. (Elsevier Science, 1986).
- [10] Pallas-Areny, R. *Transducers*. (J. Wiley & Sons, 1991).
- [11] Moss, B. K., Burford, R. P., and Skyllas-Kazacos, M. *Materials Forum*. 13, 35 (1989).
- [12] Aquino-Binag, C., Pigram, P. J., Kumar, N., and Lamb, R. *N. Chem. Mater.* 8 (11), 2579 (1996).