IMPEDEANCE SPECTROSCOPIC STUDIES ON PANI/CEO₂ COMPOSITES

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ABSTRACT

Polyaniline-Cerium oxide composites were prepared by in situ polymerization method with different weight percentage of cerium oxide in Polyaniline. The composites were characterized by infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The frequency dependent conductivity and dielectric behavior of these composites have been studied in the frequency range of 50 Hz to 5 MHz. The variation of $\sigma_{ac}$ was small in all composites in the frequency range of 50 Hz to 10 KHz. Large variations in conductivity were observed in the frequency range of 10 KHz to 5 MHz. This multiphase variation may be due to lattice polarization around a charge in localized state and due to variation of distribution of CeO₂ in polymer matrix. Dielectric constant and dielectric loss and real part of impedance were found to decrease with increase in frequency. The position of peak of Z shifts towards higher frequency side with decrease in weight percent of cerium oxide in polyaniline.

Key words: polyaniline, Cerium oxide, impedance spectroscopy, a.c.conductivity
1. INTRODUCTION

Conducting polymers are being used commonly in scientific and industrial studies and in various applications such as sensors, rechargeable batteries, diodes, transistors and microelectronic devices [1-7]. These materials provide huge scope for tuning their electrical conductivity [8-9]. Among conjugated polymers polyaniline deserves special attention because of its good environmental stability, easy processability, moderate electrical conductivity, and rich physics in charge transport mechanism [10].

The electrical and dielectric properties of these materials are altered when they are taken in the composite form. The composite materials consist of conducting filler material in the polymer matrix and provide satisfactory mechanical and electrical properties. Conducting polymer inorganic composites have been in the extensive research for the past few years [11-14]. Synthesis of many polyaniline—inorganic particle composites have been reported [15-21] and applications of such composites as electro—rheological fluids [22] and in high density information storage devices [23] have been studied.

The conductivity of these composites depends on number of factors such as the concentration of conducting fillers, their shape, size, orientation and interfacial interaction between filler molecules and host matrix [24-25]. Conduction by polarons and bipolarons is the dominant mechanism of charge transport in polymers. New models are developed to explain the mechanism of charge transport in these materials [26-27]. Kivelson was the first to use the inter-soliton hopping model [28]. Other models like electron hopping and dipolar relaxation have been used to explain the dielectric data of PANI salts. But it seems that no definite theory exists to explain the origin of electric conduction or the reported near metal insulator transition occurring in conducting PANI [29]. In the present paper, the authors report the preparation of Polyaniline / Cerium oxide composites, its characterization through FTIR spectra, scanning electron microscope (SEM), transport properties such as ac conductivity, dielectric behavior, dielectric loss and variation of impedance with frequency.

2. EXPERIMENTAL

All chemicals used are analytical grade (AR) and were used as received. The monomer aniline was doubly distilled prior to use. Synthesis of polyaniline/CeO₂ composites has been carried out by single step in situ polymerization technique. Aniline of 0.1mol was dissolved in 1M of hydrochloric acid to form aniline hydrochloride. Finely grinded powder of Cerium oxide (CeO₂) is added in the weight percent of 10, 20, 30, 40 and 50 to the above solution with vigorous stirring to keep Cerium oxide suspended in the solution. To this reaction mixture, 0.1M of oxidizing agent ammonium persulphate [(NH₄)₂S₂O₈] in 1M of hydrochloric acid was added slowly with continuous stirring for 4–8 hours at 0–5°C to polymerize. The precipitated powder was recovered, vacuum filtered and washed with deionized water. Finally, the resultant precipitate was dried in an oven for 24 hours to achieve constant weight. In this way, five different composites of polyaniline/CeO₂ with different weight of (10, 20, 30, 40 & 50) in PANI have been synthesized. The pellets of 10 mm diameter are formed with thickness varying up to 2 mm by applying pressure of 10 ton in a UTM-40 machine (40 Ton Universal testing machine). For conductivity measurement, the pellets are coated with silver paste on either side of the surfaces.
The characterization studies are employed on all the above synthesized polyaniline/CeO$_2$ composites to confirm the presence of CeO$_2$ in PANI. Fourier transform infrared (FTIR) spectra was recorded on a JASCO FT/IR 5300 spectrophotometer in KBr medium and the powder morphology of pellets was investigated with scanning electron micrographs on Phillips XL 30 ESEM.

The frequency dependent AC conductivity studies on polyaniline / CeO$_2$ composites are made using Hioki impedance analyzer (model 3532-50 programmable LCR meter) in the frequency range 50 Hz to 5 MHz at room temperature.

3. RESULTS AND DISCUSSIONS

3.1. FTIR

Figure 1(a) shows the IR spectra of Polyaniline where the transmittance is plotted as a function of wave number (cm$^{-1}$). Careful analysis of the spectra reveals the presence of intensity peaks 1302 cm$^{-1}$ for C-N stretching + C-H bending, 1240 cm$^{-1}$ C-N stretching + C-C stretching, 812 cm$^{-1}$ Deformational C-H (out of plane) of 1-4 disubstituted aromatic ring (Benzoid). The spectra shows the presence intense bands at 1568 cm$^{-1}$, 1481 cm$^{-1}$ which may be attributed to Quinoid and Benzoid rings respectively.

The IR spectra of polyaniline – CeO$_2$ composite (40 wt % of CeO$_2$ in PANI) is shown in Figure 1 (b). The prominent peaks that are observed in polyaniline – CeO$_2$ composite are 2918 cm$^{-1}$, 2361 cm$^{-1}$, 1560 cm$^{-1}$, 1471 cm$^{-1}$, 1298 cm$^{-1}$, 1240cm$^{-1}$,1107 cm$^{-1}$,798 cm$^{-1}$, 652 cm$^{-1}$, and 509 cm$^{-1}$. By careful observation of IR the characteristic stretching frequencies are considerably shifted towards higher frequency side. The data suggest that, there is a Vander walls kind of interaction between the polymer chain and CeO$_2$. 

![Figure 1 (a) IR spectrum of Polyaniline](image-url) ![Figure 1 (b) IR spectrum of composite](image-url)
3.2. SEM

SEM micrograph of polyaniline is as shown in figure 2(a). It can be clearly seen that the micrograph of polyaniline is smooth and homogeneous. Since Hydrochloric acid is used as protonic acid in the preparation of polyaniline, the presence of microcrystalline structure can be seen that is not homogeneously distributed throughout. The contrast in the image is a result of differences in scattering from different areas of the surface as a result of geometrical differences.

Figure 2(b) shows the SEM micrograph of pure CeO$_2$. High magnification SEM image reveals that CeO$_2$ particles are uniformly distributed with definite shape and size and confirms the crystallanity of the oxide. The SEM micrograph of polyaniline – CeO$_2$ composite with 40 wt % of CeO$_2$ in polyaniline is shown in figure 2(c). High magnification SEM image reveals the presence of CeO$_2$ particles uniformly distributed throughout the composite sample. A small variation in the particle dimensions of CeO$_2$ so dispersed in polyaniline has been observed. Fibrillar morphology is observed in the composite. The contrast in the image is due to the difference in scattering from different surface areas as a result of geometrical differences between polyaniline and CeO$_2$.

3.3. A.C. conductivity

Using the values of the equivalent parallel capacitance($C_p$), dissipation factor($D$), and parallel equivalent resistance($R_p$), recorded by the LCR meter at a different frequencies, ac conductivity ($\sigma_{ac}$), dielectric constant ($\varepsilon'$) and dielectric loss (tan $\delta$) parameters have been calculated. Figure 3(a), shows the variation of ac conductivity as a function of frequency of polyaniline/CeO$_2$ composites. It is observed that variation of $\sigma_{ac}$ is small in all composites in the frequency range of 50Hz to 10 KHz. Large variations in conductivity is observed in the frequency range of 10 KHz to 5 MHz. This multiphase variation may be due to lattice polarization around a charge in localized state and due to the variation of distribution of CeO$_2$ in polymer matrix. Apart from temperature and frequency, percentage of crystallinity, degree of protonation, crystalline domain size and order in crystalline and amorphous regions have a relation with the delocalization length.

Figure (3b) shows the variation of $\sigma_{ac}$ as a function of wt% of CeO$_2$ in polyaniline at three frequencies (10, 100 & 1000 kHz) at room temperature. It is observed that ac conductivity decreases in 10, 20, 30 & 50 wt % of CeO$_2$ in polyaniline and increases in 40 wt % of CeO$_2$ in polyaniline. The decrease in conductivity with increase in wt% may be due to an increase in the disorderliness of the composites. CeO$_2$ particles could possibly induce conformational changes in polyaniline, leading to a reduction in the order and a consequent reduction in the delocalization length, which is reflected with decrease in conductivity [32].
The increase in conductivity in 40 wt% of CeO$_2$ in polyaniline may be due to the extended chain length of polyaniline which facilitate the polarization of charge carriers and variation of distribution CeO$_2$ particles which may support for more number of charge carriers to polarize between favorable localized sites causing increase in conductivity.

![Figure 3(a) ac conductivity as a function of frequency (b) variation of $\sigma_{ac}$ at three frequencies.](image)

3.4 Dielectric Behaviour

Figure 4 shows the variation of $\varepsilon$ as a function of frequency for different wt% of polyaniline/CeO$_2$ composites. It is observed that, the dielectric constant is high in 20 wt % compared to 10, 30, 40 & 50 wt% at low frequency. In all the samples, dielectric constant decreases with increase in applied frequency. The dielectric constant value for different composites is ranging from $8.9 \times 10^5$ to $3.26 \times 10^6$ at 50 Hz which decreases to value ranging from 707 to 1843 at 5 MHz. Such large values of real permittivity is not unusual, which are related to effect of electrode polarization and space charge polarization [30]. The observed behavior may be due to nearly a Debye-type single relaxation mechanism taking place in these materials. All these results go in accordance with the conductivity behavior.

![Figure 4. Variation of permittivity](image)  

![Figure 5. Variation of dielectric loss](image)
3.5. Dielectric loss

The variation of dielectric loss as a function of frequency for different wt% of polyaniline / CeO$_2$ composites is represented in figure 5. The loss tangent value is ranging between 4.06 to 9.99 at 50 Hz and decreases with increase in frequency. At 5 MHz its value is ranging between 0.68 to 1.89. Similar values which increase with protonation have been reported earlier [31]. The observed behavior is in accordance with the conductivity and dielectric constant results in these composites. High dissipation loss at low frequency in all the composites may be due to DC conduction losses.

![Figure 5](image_url)

Figure 5: Variation of dielectric loss as a function of frequency for different wt% of polyaniline / CeO$_2$ composites.

Figure 6 (a) Variation of $Z'$ with frequency (b) Variation of $Z''$ with frequency (c) Nyquist plot

Figure 6 (a) shows the variation of real part of impedance with frequency in polyaniline / CeO$_2$ composites. At lower frequencies the value of $Z'$ increases with increase in weight percent of cerium oxide in polyaniline and with increase in frequency, the value of $Z'$ is found to decrease in all samples. The variation of imaginary part of impedance with frequency in polyaniline / CeO$_2$ composites is shown in figure 6(b). The position of peak of $Z''$ shifts towards higher frequency side with decrease in weight percent of cerium oxide in
polyaniline. The width of the peak points towards the possibility of distribution of relaxation times (33) and the relaxation time $\tau$ can be determined from the position of the peak ($\tau=1/\omega_{\text{max}}$). Figure 6(c) shows Nyquist (Z’ vs. Z’’) plots for polyaniline / CeO$_2$ composites. The semi circles observed in the plot are due to grains, grain boundaries and grain- electrode effect. With increase in weight percent of cerium oxide in polyaniline, the number of semi-circles increases up to three. Each semi circle can be represented by a resistance and a capacitor connected in parallel. The intercept on real axis represents the bulk resistance of the sample.

4. CONCLUSIONS

Polyaniline-cerium oxide composites with different weight percentage of cerium oxide in Polyaniline were prepared by in situ polymerization method. The formations of the composites were characterized by infrared spectroscopy, x-ray diffraction and scanning electron microscope techniques. The frequency dependent conductivity and dielectric behavior of the composites have been studied in the frequency range of 50 Hz to 5 MHz. In the frequency range of 50 Hz to 10 KHz, variations in a.c. conductivity was small in all the samples. Large variations in conductivity were observed in the frequency range of 10 KHz to 5 MHz. This multiphase variation may be due to lattice polarization around a charge in localized state and due to variation of distribution of CeO$_2$ in polymer matrix. With increase in frequency, dielectric constant was found to decrease. This behavior may be due to nearly a Debye-type single relaxation mechanism. High dissipation loss observed at low frequency may be due to D.C. conduction losses. With increase in frequency the dielectric loss and Z’’ were found to decrease. With decrease in weight percent of cerium oxide in polyaniline, the position of peak of Z’’ shifts towards higher frequency side.

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