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A Comparative Study of the Effect of a Conductive Polyaniline Doped with a various Acids on the Microstructure and Optoelectronic Characteristics

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ABSTRACT:

Polyaniline (PANI)-ES samples are created using several ionic acid dopants, including hydrochloric acid (HCl) and sulfuric acid (H_2SO_4). In the presented study, a chemical polymerization approach was employed to prepare conductive PANI Emeraldine salt. Field Emission Scanning Electron Microscopy (FESEM) is used for studying and characterizing the polymer's microstructure, while UV-vis spectroscopy is used to study its optical properties. Also, the electrical conductivities have been determined using the Van der Pauw technique. Utilizing the 2-point probe approach, it has been discovered that samples have exhibited ohmic behavior with high linear coefficient values. The doped sample, on the other hand, showed a greater electrical conductivity of 2.98×10^{-4} S/cm for HClO4-doped sample. In addition, the energy gap between the energy levels (HOMO-LUMO) is calculated and compared to the electrical conductivities, which reveal that they are inversely proportional to each other.

Keywords:*Ionic Acid,DopedPANi-ES,Electronic Properties, Structure, Conductivity.*

I. INTRODUCTION

The conducting polymers, which are described as one of the new synthetic metal classes [1], have sparked a lot of attention in recent years, as evidenced by the Nobel Prize in Chemistry Science in 2000 for development and discovery of the conductive polymers [2]. PANI is considered as a highly analyzed material, due to its high conductivity after acid doping, ease of preparation under the reproducible conditions via electro polymerization and chemical oxidation of aniline, good electrochemistry, good environmental stability, and electrical conductivity [3]. The existence of conjugated double bonds along polymer's backbone is an important characteristic of conductive polymers. The bonds between the atoms of the carbon in conjugation are alternately double and single. Each one of the bonds contains a localized (sigma) bond that contributes to the formation of a strong chemical bond. Furthermore, every double bond includes a weaker (pi) bond that is less strongly localized.

Yet, conjugation alone is insufficient for making the polymer material conductive. This is what doping accomplishes, charge carriers as extra electrons or holes must be injected into the material. In addition, a hole is a charge at a position, in which an electron is not present. In the case when an electron jumps in from a neighboring spot to fill the hole, a new hole is produced, and so on, allowing charge to migrate a long distance [4]. While the conducting processes in their conjugated carbon backbones are well-understood, the conducting mechanisms in the PANI forms are more complicated and poorly established. Only in protonation form of the emeraldine salt does PANI act as an electrically conductive material.Itmight change electronicconductivityapproximately (10) ordersofvalue, which passes frominsulatorstate(emeraldinebasewiths less than 10^{-10}S/cm)tometallicconduction

(emeraldinesaltwiths ~10^{-1}-10^{2}S/cm),based on the degreeof the protonation[5,6].We believe that by adjusting the pH, polymerization conditions, and doping level, we may vary the morphology and consequently the chemical and physical properties of the polymer [6]. The protonated structure related to PANI in ionic acid media, seen in Figure 1, piqued our interest. PANI, both sulfonated and chloride has a similar structure to ion conducting polymers.
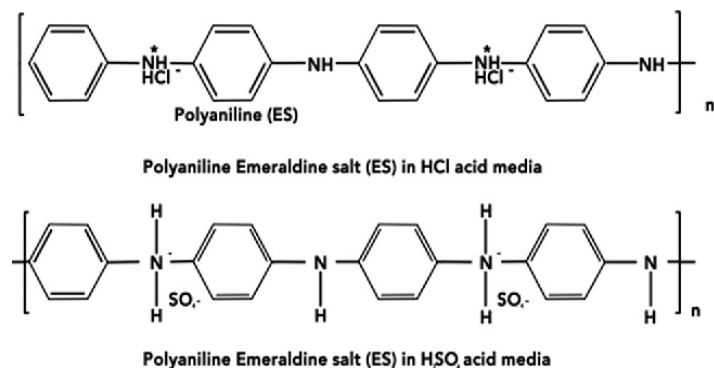

Fig.1: Diagram of transitionelectronsfor conductive Polyaniline(ES)to–Cl and SO_4 [7].

The Cl and HSO4- species in the emeraldine salt (ES) are ionic linked to the -NH groups in the polymer chains. Those types of bonds are quite weak and may be easily removed through changing the pH of the system [7]. By additional doping PANI in chloric and sulfuric acid media, we actually presented numerous charge carriers that increase electrical conduction along the polymer chain. Furthermore, we suggest that total conduction in PANI-ES is provided through adding ionic conduction and electrical conduction caused by ionic groups on aromatic rings[7].

II. CHEMICAL MATERIALS

For the synthesis of PANI, we employed the next chemical materials. All of the chemicals utilized here were of the maximum purity, and their suppliers as well as the reason for which they were utilized are stated in Table1.

Table1: Usedchemicalsas well asthesuppliercompanies.

Chemical Materials	Molecular weight (g/mole)	The Origin Company
Aniline hydrochloric ($C_6H_5NH_2.HCl$)	93.13	Merck Schuchardt, Germany
Ammonium persulphate ($(NH_4)_2S_2O_8$)	228.20	Merck KGaA, Germany
Hydrochloride Acid (HCl)	36.46	BRIGHTCHEM, Malaysia
Sulphuric Acid (H_2SO_4)	98.08	QReC, Asia, Malaysia
Hydro Formic Acid (HF)	20.0	QReC, Asia, Malaysia

III. MEASUREMENTS AND INSTRUMENTS

Morphological analysis of PANI thin films was performed with the use of FESEM (Model: Nano SEM 450) at 20 kV. The samples' UV-Vis spectra have been recorded on a Shimadzu 1800 UV-visible spectrophotometer. Interdigitated electrodes (IDE) that are made up of 2 individually addressable interdigitated comb-like structures of the electrode were proposed as ultra-sensitive for the chemical structure films [8, 9]. Figure 2 depicts an electrode made up of Aluminum lines on glass substrate. It is possible to evaluate the conductivity of the surface regarding samples with the use of interdigitated electrodes using the next relation:

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

Where, t represents thickness of polymer thin films, ℓ represents the number of the fingers, W represents distance fingers, and L represents space between the electrodes. So that;
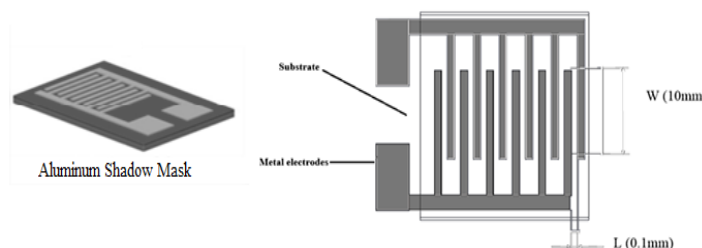

Fig2: Diagram of the interdigitated finger electrode.

IV. EXPERIMENTAL PROCEDURES

PANI was synthesized from the monomer aniline using a chemical polymerization process with protonic HCl and H_2SO_4 as stimulants of the reaction and APX (i.e. ammonium peroxydisulphate) as oxidant agent. For syntheses, 1M of acidic medium has been used, 50ml beaker, and 0.20M of the aniline solution in a 250ml beaker that is supplied by Teflon coated magnetic stirrer at a temperature of around 0-2°C. After combining 0.25M APX in an aqueous medium with an equal molarity acid of (H_2SO_4) and (HCl), 1M acid has been added in a drop-by-drop manner into the solution above. For polymerizing the mixture, the two solutions are combined in round-bottomed flask with gentle stirring. It is discovered that the process is exothermic. The temperature of such reaction as it progresses through the polymerization steps as a function of time. In addition, the precipitate (PANI) has been collected as well as washed 3 times with 0.20M acid and 150ml of Acetone. Then, PANI has been air dried for 1 hr and after that annealed in a vacuum oven at a temperature of 60°C for 8 hrs, to prevent moisture absorption. For obtaining extremely small particles, the PANI powder dark green colorful of conductive PANI-emeraldine salt (ES) form has been carefully ground in a mortar. After that, using 0.10M of the Hydrofluoric acid (HF), we solved PANI powder and made samples of the thin film, as shown in Figure (2), which depicts the process step by step.
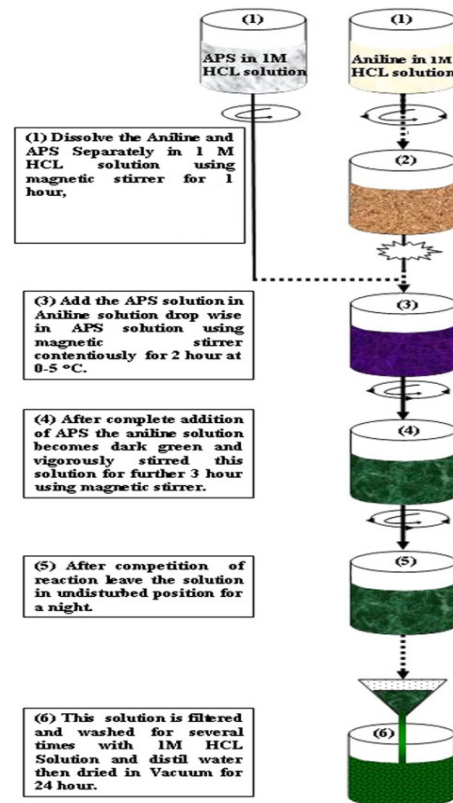

Fig 3: Fabrication Polyaniline illustration reaction steps.

V. RESULTS AND DISCUSSION

The microstructures of conductive PANI-ES samples with various dopants acid are exhibited in the FESEM images with amplification (5µm) in Figure 4(a), 4(b).Variations in microstructure results in varied sample qualities. The inclusion of the dopants of the acid had strengthened polymer crystal lattice, resulting in ionizing the polymer chain sites. The dopant ion-induced chain defects supply more mobility charge carriers upon which the conduction is dependent [10]. Figures (4a, 4b) depict a micro porosity pattern regarding the globular microstructures for PANI-ES with different acidity. The material's high porosity and clumped spherical shape were confirmed that through character FESEM analysis. Furthermore, the orientation of sample structures at the macroscopic level affected polymer conductivity [10].
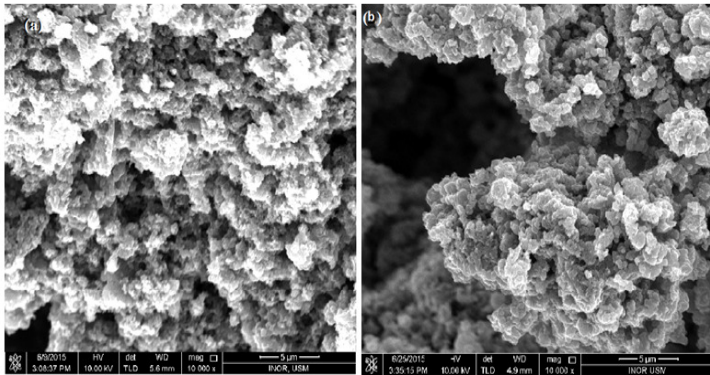
Fig (4a, 4b): Microstructure analysis by FESEM(5μm) of the doped PANI.

The optical absorption spectrum of PANI dopant samples generated at temperature degrees (-2 ^{o}C) with similar concentrations of protonic acids was discussed. This is evaluated in the visible spectrum using a Shimadzu UV-1800-spectrophotometer. There have been 3 prominent absorption peaks found approximately 300nm, 400nm, and 800nm in Figure. 5 (a, b), which confirm H_2SO_4- and HCl-doping in the PANI-ES films[11−13].
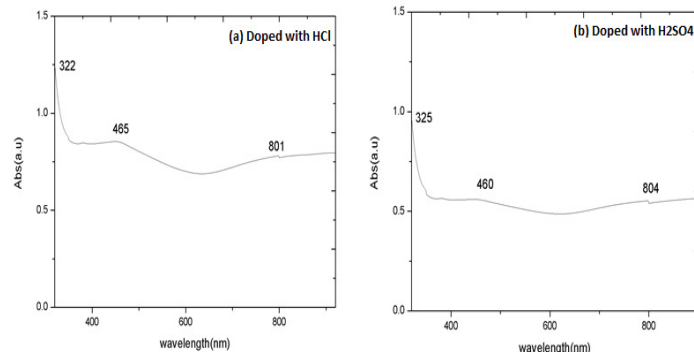

Fig. 5(a, b): Optical absorption spectra of PANI-ES that doped with acids.

PANI doped with HCl acid shows peaks at (322, 465, and 801) nm and (801 nm) and doped with H_2SO_4 acid (325, 460, and 804) nm are allocated to: (polaron→π*), (π→π*) and (π→Polaron) transitions for the PANI-ES doping with equal molars acid (HCl, H_2SO_4, respectively, as shown in Figure5 (a, b).
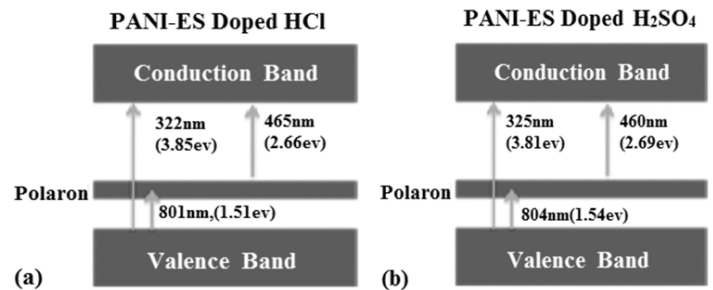

Fig6 (a, b): Aoptical transitions and HOMO-LUMO energylevels in PANI.

Which has confirmed the production of polaron bands in polymer band gap as a result of the protonic acid doping. It is obvious that there is a noticeable increase in the absorption as the reaction medium temperature decreases. Which is because lowering the temperature related to the reaction medium raises the polymerization degree, which results in an increase in the polymer's molecular weight, which results in an increase in absorption [14]. Furthermore, the localized defect states increase with decreasing temperature (0-4 °C) [15]. As can be seen in Table 5, the coefficients of absorption (α) regarding such PANI-ES films are maximal at 322nm, 325nm for PANI-ES (H_2SO_4, HCl). All obtained PANI-ES samples may be theoretically described by computing band gap energy values from their UV-visible spectra, as shown in Figure.6 (a, b). Furthermore, this photon energy is associated with the wavelength λ of UV-vis light via the next relationship[16-17].

$$\Delta E = E(HOMO) − E(LUMO) = Eg = 1240/\lambda nm.......(3)$$
hrepresents thePlanck'sconstant,νrepresents lightfrequency andcrepresents light velocity.Theestimatedbandgapforevery one of thecases has been listedinTable2.

Table2: Optical characteristics of the PANI-ES sample.

Polymer	Wavelength λ(nm)	Abs Coefficient $\alpha x10^5$ (cm^{-1})	E_g=E_{HOMO}-E_{LUMO} (eV)
PANi-HCl	322	1.2	3.85
PANi-H_2SO_4	325	0.8	3.8

For PANI doped H_2SO_4 and doped hydrochloric films with 1M doping concentrations, the coefficient of the absorption(α) in PANI doped HCl ($1.20 \times 10^5 cm^{-1}$) was higher than in PANI-H_2SO_4 ($0.80 \times 10^5 cm^{-1}$) for the same temperature, accompanied with an increase in the energy of the band gap (Eg) from 3.85eV to 3.8eV. The effects of doping concentration on PANI-ES films' optical absorbance at a constant temperature of film production has already been studied [17, 18]. According to the spectra in Figure (5a, b), films prepared at (0°-2 ^{o}C) temperature alone exhibit a weak peak about 801nm, 804nm, regardless of the concentration of doping that might be because of the reduction in the localized defect states in polaron band.

Figures (7a, 7b) shows the current-voltage property for PANI doped with H_2SO_4 and PANI-ES doped with HCl at temperatures ranging from 293°-383^oK. The film thickness was 45nm. For all applied voltages, ohmic behavior was observed. Equation (1) was used to compute the electrical conductivity for various temperatures, which is given in Table 3, and Figures (7a, 7b) illustrate electrical conductivity as a reciprocal temperature function for the PANI-HCl and PANI-H_2SO_4, respectively.

The electric conductivity has been improved because of the HCl doping to 1.20 $x10^{-4}$S/cm for PANI-HCl, whereas in the PANI-H_2SO_4 it has been higher at $2.98x10^{-4}$ S.cm^{-1}, 383^oK. The current is increased linearly with the applied voltage, and the process of conduction in the conducting polymers differs compared to that of semiconductor materials [19]. With regard to conducting polymers, the initial positive and negative charges introduced to the polymer chains do not immediately begin to fill the unbending valence or conduction bands. There are no persistent dipoles in conducting polymers. There are indeed random charges (Polaron) capturing locales in the sample. A high coupling between phonons and electrons, when affected via an applied outside field, creates lattice distortions surrounding the added charge, and as a result, charge catching gets strong, and their localized movement functions as effective electric dipole. Which results in the

formations of the semi-particles, like pi-Polaron and Polaron. In such instance, the charge is transported via such pi-Polaron. With the increase in the applied voltage, presence of pi-Polaron increases, contributing to the increments of the speedup in current as for the voltage, leading to ohmic behavior as a linear curve [20]. Table3 shows that conductivity which is related to PANI-H_2SO_4has been greater compared to that of PANI-HCl since pi-Polaron state produced by doping with the H_2SO_4hasbeen larger than that produced by the doping with the HCl [21, 22]. It is shown that localized salt in PANI-H_2SO_4has been more apparent compared to that in PANI-HCl, implying that the energy for charge transitions must be reduced [22].

Table 3: Electrical conductivity for Doped Polyaniline:

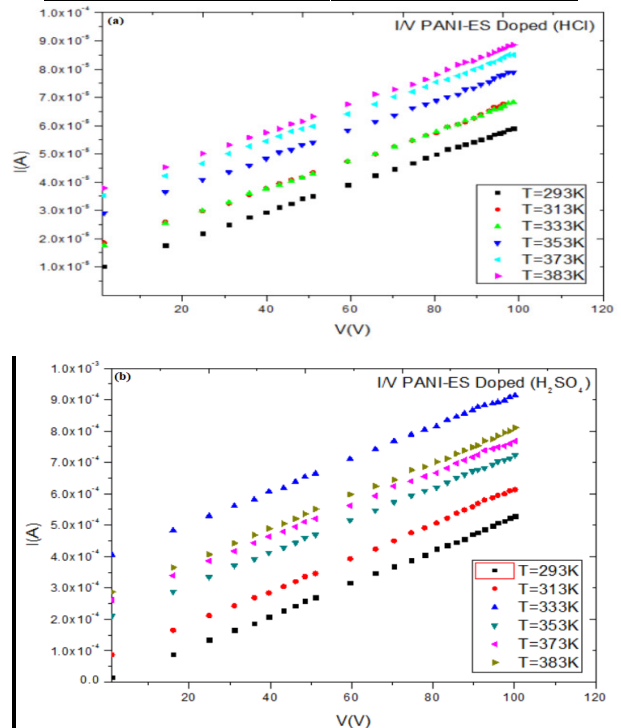| T (K)	PANi-ES (HCl) σ_{DC} (S.cm^{-1})	PANI-ES (H_2SO_4) σ_{DC} (S.cm^{-1})
293	$7.59x10^{-6}$	$2.46x10^{-5}$
313	$1.61x10^{-5}$	$4.86x10^{-5}$
333	$3.12x10^{-5}$	$8.82x10^{-5}$
353	$5.63x10^{-5}$	$1.49x10^{-4}$
373	$9.5x10^{-5}$	$2.4x10^{-4}$
383	$1.2x10^{-4}$	$2.98x10^{-4}$

Fig 7 (a, b): Current-Voltage characteristic for PANi-ES doped at different temperatures 293°-383° K.

VI. CONCLUSION

Summarize, a one-step direct and environmentally friendly, easy, cost-effective, and innovative chemical synthesis technique for producing PANI-ES devised. This could be useful for commercially synthesizing PANI. It may be demonstrated that PANI has micro-structure and chemical stability by studying its chemical and physical properties using additional approaches like UV-vis spectroscopy, FESEM, and electrical conductivity.

- The polymerization reaction of PANI in the oxidative chemical approach was exothermic, with the reaction conditions of time and temperature being directly related to the construction of ionic acid which was utilized to dope the polymer.
- The FE-SEM diagnostic results showed that polymer particle size was within micro-scale and that there was acid present.
- The optical properties of doped PANI-ES thin film validated the preparation of the micro-structure polymer, low resistivity and wide optic band gap.

- Polyaniline doped by salts ionic PANi-ES have been found to exhibit varying electric conductivity levels. The doped PANi samples have shown a dramatic increase in conductivities.
- The highest conductivity was to H_2SO_4 doped sample gave conductivity 2.98×10^{-4} S.cm^{-1}, while HCl-doped sample gave 1.2×10^{-4} S/cm. The values of the experimental conductivity have often revealed an inverse association with HOMO-LUMO energy gap values.

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