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Study of The Organic Solar Cells Based on An Emeraldine Salt of Conductive Polyaniline

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ABSTRACT
Conductive polymer of Polyaniline is synthesized by doping with inorganic and organic acids, namely Hydrochloric acid (HCl) and Sulfuric acid (H2SO4). Thin film quality depended on the method of chemical polymerization. The electrical conductivity of these films was measured by two probe methods. The direct current (DC) conductivities (σDC) are found to be about 1.2x10-4 S/cm and 2.98x10-4 S/cm for PANI (HCl) and PANI (H2SO4), respectively. The electrical conductivity is influenced by preparation conduction such as concentration of the ionic salted acid HCl, H2SO4 and temperature. The best electrical conductivity about 2.98x10-4 S/cm was found at 383K. Conductive σDC is measured down to a temperature of ~100 K and the apparent change in the activation energies Ea are found to be 0.124 eV, and 0.112 eV for PANI-HCl, and H2SO4 doping respectively. Conductivity σDC is less temperature dependent near room temperature, further decrease in temperature the σDC is strongly dependent. In material characterization, successful doping is corroborated by FESEM study. PANI (H2SO4) exhibited highest conductivity followed by PANI (HCl). Polyaniline is one of imported polymers for solar cells.

Keywords: emeraldine-salt; protonic acids; electric conductivity; organic solar cells

INTRODUCTION
The conducting polymers are a special class of organic polymers that have alternate double bond conjugated and can conductive electricity. The conducting Polyaniline (PANI) demonstrates outstanding properties due to its environmental stability, high electrical conductivity and ease of synthesis which drives it towards potential electrical device applications [1-5]. The improvement on electrical characteristics of doped Polyaniline reflecting the conditions of preparation incorporation is of fundamental importance. In comparison with metal oxides, acid doped conducting polymers influence more on electrical properties. Interest has focused upon the discovery of doping by acids with certain functionalized protonic acids may be used to render the emeraldine salt of the polymer process able from solution [6, 7]. Heeger has reported the use of functionalized protonic acids to dope emeraldine base and, simultaneously, to make soluble the resulting PANI complex in common organic solvents [8]. This procedure increases the PANI compatibility with bulk polymers with similar molecular structures. In addition, it can strongly influence the electrical properties of a device. Consequently, a wide range of conductivities are obtained by doping with various protonic acids [9, 10]. A common an inorganic acid namely Hydrochloric acid (HCl) doped PANI is soluble in pyrrolidine and concentrated acids with improved electrical conductivity [11]. On the other hand, the organic acid that confers certain solubility and high conductivity on PANI is Sulphuric acid [12] where doped in Polyaniline presents a high conductivity (>1 - 102 S·cm−1) in the presence of m-cresol solvent. It provides high conductivity and crystallinity to the PANI-H2SO4 complex system, conferring on polymer a metallic like-behavior [13]. In the recent years, HCl and H2SO4 doped PANI have been used in the composites to produce highly conductive nanofibers by electrospin technic [14-16].

Present article provides simultaneous comparison of two different acids doped PANI and electrical properties as conductivity, activation energy and organic solar cells characteristics.

EXPERIMENTAL PROCEDURES
PANI synthesized by chemical polymerization of aniline in the presence of protonic acid (HCl, H2SO4) and ammonium peroxydisulphate (APX) as an oxidant agent. For the synthesis, 1M of Hydrochloride and Sulphuric acid medium, and 0.2M of aniline solution were added with a magnetic stirrer at about 0-4°C used ice-bath. Then 0.25 M of APX in aqueous medium with an acid. Both solutions mixed in a round bottomed flask and gentle stirring to polymerize the mixture. The precipitate (PANI) was collected then filtration and washed with Acetone. After that (PANI) dried in oven vacuum at 80°C to 24h, annealed. The Polyaniline dark green colored of conductive Polyaniline emeraldine salt (PANI-ES) was thoroughly grounded to obtain very fine particles. Then used o.1M of HF acid to solving PANI powder and prepared the thin films samples. Solar cell simulator characteristic, which were study by using IV (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.

RESULTS AND DISCUSSION
Samples were synthesized using protonic acid such as Hydrochloric and Sulphuric acid as dopant. The final product was conducting of emeraldine salt PANI-ES as conductive polymer. FESEM images shown in the Figure 1, (a, b), the PANI-ES sample with (HCl, H2SO4) dopants acid exhibit type of microstructures. Acidic dopants improved an ionization of sites in the chains of polymer.

The defects in the chain due to more of the mobility of charge carriers on which conduction depends [17]. Figure 1, (a, b) image at 10 µm shows a micro porous images of globular microstructures for the PANI doped with different acid. Orientation of morphology of samples at the macroscopic level affects the mobility of charge carriers and, the conductivity of polymer [17, 18]. Porosity nature material and the roundedness spherical morphology was confirmed with a FESEM.

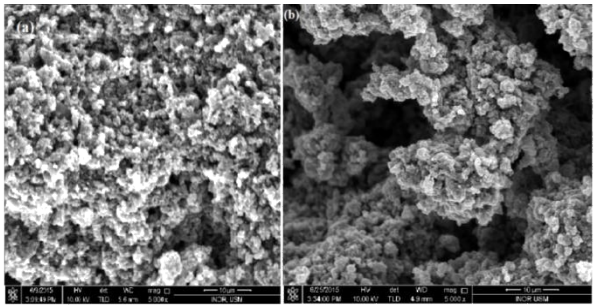

FIGURE 1: FESEM images of doped PANI-ES at (10 µm).

Current-Voltage characteristic for PANI-ES doped with HCl, H_2SO_4, as show in Figure. 2, the range temperature of 293°-383°K. Thickness of thin films was 45nm. Ohmic behavior was noticed for all the applied voltage. The electrical conductivity was calculated according to Equation (1) for different temperatures and tabulated at Table 1. Figure 2 show the electric conductivity as function of reciprocal temperature for PANI-HCl. The electrical conductivity increased due to HCl doping from reached 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 [19]. As the applied voltage increases, the existence of pi-polaron builds which contribute to the increments in current as for voltage resulting in ohmic behavior as linear curve [20]. Table, 1 demonstrates that the conductivity of PANI-HCl because the pi-polaron state which was made by doping with HCl was bigger with temperature [21, 22].

$$\sigma_{DC} = [I/V]\,[L/Wt\ell] \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

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). Figure. 2 show the I-V characteristic for PANI-ES doped with H2SO4, at same temperature range of 293°-383°K. Ohmic behavior observed for all the applied voltage. The electrical conductivity was calculated by Equation (1) for different temperatures and tabulated at Table 1. Figure. 2 shows the electric conductivity as function of reciprocal temperature for PANI- H_2SO_4. Electrical conductivity increased due to H_2SO_4 doping from 2.46x10^{-5} $S.cm^{-1}$ to 2.98x10^{-4} $S.cm^{-1}$ for PANI- H_2SO_4 doped at room temperature. In case of the conducting polymers, the negative and positive charges initially added to the polymer chains not just start to fill the unbending conduction or valence bands. In that case, the charge transport is through this pi-polaron. As the applied voltage increases, the existence of pi-polaron builds which contribute to the speedup increments in current as for voltage resulting in ohmic behavior as linear curve [17].

Table.1 demonstrates that the conductivity of PANI- H_2SO_4 because the pi-polaron state which was made by doping with H_2SO_4 was less with temperature [18].

TABLE 1: The electrical conductivity for Polyaniline doped.

T (K)	PANi-ES (HCl) 6_{DC} ($S.cm^{-1}$)	PANI-ES (H_2SO_4) 6_{DC} ($S.cm^{-1}$)
293	7.59x10^{-6}	2.46x10^{-5}
313	1.61x10^{-5}	4.86x10^{-5}
333	3.12x10^{-5}	8.82x10^{-5}
353	5.63x10^{-5}	1.49x10^{-4}
373	9.5x10^{-5}	2.4x10^{-4}
383	1.2x10^{-4}	2.98x10^{-4}

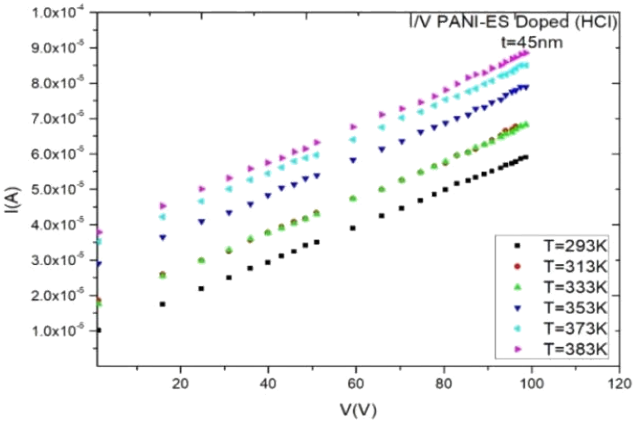

FIGURE 2: I/V characteristic for conductive PANI-ES- HCl at different temperatures (293°-383° K).

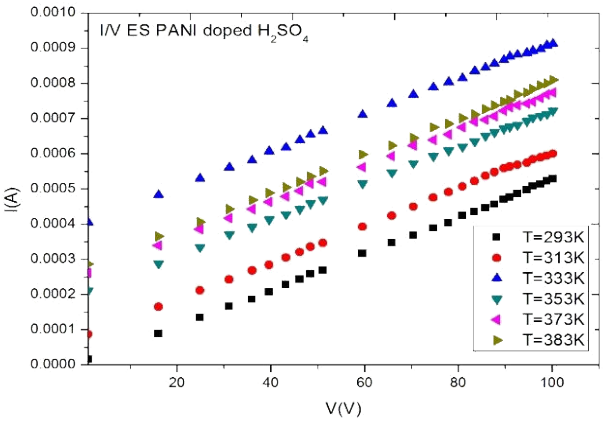

FIGURE 3: I/V characteristic for conductive PANI-ES-H2SO4 at different temperatures (293°-383° K).

The activation Energy (Ea) of polymer PANI-ES has been deduced using the expression Arrhenius Equation [23, 24]:

$$\sigma_{DC} = Ae^{-\frac{Ea}{KT}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

The activation energy Ea determined by Eq (3) from this curve was 0.124eV for PANI-HCl, and 0.112eV for PANI-H_2SO_4. The estimation of activation energy Ea for PANI-H_2SO_4 was less than PANI-HCl which shows that the localized salt in PANI-H_2SO_4 was more prominent than PANI-HCl suggesting that it needs to reduce the energy for charges transition [25].

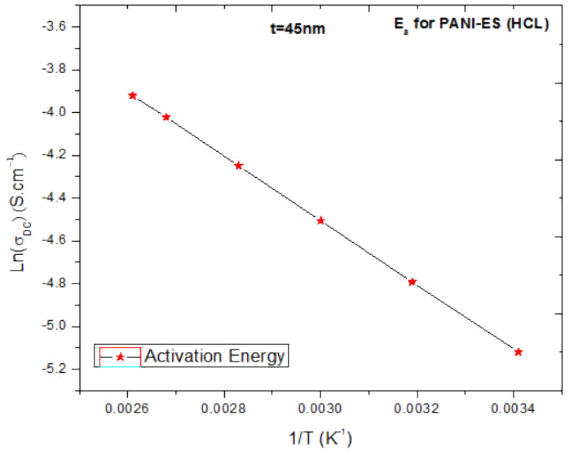

FIGURE 4: The activation energy for PANI-ES doped HCl film.

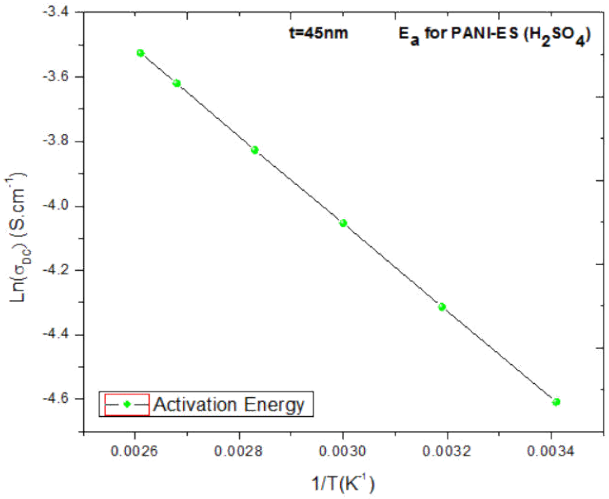

FIGURE 5: The activation energy for PANI-ES doped H_2SO_4 film.

The (J-V) characteristic of conductive Polyaniline PANI-ES is shown in Figure 6, and Figure 7. The devices were with an illumination and power intensity 100mW.cm-2. The Voc, FF, and η are recorded at Table 2. From Table 2, it can consider that the structure (PANI/ HCl, H_2SO_4) 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 amplification between chain distance, and strong interaction amongst dopant and solvent [26]. PANI-ES doped HCl. Figure 6, show the efficiency of solar cell device for PANi-ES dopes with protonic acid media such as HCl, H_2SO_4. 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, and 0.26% for PANI-H_2SO_4. The parameters Voc, J sc, P max, FF, and η, shows in Table 3. The solar conversion efficiency 0.26%, for PANI-H_2SO_4 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 4% [27, 28]. It can be clarified that PANI- H_2SO_4 has more prominent excitation states than that of PANI pure. Likewise, from the table one can consider that the structure (PANI-H_2SO_4) is the best one among other devices. The low values FF are associated with morphology the polymer film and a poor absorber morphology limiting the electron hopping transport [29, 30].

TABLE 2: Solar cells Parameters PANI doped HCl and H_2SO_4 at intensity light 100mW.cm-2:

Polymer Doped	V_{oc} mV	J_{sc} mA.cm^{-2}	V_{max} (mV)	J_{max} mA.cm^{-2}	FF	η (%)
HCl	876.4	4.5x10^{-3}	600	3.9x10^{-3}	0.59	0.3
H_2SO_4	773	3.3x10^{-3}	520	1.2x10^{-3}	0.48	0.26

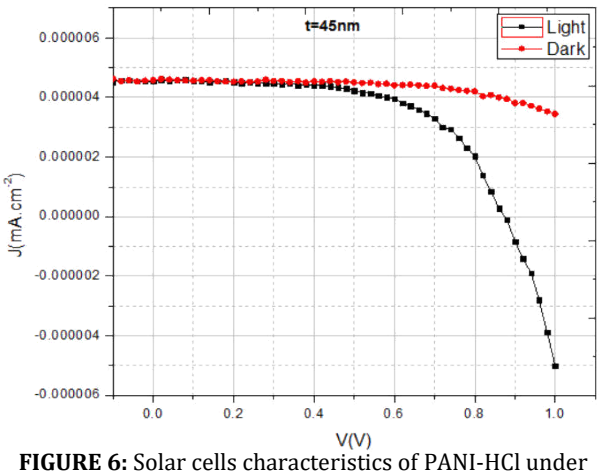

FIGURE 6: Solar cells characteristics of PANI-HCl under illumination 100mW.cm-2.

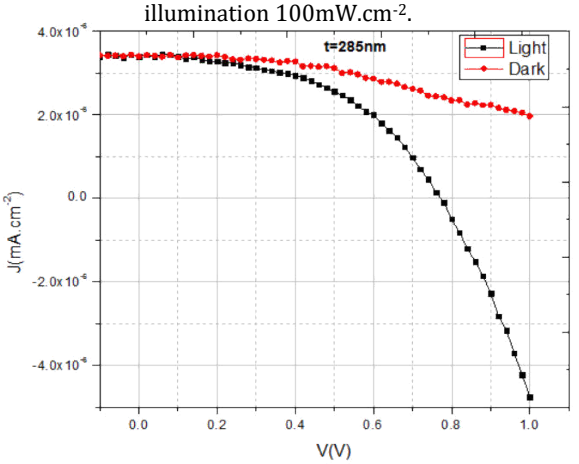

FIGURE 7: Solar cells characteristics of PANI-H_2SO_4 under illumination 100mW.cm-2.

CONCLUSION

As chemical synthesis new method has been developed to produce PANI-ES a directly by one-step and environmentally friendly simple, chipper, easy method. This may be helpful for commercially synthesis of polyaniline. Study of physical and chemical characteristics with new of techniques such as FESEM, and for direct current conductivity (σDC), it can be proved that Polyaniline has microstructure and chemical stability. The Polymerization reaction of was exothermic reaction. The effect of acid caused an increase in the properties of crystallinity. An electrical characteristic confirmed preparation of microstructure polymer, as low resistivity of doped PANI-ES thin film. An organic solar cell fabricated from the conductive polymer deposited on porosity silicon wafers. The efficiency of solar cell increased when used organic solvent as HF reached to the best value 0.26 % for PANI-Sulphuric acid.

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