

Charge Transfer in Anion Doped Polyaniline

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Abstract. The effects of anionic dopant (Cl⁻, ClO₄⁻ and SO₄²⁻) on the physicochemical properties of conducting polyaniline (PANI) were studied. The depositions of current densities were 5 mA/cm², 10 mA/cm² and 15 mA/cm². In the Infra Red Spectra (IR), the band characteristics of aniline confirmed the presence of monomer ring in the polymer. Most of the samples except SO₄²⁻-doped polyaniline showed their semiconductive behavior. The resistance of the SO₄²⁻-doped sample is much lower than those of other Cl⁻, ClO₄⁻-doped samples. Resistivity were lied in the range of (2.71~13.00) × 10⁴ ohm.cm for Cl⁻-doped, (1.66~9.16) × 10³ for ClO₄⁻-doped and 276.75 ohm.cm for SO₄²⁻-doped polyaniline.

Keywords: dopant, polyaniline, conductivity

1. Introduction

Polyaniline is one of the most promising intrinsic conducting polymers due to its relatively easy preparation, excellent environmental stability, low cost and interesting electronic [1-7]. Among the numerous electronically conducting polymers studied to-date, PANI films appear undoubtedly as the favorite for extensive work in a variety of directions. Some authors have been interested for some time in the preparation and study of stable PANI films doped with anions [8]11 255. However, electrochemically synthesized polyaniline (PANI) has conducting properties for its conjugated double bond. The electronic state of PANI can be controlled through both variation in the number of electrons per repeat unit and variation in the number of protons per repeat unit. The properties of polyaniline vary with the nature of dopant anion because protonation in PANI involves ingression of anions in such a way so as to maintain charge neutrality along with the whole polymer backbone. 1979 Diaz et al. [9] reported a new technique for the synthesis of conducting polymer by electro-chemical process. This discovery of the synthesis of polyaniline (PA) and polyparaphenylene(PPP) [10] gave the way for the synthesis of number new conducting polymers such as poly phenylene sulphide (PPS) [11], Poly thiophene (PTh), Polyfuran (PFU), poly (ethynylsulphide) [12], poly (P-phenyl acetylenic phosphine (PPPAP) [13], Poly substituted Phenol polyanilines [14], substituted polyaniline [15-16] etc. However, dopant has sufficient oxidizing or reducing power to ionize the polymer. Therefore, positive charge carriers or negative charge carriers are created by doping on the polymers backbone, because dopants are either strong oxidizing or strong reducing agents. There are three methods for the preparation of organic conducting polymers, viz. (i) chemical syntheses of a polymer followed by doping with electron acceptor or electron donor dopant; (ii) chemical synthesis of a polymer and its subsequent doping with electrochemical method (iii) electrochemical polymerization and simultaneous doping with the desired dopant. The method depends upon the nature of the monomer required for polymerization.

Moreover, the extent of conductivity of a material is dependent upon the number of mobile carrier and their effectiveness. Tendency of an organic polymer to get oxidized or reduced is determined by its electronic properties such as the lowest ionization potential and highest electron affinity. Once the charge carriers are generated, the system becomes conducting. The effective mobility of these carriers is determined

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by the corresponding band width. From the above discussion it follows that the conducting properties of an organic polymer are related to its electronic properties such as band gap, ionization potential, electron affinity and band width.

The aim of this paper is to present evidence of the influence of the electrolytes in doping process and then, the consequences of this doping on the charge transport behavior of the PANI / (Cl^- , ClO_4^- and SO_4^{2-}) compound. In the present work, various mobile charge carriers and their effectiveness on the physicochemical properties of conducting PANI were studied.

2. Experimental

IR spectra of all the PA samples were recorded on an IR spectrophotometer (model IR-470, Shimadzu, Japan) in the region of $4000\text{-}400\text{ cm}^{-1}$. IR spectra of the solid PA samples were taken by mixing and grinding a small amount of the polymeric dry materials with KBr. The powder mixture was then compressed in a metal holder under a pressure of 8-10 tones to produce pellet. The pellet was then placed in the path of the infra red beam for measurements. Conducting polyaniline were synthesized from an electrolytic solution containing aniline in acid medium (H_2SO_4 , HCl , HClO_4) by anodic electrodeposition on platinum sheet. Bath temperatures were 5°C - 25°C and deposition current densities were $5\text{-}15\text{ mA/cm}^2$.

3. Results and Discission

3.1. Characterization of functional groups of PANI

The infra red spectra (IR) of samples were recorded in $400\text{-}4000\text{ cm}^{-1}$ range. The observed bands in the spectra for different functional groups are summarized in Table 1. The absorption band at $3300\text{-}3400\text{ cm}^{-1}$ may be due to the presence of NH bond in the aromatic ring. The observed absorption band in the range $1680\text{-}1720\text{ cm}^{-1}$ may be due to stretching of C=N-bond. Therefore, it may be assumed that PANI molecules prepared in this study consists of -N= sites which might be due to the higher degree of oxidation in the polymer film of the sample. The absorption band at $1520\text{-}1560\text{ cm}^{-1}$ and $2980\text{-}3010\text{ cm}^{-1}$ may represent C=C and C-H stretching of the aromatic amine respectively. The absorption bands in the region $800\text{-}900\text{ cm}^{-1}$ may provide evidence for the mono-substituted benzene ring. The band observed in the range $1120\text{ - }1200\text{ cm}^{-1}$ may be due to the presence of anion radical of acid molecules that may be absorbed to counterbalance the positive charge on the nitrogen atom of PANI during protonation. From the above stated, it can be assumed that the PANI sample in its protonated form may have the structure where Cl^- , ClO_4^- and SO_4^{2-} corresponds to negative radical of the acid molecules. The observed band in the spectra (Table 1) in the range $3600\text{-}3700\text{ cm}^{-1}$ may indicate the absorbed water molecules by PANI molecules during the measurements.

Table 1 IR Spectra of polyaniline

Characteristic Band	Wave number cm^{-1}
Anionic radicals of acid molecules (Cl^- , ClO_4^- and SO_4^{2-})	1120-1200
Secondary NH	3300-3400
C-H stretching (aromatic)	2980-3010
C-N stretching+C-C stretching	1288-1214
C-N ⁺ stretching+C-C stretching	1228-1221
C-N+stretching+C-C stretching	1401-1383
Aromatic C-H	1000-1400
CN stretching+CH bending	1315-1285
C=N	1680-1720
Aromatic Ring	1625-1615
C=C	1520-1560
CH (ip) bending	1185-1175
Mono-substituted benzene ring	800-900
Water molecule	3600-3700
1, 2, 4-substituted aromatic ring	480 cm^{-1}

Surville et al [17] have observed that PANI has a strong affinity for water and its absorption capacity can be increased up to 40% of polymer's weight. In the infrared spectra of polyaniline, a strong absorption band at around 480 cm^{-1} , gives an evidence of 1, 2, 4-substituted aromatic ring. This indicates the bonding in polymer is through 1, 4-position of benzene ring. The elemental analysis of polyaniline synthesized in this study also supports the empirical formula of polyaniline as: $(\text{C}_6\text{H}_4\text{NH})_4 2\text{A}^-$ ($\text{A}^- = \text{Cl}^-, \text{ClO}_4^-$ and SO_4^{2-}). Similar structure of PANI molecule has also been proposed by the Mac Diarmid the Noble prize winner in 2000. The mechanism of polymerization inferred that one anion ($\text{Cl}^-, \text{ClO}_4^-$ and SO_4^{2-}) is substituted for every two phenyl rings.

3.2. Resistivity of anion doped ($\text{Cl}^-, \text{ClO}_4^-$ and SO_4^{2-}) polyaniline

The resistance $R(T)$ at any temperature (in $^{\circ}\text{K}$) can be given by an empirical relation,

$$R(T) = R_0 + m(T - T_0)$$

$$= R_0 [1 + (m/R_0)(T - T_0)]$$

$$= R_0 [1 + a(T - T_0)]$$

Where, R_0 = resistance at any suitable reference temperature,

$a = m/R_0$ = mean-temperature coefficient of resistance,

For lower temperature region the reference temperature at $t=0\text{ }^{\circ}\text{C}$ ($T=273\text{ }^{\circ}\text{K}$) and for higher temperature region reference temperature at $50\text{ }^{\circ}\text{C}$ ($T=323\text{ }^{\circ}\text{K}$) were taken. From the slopes (m_1 and m_2) obtained from resistance vs. temperature ($^{\circ}\text{K}$) curve the mean-temperature coefficient 'a' of resistance in the two regions of temperature were evaluated. The linear increase of resistance at lower range of temperature ($30\text{ }^{\circ}\text{C}$ - $60\text{ }^{\circ}\text{C}$) was different from that at high temperature range ($100\text{ }^{\circ}\text{C}$ - $150\text{ }^{\circ}\text{C}$). For both regions mean-temperature coefficients of resistivity have been calculated. There was a linear correlation between resistances vs. temperature (R vs. $1/T$). But this linearity was not uniform monotonically. Two distinct slopes are observed, one in the temperature range $30\text{ }^{\circ}\text{C}$ - $60\text{ }^{\circ}\text{C}$ with slope $m_1 = 0.1640\text{ ohm}/^{\circ}\text{K}$ and other in the range $100\text{ }^{\circ}\text{C}$ - $150\text{ }^{\circ}\text{C}$ with slope $m_2 = 0.8042\text{ ohm}/^{\circ}\text{K}$. The resistivity of the samples was found to vary in the range of 157.18 - 100.971 ohm.cm , average value being 118.17 ohm.cm . This value may be compared with those of non metals like $\text{Al}(2.65)$, $\text{Cu}(1.68)$, $\text{Au}(2.21)$, $\text{Ag}(1.58)$, $\text{Bi}(106.8)$, $\text{C}(\text{graphite}:1375)$ etc. All these values are observed at or around $20\text{ }^{\circ}\text{C}$ and expressed in ohm.cm .

This study reveal that three types of polyanilines prepared by electrolytic method using three acid-aqueous media i.e. HCl , HClO_4 and H_2SO_4 behave as semiconductor with one exception sample of H_2SO_4 treated polyaniline. Resistivity of these polyanilines lies in the range of $(2.71 \sim 13.00) \times 10^4\text{ ohm.cm}$ (for HCl -aqueous medium), $(1.66 \sim 9.16) \times 10^3$ (for HClO_4 - aqueous medium), and 276.75 ohm.cm (for H_2SO_4 aqueous medium). These values were different from each other, highest being for HCl and lowest for H_2SO_4 treated polyaniline.

The particular sample (SO_4 -doped PANI) of polyaniline behaves like a metal rather than a semiconductor, as its resistance vs. temperature curve shown (Fig.1). There was a linear correlation between resistance vs. temperature (R vs. T). Variation of resistivity from sample to sample of the same polymer is probably lies in the method of preparation of pellets, uniform compact pellets are difficult to make, maintaining the same pressure of the hydraulic press. SO_4^{2-} -doped polyaniline showed in most cases semi-conducting behavior (e.g. sample-2), and in one case (sample-1) it behaves like a metal. Metallic behavior of this particular sample-1 of H_2SO_4 polyaniline puzzles us and the resistance of the sample-1 increases with the rise of temperature. The resistivity of the sample-1 is quite low lying in the range of 100.97 - 157.18 ohm.cm , indicating the overlap of conduction band and valency band. On the other hand other samples of H_2SO_4 polyaniline (sample-2) behave as semiconductor i.e. resistivity decreasing with rise of temperature.

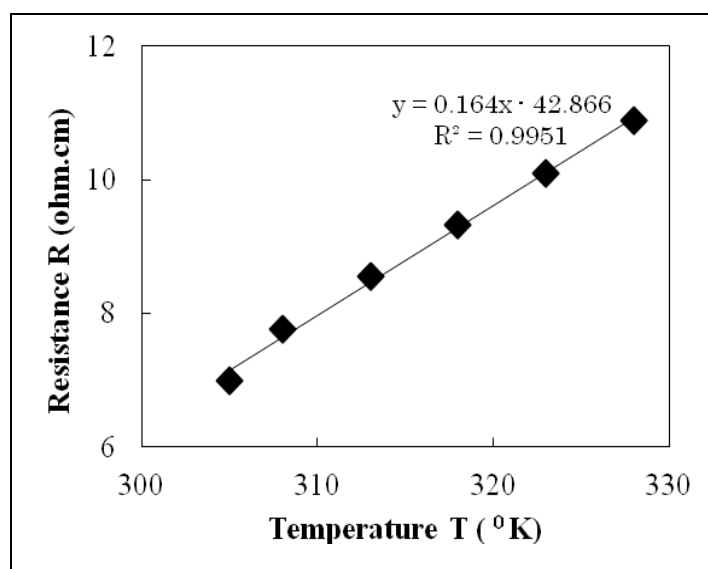


Fig.1. Resistance vs. temperature curve of H₂SO₄ (sample-1) treated polyaniline.

With average value being 276.75 Ω.cm. HCl-polyaniline gave resistivity in range of (2.17–13.00)×10⁴ ohm.cm and the behavior was as semiconductor (Table 2). These values may be compared with the intrinsic resistivity of (23×10⁴ ohm.cm). The H₂SO₄ treated polyaniline sample showed metallic behavior i.e. as the sample is heated to higher temperature its resistance is found to increase.

Table 2 Resistivity of anion doped (Cl⁻, ClO₄⁻ and SO₄²⁻) polyanilin

Polyaniline	Behavior	Range or average Resistivity (ohm.cm)
HCl treated	semi-conducting	(2.71-13.00)×10 ⁴
HClO ₄ treated	semi-conducting	(1.66-9.16) ×10 ³
H ₂ SO ₄ treated (sample –2)	semi-conducting	276.75
H ₂ SO ₄ treated (sample –1)	metallic	118.17

H₂SO₄ can be used as better dopant source than HCl and HClO₄ electrolyte. The resistivity of the SO₄⁻-doped polyaniline is quite low compare to other doped (Cl⁻ and ClO₄⁻) (Table 2), lying in the range of 100.97~157.18 ohm.cm, indicating the overlap of conduction band and valence band. The resistance for SO₄⁻-doped samples increases with the rise of temperature.

4. Conclusions

The mechanism of polymerization inferred that one anion (Cl⁻, ClO₄⁻ and SO₄²⁻) is substituted for every two phenyl rings. In the infrared spectra of polyaniline, a strong absorption band at around 480 cm⁻¹, gives an evidence of 1, 2, 4-substituted aromatic ring. Electrolyte H₂SO₄ can be used as better dopant source than HCl and HClO₄. The resistivity of the SO₄⁻-doped polyaniline is quite low (compare to Cl⁻ and ClO₄⁻ dopant), lying in the range of 100.97~157.18 ohm.cm, indicating the overlap of conduction band and valence band. The resistance for SO₄⁻-doped samples increases with the rise of temperature.

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6. References

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