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# 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, l0 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 4000-400$^{-1}$ 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 $5^0$C -$25^0$C and deposition current densities were 5-15 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 400-4000 cm$^{-1}$ range. The observed bands in the spectra for different functional groups are summarized in Table 1. The absorption band at 3300-3400 cm$^{-1}$ may be due to the presence of NH bond in the aromatic ring. The observed absorption band in the range 1680-1720 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 1520-1560 cm$^{-1}$ and 2980-3010 cm$^{-1}$ may represent C=C and C–H stretching of the aromatic amine respectively. The absorption bands in the region 800-900 cm$^{-1}$ may provide evidence for the mono-substituted benzene ring. The band observed in the range 1120 - 1200 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 3600-3700 cm$^{-1}$ may indicate the absorbed water molecules by PANI molecules during the measurements.

Table 1 IR Spectra of polyanilline

| **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 all [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: $(C_6H_4NH)_4$ $2A^-$ ($A^-$ = $Cl^-$, $ClO_4^-$ 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 ($Cl^-$, $ClO_4^-$ and $SO_4^{2-}$) is substituted for every two phenyl rings.

## 3.2. Resistivity of anion doped ($Cl^-$, $ClO_4^-$ and $SO_4^{2-}$) polyaniline

The resistance R (T) at any temperature (in $^0$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 $^0$C (T=273$^0$K) and for higher temperature region reference temperature at 50$^0$C (T=323$^0$K) were taken. From the slopes ($m_1$ and $m_2$) obtained from resistance vs. temperature ($^0$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$^0$-60 $^0$C) was different from that at high temperature range (100$^0$-150 $^0$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$^0$-60$^0$ C with slope $m_1$ = 0.1640 ohm/$^o$K and other in the range 100$^0$-150$^0$C with slope $m_2$= 0.8042 ohm/$^0$ K. The resistivity of the samples was found to vary in the range of 157.18-100.971 ohm.cm, average value being 118.17ohm.cm. This value may be compared with those of non metals like Al(2.65), Cu(1.68), Au(2.21), Ag(1.58), Bi(106.8), C(graphite:1375) etc. A11 these values are observed at or around 20 $^0$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 $(2.71 \sim 13.00)\times10^4$ ohm.cm (for HCl-aqueous medium), $(1.66 \sim 9.16)\times10^3$ (for $HClO_4$- aqueous medium), and 276.75 ohm.cm (for $H_2SO4$ aqueous medium). These values were different from each other, highest being for HCI 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-l) 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.

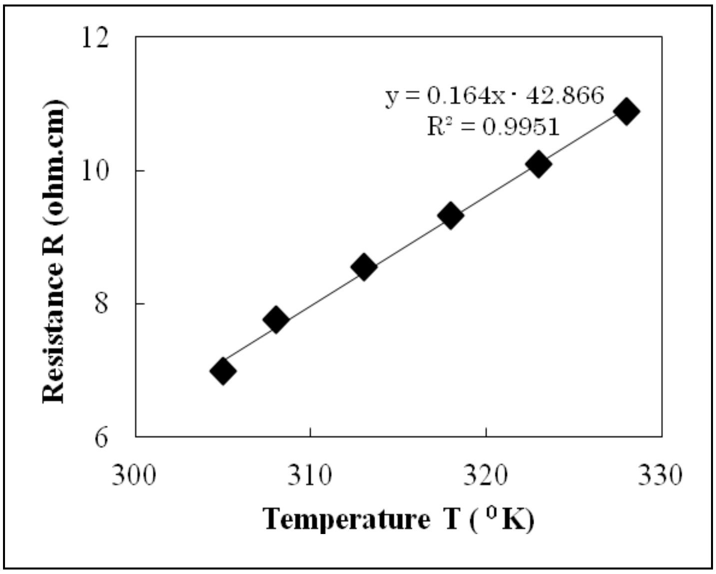


Fig.1. Resistance vs. temperature curve of H2SO4 (sample-1) treated polyaniline.

With average value being 276.75 Ω.cm. HCI-polyaniline gave resistivity in range of $(2.17-13.00)\times10^4$ ohm.cm and the behavior was as semiconductor (Table 2). These values may be compared with the intrinsic resistivity of ($23\times10^4$ ohm.cm). The $H_2SO_4$ 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 | $(2.71\text{-}13.00)\times10^4$ |
| $HClO_4$ treated | semi-conducting | $(1.66\text{-}9.16)\times10^3$ |
| $H_2SO_4$ treated (sample −2) | semi-conducting | 276.75 |
| $H_2SO_4$ treated (sample −1) | metallic | 118.17 |

$H_2SO_4$ can be used as better dopant source than HCI and $HCIO_4$ electrolyte. The resistivity of the $SO_4^{-}-$ doped polyaniline is quite low compare to other doped ($Cl^-$ and $ClO_4^-$) (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 $SO_4^{-}-$ doped samples increases with the rise of temperature.

## 4. Conclusions

The mechanism of polymerization inferred that one anion ($Cl^-$, $ClO_4^-$ and $SO_4^{2-}$) 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 $H_2SO_4$ can be used as better dopant source than HCI and $HCIO_4$. The resistivity of the $SO_4^{-}-$ doped polyaniline is quite low (compare to $Cl^-$ and $ClO_4^-$ dopant), lying in the range of 100.97~157.18 ohm.cm, indicating the overlap of conduction band and valence band. The resistance for $SO_4^{-}-$ doped samples increases with the rise of temperature.


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