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Investigation of MEH-PPV OLED Assisted by An IoT Environment Monitoring System

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Abstract **- Single layer organic light emitting diode (OLED) devices based on poly{[2-methoxy-5-(-2ethylhexyloxy)-1,4-phenylene]vinylene} (MEH-PPV) are fabricated and studied in this work. There are several factors that affect the performance of the fabricated OLED samples. Some of these factors are related to the fabrication parameters chosen for the OLED fabrication process. The effect of concentration and annealing temperature are investigated. Other environmental factors such as humidity or temperature affect the performance of fabricated OLED samples under long term exposure. An internet of things environment monitoring system (IoT-EMS) is developed to monitor and study the effect of these factors on the performance of the OLED samples. Exposure to humidity is found to severely degrade the samples. In summary, the optimum concentration for MEH-PPV is concluded to be 4 mg/ml, and the best annealing temperature is 90°C in this study. It is also deduced that humidity of 72-75 % caused degradation of the samples in less than 20 hours.**

Keywords— Organic light emitting diodes (OLED), Electroluminescence (EL), Indium Tin Oxide (ITO), IoT environment monitoring system (IoT-EMS), degradation, poly(2-Methoxy-5-(20-Ethyl-Hexoxy)-P-PhenyleneVinylene) (MEH-PPV).

I. INTRODUCTION

Electroluminescence phenomenon was discovered in 1907. The discovery changed the history of display and opened up endless possibilities for newer display technologies. OLED was discovered later, and showed that it possesses attractive manufacturing advantages such as having a lower cost and higher flexibility as compared to inorganic devices [1]. Electroluminescence behavior from a polymer was first reported in 1990 [2] and since then it was discovered in a wide range of polymers [3]. One of the polymers that allowed low voltage operation is PPV based polymers such as MEH-PPV [4,5].

The efficiency of the fabricated OLED sample can be optimized by controlling the parameters in the fabrication processes of said sample. In the fabrication process, increasing the concentration of the emissive layer will increase the thickness of the sample. Changing the annealing temperature will also cause changes to the OLED's efficiency. The annealing temperatures chosen are usually higher than the glass transition temperature (T_g) of MEH-PPV which is around 65°C [6] because the electrical characteristics of the sample depends on the polymer chains. When heated above T_g, the polymer chains could move freely and hence enhance the packing of the polymer film. That will improve the electrical efficiency of the polymer. As the annealing temperature increases, the hole injection efficiency also increases, hence, increasing the electrical efficiency (characteristics) of the OLED sample [7,8].

There are external factors that affect the OLED's efficiency negatively [9]. These external factors cause the OLED sample to degrade and lose its efficiency rapidly until the sample fails. There are two types of degradation, recoverable and unrecoverable [10]. Recoverable degradation occurs a few minutes after a bias have been applied to the sample; however, a change in the physical appearance of the sample will be noticed. Example of recoverable degradation is ionic impurities. The ionic impurities cause the formation of internal electric field, which is opposite to the external applied electric field. After the first forward bias, the internal electric field is formed and it reduces the current density in the sample. However, if a reverse bias is applied to the sample for 10 s, the internal electrical field can be removed and the current density of the sample will be improved [10]. Compare to

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recoverable degradation, unrecoverable degradation causes permanent damage to the OLED samples. Unrecoverable degradation is caused by oxidation and moistures in the air. As the sample is left in an environment with high density of oxygen and moistures in the air, the sample is prone to degrade as oxygen and water diffuse into the active layer. The current density then decreases [11].

The work is divided into two parts. In the first part, the effect of fabrication parameters on the performance of the fabricated OLED samples are investigated. The parameters are namely the concentration of MEH-PPV, and annealing temperature. In the second part, the properties of the OLED samples stored in different environment studied, monitored by an IoT environment monitoring system (IoT-EMS). The device characteristics of the samples are then measured at different time interval.

II. Methodology

A. Fabrication of Organic Light Emitting Diode

The OLED fabrication process consists of preparation of indium tin oxide (ITO) anode, coating of MEH-PPV active layer and the deposition of aluminum (Al) cathode. To prepare ITO strips from an ITO coated glass, the ITO samples are cleaned using Acetone, Isopropyl Alcohol (IPA) in an ultra-sonic bath and rinsed with deionized water. After drying, the ITO glass is then masked for etching. The etching is done by immersing the masked substrate into hydrobromic acid (HBr) at 70°C. An optimized duration of 25 s is obtained in this work. The cleaning process is repeated after etching. In order to prepare the active layer, MEH-PPV powder (Sigma Aldrich) are dissolved in chloroform ($CHCl_3$) (Merck) to obtain the desired concentration. It is left to stir for 2 hours. Prior to coating, cleaned ITO substrates are treated in UV-Ozone for 10 minutes. The spin-coating is performed in a glove-box where the humidity was below 30 %. After spin coating, the sample is annealed at either 50°C or 90°C. The last procedure is depositing Al layer on top of the polymer layer as the negative (cathode) electrode by using a thermal evaporator. The fabricated OLED sample's structure is shown in Fig. 1. The spin coating parameters of OLED samples with different concentration is shown in Table I.

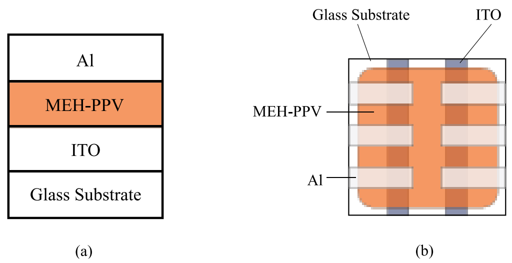

Fig. 1. OLED structure (a) side view of structure, (b) Top view of the structure.

Table I. Concentration of MEH-PPV and spin coating parameters.

Conc. (mg/ml)	Temp. (°C)	Stage 1 speed (rpm)	Time (s)	Stage 2 speed (rpm)	Time (s)
4	26.4	700	9	1700	30
2	26.4	700	9	1700	30
1	26.4	700	9	1700	30

B. IoT Environment Monitoring System

The IoT environment monitoring system is designed to monitor the conditions of the environment periodically and automatically for 117 hours. Data will be acquired and sent to the user. The data gathered could then be analysed and actions could be taken. The main components of the system consist of: sensors, a microcontroller to translate the readings from the sensors and process the binary values received from the sensors, programming software for the microcontroller, a web host and a webserver on which the data is stored. Figure 2 shows the main components used in this work.

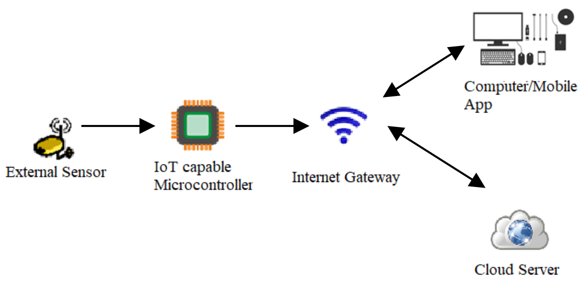

Fig. 2. IoT-EMS components.

The flowchart of the IoT-EMS is shown in Fig 3. The IoT-EMS use temperature and humidity sensors (DHT11), IoT capable microcontroller (Wemos D1 R1) that uses the Arduino layout, internet router, and a cloud server (Thingspeak.com). Two applications were used to view the data stored in the cloud server: ThingView and a IoT-EMS which is developed to overcome shortcomings of the ThingView. Figure 4 (a) shows a screen shot of ThingView application, while (b) shows a screen shot of IoT-EMS application.

Figure 5 shows the connection between Wemos D1 R1 and the external DHT 11 sensors. The IoT-EMS is used to measure the humidity and temperature inside the glovebox and the humidity-controlled sample box for storage of the OLED sample.

C. Device Characterization

Absorbance of MEH-PPV is measured by the UV-visible spectrophotometer (AvaLight-DHc and Avantes AvaSpec-3648), while the photoluminescence spectra is obtained by excitation at 368 nm Avantes and recorded using a spectrometer (AvaSpec2048L). The I-V characteristics and electroluminescence (EL) of the fabricated OLED is obtained using a source measuring unit (Keithley SMU 236). The thickness of the samples are measured by using a profilometer (Mahr Perthometer S2).

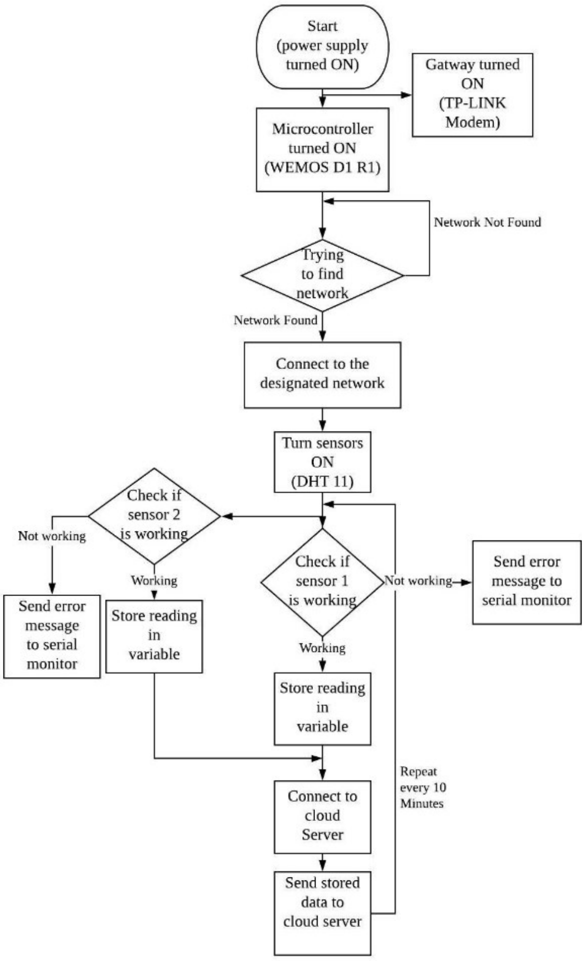

Fig. 3. Flowchart of IoT-EMS.

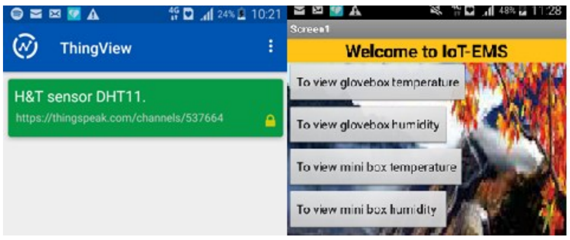

Fig. 4. (a) ThingView application (b) IoT-EMS application.

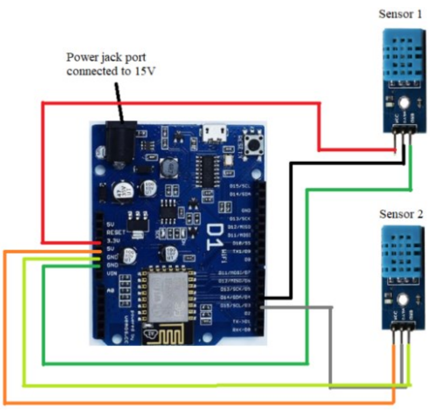

Fig. 5. IoT-EMS schematics.

III. Results And Discussion

A. Device Characteristics of MEH-PPV OLED at Different Concentrations

The thicknesses of ITO, Al and MEH-PPV with different concentration are shown in Table II. As the concentration increases, the viscosity of the solution increases and the thickness of the polymer layer (emissive layer) increases as well.

Table II. Layer thickness of the samples for MEH-PPV wth different concentration.

Concentration (mg/ml)	**Layer Thickness**		
	ITO (nm)	***Polymer (nm)***	***Al (nm)***
4	100	120	70
2	100	100	70
1	100	90	70

The absorbance of all OLED devices is shown in Fig 6. The 4 mg/ml sample has the highest absorbance, centered at ~500 nm. As the concentration of the polymer decreases, the absorbance peak decreases. Thus, 4 mg/ml sample has the highest absorbance peak, followed by 2 mg/ml and 1 mg/ml.

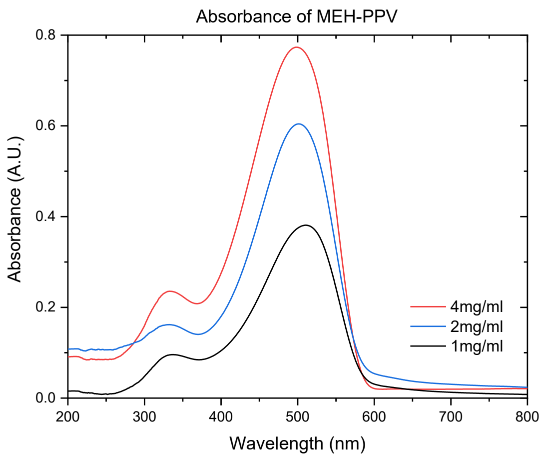

Fig. 6. Absorbance graph of MEH-PPV at different polymer concentration.

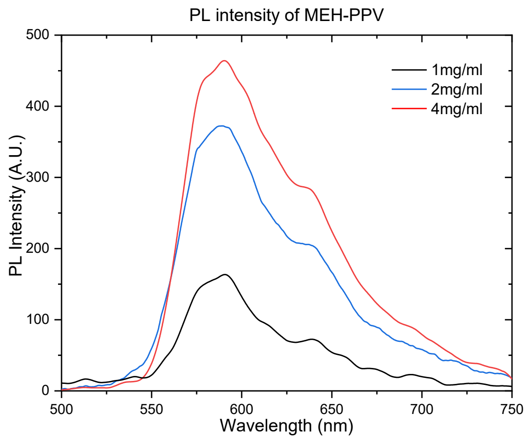

Fig. 7. Photoluminescence graph of MEH-PPV at different polymer concentration.

The photoluminescence (PL) of the OLED samples is shown in Fig 7. The PL peak ranged from 581-596 nm (red) for all the sample. As expected, the intensity of the emitted light increases as the concentration of the polymer increases.

I-V characteristic is performed by the sweeping the voltage from 0-18 V for the samples with concentration of 1, 2 and 4 mg/ml, and that is shown in Fig. 8. The 2 mg/ml and 4 mg/ml samples exhibit diode characteristics, while 1 mg/ml sample is more ohmic in nature. The 1 mg/ml sample maybe too thin that it caused the sample to be shortened. Among the 3 samples, only the 4 mg/ml sample has lit up. The EL spectra of an OLED device with a polymer concentration of 4 mg/ml is shown in Fig. 9. As shown in Fig 9, the OLED sample started emitting from 5 V, at a wavelength of 580 nm. The electroluminescent intensity increases with higher voltage and the highest EL intensity is obtained at 13 V. The emission reduces above 13 V.

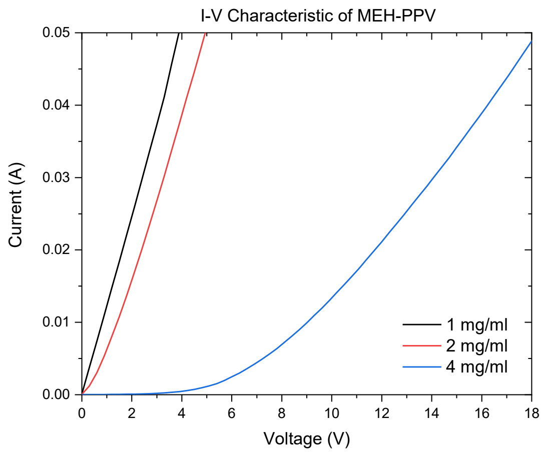

Fig. 8. I-V characteristics of MEH-PPV polymer with 3 different concentrations.

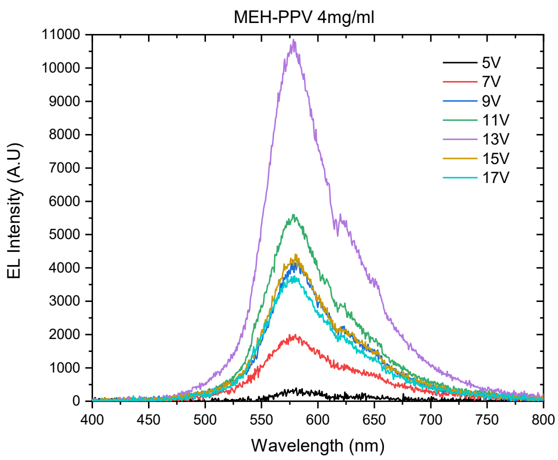

Fig. 9. EL characterization of MEH-PPV polymer with a concentration of 4 mg/ml.

B. Effect of Annealing Temperature and the Effects of Humidity on the Degradation Characteristics

The IoT-EMS is first calibrated before actual measurement of humidity or temperature. It is calibrated with a scientific humidty and temperature sensor (YESAIR, Canada). The results show that the IoT-EMS reading is within 5 % accuracy compared to the standard sensor for both humidity and temperature.

Three OLED samples at 4 mg/ml are fabricated at fixed conditions but annealled at 50°C and 90°C respectively, and that is shown in Table III. One of the samples is stored in a standard room conditions / uncontrolled environment, while another two are stored in a humidity controlled sample box / controlled environment. The storage conditions are monitored by the designed IoT-EMS system at every 5 mins for a duration of 117 hours. In the uncontroled environment, the temperature fluctuate around 26-28°C and the humidity is 72-75 %. In the controlled environment, the temperature is 26-28°C and the humidity has ranged from 15-18 %. It is noted that the main difference in controlled and uncontrolled environment is the humidity.

Table III. The annealing temperature of the samples, and the storage conditions.

Sample	Annealing temperature (°C)	Storage condition
1	50	Uncontrolled*
2	50	Controlled**
3	90	Controlled**

* Temperature: 26-28°C, humidity: 72-75 %
** Temperature: 26-28°C, humidity: 15-18 %

In order to find out the effect of humidity on the samples stored under different conditions, the I-V characteristics of samples 1 and 2 are compared after 20 hours, 92 hours and 117 hours as shown in Fig. 10.

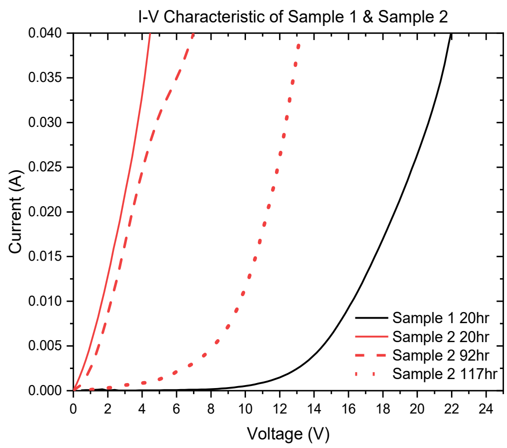

Fig. 10. I-V characteristic of sample 1 (72-75 % humidity) and sample 2 (15-18 % humidity).

As seen from the graph of I-V curve response of sample 1 after 20 hours; the current-on voltage of sample 1 is 14 V, which is extremely high compare to a current-on voltage of 0.7 V that was recorded by sample 2 at the same period. The light-on voltage of sample 1 after 20 hours was 12 V, while sample 2 had a light-on voltage of only 8 V, which is considerably higher compare to sample 2. After 92 hours, sample 1 broke down while sample 2 was still showing a diode curve I-V response and gave a current-on voltage of 0.7 V and light-on voltage of 10 V. After 117 hours, both the current-on voltage and light-on voltage of sample 2 increased significantly to 8 V and 11 V respectively. The results indicate that MEH-PPV samples degrade rapidly in the presence of humidity. It is also noted that, the degradation occurred on sample 2 as well, and that caused an increase in the current on and light on voltage. The degradation is due to of the presence of oxygen which is not controlled in this study [11].

In order to understand the effects of annealing temperature on the performance of the OLED samples. Sample 2, annealed at 50°C is compared to sample 3 which is annealed at 90°C . The result of the I-V characteristics of sample 2 vs sample 3 is shown in Fig. 11.

After 20 hours, both sample 2 and sample 3 exhibit diode characteristics with quite similar I-V responses. Sample 2 has a current-on voltage of 0.7 V and sample 3 had current-on voltage of 0.5 V. Sample 2 has a light-on voltage of 8 V while sample 3 has a lower light-on voltage of 6 V.

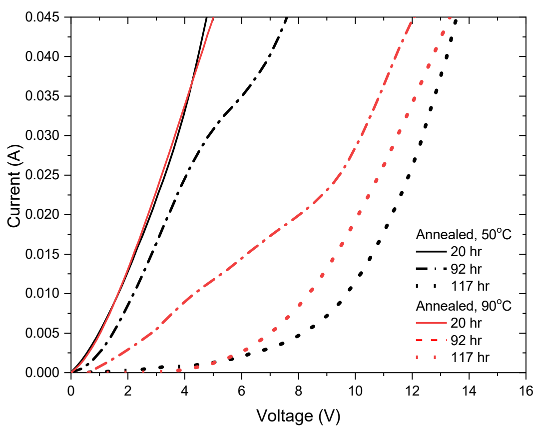

Fig. 11. I-V characteristics of sample 2 (annealed at 50°C) and sample 3 (annealed at 90°C) stored under low humidity (15-18 %).

After 92 hours, sample 2 has a better I-V response curve compare to sample 3. Sample 2 had a current-on voltage of 1 V and light-on voltage of 10 V. Sample 3 on the other hand had current-on voltage of 3 V and a light-on voltage of 8 V. After 117 hours, both samples are still emitting. Sample 2 had a current on voltage of 8 V and light-on voltage of 11 V while sample 3 had current-on voltage of 7 V and light-on voltage of 9 V. Thus, over the test duration, under controlled environment, the sample that is annealed at 90ºC emitted at lower voltage. It is more stable than the sample that is annealed at 50°C.

IV. Conclusion

OLED samples made of nano-scale materials are very sensitive to internal or external changes. Internal changes such as concentration can affect the efficiency of the fabricated OLED sample. As seen from the results, an optimized concentration is required for best performance. Within the solubility limit, it is affected by the viscosity of solution that affected the thickness of the films. Our results show that humidity was one of the major external factors that degrade the MEH-PPV OLED where the sample exhibit poor charge transport and the device impedance increases. Sample 1, stored under uncontrolled conditions failed after 92 hours, as compare to sample 2 that is stored at low humidity environment which still functioned even after 117 hours. Both the MEH-PPV samples annealed at 50°C and 90°C, stored under controlled condition degraded slightly but were still emitting after 117 hours. Comparing the annealing temperature, sample 3 annealed at 90°C had a better I-V response after all three-degradation period compare to sample 2 that was annealed at 50°C.

Acknowledgement

The contributions by all are acknowledged.

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