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# Spectroscopic and Electrical properties of Polyaniline/$Y_2O_3$ composites and their application as Humidity sensor

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***Abstract—Conducting Polyaniline/Yattrium oxide (PANI/$Y_2O_3$) composites have been synthesized by insitu deposition technique by placing fine graded $Y_2O_3$ in polymerization mixture of aniline. The results were also well supported by X-ray diffractometry (XRD), Infrared (IR) spectral analysis, scanning electron microscope (SEM) and conductivity measurements. It is observed from the XRD studies that $Y_2O_3$ has retained its structure even though it is dispersed in PANI during polymerization reaction. By observation of IR spectra, it is seen that some of the characteristic stretching frequencies are considerably shifted towards higher frequency side. The surface morphology of these composites was studied by SEM and it was found that, composites possess grains and porous structure. High conductivity measurements show thermal activated behavior. The change in resistance with respect to percentage relative humidity (% RH) is observed. The composites in the pellet form exhibit almost linear behavior within a chosen range of humidity (ranging between 10 and 95% RH)..***

***Index Terms— Polyaniline composites;$Y_2O_3$; conductivity; Humidity sensors***

## I. INTRODUCTION

For the past two decades, conducting polymers have enjoyed significant research interest, both pure and applied [1-5]. The latter has its stimulation from the application potential of conducting polymers in solid state devices such as solar cells, Schottky junctions, displays, sensors, and microelectronics. However, many conducting polymers have poor mechanical properties and environmental stability which make them unsuitable for device fabrication. To overcome this difficulty, efforts have been made to synthesize various composites in which conducting polymers are embedded in an insulating polymer matrix having good mechanical properties [6-9].The study of electrical transport in conducting polymers has been an interesting area of research. During the injection of charge carriers with various dopants like $ClO_4$, $BF_4$, etc. the polymer chain gets easily distorted around the injected charge and polaron is formed. At low doping levels polarons are the only charge carriers and as doping level increases, two polarons come close to each other resulting in the formation of bipolarons [10].

For using a composites material incorporating conducting polymers in device fabrication, it is necessary to know the nature of charge carriers, conduction mechanism, and the effect of other phases present in the system. Frequency dependent measurement is a useful tool to understand the nature of charge carriers (polarons and bipolarons) and the conduction mechanism [11]. Epstein and co-workers [12] have carried out such measurements on poly acetylene. They have suggested that charge transport occurs by charged solitons. In particular, at low doping level, an intersoliton electron hopping mechanism has been proposed by Kivelson [13].

Among all conducting polymers polyaniline (PANI) achieved widespread importance because of its unique conduction mechanism and environment stability. The survey of literature reveals that the detailed conductivity studies on PANI/ $Y_2O_3$ are scarce. In the present study, PANI and polyaniline yttrium oxide (PANI/ $Y_2O_3$) composite (with varying weight percentage of yttrium oxide in polyaniline) have been synthesized. These samples are characterized by the various techniques such as XRD, FTIR, SEM and electrical properties are measured and studied.

## 2. Experimental

### 2.1 Synthesis of PANI/ $Y_2O_3$ composites

Aniline (AR grade) was purified by distillation before use and ammonium per sulphate $[(NH_4)_2S_2O_8)]$, HCl were used as received. 0.1 mol aniline monomer is dissolved in 1 mole hydrochloric acid to form polyaniline. Fine graded pre-sintered yttrium oxide (AR grade, SD-Fine

Chem.) powder in the weight percentages (wt %) of 10, 20, 30, 40 and 50 is added to the polymerization mixture with vigorous stirring in order to keep the yttrium oxide powder suspended in the solution. To this reaction mixture, $[(NH_4)_2S_2O_8)]$ which is used as oxidant is added slowly drop-wise with continuous vigorous stirring for the period of 4-6 hours at temperature 0-5$^0$ C. Polymerization of aniline takes place over fine grade yttrium oxide particles. The resulting precipitate is filtered under suction and washed with distilled water until the filtrate becomes colorless. Acetone is used to dissolve any unreacted aniline. After washing, the precipitate is dried under dynamic vacuum at 60-80$^0$C for 24 hrs to get resulting composites. In this way five different polyaniline yttrium oxide composites with different weight percentage of yttrium oxide (10, 20, 30, 40 and 50) in polyaniline have been synthesized. All the composites are crushed into fine powder in an agate mortar in the presence of acetone medium. The composite powder is pressed to form pellets of 10mm diameter and thickness which varies from 2 to 2.75 mm. The electrical measurements on these samples were made using the silver paint as electrodes on both sides.

**2.2 Measurements.**

X-ray diffraction patterns of PANI/ $Y_2O_3$ were obtained with Philips X-ray diffractrometer using CuKα (λ = 1.5404Å). The Fourier transform infrared (FTIR) spectra of the composites were recorded on Perkin Elmer (model 783) IR spectrometer in KBr medium at room temperature, in the region 4000 – 450 Cm-$^1$. The powder morphology of PANI and PANI/ $Y_2O_3$ samples in the form of pellets was investigated using Philips XL 30 ESEM scanning electron microscope (SEM). The dc conductivity of the PANI/ $Y_2O_3$ composites were measured by two probe technique at temperature range 40 to 150$^o$C. The planar resistance of the sensors was recorded by controlling the humidity in a closed chamber at room temperature.

**3. Results and discussion.**

**3.1 X-ray diffraction (XRD)**

Figure 1 shows XRD patterns for PANI/ $Y_2O_3$ composite with 50 wt% of $Y_2O_3$ in PANI. It is seen from figure 1, that the cubic peak of $Y_2O_3$ indicates the crystalline nature of the composite. By comparing the XRD pattern of the composite with that of $Y_2O_3$, the prominent peaks corresponding to 2θ = 29.79 ,34.52, 49.19 and 58.25 are due to (2 2 2), (4 1 1), (4 4 0) and (6 2 2) planes of Y2O3 [JCPDS file no. 41-1105]. By comparing the XRD pattern of the composite and $Y_2O_3$, it is confirmed that $Y_2O_3$ has retained its structure even though it is dispersed in PANI during polymerization reaction.

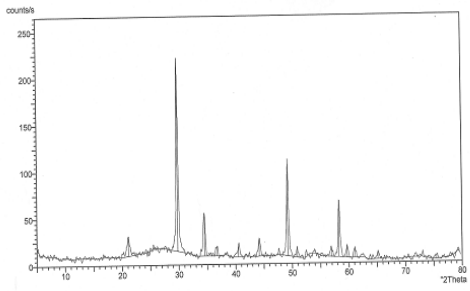


**Figure 1. XRD patterns for PANI/ $Y_2O_3$ composite with 50 wt% of $Y_2O_3$ in PANI.**

**3.2 FTIR Spectra**

Figure 2 shows the FTIR spectra of PANI/ $Y_2O_3$ composite (50% wt of $Y_2O_3$ in PANI). The FTIR transmission spectra of powder using KBr pellets having different weight percentage of $Y_2O_3$ in PANI were recorded in the range 450 – 4000 Cm$^{-1}$ to confirm polymerization of polyaniline. The spectra for all the samples showed strong bands in the region 470 – 1800 Cm$^{-1}$ that are the characteristics of PANI [14]. Similar

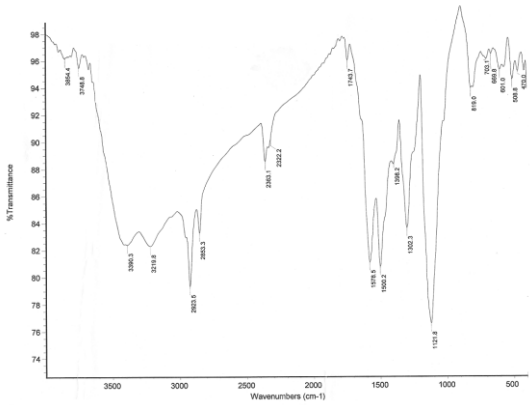


**Figure 2. FTIR spectra of PANI/$Y_2O_3$ composite (50% wt of $Y_2O_3$ in PANI).**

stretching frequencies can also be found in other composites but intensity of metal oxygen peak increases as the weight present of $Y_2O_3$ is increased. The important peaks that are observed in this composite in FTIR spectra are observed at 1743 Cm$^{-1}$, 1578 Cm$^{-1}$, 1500 Cm$^{-1}$, 1398 Cm$^{-1}$, 1302 Cm$^{-1}$, 1121 Cm$^{-1}$, 819 Cm$^{-1}$, 703 Cm$^{-1}$ 668 Cm$^{-1}$, 601 Cm$^{-1}$, 508 Cm$^{-1}$ and 470 Cm$^{-1}$. By observation of IR spectra, some of the characteristic stretching frequencies are considerably shifted towards higher frequency side. The typical peaks observed are at 1578 Cm$^{-1}$,1302 Cm$^{-1}$,1121 Cm$^{-1}$,819 Cm$^{-1}$ and 508Cm$^{-1}$ which may be attributed due to the Vander walls kind of interaction between $Y_2O_3$ and PANI chain [15].

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**3.3 Scanning electron Micrograph (SEM).**

SEM of PANI/ $Y_2O_3$ composites with 50 wt% of Y2O3 in PANI is shown in figure 3. High magnification SEM image reveals the presence of $Y_2O_3$ particles uniformly distributed throughout the composite sample. The composite possess grain and porous structure, and, further the composites have capillary pores connected by pores. The SEM studies performed on all the samples indicated a transformation from a cluster pattern to branched chain structure (or a fibrillar morphology) with increase in wt% of yttrium oxide [16]. The contrast in this image is due to the difference in scattering from different surface areas as a result of geometrical difference between PANI and $Y_2O_3$.

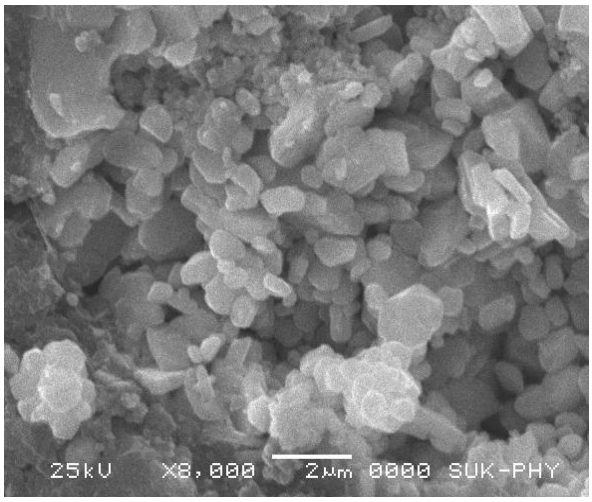


**Figure 3. SEM of PANI/ $Y_2O_3$ composites with 50 wt% of $Y_2O_3$ in PANI**

**3.4 Temperature dependent conductivity.**

Figure 4 shows the temperature dependent conductivity of PANI/ (50 wt% of $Y_2O_3$ in PANI) composites. From the figure, it is observed that the conductivity is found to be increase with temperature. Among the five composites, PANI/ $Y_2O_3$ (50 wt% of $Y_2O_3$ in PANI) was seen to yield with highest conductivities. The increase in conductivity with increase in temperature is the characteristic of 'thermal activated behavior'. The increase in conductivity would be due to the increase of efficiency of charge transfer between Y2O3 and polymer chains with increase in temperature [15, 16]. It is also be suggested that the thermal curing effects the chain alignment of the polymer, which leads to the increase of conjugation length and that brings about the increase of conductivity. Also, there had to be molecular rearrangement on heating, which made the molecular conformation favorable for electron delocalization [17].

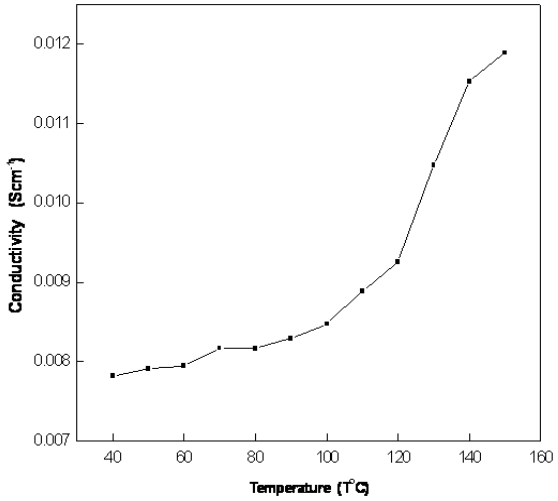


**Figure 4. Temperature dependent conductivity of PANI/ (50 wt% of $Y_2O_3$ in PANI) composites.**

**3.5 Humidity Sensing Propertity.**

Figure 5 shows the characteristic response of the PANI/ $Y_2O_3$ composites (10, 30 and 50 wt% of $Y_2O_3$ in PANI) as a function of relative humidity (% RH). From the figure, it can be noted that the resistance is varying almost linearly from 20 to 90% RH and is found to decrease from low humidity (dry state) to high humidity (wet state). At low humidity, when adsorption starts on the clean oxide surface, a layer of hydroxyl group is formed. The water vapor molecules are chemisorbed through a dissociative mechanism by which two surface hydroxyls per water molecule are formed. At higher relative humidity, the water molecule adsorbed on the PANI/$Y_2O_3$ composite (50 wt% of $Y_2O_3$ in PANI) having grains and capillary pores enhance the electrolytic conduction as well as the protonic conduction by permitting capillary condensation of water molecules within the pores. The response time for sensing the humidity for an increase in relative humidity values by 10% was measured to be about 4-5s, wherein it recovers back to the normal value in around 10 s. The samples were found to be stable for more than 1 year.

The decrease in resistance or increase in the conductivity with increasing humidity can be attributed to mobility of the $Y_2O_3$ ion, which is loosely attracted to the polymer chain by weak Vander-walls force of attraction. At low humidity, the mobility of the $Y_2O_3$ ion is restricted because under dry conditions the polymer chains would tend to curl up into compact coil form. On the contrary, at high humidity, the polymer absorbs water molecules and gets hydrated, followed by the uncurling of the compact coil form into straight chains that are aligned with respect to each other. This geometry of the polymer is favorable

for enhanced mobility of the $Y_2O_3$ ions or the charge transfer across the polymer chains and hence the conductivity.

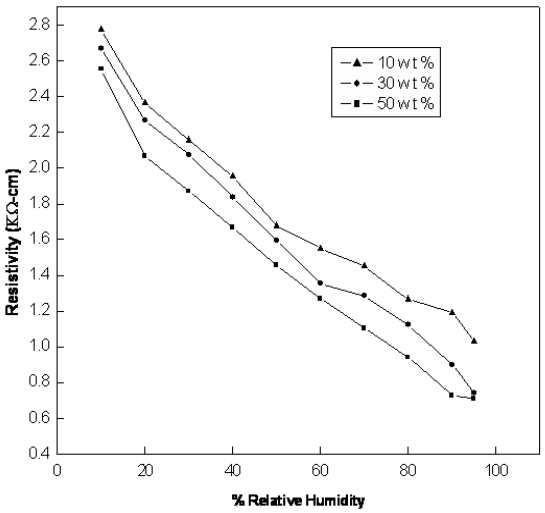


**Figure 5. Characteristic response of the PANI/ $Y_2O_3$ composites (10, 30 and 50 wt% of $Y_2O_3$ in PANI) as a function of relative humidity (% RH).**

Also, it has been reported that the conductivity of a conducting polymer increases when the sample absorbs the moisture. Decrease of resistance with the increase in the humidity proves the adsorption of the water molecules, which makes the polymer more p-type in nature, that is, the whole concentration is increased by the donation of lone pair from the conducting complex towards the $Y_2O_3$ water molecules. Thus, the partial charge transfer process of conducting species with that of water molecules results in the decrease of sheet resistivity. At higher humidity level, the mechanism may be different. The almost linear variation with respect to percentage relative humidity (%RH) can be used in an amplifier circuit for converting the measured values into measurable % RH values. On careful observation of figure 5, it is clearly seen that the PANI/ $Y_2O_3$ (50 wt% of $Y_2O_3$ in PANI) composite shows a linear response from 20 to 90% RH. On the other hand, in PANI/ $Y_2O_3$ composites (10 and 30 wt% of $Y_2O_3$ in PANI), the resistance is found to drop down from 20 up to 50% RH in a linear fashion while, after 60% RH slightly saturation is observed with a very small decrease in the resistance up to 95% RH. In other words, we can say that PANI/ $Y_2O_3$ (10 and 30 wt% of $Y_2O_3$ in PANI) shows two step sensing response. Thus PANI/ $Y_2O_3$ (50 wt% of $Y_2O_3$ in PANI) shows better sensing properties and exhibits good linearity in sensing response curve [18]

## 4. Conclusion

In this paper, we have presented a humidity sensor based on polyaniline/Yattrium oxide (PANI/$Y_2O_3$) composites synthesized by 'insitu' polymerization. This is the novel polymerization process for the direct synthesis of emeraldine phase of the polymer. Formation of mixed phases of polymer together with conducting emeraldine salt phase is confirmed for the spectroscopic techniques. High temperature conductivity measurements show thermal activated behavior. The almost linear response of PANI/$Y_2O_3$ (50wt% of $Y_2O_3$ in PANI) to the broad range of humidity proves to a competent material as humidity sensor.

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