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Evaluation an Activation Energy and its Impact on The Electrical Properties of Conductive Polyaniline

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ABSTRACT

Objective: *Polyaniline one of most Conductive polymer as prepared by chemical polymerization method at room temperature and studied the side effect the dopant with ionic acid such as sulfuric on the structure of the polymer.* ***Method :*** *The changes taking place by the following measurements: FESEM, HR-XRD, Electrical properties, and an evaluation activation energy. The FE-SEM properties of the surface study using the imaging analyzed by Field Emission Scanning Electronic Microscopic, and calculated the particle revealed, that the compound has micro granular effected with the presence of acid.* ***Results :*** *High resolution x-ray diffraction, crystalline nature of the polymer it has a semi-crystalline with the effect of the acid doped clear improvement happened to the installation of the crystalline nature of the polymer. Electrical characteristic study by using the 2-probe method, it found that the samples had ohmic curve. Thin films of samples that doped of polymer had a highest conductivity of $2.9x10^{-4}$ $S.cm^{-1}$ at 383 K, which observed for the H_2SO_4 doped sample, which shows that was more prominent of localized salted in polymeric chain.* ***Novelty :*** *Polyaniline one of most Conductive polymer as prepared by chemical polymerization method at room temperature and studied the side effect the dopant with ionic acid such as sulfuric on the structure of the polymer.*

INTRODUCTION

Electrically conducting of polymers described as a new class of synthetic materials [1] reached a high interest in the last years, confirmed by the Nobel Prize in chemistry for the discovery and development of conductive polymers [2]. Polyaniline is one of the most studied materials because of its good behavior physical-chemical and easy fabrication under reproducible conditions chemically oxidation method of aniline, as well as high conductivity upon doping with acids, and good environmental stability [3]. A key property of a conductive polymer is the presence of conjugated double bonds along the backbone of the polymer. In conjugation, the bonds between the carbon atoms are rotating single and double. Every bond contains a localized bond as strong chemical bond. In addition, every double bond also contains a localized bond as weaker bond. However, conjugation is not enough to make the polymer material conductive, [4].

Polyaniline acts as an electrically conductive material only in the protonation form of emeraldine salt. It can change the electronic conductivity about (10) orders of magnitude, passing from pure insulator state to metallic conduction, depending upon the protonation degree [4, 5]. Controlling the doping state and polymerization conditions, we assume that is possible to change the structure and thus the chemical character of polymer [6]. In the emeraldine salt (ES), the sulfuric acid HSO_4 species are ionic bonded with the -NH groups presented in the polymer chain. Actually, these kinds of bonds are

very weak and can removed easy by changing system pH [6]. By requirement doping of polyaniline in acid media, actually we introduced multiple charge carriers, which determine an improvement of the electrical conduction along the polymer chain.

RESEARCH METHOD

Synthesis of Conductive Polyaniline

The PANI-ES samples were chemical prepared at the actualization conditions at room temperature by using aniline monomer , ammonium peroxide sulfate (APS), and the appropriate dopant (H_2SO_4). The common procedure for the polymerization an aniline by hydrochloride [7]. A solution around 0.25 M of APS was mixed with 1 M of aniline and in 1M of the acid dopant. Both solutions are mixed in a round bottomed flask and gentle stirring to polymerize the mixture. The mixture was stirred and maintained at -5°C in presence ice bath. The temperature as a function of time for this reaction was recorded through the polymerization processes. The precipitate as green color formed was filtered, washed to several times with distilled water and acetone, and then dried in oven vacuum for 5 h at 75°C. The Polyaniline powder was thoroughly in a mortar to obtain the very fine particles.

Caracteristic Properties of Polyaniline

Thin films of polyaniline samples studied of microstructure using a FE-SEM, X-ray and studied an electrical conductivity. Electrical property, the conductive paste was use to attach as contacts. Then, current-voltage measurements done using the four-probe method and resistivity measurements derived by the Van der PAUW method [8]. Before taking the FE-SEM images, the samples coated with Pt for 6 min for usually sufficient coating using an RF magnetron sputtering system to increase the source of electrons. Structural of the thin films PANI was study carried out using field effect scanning electron microscopy FESEM (Model: FEI Nova Nano SEM 450) operating at 20 KV. The samples studied at different magnifications for topographic comparisons. High Resolution (Model: PANalytical X pert Pro MRD PW3040). The patterns were recorded in the range of 2θ: 10–70^o with a step width of 0.02^o and a step time 1.25sec by using (CuKα) radiation (λ=1.5406A^o). X-ray patterns were analyzed by matching the observed peaks with the standard pattern provided by a JCPDS file. Electrical conductivity characteristic and activation energy property study using by a four-probe resistivity (Model Keithley 82). Metal electrodes shadow mask assembled from two individually addressable as electrode structures have frequently as very sensitive for chemical materials .Figure. 1 shows electrode that consists of Aluminum fingers lines on a glass substrate. It be achieved using inter-digitated electrodes to measure the surface conductivity of the samples from the following relationship:

$$\sigma_s = [I/V]\,[L/Wt\ell] \qquad (1)$$

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

$$\sigma_s = I/Vt\ (10^{-3}\ S.cm^{-1}) \qquad (2)$$

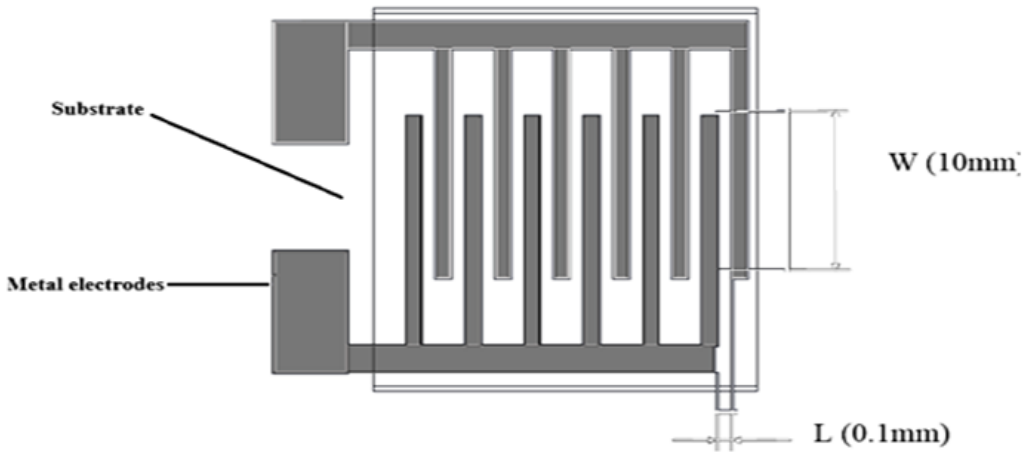

Figure 1. Finger electrode Shadow mask.

RESULTS AND DISCUSSION

FE-SEM images shown in Figure 1 (a, b) the samples with polymer dopant exhibit high microstructures. The difference in microstructure leads to variations in conductivities of the samples. Addition to the polymer chain, which lead to the ionization state. The defects in the chain due to the dopant ions provide the mobility of the charge carriers on which conduction depends [9]. The conductivity is also dependent on amount the charge carriers. The doped sample in Figure 1 displays globular structure morphology. Figure 2 (a, b) shows a high micro porosity of globular structures for the PANI-ES doped with sulfuric acid. The exceedingly porosity nature of the polymeric material and the packaged circular morphology was confirmed with a FESEM.

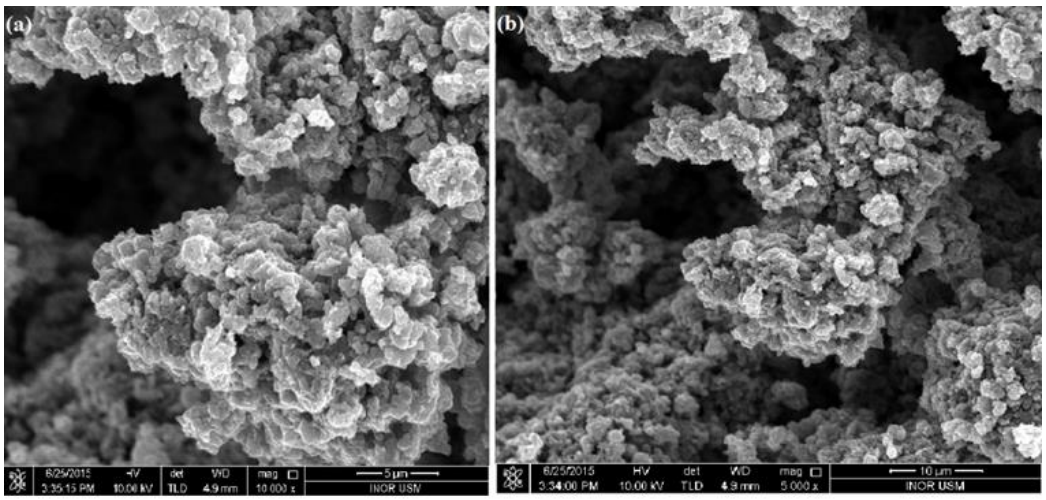

Figure 2. FE-SEM images of PANI-ES doped acid at (a) 5µm (b) 10µm.

Figure. 3 which represents the x-ray diffraction of polyaniline doped with acid show tow wide peaks at (2θ=22^{o} ,25^{o}). The spectrum of x-rays to film of Polyaniline as the angel at (22^{o}) show diffraction levels parallel in the polymeric chain, the angle at (25^{o}) shows diffraction levels orthogonal these results are compatible to results Singla et al [8]. The diffraction of the films of polyaniline when researcher used a different acid to doping

polymer and the results was one of the terms of the film of the peaks at angle (22^o, 25^o). The crystallite grain size is calculated according to Debye Scherer equation:

$$Gs=K\lambda/\beta \cos\theta \quad (3)$$

Where: K is the shape factor (0.9), *Gs* is the grain size; λ is the wavelength of X-ray radiation use (1.54Å); β is the full width at half maximum, θ is the diffraction angle. The pattern thin film polymer PANI-ES, that shows structure by the study of x-ray peaks confirmed amorphous and the semi crystalline nature of the synthesis polymer [10], [11]. The peaks at ($2\theta=22^o$, 25^o) may also represent the characteristic distance between the crystalline planes of benzene and quoined respectively in the polymeric chains [12]. The characteristic broadening of the observed peaks implies that the films are nano-crystalline. Table 1 show an affected of strong acid on Bragg angle with intensity of conducting polyaniline.

Table 1. Affected of ionic acid on Bragg angle and intensity in conducting PANI doped.

Sample	Pos. [2θ °] (degree)	FWHM (degree)	*d*- spacing (Å)	G_s (nm)
PANI-ES (H_2SO_4)	22^0	0.8	3.9	97.7
	25^0	0.98	3.5	18.15

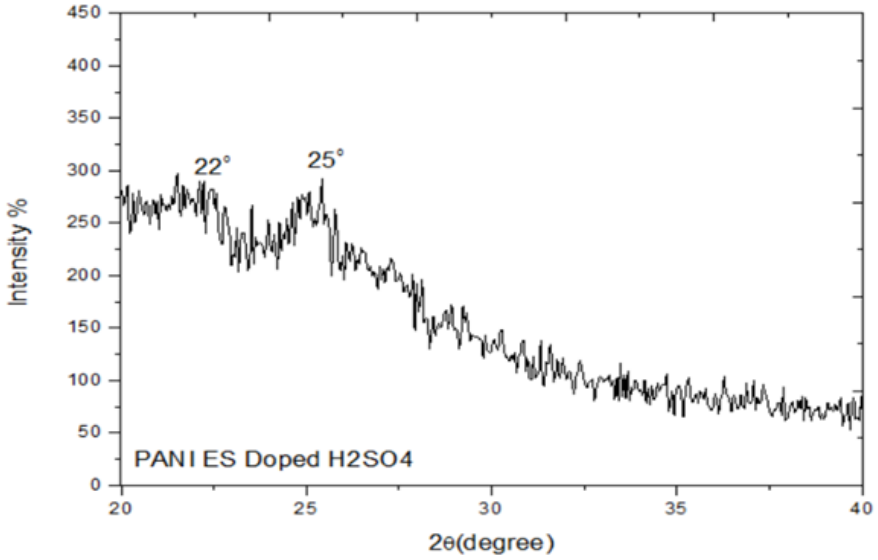

Figure 3. X-ray diffraction of doped Polyaniline with ionic acid.

Figure 4 show the electrical properties for Polyaniline doped with H_2SO_4, at temperature range around 293^o-383^oK, with the same thickness of thin films at 45nm. The ohmic behavior showed for all the applied voltage. The electrical conductivity was calculated by equation (4) for different temperatures and tabulated at Table 2. Figure. 4 show the electric properties and electrical conductivity as function of inverse temperature for PANI. Electrical conductivit exhibited increased due to acid doping from $2.4x10^{-5}$ $S.cm^{-1}$ to $2.9x10^{-4}$ $S.cm^{-1}$ for PANI-H_2SO_4 doped at room temperature. Actually, the current increased linearly with amount voltage and the electrical conductivity in the conducting

polymers is not same as semiconductors materials [11]. 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 plot [12]. Table.2 showed that the conductivity of polyaniline because the bi-Polarons state which was made by doping with sulfuric acid was become a very lower with temperature [13]. Activation Energy (Ea) in Figure. 5 of doped polyaniline has been deduced using the expression Arrhenius equation [14], [15]:

$$\sigma_{DC} = Ae^{-\frac{E_a}{KT}} \qquad (4)$$

The activation energy (E_a), Figure. 5 determined from this curve was 0.11eV for doped polyaniline. The estimation of activation energy E_a for PANI-H_2SO_4 is very large value, which shows that the localized salt dopant polymer was more prominent suggesting that it needs to reduce energy for charges transition [16].

Table 2. Electrical conductivity for Doped Conductive Polyaniline (PANI-ES).

T (K)	PANI-ES (H_2SO_4) 6 DC ($S.cm^{-1}$)
293	$2.46x10^{-5}$
313	$4.86x10^{-5}$
333	$8.82x10^{-5}$
353	$1.49x10^{-4}$
373	$2.4x10^{-4}$
383	$2.98x10^{-4}$

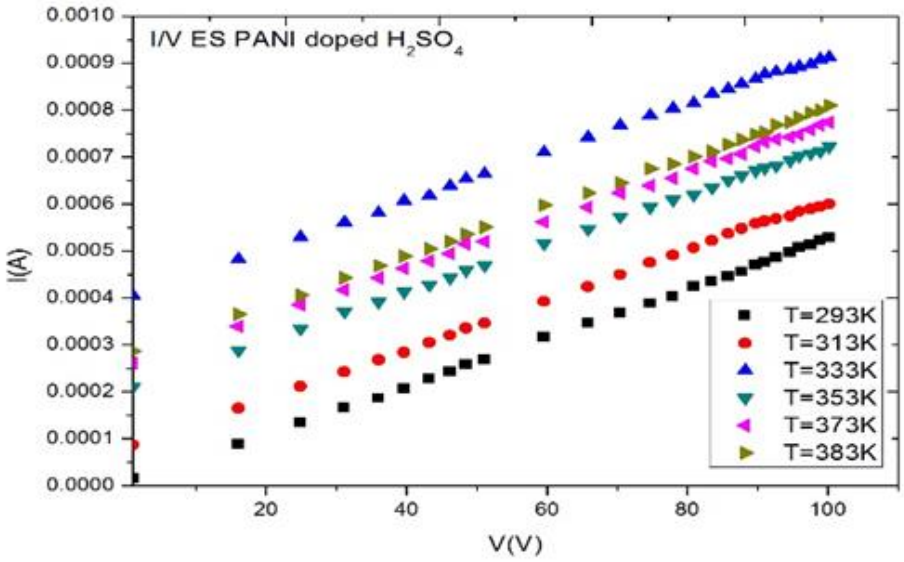

Figure 4. Electric Properties for PANI-ES doped H2SO4 at different temperatures 293o-383o K.

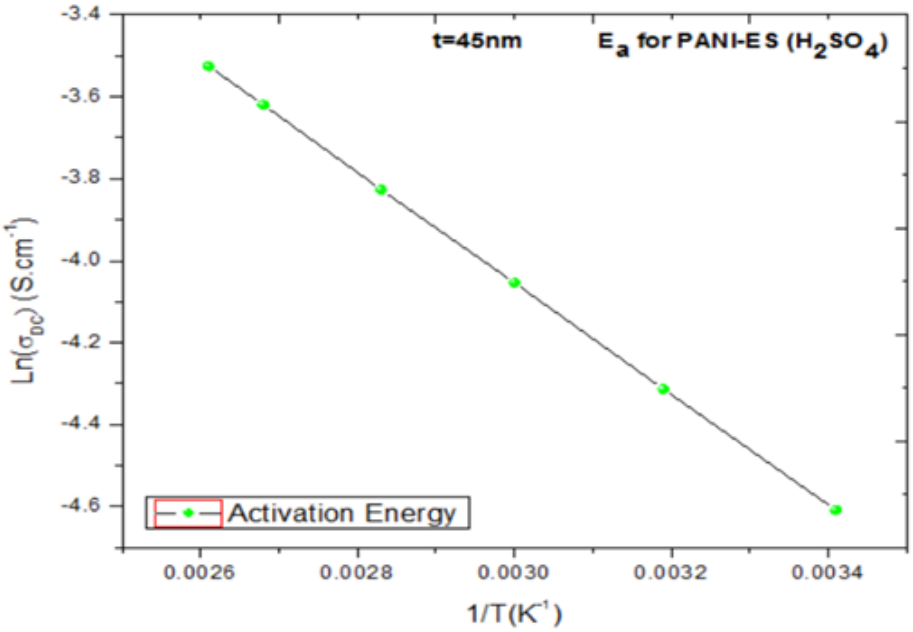

Figure 5. The activation energy for PANI-ES doped H2SO4 film.

CONCLUSION

Fundamental Finding : The field emission scanning electron microscope FE-SEM images of the doped polymer samples showed height porosity microstructures, the acidic doped sample exhibited a high micro porous structure. The conductive of polymer was synthesized by chemical oxidative method in which the fabrication time was approximately 20h. Polyaniline ionic salts were found to exhibit varying electrical conductivities. All samples showed an ohmic curve. The doped polyaniline samples showed a sudden increase in conductivities. The strong acid doped sample gave the highest conductivity 2.98×10^{-4} S.cm^{-1} which is greater than more times that of the pure sample. **Implication :** The experimental conductivity values generally showed an inverse correlation with the values of the energy band gap for energy levels of HOMO-LUMO. This suggests that doping significantly modifies the electronic structure and enhances conductivity properties, supporting the potential of acid-doped polyaniline in electronic and sensor applications. L**imitation :** Activation energy Ea for the conductive polyaniline doped was an increased to 0.11 eV for the polymer doped by sulfuric acid. While this increase indicates successful doping, the value also implies a limitation in charge carrier mobility that may influence performance in certain high-frequency or low-voltage applications. **Future Research :** Further investigation of the morphology of samples will give a better understanding of the bulk conductivity. This will allow for a more precise correlation between microstructural features and electrical behavior, potentially guiding optimized synthesis conditions in future studies.

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