Fabrication and Characteristics of Organic Solar Cell Based on Conductive Polymer

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Abstract:
Polyaniline (PANI) is one of imported polymers for synthesis solar cells. The quality of thin film depended on the method of polymerization. In this paper PANI have been prepared by the chemical oxidative polymerization of aniline by presence oxidative agent. The electrical conductivity of these films was measured by two probe methods. The electrical conductivity is influenced by preparation conduction such as concentration of the protonic acid HCl and temperature. The best electrical conductivity about $1.2 \times 10^{-4}$ S/cm was found at 383K.

Keywords: Solar cells, conductive polymer PANi-ES, electrical characterization

1. Introduction
Polyaniline (PANI) is one of the most promising conducting polymers [1-3]. The most important feature that makes PANI so interesting as sensitive p-n junction layer for the solar cell is the variation of its electrical and optical properties at room temperature [4,5] Polyamine PANi is one of (ICP) and an attractive due to its considerable conductivity, easy synthesis route and good thermal stability. The conductivity could be increased by more than ten orders of magnitude by doping with protonic acids [6]. Depending on the oxidation level, PANi can be synthesized in various insulating forms such as the fully reduced leucocemeraldine base LEB, the half oxidized emeraldine base PANi-EB, and the fully oxidized pernigraniline base PNB [7-9]. Of these three forms PANi-EB is the most stable and widely investigated polymer in this family. PANi-EB differs substantially from LEB and PNB in the sense that its conductivity can be doping from $10^{-10}$ S/cm up to 100 S/cm and more where as the LEB and PNB forms cannot be made conducting [2,3]. The insulating emeraldine base form of polyaniline PANi-EB consists of equal numbers of reduced $[-(\text{C}_6\text{H}_4)-\text{N}(\text{H})-(\text{C}_6\text{H}_4)-\text{N}(\text{H})]$ and oxidized $[-(\text{C}_6\text{H}_4)-\text{N}=(\text{C}_6\text{H}_4)\text{N}^-].$

As show in Fig (1). In the present study polyaniline films have been prepared by chemical oxidative polymerization method of aniline monomer by presence of protonic HCl. The polymer films have been characterizes by FTIR spectrophotometer. The conductivity measured by two probe methods [9].

2. Characterization and Measurement Methods
Morphological study of the thin films of PANi was carried out using field effect scanning electron microscopy (FE-SEM) (Model: FEI Nova Nano SEM 450) operating at 20 kV. Fourier transform infrared spectroscopy FTIR (Model: Perkin Elmer spectrum Gx) of polymer was studied in the frequency range of 400–4000 cm$^{-1}$. Electrical conductivity characteristic study using were found by a two-probe resistivity meter at room temperature (Model Keithley 82), and
solar simulator which were study by using IV (Model: Keithley-2400 SOURCE METER). The solar simulator intensity, values were measured by using a solar simulator light source led, power output 100mW.cm⁻², white light, 100% intensity is adjustable, The lamp had spectral distribution closely matching that of the solar spectrum.

3. Materials and Methods

Polyaniline was synthesized by chemical oxidative polymerization of aniline in the presence concentration of hydrochloric acid as a catalyst and ammonium peroxidesulphate as an oxidant agent by chemical oxidative polymerization method. For the synthesis, 50 ml 1M HCl, and 2ml of aniline were added into a 250 ml equipped with electromagnetic stirrer. Then 4.9 g of (NH₄)₂S₂O₈ ammonium peroxidesulphate in 50 ml, 1M HCl was suddenly added into the above solution. The polymerization temperature ≈ 0°C was maintained for 6 h to complete the reaction. Then the precipitate obtained was filtered. The product was washed successively by 1M HCl followed by distilled water and respectively until the wash solution turned colorless. Then it was prefiltered and washed once again successively by of distilled water, thoroughly to obtain the emeraldine salt form of polyaniline PANi-ES. To obtain emeraldine base form of PANi, undoped EB form of PANi with 0.1M NH₂OH solution then dried at 60°C in vacuum for 24 h. Thus, finally obtained powder of insulating polyaniline EB polymer [10].

4. Results and Discussion

The polyaniline samples were synthesized using protonic acid such as hydrochloric acid as dopant. The final product was a dark green conducting of emeraldine salt PANi-ES as conductive polymer. FESEM shown in the Figure 2 (a, b), the PANi-ES sample with HCl dopants acid exhibit varying microstructures. The addition of acid dopants improved the polymer lattice, which leads to the ionization of sites in the chains of polymer. The defects in the chain due to the dopant ions provide more of the mobility of the charge carriers on which conduction depends [11]. Figure 2, (a, b) image at 5 µm, 10 µm shows a micro porous pattern of globular microstructures for the PANi-ES doped with HCl. The orientation of morphology of samples at the macroscopic level affects the mobility of charge carriers and, the conductivity of polymer [11]. The highly porosity nature of the material and the clumped spherical morphology was confirmed with a FESEM study.

Figure 2: FESEM Morphology of Doped Polyaniline-ES at (5 µm and 10 µm)

Figure 3, shows the FTIR spectra of PANi-ES sample prepared at temperature ≈ 0°C with 1M dopant concentration. The spectra recorded in wave number rang 400-4000 cm⁻¹. FTIR properties can distinguish between the benzenoid and quionied rings in rang 1350-1960 cm⁻¹ region of the spectrum. It is clear from the figure that temperature of thin film has effective changed the molecular media of PANi-ES than the dopant concentration. The peaks around (801 cm⁻¹,1303 cm⁻¹,1474 cm⁻¹, and 1560 cm⁻¹) of all spectra correspond to PANi-ES [12]. The peak around 1243 cm⁻¹ corresponds to the electrically conductive state of doped polymer PANi-ES [13]. Decrease in temperature of film prepared will shift few peaks toward lower wave number region (1134cm⁻¹, 1296 cm⁻¹, and 1589 cm⁻¹) along with increase in intensity of the peaks. This due to increase in the degree of polymerization of PANi-HCl with decrease in dopant concentration of PANi-HCl show less variation in the intensity of peaks. This shows that the degree of polymerization is very highly pronounced for PANi-HCl sample prepared at low temperature. Table 3; show the list of observed peaks with their corresponding functional groups.
Figure 3: FTIR Spectra of PANi-ES Doped HCL

| Wave Number(cm⁻¹) | Assigned Functional Groups                      |
|-------------------|-------------------------------------------------|
| 801               | C-Cl aromatics out of plane band                |
| 1134              | Vibration of (–NH=) structure                   |
| 1243              | Stretching of (C-N*) polaron structure          |
| 1296              | C-N stretch of Benzenoid ring                   |
| 1474              | C-C stretch of Benzenoid ring (N-B-N)           |
| 1589              | C=C stretch of Quinoid ring (N=Q=N)             |
| 2366              | C-H stretching band                             |
| 3407              | N-H stretching band                             |

Table 1: FTIR Peaks in the PANi-ES Doped HCl Sample

Figure 4 show the current-voltage characteristic for PANi-ES doped with HCl, at temperature range of 293°-383°K. The thickness of thin films was 45nm. Ohmic behavior was noticed for all the applied voltage. The electrical conductivity was calculated by Equation (1) for different temperatures and tabulated at Table 2. Figure 4 show the electric conductivity as function of reciprocal temperature for PANi-HCl. The electrical conductivity increased due to HCl doping from 7.59x10⁻⁶ S.cm⁻¹ to 1.2 x10⁻⁴ S.cm⁻¹ for PANi-HCl doped at room temperature. Actually, the current increments linearly with applied field and the conduction mechanism in the conducting polymers is not same as characteristic of semiconductors materials [14]. As the applied voltage increases, the existence of bi-polarons builds which contribute to the increments in current as for voltage resulting in ohmic behavior as linear curve [15]. Table 2 demonstrates that the conductivity of PANi-HCl because the bi-polarons state which was made by doping with HCl was bigger with temperature [16,17].

\[
\sigma_s = \frac{I}{V} \frac{L}{Wt} \ell
\]  
(1)

Where, t is thickness (45nm) of polymer thin films, W is the distance fingers (10mm), ℓ is number of fingers is to be (10), and L is the space between electrodes (100μm).

| T (K) | PANi-ES (HCl) 6 Đc (S.cm⁻¹) |
|-------|-----------------------------|
| 293 (RT) | 7.59x10⁻⁶           |
| 313    | 1.61x10⁻⁵            |
| 333    | 3.12x10⁻⁵            |
| 353    | 5.63x10⁻⁵            |
| 373    | 9.5x10⁻⁵             |
| 383    | 1.2x10⁻⁴             |

Table 2: The Electrical Conductivity For Polyaniline PANi-ES (Hcl)
The (J-V) property of conductive polymer PANi-ES is shown in Figure 5. The devices were with thickness 45nm, an illumination and power intensity 100mW.cm$^{-2}$. The $V_{oc}$, FF, and $\eta$ are recorded at Table 3. From the Table 3 one can consider that the structure (Si/ PANi-HCl) is the good devices of organic solar cell. It has been exhibited that PANi-ES doped by large sized organic hydrochloric acid, have a perfect solubility in common with organic solvents. It is due to an amplification between chain distance, and strong interaction amongst dopant and solvent [18]. PANi-ES doped HCl, powder is solvent in DMF. Figure 5, show the efficiency of solar cell device with thicknesses of 45nm for PANi-ES dopes with protonic acid media such as HCl. The efficiency then becomes larger with the application of hydrofluoric acid HF as a solvent where reaches to the value 0.3% for PANi-HCl. The parameters $V_{oc}$, $J_{sc}$, $P_{max}$, FF, and $\eta$ are tabulated in Table 3. The best value of efficiency is obtained from devices at thickness 45nm. A typical solar conversion efficiency of 0.3%, which is small values as compared with Al/PANI/GaAs, metal-insulator semiconductor solar cell which was found to give efficiency in the region of 5% [19,20]. The low values of (FF) is associated with morphology of the polymer film and a poor absorber morphology limiting the electron hopping transport [21,22].

| Polymer/ (DMF) (45nm) | $V_{oc}$ (mV) | $J_{sc}$ (mA.cm$^{-2}$) | $V_{max}$ (mV) | $J_{max}$ (mA.cm$^{-2}$) | $P_{max}$ (mW.cm$^{-2}$) | FF | $\eta$ (%) |
|----------------------|--------------|---------------------|--------------|---------------------|---------------------|-----|-------------|
| PANi-ES              | 876.4        | 4.5x10$^{-3}$       | 600          | 3.9x10$^{-3}$       | 2.3x10$^{-3}$       | 0.59| 0.3         |

Table 3: (J-V) Parameters of solar cells PANi-ES at Intensity Light 100mW.cm$^{-2}$

Figure 5: (J-V) Characteristics Solar Cells of PANi-ES under Illumination 100mW.cm$^{-2}$

Figure 4: I/V Characteristic for Conductive PANi-ES Doped at Different Temperatures (293°-383° K)
5. Conclusion
The conductive polyaniline (PANi) was synthesized by chemical oxidative polymerization method in which the fabrication time was approximately 24 h whereas other methods require longer time. The field emission scanning electron microscope FESEM pictures of the doped PANi samples showed varying microstructures, the HCl-doped sample exhibited a microporous structure. Morphology of polymer polyaniline by FESEM analyzing showed that the particle size of polymer is inside the micro-scale with the existence of acid. Further investigation of the morphology of samples will give a better understanding of the bulk conductivity. FT-IR spectroscopy analyzing confirmed the inner structure of the polymer with the existence of protonic acid; and the position of the bonds did not more change. The doped sample gave the highest conductivity 1.2x10^4 S/cm. The experimental conductivity values generally showed an inverse correlation with the values of the energy gap. An organic solar cell was fabricated from the conductive polymer deposited on silicon wafers. The efficiency of solar cell increased when used strong organic solvent as DMF to 0.3% for PANi- hydrochloric acid.

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