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Electrical Conductivity of Conductive Polymer Polyaniline (PANI-ES) Preparation by Chemical Oxidative Method

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Abstract: Conductive polymer as Polyaniline (PANI-ES) prepared by chemical oxidation polymerization method at room temperature and studied the effect the dopant sulfuric acid on the structure of the polymer, which prepared with molarity of sulfuric acid (1M), the changes taking place were follow-up by the following measurements: FESEM, FT-IR, I-V character. The diagnosis of the output polymer films by using infrared spectroscopy FT-IR, for doped samples with 1M of sulfuric acid observed change in the intensity of emission opposite the wave number corresponding to each bond, while not noticed any change in the position of the bonds with appearance anew peak return to SO_4 compound. By the FESEM properties of the surface study using the topography FESEM (Field Emission Scanning Electronic Microscopic) and calculated the particle revealed, that the compound has micro granular affected with the presence of acid. Electrical characteristic study by using the two-probe manner, it found that the samples had ohmic plots in which high linear coefficients. The doped samples of polymer had a highest conductivity of 2.98×10^{-4} $S.cm^{-1}$ at 383 K, which observed for the H_2SO_4 doped sample, which shows that was more prominent of localized salt in polymer.

Keywords: Electrical Conductivity, Acidic doped, PANi-ES.

I. INTRODUCTION

Electrically conducting polymers described as a new class of synthetic materials [1] reached a high interest in the last years, confirmed by the Nobel Prize 2000 in chemistry for the discovery and development of conductive polymers [2]. Polyaniline is one of the most studied materials because of its high conductivity upon doping with acids, good behavior physic-chemical and easy fabrication under reproducible conditions by electro-chemical polymerization and chemically oxidation of aniline, 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] charge carriers in the form of extra electrons or holes have to inject into the material. Polyaniline acts as an electrically conductive material only in the protonation form of emeraldine salt. It can changes the electronic conductivity about (10) orders of magnitude, passing from insulator state (emeraldine base) to metallic conduction (emeraldine salt), depending upon the protonation degree [4, 5]. Controlling the doping state and polymerization conditions, we assume that is possible to change the morphology and thus the chemical properties of polymer [6]. In the emeraldine salt (ES), the 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 very easy by changing the system pH [6]. By requirement doping of polyaniline in sulfuric acid media, actually we introduced multiple charge carriers, which determine an improvement of the electrical conduction along the polymer chain. Moreover, we assume that the total conduction in PANI given by summing the electrical conduction and ionic conduction that occurs by sulfonic groups on the aromatic rings [6].

II. METHODOLOGY: Synthesis of Conductive Polyaniline PANI-ES

The PANI-ES samples were chemical prepared at the ambient conditions at room temperature by using reagent aniline, ammonium peroxide sulfate (APS), and the appropriate dopant (H_2SO_4). The standard procedure for the polymerization of aniline hydrochloride was followed [7]. A 0.25 M solution 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 -4°C in presence ice bath. The temperature as a function of time for this reaction was recorded through the polymerization processes. The green precipitate formed was filtered, washed with distilled water and acetone, and then dried in oven vacuum for 6 h at 80°C. The Polyaniline powder was thoroughly in a mortar to obtain very fine particles.

III. CARACTERIZATION OF POLYANILINE

All the prepared polyaniline thin films samples characterized of microstructure using a microscope FESEM, Spectroscopy Fourier and electrical conductivity. For conductivity and electrical properties, conductive paste was use to attach the wires as contacts. Then, current-voltage (*I-V)* measurements done using the four-probe method and resistivity measurements derived using the Van der PAUW method [8]. Before taking the FESEM images, the samples coated with platinum for 5 min for usually sufficient coating using an RF sputtering system to increase the source of electrons. Morphology 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. Spectroscopy Fourier transform infrared FT-IR (Model: Perkin Elmer Spectrum Gx) of polymers films was studied in the frequency range of 400–4000 cm^{-1}. Electrical conductivity characteristic study using by a four-probe resistivity meter at room temperature (Model Keithley 82). Metal electrodes mask assembled from two individually addressable (Interdigitated) comb-like electrode structures have frequently been suggested as ultra-sensitive for chemical structure. Electrode mask with size in the nanometer scale is popular in the solid-state physics [9]. Figure. 1 shows electrode that consists of Aluminum fingers lines on a silicon or glass substrate. It be achieved using inter-digitated electrodes to measure the surface conductivity of the samples from the following relationship:

$\sigma_s = [I/V]\,[L/Wt\ell]$ …………………… (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;

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

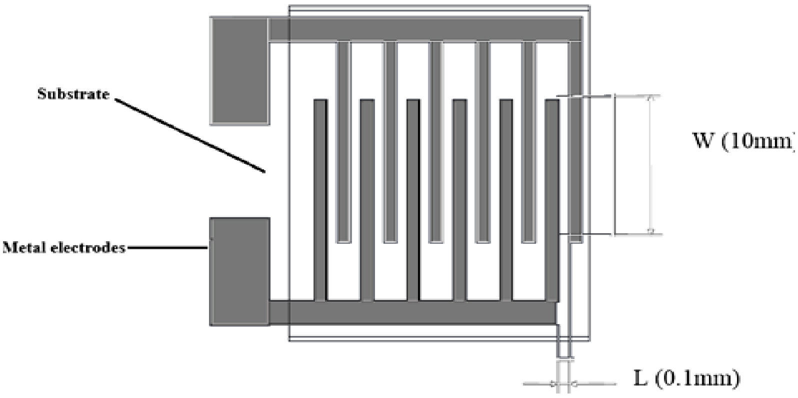

Fig. 1: An Interdigitated finger electrode mask.

IV. RESULTS AND DISCUSSION

Figure. 2 show the *I-V* characteristic for PANI-ES doped with H_2SO_4, at temperature range of 293^o-383^oK, with the thickness of thin films was 45nm. Ohmic behavior observed for all the applied voltage. The electrical conductivity was calculated by Equation (2) for different temperatures and tabulated at Table 1. Figure. 2 show 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. Actually, the current increments linearly with applied voltage and the electrical conductivity in the conducting polymers is not same as semiconductors materials [10]. 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 these bi-Polarons. As the applied voltage increases, the existence of bi-Polarons builds which contribute to the speedup increments in current as for voltage resulting in ohmic behavior as linear curve [11]. Table.1 demonstrates that the conductivity of PANI-H_2SO_4 because the bi-Polarons state which was made by doping with H_2SO_4 was less with temperature [12]. The Activation Energy (Ea) of doped polymer PANI-ES has been deduced using the expression Arrhenius Equation [13, 14]:

$\sigma_{DC} = Ae^{-\frac{E_a}{KT}}$ …….. (3)

The activation energy E_a determined from this curve was 0.112eV for PANI-H_2SO_4. The estimation of activation energy E_a for PANI-H_2SO_4 is big value, which shows that the localized salt dopant polymer was more prominent suggesting that it needs to reduce the energy for charges transition [15].

Table 1: 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}**

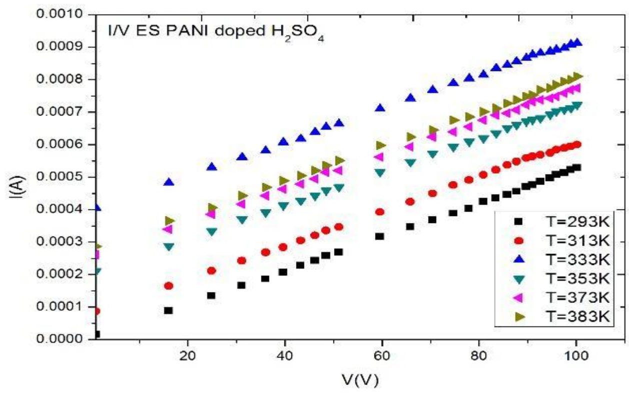

Fig.2: I-V characteristic for PANI-ES doped H_2SO_4 at different temperatures 293°-383° K.

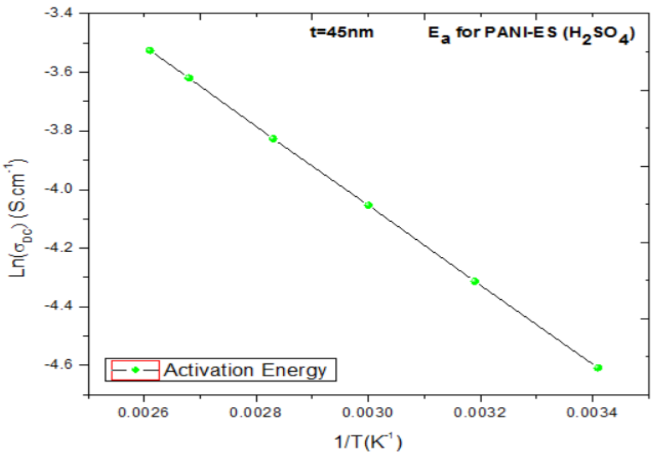

Fig. 3: The activation energy for PANI-ES doped H_2SO_4 film.

As shown in the FESEM images of Figure. 4 (a, b) the PANI-ES samples with H_2SO_4 acid dopant exhibit varying microstructures. Variation in microstructure leads to different conductivities of the samples. The addition of acid dopants alters the polymer lattice, which leads to the ionization of sites in the chains. The defects in the chain due to the dopant ions provide the mobility of the charge carriers on which conduction depends [16]. The conductivity is also dependent on the number of charge carriers. The doped sample in Figure. 4 displays globular structure morphology. Figure 4 (a, b) shows a high micro porous pattern of globular microstructures for the PANI-ES with H_2SO_4-doped sample. The exceedingly porosity nature of the material and the bunched circular morphology was confirmed with a FESEM study.

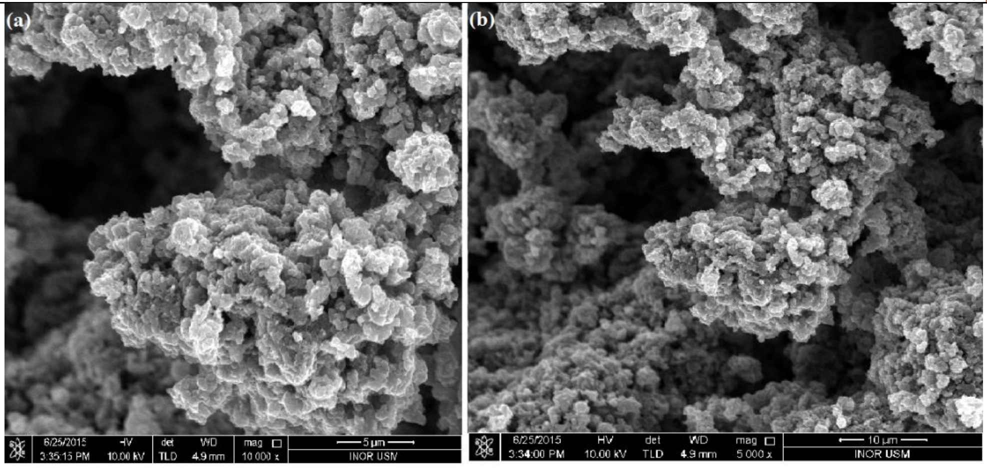

Fig 4: FESEM images of PANI-ES doped with H_2SO_4 acid at (a) 5µm (b) 10µm.

The peaks observed for the Polyaniline doped at room temperature with 1M concentration of H_2SO_4, listed in Table. 2 demonstrates the fundamental transmission groups of the Polyaniline. The FT-IR spectroscopy properties as shows in Figure. 5 for polyaniline doped, from the spectrum, it can distinguish between benzenoid rings and quiniod rings in the 1300-1600 cm^{-1} region of the spectrum. Assign the vibration bands characteristic of the conducting protonated form found between 1226 cm-1 and 1144 cm-1 to a vibrational mode of a protonated imines group [17]. The peak at 1260-1350 cm^{-1} could be related to the Sulphate compounds and amine, which produced by dopant acid. Likewise, peaks at 1380, 1475cm^{-1} can be assigned to a state of Sulphate bonds added to rings on top of that alcohol as products. The most important property bands groups for prepared PANI are the bands watched at 1650 cm^{-1} and 1961cm^{-1}, which represent the benzenoid rings and quinoid rings respectively. Alternative groups, which showed existence of vibration bonds of water molecules in the generality of the spectra presented in Figure. 5, demonstrated a high-level humidity during estimations that made [18].

Table 2: List of the observed peak in the polyaniline doped samples

Peak (cm^{-1})	**Assignment Functional groups**
1650-1961	**C=N Benzenoid ring conjugate cycle alkenes band**
1380-1475	**S=O Sulphuric Chloride, stretching band**
1299-1350	**S=O Sulphuric stretching band strong**
1200-1297	**C-N amine stretching strong band**
1020-1125	**C-N Benzene derivative amine stretching band**
850-500	**C-Cl compound stretching band**

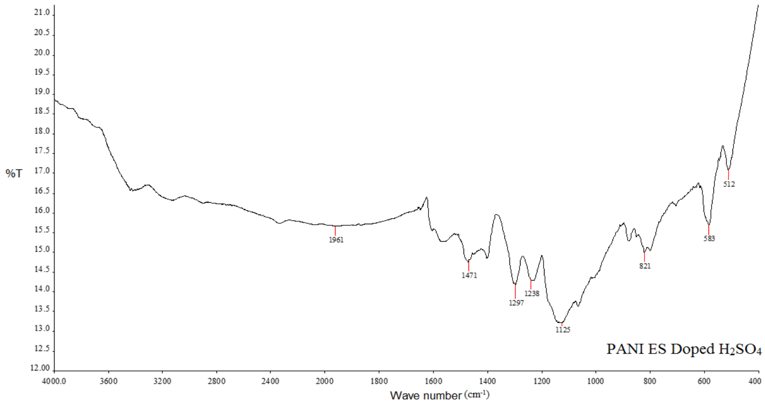

Fig .5 FT-IR spectrum of PANI-ES powder doped H_2SO_4.

V. CONCLUSION

The conductive of polyaniline (PANI-ES) was synthesized by chemical oxidative polymerization method in which the fabrication time was approximately 22h. Polyaniline salts PANI-ES were found to exhibit varying electrical conductivities. All prepared samples showed ohmic behavior. The doped PANi samples showed a dramatic increase in conductivities. The H_2SO_4 doped sample gave the highest conductivity $2.98x10^{-4}$ $S.cm^{-1}$ which is times greater than that of the undoped sample. The experimental conductivity values generally showed an inverse correlation with the values of the HOMO-LUMO energy band gap. An activation energy E_a for the polyaniline doped PANI-ES was an increased to 0.112 eV for the polymer doped by hydrochloric acid. The field emission scanning electron microscope FESEM images of the doped PANI samples showed height porous microstructures, the H_2SO_4 doped sample exhibited a micro porous structure. Further investigation of the morphology of samples will give a better understanding of the bulk conductivity.

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