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Electrical and Sensor Behavior of Polyaniline / Neodymium Composites

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Abstract: ***Polyaniline (PANI)/Neodymium oxide (Nd_2O_3) composite has been synthesized by using insitu polymerization method for different concentrations of Nd_2O_3 powder. DC conductivity studies of PANI- Nd_2O_3 composites for different weight percentage (wt%) show thermally activated behaviour. The conductivity was found to increase with the increase in temperature indicating the semiconducting behaviour of all the compositions. Maximum conductivity was observed in 30 wt% of Nd_2O_3 in polyaniline. The ac conductivity has been studied in the frequency range of 50 Hz to 1 MHz and it is found that 40 wt% shows high conductivity compared to pure polyaniline and other complexes. On exposure of the composites to liquefied petroleum gas (LPG), increase in resistance was observed with the increase in gas concentration. Maximum sensitivity for gas sensing was observed in the composite of 50 wt% Nd_2O_3 in polyaniline.***

Keywords: Polyaniline,Neodymium,DC conductivity, AC conductivity,Sensor..

1. Introduction

Conducting polymers such has polyaniline and polypyrrole have received greater attraction due to their favorable economics, easy synthesis, envi ronmental stability and unique chemistry. The electrical conductivities of the intrinsically and conducting polymer systems range from those insulators ($<10^{-5}$ and 10^{-10} S/cm) to those of typical semiconductors such as silicon ($\approx10^{-5}$ S/cm) and to those of metals such as copper ($\approx5\times10^{5}$ S/cm). Applications of these polymers have begun to emerge a new era. In the recent past, the conducting polymer-based composite have drawn attention in their application as gas sensing . Therefore, Pani/Nd_2O_3 composites have been most intensively studied among various composites, because it could combine the merits of Pani and crystalline Nd_2O_3 within a single material and are expected to find applications in electro chromic devices, photo electrochemical devices, nonlinear optical system, and sensors. Polyaniline composites with inorganic particles were also performed, such as with montomorrillonite and y-zeolite[1-6] .

In the present work, attempts have been made to synthesize the Nd_2O_3 particles and PANI- Nd_2O_3 composite and study the electrical properties such as DC and AC conductivity measurements are done by using two probe set-up and the sensor studies of the sample using the laboratory set-up, has been discussed.

2. Materials and Methods

All the chemicals used for synthesis were of Analytical Reagent (AR) grade. The monomer aniline was doubly distilled prior to use. Ammonium persulfate [$(NH4)_2S_2O_8$], hydrochloric acid (HCl) and Neodymium oxide (Nd_2O_3) powder were procured and were used as received.

a) Synthesis of Polyaniline

The monomer aniline was distilled twice before use. Analytical reagent-grade ammonium persulfate [$(NH_4)_2S_2O_8$], hydrochloric acid (HCl) and Neodymium oxide Nd_2O_3were used for synthesis. The polyaniline – Neodymium oxide composites were synthesized by insitu polymerization. Aniline solution was formed by dissolving aniline (0.1 mol) in 1M HCl. Neodymium oxide was added to the aniline solution with vigorous stirring to keep Neodymium oxide suspended in the solution. 0.25M ammonium persulfate, which acts as the oxidant, was added to this reaction mixture slowly with continuous stirring at 0–5 ^{0}C. The reaction mixture was kept stirring for 24 hours. The polymer in the form of greenish precipitate was recovered by vacuum filtration and washed with deionized water. To achieve a constant weight, the precipitate was dried for 24 hours in an oven. In this way polyaniline – Neodymium oxide composites with 5 different wt % (10, 20, 30, 40 and 50) of Nd_2O_3 in polyaniline were synthesized [7].

3. Conductivity and Sensor Measurements

For temperature dependent DC conductivity studies and sensing studies, the test samples were prepared in the pellet form (10 mm diameter and thickness varying up to 2 mm) by applying pressure of 10 tons in a Universal testing machine. The pellets were coated with silver paste on either side. Temperature dependent electrical conductivity was measured from 30^{0}C to 180^{0}C using Keithley 6514 electrometer.AC conductivity. Dielectric tangent loss and dielectric constant are studied by sandwiching the pellets of these composites keep in between the silver electrodes and is studied in the frequencies 50Hz –10^{6}Hz, using LCR meter Newton Model PSM-1735.For gas sensing, the pellets were kept in the gas sensing chamber. With the help of a regulator and a flow meter, LPG is allowed to enter the chamber at a constant rate of 20 cc/min. The variation in resistance of the composite pellets with increase in gas concentration is recorded at a regular interval of 30 seconds using a high accuracy dot-tech meter.

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4. Results and Discussion

4.1 DC Conductivity

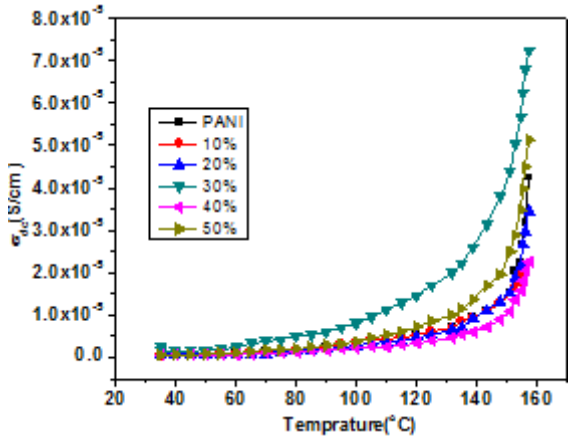

Figure 1: Variation of σ_{dc} as a function of temperature of PANI / Nd_2O_3composites

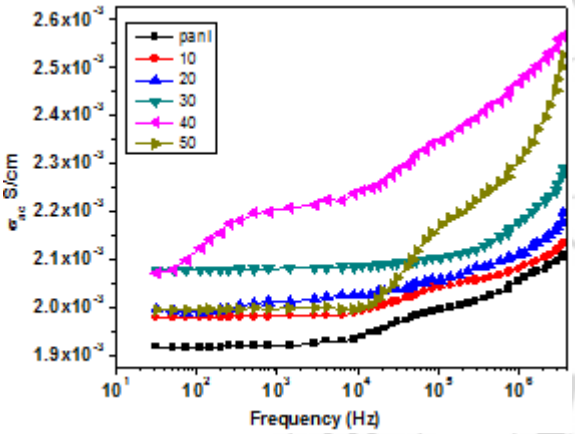

Figure 2: shows the variation of ac conductivity as a function of frequency for Polyaniline – Nd_2O_3 composites (different wt %).

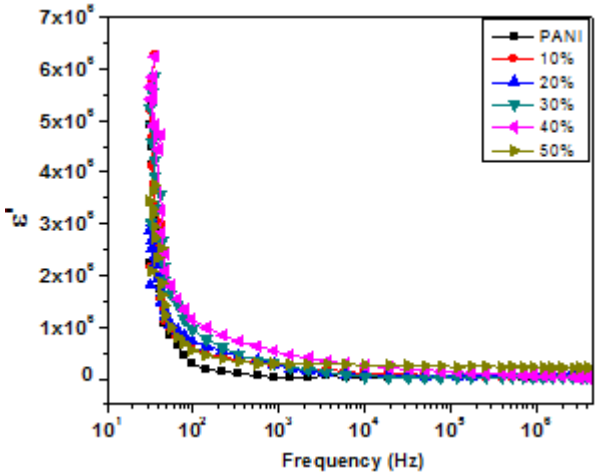

Figure 3: shows the real part permittivity as a function of frequency of PANI- Nd_2O_3 composites at different weight percentages.

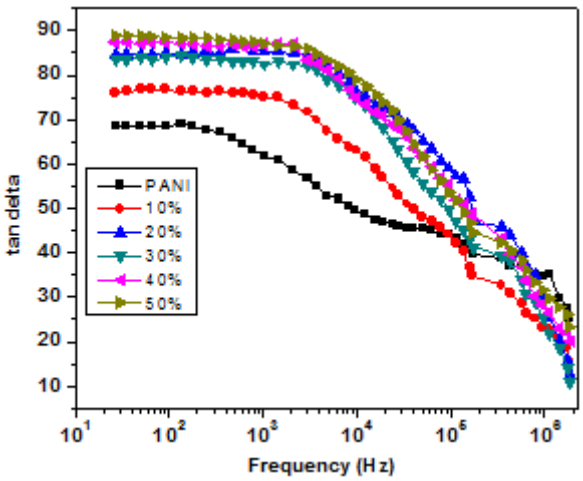

Figure 4: shows the variation of tanδ as a function of frequency of PANI-Nd_2O_3 composites at different weight percentages.

Figure 1 shows the ζ_{dc} conductivity as a function of temperature for PANI/Nd_2O_3 composites at various weight percentages. It is observed that the conductivity of the composites increases with increase in temperature ranging from 30^0C to 160^0C. Among all the PANI/Nd_2O_3 composites, 30 wt% shows highest conductivity. This clearly indicates that the conductivity is not only the motion of ions (Nd_2O_3) but also hopping of charge carriers like polarons and bipolarons from one island to another. It is also suggested here that the thermal curling effects of the chain alignment of the polyaniline leads to the increase in conjugation length and that brings about the increase of conductivity. Also, there will be molecular rearrangement on heating which makes the molecules favorable for electron delocalization. The conductivity varies directly with the temperature obeying an expression of the following form.

$$\zeta(T) = \zeta_0 \exp[-(T_0/T)^{1/4}] \quad \ldots\ldots\ldots\ldots (1)$$

where ζ is the conductivity, T is the temperature, and ζ_0 is the conductivity at characteristic temperature T_0. Conductivity varying with various values of the exponent (e.g., $T^{-1/4}$, $T^{-1/3}$ and $T^{-1/2}$) has been reported and different models have been used to interpret this data[8].

Figure 2 shows the variation of ac conductivity as a function of frequency for PANI – Nd_2O_3 composites (different wt %). It is observed that in all the cases, ζ_{ac} remains constant up to 10^4 Hz. Among all the composites, 40 wt% of PANI/Nd_2O_3composites shows high conductivity due to interfacial polarization. However, in case of polyaniline and other composites 10, 20, 30 and 50 wt%, the conductivity value is low because of dipole polarization. This behavior of these composites may be due to the variation in the distribution of Nd_2O_3 particles in polyaniline.

Figure 3 shows the variation of ε' as a function of frequency for PANI – Nd_2O_3 composites (different wt %). In all the cases it is observed that, the dielectric constant is quite high at low frequency and decreases with increase in applied frequency. The observed behavior may be due to Debye like relaxation mechanism taking place in these materials. Among all, the 40 wt% of PANI - Nd_2O_3 composites shows high

permittivity due to relaxation mechanism and may be also as it exceeds critical contraction[9] .

Figure 4 shows the variation of dielectric loss as a function of frequency for PANI – Nd_2O_3composites (different wt %) is represented in figure 4. Even though $Nd_2O_3$is added up to 40 wt% in polyaniline, the behavior of dielectric loss with respect to frequency follows the same trend as that of pure polyaniline. At higher frequencies, these composites exhibit almost very low dielectric loss which suggests that these composites are lossless materials at frequencies beyond 1 MHz[10].

B) Sensor Behavior

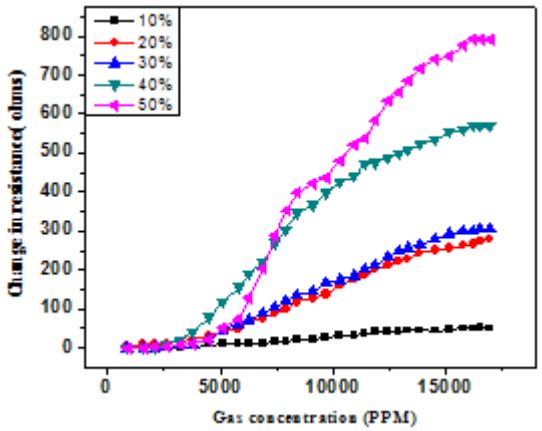

Figure 5: Variation of resistance in PANI/ Nd_2O_3 composites with gas concentration

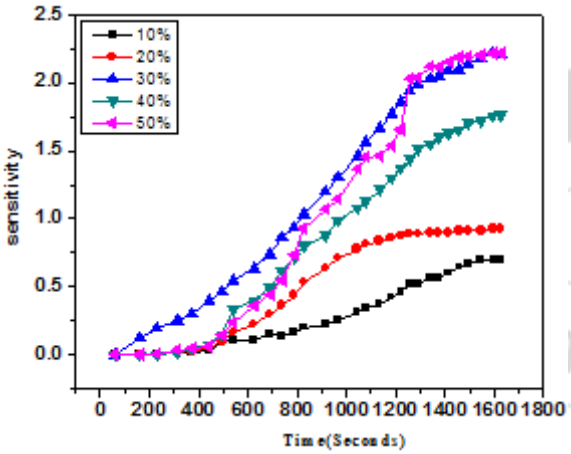

Figure 6: Sensitivity of PANI/Nd_2O_3 composites for LPG,

The change in resistance with gas concentration for PANI/ Nd_2O_3 composites are shown in Figure 5. With increase in gas concentration the resistance of all the samples was found to increase. Maximum change in resistance was observed in composites of 50 wt% of Nd_2O_3in PANI. The sensitivity for LPG with time for PANI/ Nd_2O_3composites are shown in Figure 6. Maximum sensitivity is observed in the composite with 50 wt% of Nd_2O_3 in polyaniline[11-13].

The gas sensing mechanism in Polyaniline – Nd_2O_3 composites is expected mainly because of two reasons. First, the trapping of LPG molecules in between the PANI – Nd_2O_3 composites islands by electrostatic forces and second is a surface controlled phenomenon i.e., it is based on the change in surface resistance of the composites at which the LPG adsorb and reacts with pre-adsorbed oxygen molecules . The Polyaniline – Nd_2O_3 composites is more surface area due to the distribution Nd_2O_3 particles in the leaf structure[14] . Therefore, the oxygen chemisorptions centres viz., oxygen vacancies, localized donor and acceptor states and other defects are formed on the surface during synthesis. These centres are filled by adsorbing oxygen from atmospheric air. When the composites is placed inside the gas sensing setup, after some time equilibrium is established between oxygen adsorbed at the surface of sensing element and atmospheric oxygen through the chemisorptions at room temperature. The stabilized resistance at this state is known as resistance in the presence of air (Ra). The electron transfer from the conduction band to the chemisorbed oxygen results in the decrease of electron concentration at the film surface. As a consequence, a decrease in the resistance of the film is observed. In LPG, the reducing hydrogen species are bound to carbon, therefore, LPG dissociates less easily into the reactive reducing components on the film surface. When the film is exposed to reducing gas like LPG, it reacts with the chemisorbed oxygen and is adsorbed on the surface of the film then the exchange of electrons take place between the LPG and oxide surface upon adsorption i.e., a surface charge layer will be formed. When the LPG reacts with the surface oxygen ions of the composites, a potential barrier would be developed i.e., this mechanism involves the displacement of adsorbed oxygen species by formation of water. The overall reaction of LPG with the chemisorbed oxygen may take place as shown in figure [6]. CnH_{2n+n} represent the various hydrocarbons. The free electrons released through reaction between the LPG molecules and the pre-adsorbed O2− neutralize the holes, which are the majority carrier in n-type Nd_2O_3particles. This compensation results in a decrease in the concentration of hole carriers in composites, and consequently, an increase in sensor resistance was observed. Here the oxygen molecules are continuously supplied from the dilution gas (dry air) and are adsorbed on the polyaniline – Nd_2O_3composites surface while the interaction with LPG continuously forms water molecules to escape from the surface. When the flow of LPG is stopped for recovery, the oxygen molecules in air will adsorb on the surface of polyaniline – Nd_2O_3 composites and the capture of electrons through the processes indicated in equations will reduce the sensor resistance towards the initial stable surface state of composites. In the first cycle of exposure, LPG molecules interact with the pre-adsorbed oxygen on the surface of PANI Nd_2O_3composites and the sensor resistance increases[15-16]. Since the sensing mechanism of these devices is based on the chemisorptions reaction that take place at the surface of the polymer and metal oxide, so increasing specific surface area of the sensitive materials leads to more sites for adsorption of surrounding gases.

5. Conclusion

The inorganic Nd_2O_3 doped polyaniline composites has been prepared at different weight percentages (10, 20,30, 40, and 50 wt %) were synthesized by insitu polymerization method. DC conductivity shows thermally activated behavior of PANI/ Nd_2O_3 composites. Maximum conductivity $7.1x10^{-6}$

was observed in samples with 30 wt% of Nd_2O_3 in polyaniline. The ac conductivity has been studied in the frequency range of 50 Hz to 1 MHz and 40 wt% shows high conductivity of $2.6x10^{-3}$ S/cm as well as low dielectric constant compared to pure polyaniline and other composites. Variation of impedance as a function of frequency suggests nearly Debye type relaxation. On exposure to LPG, change in resistance was observed in all the composites with increase in gas concentration. Maximum sensitivity for gas sensing was observed in the composite with 50 wt% Nd_2O_3 in polyaniline.

6. Acknowledgment

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