Fabrication of Polyaniline Thin Film Using Electrodeposition Method as Alcohol Sensor

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Abstract: The use of aliphatic alcohols such as methanol as an alternative renewable fuel in high-density engines can harm both the environment and human health. Polyaniline (PANi), a conductive polymer, has emerged as a solution to this problem because of its benefits as a sensor with relatively high conductivity. In this study, PANi was synthesized using a potentiostat electrodeposition method at a constant potential of -0.4 to +1.0 V at a scan rate of 100 mV/s, resulting in a thin film of PANi on the ITO surface. The formed PANi samples were used to determine the sensitivity level of the sensor to methanol at different concentrations. Morphological results of PANi deposited on the ITO surface were observed using SEM showing the shape of nanoparticles with an interconnected-sponge structure and a porous shape with a diameter of 35.3 nm. The PANI sample can be applied as a sensor material for detecting alcohol vapour in indoor air (at room temperature). The sensing measurement results show that the PANi-based sensor can detect methanol vapour at low concentrations up to 5 ppm. The higher the methanol concentration used, the higher the sensor sensitivity.

Keywords: PANi; ITO; electrodeposition; alcohol sensor.

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I. INTRODUCTION

Along with increasing economic growth, the supply of fossil fuels has decreased due to the increasing use of fuel oil, especially in the transportation sector [1]. However, the current development of science and technology has led to new ideas related to the provision of renewable alternative energy as a substitute for fossil fuels, one of which is aliphatic alcohol in engine combustion systems [2]. The production process of aliphatic alcohol is simple, so its use will continue to increase [3, 4]. However, the increasing use of alcohol with high levels can harm human health and the environment, as it is the characteristic of volatile aliphatic alcohol, especially the type of methanol which has a high alcohol vapour pressure so that it is easily flammable and produces hazardous toxic substances [5, 6]. The adverse effects of methanol vapour include affecting the human nervous system, irritation to the respiratory system, and the possibility of death depending on the level of alcohol used [5, 7]. In addition, excessive exhaust emissions can also affect the process of photosynthesis in plants. Thus, we need a device capable of detecting methanol vapour in the environment.

An analysis of the test of a sensor using an active ingredient has been carried out by applying a resistance change technique resulting from the interaction of analyte molecules with the active ingredient on the sensor surface [8]. The active material used can be a conductive polymer. Conductive polymers are intrinsically capable of conducting electrical properties that can be adjusted by controlling the concentration of electrolyte or monomer, temperature, and polymerization time. Conductive polymers have been extensively investigated to detect various organic vapours due to their application at room temperature [9]. Polyaniline (PANi) has been widely studied among the conductive polymers because of its good environmental stability, ease of fabrication, stability in aqueous solutions, and relatively high electrical conductivity [10, 11]. PANi has been applied in various applications such as biochemical sensors, electrochromic windows, sensor devices, electromagnetic interference shielding, and corrosion protection [10, 12, 13]. There are many methods to synthesize PANi. One of them is the potentiostat electrodeposition method, which researchers widely use because it has an easy, fast process, and does not require any solvents in the synthesis process [14, 15]. This method works at a constant potential. The electrode potential range can be set in advance so that it is easier to find the electron transfer reaction through the current obtained during polymerization.

The characterization of PANi as an active sensor material has previously been investigated by Joulazadeh and Navarchian [16], applying PANi coated on a glass substrate to detect several alcohol vapours, namely ethanol, methanol, propanol, and butanol. The results show that the best performance occurs when detecting alcohol vapours with low molecules, namely methanol and ethanol. Sáaedi *et al.* [17] composited PANi with ZnO for sensing methanol gas synthesized under magnetic flux density. The results showed that the sensor response increased with increasing magnetic flux density and good selectivity at 0.5 T. Mahato and Adhikari [8] composited PANi with PVA in detecting alcohol vapours of

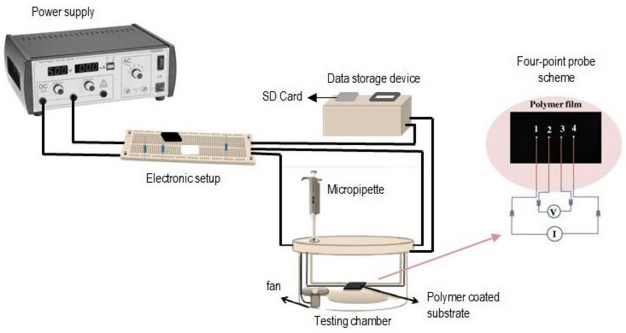

FIG. 1: Schematic of the alcohol sensing measurement set-up.

ethanol, methanol, propanol, and isopropanol types, where the results showed that the conductive polymer of the PANi/PVA composite was able to be used to detect alcohol vapour with a reasonably good sensitivity level for all samples with different concentrations.

In this study, a thin layer of PANi was fabricated using the potentiostat electrodeposition method using ITO as a working electrode to determine the characteristics of the PANi layer deposited on the ITO surface and the sensitivity of PANi-based alcohol sensors to methanol at different concentrations. The ITO substrate was chosen because it is one of the materials with good optical transparency, a wide working window, and high electrical conductivity [18], so it is expected that the PANi thin film obtained from this study has a good sensitivity level.

II. METHOD

A. Synthesis of Polyaniline (PANi)

In this study, transparent Indium Tin Oxide (ITO) glass was used as a substrate with a surface area of 2.5 cm x 2.5 cm. Before the deposition process, the substrate was cleaned with acetone and continued using distilled water to remove the adsorbed substance on the substrate surface, so that a better layer was produced. The cleaned substrate was then dried until it was ready for deposition.

PANi deposition on the ITO surface was carried out by the potentiostat electrodeposition method using the Gamry Reference 3000 Potentiostat/Galvanostat instrument. ITO was used as the working electrode, platinum metal as the counter electrode, and Ag/AgCl as the reference electrode. Cyclic Voltammetry (CV) was used to determine the electropolymerization process in an electrolyte solution consisting of 0.25 M aniline and 0.5 M HCl. Electropolymerization was carried out at a constant potential of -0.4 to +1.0 V at a scan rate of 100 mV/s [19]. The polymerization process occurs when a voltage input is connected to the three electrodes to produce a PANi thin layer on the ITO surface.

B. Characterization Techniques

The PANi samples deposited on the ITO surface were then subjected to Fourier Transform Infrared (FTIR) spectroscopic characterization to identify the type of bond present in the sample. The morphology of the samples was observed using a Scanning Electron Microscope (SEM). Furthermore, the sample has also measured the sensitivity of the alcohol sensor to methanol vapour at different concentrations, namely 5, 10, 20, 50, and 100 ppm, using a four-point probe instrument (four sensing terminals) as shown in Fig. 1. In this measurement, the four probes touch the sample surface, where two probes are for measuring voltage, and the other two are for measuring current. The probes are placed in a row in a straight line where the distance between the probes is arranged to have the same distance. This instrument is used to determine the value of the output voltage and output current more accurately so that the resistance value of the sample will be obtained. Thus the sensitivity value of the sensor will also be known by measuring the change in sample resistance before and after exposure to methanol vapour at room temperature.

For alcohol sensing measurements, the sample is fed into a DC electrical circuit connected directly to the testing chamber or sensing chamber. Then alcohol with a specific concentration is injected into the sensing chamber, equipped with a circulation fan that works continuously during the measurement process. The amount of alcohol vapour concentration is calculated at room temperature (30 ^{o}C) using Eq. 1.

$$C = (22.4 \times V_L \times \rho_L \times \phi \times 100) \,/\, (M \times V) \qquad (1)$$

Where C is the target alcohol concentration (ppm), V_L is the alcohol volume (mL), ρ_L is the alcohol density (g/mL), ϕ is the volume fraction of alcohol required, M is the target alcohol molecular weight (g/mol), and V is the volume of the room (L) [20].

The performance of the sample when detecting methanol vapor was observed in terms of response time, recovery time, and sensor sensitivity. The response (S) of the sensor, namely the sensitivity of the sensor is expressed as the ratio of the change in resistance (ΔR= R-R_0) of the sample resistance (R) due to exposure to alcohol vapor in the test chamber to the sample resistance (R_0) before exposure to alcohol vapor which is calculated using Eq. 2 following [21].

$$S = \frac{\Delta R}{R_0} \times 100\% \qquad (2)$$

III. RESULTS AND DISCUSSION

A. Cyclic Voltammetry Results of PANi Deposition

Electropolymerization results using Cyclic Voltammetry (CV) can affect the morphology, thickness, and composition of the layer on the substrate surface. The higher of scan rate used in the electropolymerization process, the faster rate of the

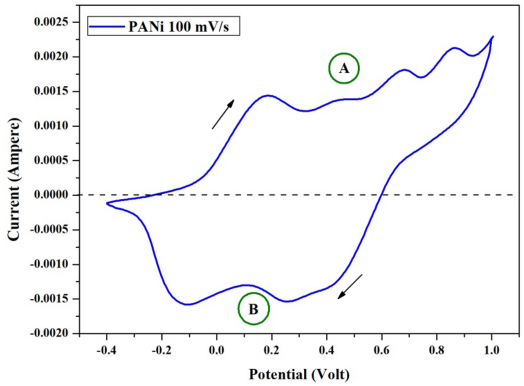

FIG. 2: Cyclic voltammogram curve of the PANi thin films deposited on ITO substrate with a scan rate of 100 mV/s.

FIG. 3: Observation of the color of PANi thin film deposited on the ITO substrate.

growth of a PANi layer on the ITO surface, resulting in a thinner layer, which indicates that the PANi layer adheres firmly and forms bonds on the ITO surface. This study used a thin layer of PANi as an alcohol sensor material. Then, the voltammogram curve of the PANi electropolymerization was taken in one scan/cycle from ten cycles carried out, as shown in Fig. 2. The ideal number of cycles is a maximum of ten cycles because the ions from the solution will be bound to each other and form layers during the electropolymerization process. If the polymerization cycle is more than ideal, it will produce a thick layer and allow rapid degradation from the substrate surface [22]. The use of a constant potential between 0.4 to + 1.0 V at a scan rate of 100 mV/s has triggered the polymerization of PANi on the ITO surface, which is characterized by the appearance of several oxidation peaks (several peaks around point A) and reduction peaks (several peaks around point B).

The increase in the value of the reduction-oxidation (redox) current is evidence of the growth of the PANi layer on the ITO surface. There are three oxidation peaks at +0.19, +0.68, and +0.90 V and two reduction peaks at +0.25 and 0.15 V, which at these peaks indicate the presence of an electroactive region in layers. This potential also explains the presence of aniline monomers which undergo deprotonation reactions, as reported by [19, 23]. The oxidation peak indicates a change from the leucomeraldine phase to the emeraldine phase. When approaching the potential limit of the voltammogram, there is a change from the emeraldine phase to the pernigraniline

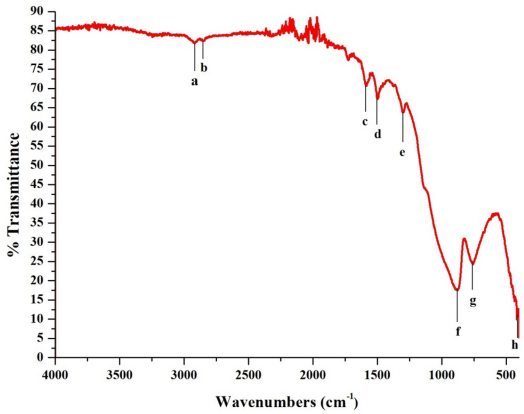

FIG. 4: FTIR spectra of the PANi thin films deposited on ITO substrate .

phase, which occurs at the oxidation peak of +0.90 V. While the reduction peak indicates a shift from the pernigraniline phase to the emeraldine phase [24]. This electropolymerization process resulted from a green PANi thin layer deposited on the ITO surface, as shown in Fig. 3, which is the result of direct observation of the colour of the PANi thin layer on the ITO surface. According to the redox state, the green colour on the layer indicates the form of the phase is emeraldine salt, where the emeraldine phase produces a conductive PANi layer whose conductivity can be adjusted through a doping process using an acid solution such as HCl. The results of the literature show that in the potentiostat electrodeposition method, the greater the scanning rate, the higher the oxidation peak, and the more it moves towards a positive potential. As a result, the current density increases, indicating that the growth of PANi on the ITO surface is increasing. Meanwhile, the reduction peak moves in the negative direction, which indicates that the working electrode provides ample space when interacting with the electrolyte solution [25].

B. FTIR Characterization Results

The results of electropolymerization of the PANi thin film deposited on the ITO surface were then tested by FTIR. Fig. 4 shows the FTIR spectrum of a PANi sample using 0.5 M HCl dopants. The summary of the FTIR spectrum observations is listed in Table I. The results of the FTIR spectrum show that the PANi sample has several types of bonds, including C-H aliphatic stretching, N=Q=N stretching vibration, C=C stretching (Q), C=C stretching (B), N-B-N stretching, C-N-C stretching vibration, C-H out-of-plane bending, C-H out-of-plane bending vibrations in benzenoid units. When compared with several references, the FTIR characterization of PANi samples has a lot of agreement. Thus, it can be concluded that the electropolymerized sample consists of PANi molecules.

However, in the type of C-H bending bond, the wavenumber is 877.27 cm^{-1}, while this type of bond is in the wavenumber 850-550 cm^{-1}. This is possible because of the out-of-plane deformation of the C-H bond in the ring structure of 1,4-

TABLE I: Summary of FTIR spectra observations for PANi with HCl dopants.

Code	Wavenumber (cm-1)				Bond Types	References
	Datasheet		Reference (PANi/HCl)	Sample (PANi/HCl)		
a & b			2925	2917.15	C-H aliphatic stretching	[28]
			2856	2841.16		
c	1650	1560	1551 and 1556	1585.61	N=Q=N stretching vibration C=C stretching (Q)	[27, 28]
d	1500	1400	1472 and 1476	1499.02	N-B-N stretching N-B-N stretching	[27, 28]
e	1335	1250	1291	1296.04	C-N-C stretching vibration	[27]
f & g	850	550	800	877.27	C-H out-of-plane bending	[26]
			794	759.13	C-H out-of-plane bending vibrations in benzenoid units	[27]
h			497	415.83	C-C out-of-plane bending vibrations in benzenoid units	[27]

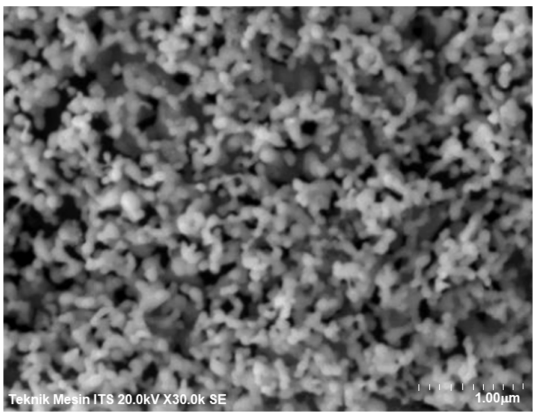

FIG. 5: SEM results of the PANi thin films deposited on ITO substrate with a magnification of 30,000X.

distributed during the electropolymerization process. Then the type of bond C-H out-of-plane bending vibrations in benzenoid units also appears due to the influence of chloride ions which confirms doping on PANi during the electropolymerization process [26, 27].

C. SEM Characterization Results

The morphology of the PANi sample with HCl doped deposited on the ITO surface observed using SEM with a magnification of 30,000 times at a voltage of 20 kV is shown in Fig. 5. The formed PANi layer has an interconnected sponge and porous structure, and the results of using the Image-J software show that PANi has a particle size of 35.3 nm in diameter. It can be seen that the PANi growing on the ITO surface was relatively evenly distributed. However, there were still black pores which indicated that there was still an ITO surface that had not been coated with PANi. This is possible because the coating process uses a high scan rate of 100 mV/s so that PANi is not evenly deposited on the ITO surface. The particle size obtained from this study corresponds to that reported by Buron *et al.* [28] showing that the PANi layer growing on the ITO surface has a diameter of less than 50 nm. From this study, the particle size obtained was around 35.3 nm. The typical structure of PANi nanoparticles resulting from electrodeposition is that it has a sponge, branched, and porous shape depending on the electropolymerization time.

D. Alcohol Sensor Analysis

The alcohol sensor sensing mechanism is when the alcohol sensor is connected directly to the system panel. Then it is sealed in a chamber with stable air, as shown in Fig. 1. When $V_{\rm out}$ is stable, the target alcohol liquid volume is injected into the test chamber. The target alcohol liquid can turn into alcohol vapour quickly as it mixes with the air. Simultaneously, the measurement of the sensitivity of the sensor begins. When the $V_{\rm out}$ value is stable, the measurement is stopped, and the remaining alcohol vapour is removed from the test chamber. Finally, the chamber is closed again to allow the alcohol sensor to re-expose to stable air and wait for further testing. The sensing behaviour of PANi-based sensors exposed to methanol vapour with different concentrations is shown in Fig. 6 (a), (b), and (c). Fig. 6 (a) shows that the sensor immediately responds to methanol vapour, and there is a gradual decrease in resistance from low to high concentrations. This is possible due to the increased activity of the sensor surface due to exposure to alcohol vapor, where there is an interaction between the H bond and the OH group of the alcohol and the nitrogen atom in the PANi structure. In addition, alcohol molecules trapped in PANi macromolecules cause the chains to swell and break some of the charge carrier conduction pathways [16]. This factor makes the resistance value high.

In Fig. 6 (b), the sensor response time to the sensitivity of 5 ppm methanol vapour is about 84 seconds. The sensor response time will continue to increase as the concentration of the injected alcohol increases. The sensor will be restored after the alcohol vapour is removed from the test chamber with a recovery time of 15 s. At the same time, the effect of differences in alcohol concentration on sensor sensitivity is observed in Fig. 6 (c). It can be seen that the higher injected

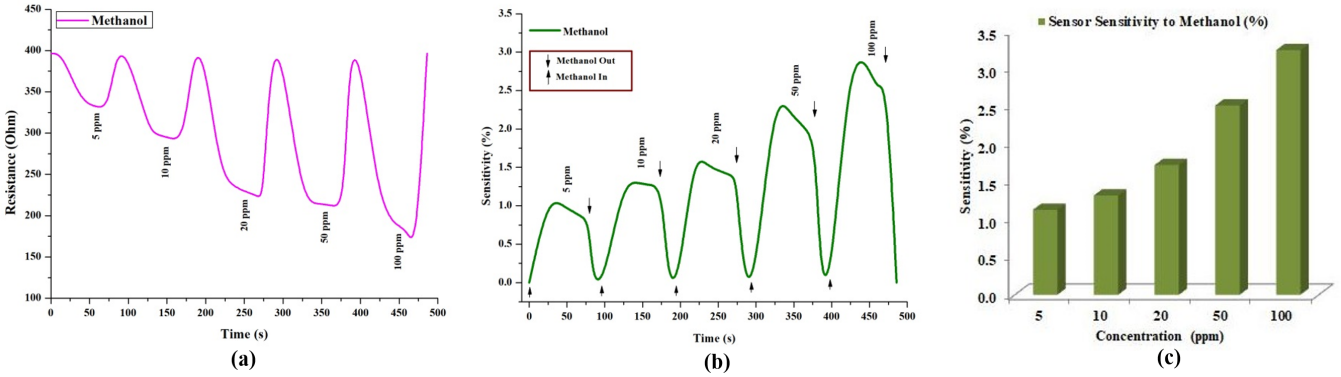

FIG. 6: Graph of the response time of alcohol sensors at different concentrations to (a) resistance value, (b) sensor sensitivity, and (c) graph of the effect of different alcohol concentrations on sensor sensitivity.

alcohol concentration, the more sensitive the sensor will be. Very few target alcohol molecules are available to interact at low concentrations. While the number of target alcohol molecules at high concentrations is more [29], this also makes the sensor response time longer. The sensor's increasing sensitivity indicates that the sensor's conductivity is also getting higher. Thus, the PANi sample obtained from this study allows it to be applied as a sensor material to determine air quality, especially for detecting alcohol vapor in indoor air (at the room temperature), where the results of the PANi-based sensor sensing measurement for methanol vapor at different concentrations indicate that the PANi-based sensor can detect methanol vapor at low concentrations up to 5 ppm.

IV. CONCLUSION

Based on the study results, it can be concluded that polyaniline (PANi) was successfully synthesized using a potentiostat electrodeposition method with a scan rate of 100 mV/s which resulted in a thin layer of PANi on the ITO surface. The morphology result of PANi on the ITO surface was investigated through an SEM test which showed the shape of nano-sized particles with an interconnected-sponge structure. The PANi sample was used as a conductive polymer in sensing alcohol sensors to methanol vapor at different concentrations. The results showed that the sensor's sensitivity increased as the concentration of alcohol injected into the sensing chamber increased.

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