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Electrochemically- Synthesized Polypyrrole Thin Films for Ethanol Vapor Sensing

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Abstract: The possible technological application of conducting polypyrrole as an electronic nose or aroma sensor is based on the change in its resistance upon exposure to certain volatile gases. In this study, conducting polypyrrole films were galvanostatically synthesized at constant temperature in aqueous solution containing 0.1M pyrrole monomer and varying concentrations of sodium p-toluenesulfonate (0.08M, 0.10M and 0.12M) as dopant and anion salt. Film resistivities in air were determined using Van der Pauw technique and were found to range from 0.2012 to 10.53 Ωcm. Upon exposure to 500ppm ethanol vapor, the resistivity of the polypyrrole films was found to decrease significantly. The sensitivity of the film sensor to ethanol vapor was detemined by obtaining the fractional change in resistivity $\Delta\rho/\rho_o$ upon exposure to the said vapor. Relatively high values of $\Delta\rho/\rho_o$ were obtained, ranging from 76.36% to as high as 99.40%. These high values show that the polypyrrole films synthesized in this study are highly sensitive to ethanol vapor and could be a very good material as an ethanol sensor. Furthermore, the resistance of the film sensors calculated from the I-V curves showed a significant drop after exposure to ethanol vapor. The calculated fractional change in resistance based on the I-V curves ranged from 60% to 91%. The conducting polypyrrole film with the highest resistivity in air showed the highest fractional change in resistance and the film with the lowest resistivity in air showed the lowest fractional change in resistance.

Keywords: ethanol; sensor; conducting polymer; polypyrrole; thin film

1. INTRODUCTION

Since the discovery of conducting polypyrrole, several studies have been made to control the electrical conductivity of polypyrrole by doping, from insulating to highly conducting. One method of synthesizing polymers is by electrochemical oxidation where monomers polymerize at the anode of an electrochemical cell and doping the polymer is achieved by oxidation or reduction. Due to the ease in growing and doping this organic semiconductor material, several technological applications have been proposed, studied and reported. Possible applications include rechargeable batteries, electrochromic displays and smart windows, light emitting diodes (LEDs), toxic waste cleanup, sensors, corrosion inhibitors, field effect transistors (FETs), and electromagnetic interference (EMI) shielding.

This study aims to electrochemically synthesize conducting polypyrrole films for ethanol vapor sensing application. By determing the fractional change in the reisticance of the film sensor,

the sensitivity of the polypyrrole film to ethanol vapor may be established.

2. METHODOLOGY

2.1 Synthesis and Characteriztion of Conducting Polypyrrole Films

The conducting polypyrrole films were electrochemically synthesized in an aqueous solution containing 0.1M pyrrole monomer and sodium p-toluenesulfonate (Na p-TS) as dopant and anion salt. Different concentrations of the anion salt were prepared, specifically 0.08M, 0.10M and 0.12M to produce films with varying conductivities. For the working and counterelectrodes, stainless steel plates with dimensions 9cm x 9cm were used. Furthermore, a constant current density of 3 mA/cm^2 was maintained and all synthesis was done at room temperature, under nitrogen environment and low light conditions. In order to obtain films of varying thicknesses, film growth time was varied (1 hour, 1.5 and 2 hours). Films of different thicknesses is desired to determine the effect of film sensor thickness on its sentisitivity to changes in vapor concentration.

Energy dispersive x-ray (EDX) was used to verify the films' elemental composition and a JEOL JSM-5310 scanning electron microscope (SEM) to measure film thickness and surface morphology. Moreover, the resistivity of the films were determined using Van der Pauw four-point-probe technique and the current-voltage (I-V) characteristics were measured using a Rigol DS 1102E digital oscilloscope.

2.2 Vapor Sensor Film Characterization

The synthesized polypyrrole film sensor was mounted in a glass chamber (Fig. 1) where 250 ppm concentration of ethanol vapor was passed. The film sensor was then connected to a circuit where a function generator applies voltage across the sensor while a digital oscilloscope measures the current-voltage characteristics. All measurements were done under normal atmospheric condition at room temperature (26°C ± 2°C). Figure 2 shows the experimental set-up for the measurement of the I-V characteristics of the film sensors upon exposure to ethanol.

Fig. 1. Conducting polypyrrole film sensor mounted in a glass chamber for vapor sensor measurements.

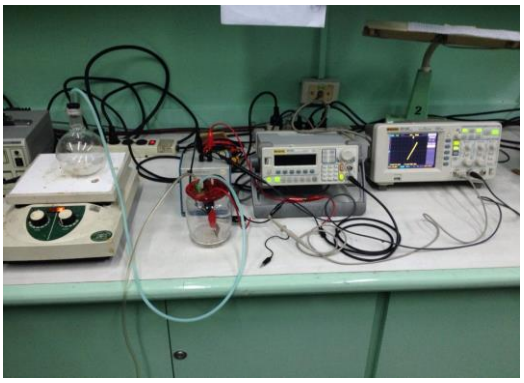


Fig. 2. Experimental set-up used in the I-V characterization of film sensor.

3. RESULTS AND DISCUSSION

3.1 Elemental Analysis and Surface Morphology

EDX analysis was performed in order to determine the elemental composition of the films synthesized. Specifically, the method was used to check if the deposited film on the stainless steel was polypyrrole (PPy) and confirm the incorporation of the dopant during the polymeriztion process. The bar graph shown in Figure 3 illustrates the percentage values of the elements present in the PPy film synthesized using 0.12M of Na-PTS. The elemental

analysis results show that carbon (52.59%), nitrogen (15.92%), oxygen (17.82%) and sulfur (13.36%) were detected which are the elemental composition of polypyrrole. The results also confirm the incorporation of a relatively small amount of sodium (0.31%) in the PPy film as dopant.

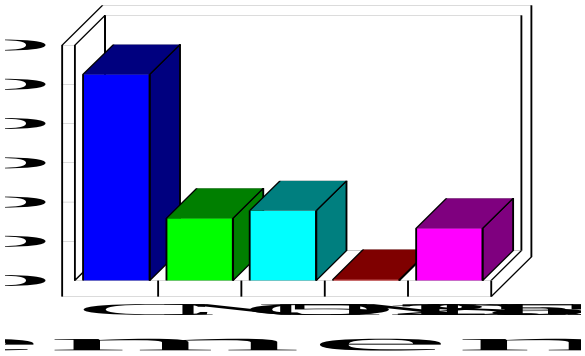


Fig. 3 Elemental analysis of conducting polypyrrole film synthesized using 0.12M Na-pTS.

The SEM images of the films prepared using 0.10M Na-pTS with varying synthesis time are shown in Figure 4. It was observed that longer synthesis time produced thicker films, consistent with previous studies. Longer film growth time allows lengthier period for the deposition and polymerization of the polypyrrole film on the electrode. Measured polypyrrole film thickness range from 0.5883 µm to 35.50 µm.

The surface morphology of the PPy film magnified 2000x (Figure 4B) shows globular structures typical of electrochemically synthesized polypyrrole films. However, the PPy films grown on stainless steel plates in this study have a relatively smooth surface compared to PPy films grown on ITO-coated glass slides, from previous studies, under similar synthesis conditions.

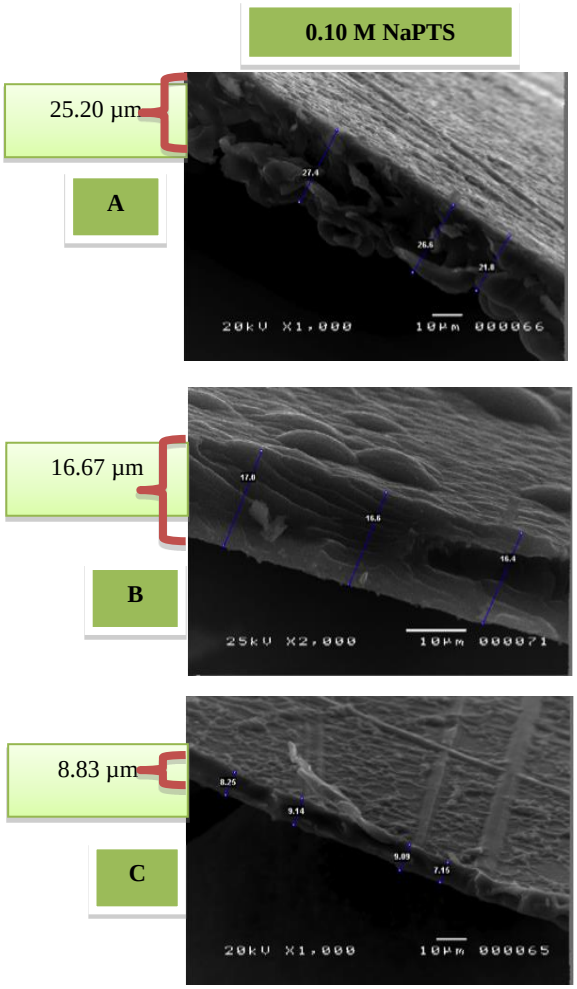


Fig. 4. SEM images of the polypyrrole films synthesized using 0.10M NaPTS dopant with the following synthesis time: A) 1hr (magnified 1000x) m; B) 1 ½ hr (magnified 2000x); and C) 2 hrs (magnified 1000x).

3.2 Resistivity Response of Film Sensor to Ethanol Vapor

Using the Van der Pauw four-point-probe technique, the resistivities of the PPy film sensors were determined in air and then upon exposure to 250ppm ethanol vapor. Tables 1A, 1B, and 1C presents the resistivities of the film sensors before and after exposure to ethanol vapor.

Table 1. Resistivity of PPy film sensors synthesized using (A) 0.08M, (B) 0.10M, and (C) 0.12M Na-PTS in

air and upon exposure to ethanol vapor

A. PPy film sensors synthesized using 0.08M Na-PTS						
Synthesis Time	1 hour		1 and ½ hour		2 hours	
Thickness (μm)	24.56 μm		4.39 μm		35.13 μm	
Resistivity (Ω cm)	Air	Ethanol	Air	Ethanol	Air	Ethanol
Film 1	7.49	0.35	1.09	0.0052	6.92	0.04
2	6.95	0.56	0.645	0.031	10.5	0.13
3	6.26	1.48	0.494	0.016	7.77	0.43

B. PPy film sensors synthesized using 0.10M Na-PTS						
Synthesis	1 hour		1 and ½ hour		2 hours	
Film Thickness	25.20 μm		16.67 μm		8.83 μm	
Resistivity (Ω cm)	Air	Ethanol	Air	Ethanol	Air	Et
Film 1	5.86	0.51	6.33	0.09	2.35	0
2	5.58	0.40	3.80	0.06	2.90	0
3	4.97	0.35	5.57	0.07	2.75	0

C. PPy film sensors synthesized using 0.12M Na-PTS						
Synthesis	1 hour		1 and ½ hour		2 hours	
Film Thickness	58.83 μm		31.83 μm		25.40 μm	
Resistivity (Ω cm)	Air	Ethanol	Air	Ethanol	Air	Et
Film 1	0.2012	0.00142	5.08	0.12	7.	0
2	0.2313	0.00697	8.75	0.12	5.	0
3	0.2625	0.00747	4.22	0.12	8.	0

From the table above, it can be seen that the resistivities of the PPy films decreased significantly upon exposure to ethanol vapor. The resistivities decreased by a factor of a tenth to as low as a hundredth. The fractional change in resistivities were also computed and showed in Tables 2A, 2B and 2C.

The response of thin films to vapor exposure is commonly determined by calculating the fractional change in resistance or resistivity. In this paper, the fractional change in resistivity was determined by

$$\frac{\Delta\rho}{\rho} = \frac{|\rho_e - \rho_o|}{\rho_o} x\,100$$

where ρ_e is the resistivity of the film after exposure to ethanol vapor and ρ_o is the resistivity in air, i.e. before exposure to ethanol vapor.

Table 2. Fractional change in resisitivity of PPy film sensors synthesized using (A) 0.08M, (B) 0.10M, and (C) 0.12M Na-PTS.

A. PPy film sensor synthesized using 0.08M Na-PTS				
Synthesis Time		1 hour	1 and ½ hour	2 hours
Film Thickness (μm)		24.56 μm	4.39 μm	35.13 μm
Fractional change in resistivity	Film 1	95.33 %	99.52 %	99.34 %
	Film 2	91.94 %	95.19 %	98.77 %
	Film 3	76.36 %	96.76 %	94.47 %
	Average	87.88 %	97.16%	97.52%

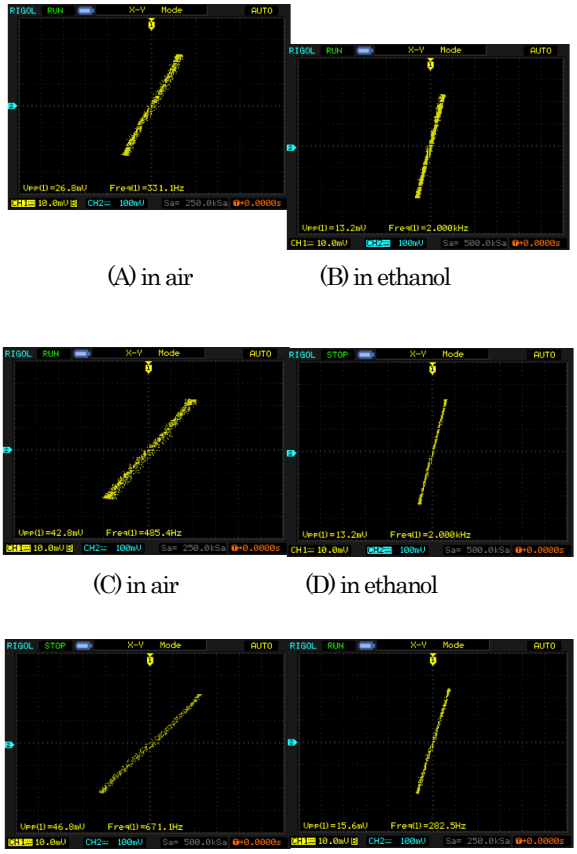
B. PPy film sensor synthesized using 0.10M Na-PTS				
Synthesis Time		1 hour	1 and ½ hour	2 hours
Film Thickness (μm)		25.20 μm	16.67 μm	8.83 μm
Fractional change in resistivity	Film 1	91.30 %	98.58 %	98.26 %
	Film 2	92.83 %	98.42 %	98.45 %
	Film 3	92.96 %	98.74 %	98.25 %
	Average	92.36%	98.58%	98.32%

C. PPy film sensor synthesized using 0.12M Na-PTS				
Synthesis Time		1 hour	1 and ½ hour	2 hours
Film Thickness (μm)		58.83 μm	31.83 μm	25.40 μm
Fractional change in resistivity	Film 1	99.29 %	97.64 %	99.01 %
	Film 2	96.99 %	98.63 %	99.29 %
	Film 3	97.15 %	97.16 %	99.40 %
	Average	97.81 %	97.81%	99.23%

From Tables 2A, 2B and 2C, it can be seen that the calculated fractional change in resistivity ranged from 76.36% to as high as 99.40% which demonstrates that the polypyrrole films synthesized in this study are highly sensitive to ethanol vapor and could be a very good material as an ethanol vapor sensor. There is, however, no significant relationship observed between the thickness of the film and the fractional change in resistivity after exposure to ethanol vapor.

3.3 I-V Characteristics of PPy Film Sensors

The I-V characterisitics of the film sensors were obtained in air and upon exposure to ethanol vapor (Figure 5).



(A) in air (B) in ethanol

(C) in air (D) in ethanol

(E) in air (F) in ethanol

Fig. 5. I-V characteristics in air and in ethanol vapor of film sensors synthesized using (A)/(B) 0.08M, (C)/(D) 0.10M and (E)/(F) 0.12M Na-PTS.

The reisitance of the film sensor was computed by getting the reciprocal of the slope of the I-V curve. Based on the I-V curves her than the resistance upon exposure to ethshown above, the resistance of the films in air are higanol vapor. This supports the results on the resistivity measurements discussed earlier; that the resistivity of all the films decreased significantly upon exposure to ethanol vapor.

The slope of the I-V curve of the film sensor exposed in air is small, corresponding to a large resistance. On the other hand, the I-V curve in ethanol of the polypyrrole film showed a larger slope which means its resistance drops when exposed to ethanol vapor. The gradual increase in resistance of the electrochemically-synthesized polypyrrole films that was observed upon exposing the polypyrrole films on alcohol is due to the extraction of some dopant molecules, which resulted to the densification of the polymer (Mabrook et. al, 2005). In a similar study by Segal E. et. al (2005) discussed that the observed resistance change of the electrochemically-synthesized film doped in sodium p-toluenesulfonate (NaPTS) resulted from enhanced charge carrier mobility through hopping processes between the sodium p-toluenesulfonate particles. The dopant content and method of processing affected the sensing performance of the polypyrrole film.
The fractional change in resistance was also determined and the calculated values are shown in the table below. The fractional change in resistance is determined by

$$\frac{\Delta R}{R} = \frac{|R_e - R_o|}{R_o} x\,100$$

where R_e is the minimum or maximum resistance of the sensor after exposure to the vapor and R_o is the resistance in air.

Table 3. Fractional change in resistance of film sensors after exposure to ethanol vapor

NaPTS dopant Molarity	Film Thickness (μm)	Resistivity in air (Ωcm)	Fractional change in resistance
0.08M	24.56	6.95	80%
	4.39	0.645	85%
	35.13	10.53	91%
0.10M	25.2	5.86	70%
	16.67	5.57	67%
	8.83	2.35	72%
0.12M	58.83	0.263	60%
	31.83	5.08	73%
	25.4	5.6	71%

Based on table 3, the resistance of the film sensors decreased by as much as 91% following

exposure to ethanol vapor. The film sensor with the highest resistivity (10.53 Ωcm) in air showed the highest fractional change in resistance. And the film with the lowest resistivity (0.263 Ωcm) showed the lowest fractional change is resistance. The values obtained in this study is relatively higher than the ones reported by Mabrook et. al. (2005), in which the fractional change in resistance of theIR inkjet-printed conducting PPy film sensors is 68%.

4. CONCLUSIONS

Conducting polypyrrole films were electrochemically synthesized at a constant current density of 3 mA/cm^2 and temperature (26°C ± 2°C) in an aqueous solution containing 0.1M pyrrole monomer and varying concentrations of NaPTS dopant and anion salt. (26°C ± 2°C). The NaPTS dopant concentrations used were 0.08M, 0.10M and 0.12M. EDX measurements verified the elemental composition of the PPy films and the incorporation of the dopant into the film during the polymerization process. Scanning electron microscopy was used to determine the surface morphology of the films and the film thickness. Measured film thickness ranged from 0.5883 µm to 35.50 µm.

The resistivity of the films before and after exposure to ethanol vapor was determined using Van der Pauw four-point-probe technique. Film resistivities in air range from 0.2012 Ωcm to 10.53 Ωcm. Thicker films were found to have relatively higher resistivities than thinner films. Upon exposure to ethanol vapor, the resistivity of the polypyrrole films decreased by a factor of a tenth to a hundredth. The calculated fractional change in resistivity ranged from 76.36% to as high as 99.40% which shows that the polypyrrole film sensors synthesized in this study are highly sensitive to ethanol vapor and could be a very good material as an ethanol sensor.

The I-V curves before and after exposure to ethanol vapor was also determined using a digital oscilloscope. The resistance of the film sensors showed a significant drop upon ethanol vapor exposure. The calculated fractional change in resistance ranged from 60% to 91%. The film sensor with the highest resistivity in air showed the highest fractional change in resistance and the sample with the lowest resistivity in air showed the lowest fractional change in resistance.

It is recommended for further studies that the resposnse time of the film sensors and its sensitivity to varying ethanol vapor concentrations be measured. Furthermore, the researchers of also recommend measurement of the thickness of the films after exposure to ethanol vapor to determine the degree of swelling and its effect on the sensitivity and response of the film sensors to varying concentrations of ethanol vapor.

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