

Preparation a Conducting Polyaniline by Chemical Oxidative Method and Study Electrical Conductivity Properties

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Abstract— Samples of doped polyaniline (emeraldine salt) were prepared with protonic acid dopants, namely, hydrochloric acid (HCl). Using the two-point probe method, it was found that the samples had ohmic behavior in which high linear coefficients. The doped sample had a highest conductivity of 1.2×10^{-4} S/cm was observed for the HCl doped sample, while the lowest value 7.59×10^{-6} S/cm. These conductivities were compared with the computed energy gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) where it was found that they are inversely proportional to each other. Field scanning electron microscopy revealed significant differences among the samples in terms of morphology.

Keywords— Emeraldine salt, Conducting PANi, Electric conductivity.

I. INTRODUCTION

Conducting polymers is widely used in microelectronics devises, the importance, these microelectronics application is that it has physical properties tailored to a particular application and to understand the mechanisms controlling these properties [1-3]. Polymeric materials can be synthesized and processed into different shapes according to the required application such as thin films, rods, disk...etc. Polymers have many advantages to the electrical application due to their simple synthesis technology, relatively low-cost materials and can be deposited on different substrates, moreover, they have special characteristic that made them very important, such that, they have a wide range of electrical conductivity [10^{-24} - 10^6 S/cm] [4]. In this work we study the electrical properties of (PANi -HCl). The effect of temperature on the conductivity of conducting polymer was also investigated. The activation energy of conducting polymer was also determined.

II. INSTRUMENTS AND CHARACTERIZATION

The synthesized polymer PANi was used to study the morphology through FESEM. The Morphological by FESEM study the thin films of PANi was carried out using by field effect scanning electron microscopy (Model: FEI Nova Nano SEM 450) operating at 20 kV. Interdigitated electrodes (IDE) assembled from two individually addressable interdigitated comb-like electrode structures have frequently been suggested as ultra-sensitive for chemical structure films. Interdigitated electrode structure with feature size in the nanometer scale is popular in the solid-state physics [5,6]. Figure 1 shows electrode that consists of interdigitated Aluminum lines on a

glass substrate. It can be achieved using interdigitated electrodes to measure the surface conductivity of the samples from the following relationship.

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

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 (100 μ m). So that;

$$\sigma_s = I/Vt (100 \times 10^{-6} / 10 \times 10 \times 10^{-3}) = I/Vt (10^{-3} \text{ S/M}) \quad (2)$$

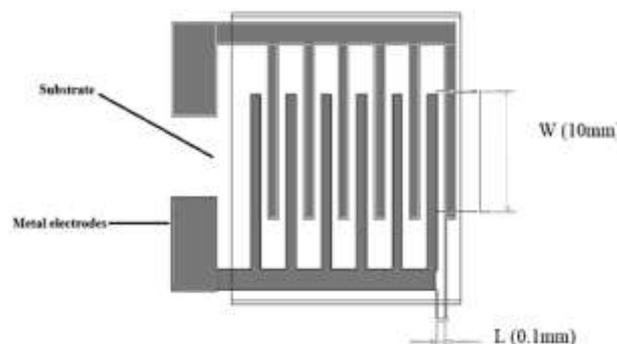


Fig. 1. A schematic diagram of interdigitated finger electrode.

III. CHEMICAL PREPARATION OF PANI-ES (EMERALDINE SALT)

The PANi-ES samples were chemically synthesized using reagent-grade aniline, 6g ammonium persulphate (APS), and the appropriate dopant 100ml (HCl). The standard procedure for the polymerization of aniline was followed [7]. About 20ml aqueous solution of APS was mixed with 0.2 M of aniline in 1M of the acid dopant. The mixture was stirred and maintained at 5°C in an ice bath. The obtained green precipitate formed was filtered, washed with distilled water to remove APS in the material, then with acetone to remove any organic impurities. And dried in a vacuum oven for 6 h at 80°C and stored overnight in air tight container.

IV. RESULTS AND DISCUSSION

Figure 2 and Figure 3 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 (2) for different temperatures and tabulated at Table I. Figure 2 show the electric conductivity as function of reciprocal temperature

for PANi-HCl. The electrical conductivity increased due to HCl doping from $7.59 \times 10^{-6} \text{ S.cm}^{-1}$ to $1.2 \times 10^{-4} \text{ S.cm}^{-1}$ 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 [8]. In case of the conducting polymers, the negative and positive charges initially added to the polymer chains don't 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 [9]. Table I demonstrates that the conductivity of PANi-HCl because the bi-polarons state which was made by doping with HCl was bigger with temperature [10]. The Activation Energy (E_a) is the energy level that the reactant molecules must overcome before an interaction can happen. The activation energy of doped polymer PANi-ES has been deduced using the expression Arrhenius Equation [11, 12]:

$$\sigma_{DC} = Ae^{-\frac{E_a}{kT}} \quad (3)$$

The activation energy E_a determined from this curve was 0.125eV for PANi-HCl. The estimation of activation energy E_a for PANi-HCl is big value which shows that the localized salt in PANi-HCl. was more prominent suggesting that it needs to reduce the energy for charges transition [13].

TABLE I. The electrical conductivity for Conductive Polyaniline (PANI-ES).

T (K)	PANI-ES (HCl) $\sigma_{DC} (\text{S.cm}^{-1})$
293 (RT)	7.59×10^{-6}
313	1.61×10^{-5}
333	3.12×10^{-5}
353	5.63×10^{-5}
373	9.5×10^{-5}
383	1.2×10^{-4}

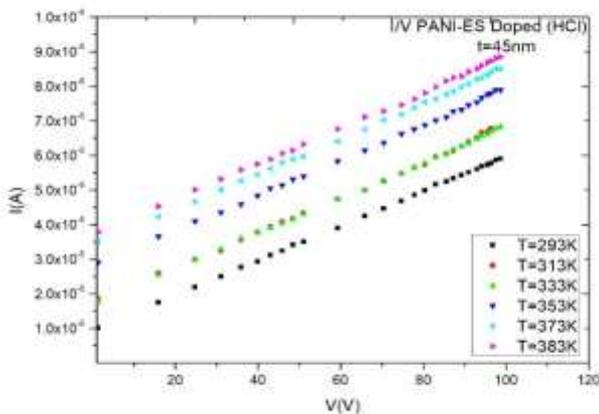


Fig. 2. The current-voltage characteristic for PANi-ES doped HCl at different temperatures 293°-383° K.

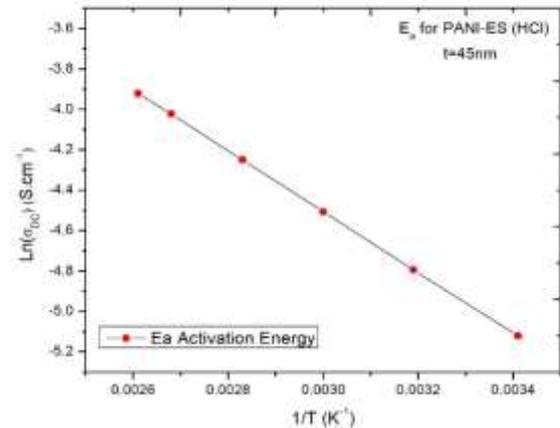


Fig. 3. The activation energy for PANi-ES doped HCl film.

The FESEM images show in Figure 4. (a, b) ordinary features of the polymer structure. All images are mostly made out of irregularly composed granular and flakes with sharp edges. In addition, the structure looks more porous. It can be observed from Figure 4. (a, b), that polyaniline composition particles have much more cavities morphology. The enlargement addition of acid dopant enhanced the crystal lattice of the polymer which gives rise to the growth of the ionization of areas in the chains. The imperfections in the chain of polymer due to the dopant particles give large number of the charge carriers on which conduction depends [14,15]. Figure 4. exhibiting a fine porous consolidated structure. The exceedingly porosity nature of the material and the bunched circular morphology was confirmed with a FESEM study.

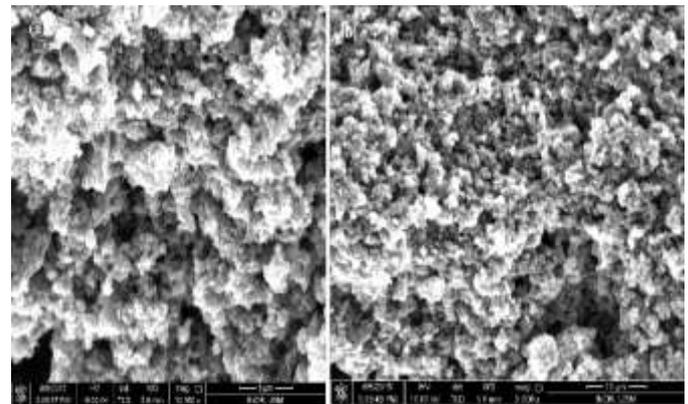


Fig. 4. FESEM images of PANi-ES powder doped with HCl (a) magnification to 5µm (b) magnification to 10µm.

V. 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. 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 compared with

undoped PANi. The HCl-doped sample gave the highest conductivity 1.2×10^{-4} S/cm which is times greater than that of the undoped sample. The experimental conductivity values generally showed an inverse correlation with the values of the energy gap. The activation energy E_a for the polyaniline doped PANi-ES was increased to 0.125 eV for the polymer doped by hydrochloric acid. 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.

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