



CHALCOGENIDE SEMICONDUCTOR NANOPARTICLES EMBEDDED IN POLYMER MATRIX: CRITICAL APPROACH

Manoj Kumar

Department of Physics, Dayanand Anglo-Vedic. College, Abohar, India

E-Mail: mkverma782006@gmail.com

ABSTRACT

Nanocomposites of polymer electrolyte are prepared by embedding copper sulfide or bismuth sulfide chalcogenide semiconductor particles in polymer electrolyte (PEO:NH₄ClO₄). The process of preparation is established by passing the hydrogen sulphide (H₂S) through the polymer complex (PEO:NH₄ClO₄+ x wt.% copper sulphate/bismuth nitrate). Total conductivity is measured by semicircled cole-cole plots which indicated one order of increase of bulk conductivity (10⁻⁶ S/cm to 10⁻⁵ S/cm) with the dispersal of chalcogenide semiconductor particles (Bi₂S₃/CuS) in the complex. Contribution of electronic conductivity or ionic conductivity to the total conductivity is measured the Wagner's polarisation plots. SEM studies showed the non-uniform distribution of the chalcogenide particles ranging from in the composites ranging from micro to nano sizes, TEM studies showed chain type structure for the interconnected (Bi₂S₃/CuS) dispersoid. The band gap of different coloured composite films are measured by optical absorption studies which showed change in the band gap with change of size of dispersoid from micro to nano size.

Keywords: polymer electrolyte nanocomposites, bulk conductivity, band gap, SEM, TEM.

INTRODUCTION

Polymer electrolytes or ion conducting polymer have been the focus of extensive research for the last three decades. The early work on ion conducting polymer electrolytes was pioneered by Fenton [1, 2]. Armand stressed on their immense potential applications in solid state batteries fuel cell, supercapacitor, dye sensitized solar cell, sensors and electro chromic display devices [3-7]. Ion conducting polymer electrolytes have been extensively focus of study due to more advantages over the liquid electrolyte like ease of preparation in thin film, wide range of composition, good electrode-electrolyte contacts apart from mechanical stability and flexibility. Earlier most of the polymer electrolyte are concerned with the doping of metal salts or ions with the polar polymers like polyethylene oxide (PEO), polypropylene oxide (PPO), polyacrylic acid (PAA), polyethylene imine (PEI), polyethylene glycol (PEG) etc.[8-10]. Among all the above mentioned polymers, PEO forms the most exhausted system because of its extraordinary property of large solvation with wide variety of ionic salts resulting good electrochemical stability. But the ionic conductivity of PEO based system is in the range 10⁻⁴-10⁻³ Scm⁻¹ at 80-100°C temperature range, where PEO remains in amorphous state and ions have large degree of freedom. Hence, this low value of conductivity of PEO based polymer electrolytes restricted their applications in the electrochemical devices. Different researchers worked out on different techniques to enhance the conductivity and performance of the polyethylene oxide based polymer electrolytes in the solid state devices. Out of many techniques like changing polymer chain length, changing the nature of the complexing salt, mixing of the two polymers (copolymerisation), plasticization, the formation of polymer nanocomposites is most challengeable [11-15]. Major focuses in above techniques were in enhancing bulk conductivity while preserving the mechanical stability and good electrode electrolytes interface.

The preparation of polymer electrolyte nanocomposites has emerged a versatile technique to improve the performance of solid polymer electrolytes. This technique involves dispersion of the nano sized ceramic and inorganic fillers. Most of the polymer electrolytes nanocomposites are purely ionic in nature i.e. charge carriers are primarily ions with transference number, $t_{ion} \sim 1$. Electronic contribution to the total conductivity in polymer electrolytes composites is approximately nil with $t_e \sim 0$. A new class of polymer electrolyte composites is chalcogenide semiconductor dispersed polymer electrolyte composites, which introduces the partial electronic conductivity in addition to ionic conductivity of polymer electrolytes. The technique embeds in-situ chalcogenide semiconducting particles like lead sulfide (PbS), cadmium sulfide (CdS), bismuth sulfide (Bi₂S₃), copper sulfide (CuS) in the pure polymer electrolyte [16-19]. These chalcogenide/semiconducting particles like PbS, CuS, CdS, Bi₂S₃, being the semiconducting /electron conducting nature may introduce the partially electronic conductivity in the otherwise pure ionic conducting matrix. Such a composites is termed as mixed ion and electronic conductor (MIEC). The research paper presents some of critical studies of properties of these above mentioned chalcogenide semiconductor embedded in polymer composites. The detailed properties are published elsewhere [17-20]. The motivation behind present work is many fold as under. The various semiconducting particles (PbS, CdS, CuS, Bi₂S₃) differ in their sizes. Hence it will be interesting to note the formation of polymer nanocomposites from these chalcogenide particles in micro to nano ranges. As these particles differ in type and conductivities too, hence may introduce the partial electronic contribution to the different extent. It would also be interesting to note that these semiconducting particles have the different band gap depending on the colour of polymer nanocomposites and there would may any change in band gap as the function of



sizes dispersal of semiconducting particles, The bulk conductivity had been function of dispersed phase concentration in any type of the composites viz polycrystalline solid-solid or polymer solid composite electrolyte. Solid solid composite show one conductivity maxima which appear at 30-40 wt.% concentration of dispersed phase. While polymer solid composites show the two maxima one at lower concentration 3-6 wt.% and other some higher 10-15 wt.% of dispersed phase in the bulk conductivity vs dispersoid concentration plot [21]. According to Mayer's absorption model [22], the total bulk conductivity should be enhanced with the dispersion of third phase materials. It would be interesting to see all above mentioned aspects in the present paper.

EXPERIMENTAL

Material preparation

The Figure-1 shows the methodology for the preparation of the polymer electrolyte composites.

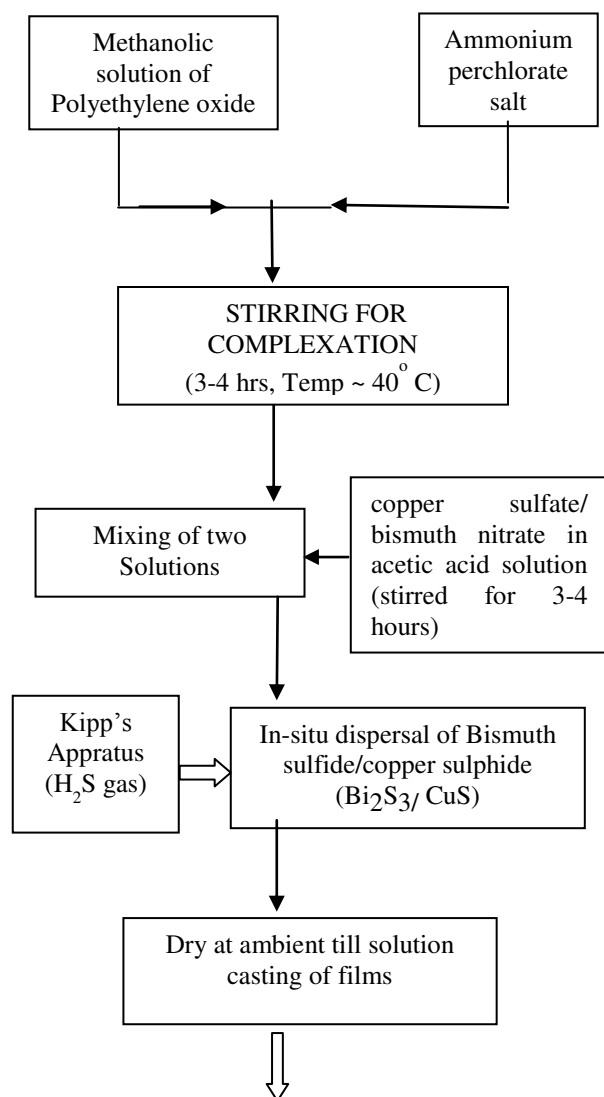


Figure-1. Various steps involved in the preparation of polymer-electrolyte nanocomposites.

In the beginning the polyethylene oxide (Mol. Wt. $\sim 6 \times 10^5$, Aldrich) and ammonium perchlorate (Aldrich) are taken in the weight percentage of [PEO:NH₄ClO₄ (96:4)], the concentration ratio of maximum conductivity of the pristine polymer electrolyte. The two materials are mixed in solvent methanol and stirred for 3-4 hrs till viscous solution is obtained. In another beaker, bismuth nitrate/copper sulfate in the solvent acetic acid/methanol is stirred. Two solutions are added with continuous stirring for thorough mixing. Hydrogen sulfide gas (H₂S) from the Kipp's apparatus is passed in the above prepared complexed solution resulting in situ formation and dispersal of the bismuth sulfide/copper sulfide particle in the composite solution. The composite films are vacuum dried at $\sim 10^{-5}$ Torr.

CHARACTERISATION

The ionic or electronic transference number is calculated by Wagner's polarization method [23]. When small d.c. potential (3-5 V) is applied across the polymeric composite film, the charge carriers move under the influence of electric field due to applied potential and collect at the respective electrodes. Initial current is due to both the charge carriers (ions and electrons) and called total current (I_T). But after some time due to polarization phenomenon, the final current (I_F) is only due to electrons/holes conduction. The calculating the value of initial current (I_T) and final current, (I_F), ionic and electronic transference number are given as

$$t_{ion} = (I_T - I_F) / I_T$$

$$t_e = 1 - t_{ion}$$

Ionic and electronic conductivities values can be obtained from following relations:

$$\sigma_i = t_{ion} \cdot \sigma_T$$

$$\sigma_e = t_e \cdot \sigma_T = (1 - t_{ion}) \cdot \sigma_T$$

where, σ_T is the total measured bulk conductivity.

For the measurement of total bulk conductivity of various composite films, the Cole-Cole plots or impedance plots between conductance G (S) and susceptance B (S) are plotted in frequency range 40 Hz to 100 KHz. The impedance plots are broadened semicircles and the intercept on the conductance (G) axis at the low frequency range gives the value of bulk conductance (G). The bulk conductivity can be given as follows.

$$\sigma = GL/A \quad (1)$$

where L is the thickness and A is the area of polymer sample.



RESULT AND DISCUSSIONS

Band gap of the different polymer composites films is measured from the optical studies and related to

the colour of the composites films. The band gap of different composites film along with the composition is shown in the Table-1.

Table-1. Optical characteristics of PEO/ NH_4ClO_4 +x wt.% bismuth sulfide /cupper sulfide.

Concentration of dispersoid (x wt.%)	Colour of composites	Range of particles sizes	Band gap from optical absorption (eV)
(A) Bismuth sulfide			
1	Light brownish	Bulk + few nano	1.65
4	Light brownish	Bulk + nano	1.74
8	Dark brownish	Bulk + more nano	1.76
10	Dark brownish	Bulk + more nano	1.80
(B) Cupper sulfide			
1	Light bluish	Bulk	2.2
2	Light bluish	Bulk + few nano	2.3
3	Greenish blue	Bulk + nano	2.36
5	Greenish blue	Bulk + nano	2.4

The composite films PEO/ NH_4ClO_4 +x wt.% Bi_2S_3 are brownish (light and dark) in colour with the band gap 1.8 eV. The composite films PEO/ NH_4ClO_4 +x wt.% CuS films is greenish blue in colour with band gap 2.4 eV. It can be seen from the

Table-1, there is change in the band gap with the size of the dispersoid. increases as the size of the dispersoid bismuth sulfide/cupper sulfide in the composites changes from micro to nano range. This could be explained by well-known quantum effect.

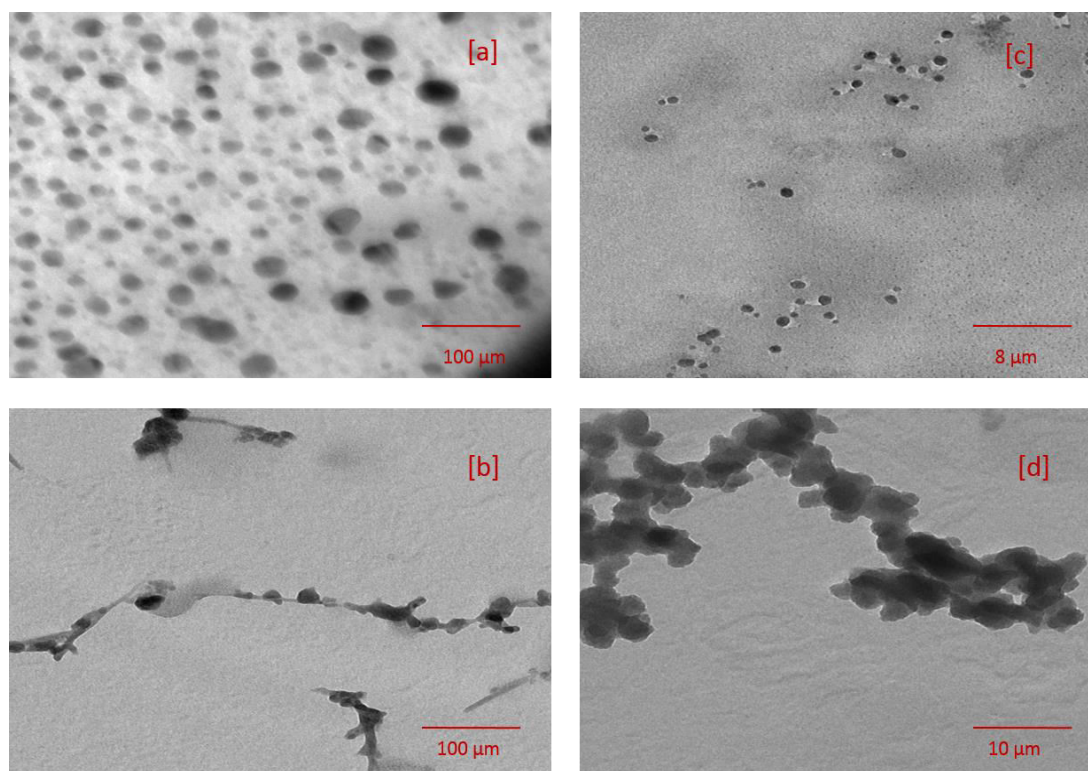


Figure-2. Micrographs of PEO: NH_4ClO_4 + x wt% Bi_2S_3 , [a] SEM (x=2 %) [b] TEM (x=4 %) and micrographs of PEO: NH_4ClO_4 + x wt% CuS [c] SEM (x=1 %) [d] TEM (x=4 %)



TEM/SEM micrographs for the polymer composites are shown in the Figure-2. From the TEM micrographs (b & d), it can be seen there is inherent chain type structure and percolation pathways for charge carriers via interconnected dispersed particles. From SEM micrographs (a & c), there are well dispersed spherical shaped copper sulfide particle in the composites films with sizes from ~ 20 nm to several hundred nm. In some other places, there is formation of large agglomerates of dispersed particles.

The electrical bulk conductivity measurement is done by complex impedance plots as explained in the section 2 (equation 1). The cole-cole plots the various composite films are shown in the Figure-3(a). The

polarization plots for the measurement of ionic and electronic transference number are shown in the figure 3 (b). Figure-3 (c) gives the variation of the total conductivity with the concentration (wt.%) of both dispersoids in the composite. From the Figure-3, it is found that dispersion of $\text{Bi}_2\text{S}_3/\text{CuS}$ in the ionic matrix can change the bulk conductivity behavior in the following ways.

From the figure 3(b), the final current increases with the increase of concentration of the dispersoid which results in increase of electronic conductivity. The dispersal of the semiconducting particles have introduced the partial electronic conductivity than pure ionic conductivity of pure polymer electrolyte.

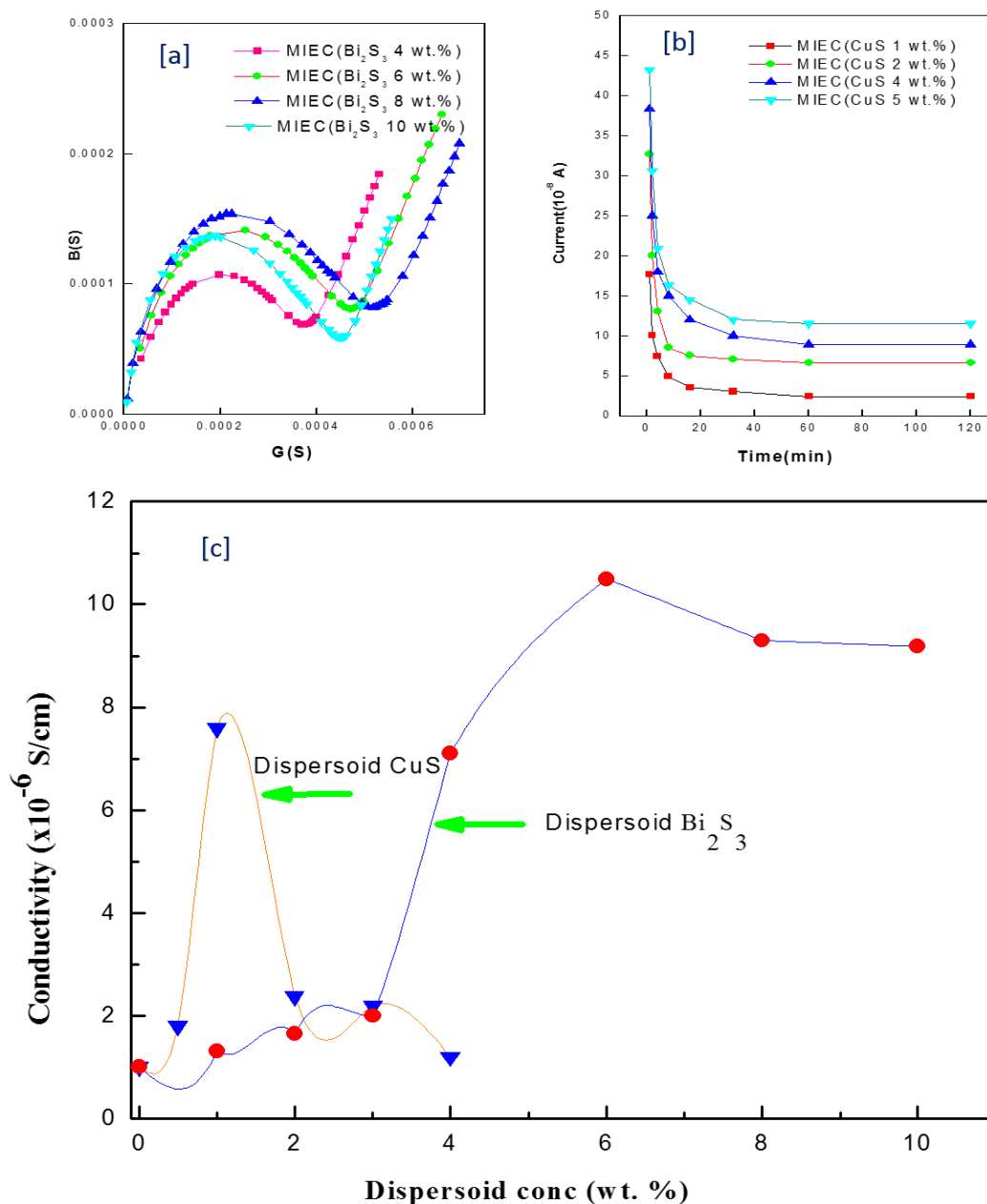


Figure-3.(a) Cole cole plots of PEO: NH_4ClO_4 + x wt.% Bi_2S_3 composites (b) Polarisation plots of PEO: NH_4ClO_4 + x wt.% CuS composites (c) Variation of conductivity of composite PEO: NH_4ClO_4 + x wt.% $\text{Bi}_2\text{S}_3/\text{CuS}$.



Total conductivity of composite for both the dispersoid ($\text{Bi}_2\text{S}_3/\text{CuS}$) is also enhanced which peaks at certain low concentration of the dispersoid and then further decreases. This shows its conductivity behavior as typical type of composite (a peak is found in σ vs. material's wt.% at a particular dispersed phase concentration). With the addition of dispersoid bismuth sulfide or copper sulfide in the pure ion conducting matrix, the total bulk conductivity increases. This could be explained as follows. With the presence of above mentioned dispersoid, the concentration of ions increases due to decrease of ions neutralization or salt aggregation. Hence the third phase dispersoid act as plasticizer. The bulk conductivity obtains the maxima and then decrease after certain higher concentration of the dispersoid in the composites. The decrease in the conductivity is due to the again charge neutralization of the ions in the matrix. In the present polymer composites, the peaking in the conductivity is found at the low concentration 3-6 wt.% of the dispersoid as expected in the dispersed phase composites. The peak at the higher concentration could not found as the composites are not stable and brittle. From the figure 3(b), it can be seen that with the increase of concentration of the dispersoid bismuth sulfide/copper sulfide in the composite, electronic transference no. also increases. This is due to increase of semiconducting particle concentration ($\sigma = n\mu e$) which results in the increase of electronic transference no. From the figure 3 (c) it is found that total conductivity follows the trends as that of ionic conductivity. It means that electronic conductivity is the small part and ionic conductivity is still dominating. The composites with the dispersoid Bi_2S_3 has high peaking conductivity than CuS dispersed composite. Bismuth sulfide is large molecular size than CuS and it disperse more no. of ions in ionic matrix and prevents from neutralization.

CONCLUSIONS

Polymer electrolyte nanocomposites dispersed with bismuth sulfide/coppers sulfide to the pristine polymer electrolyte ($\text{PEO}:\text{NH}_4\text{ClO}_4$) at different weight concentration are prepared successfully by in-situ method. $\text{PEO}:\text{NH}_4\text{ClO}_4 + x$ wt.% Bi_2S_3 the composites films are light and dark brown coloured. The band gap of composite film changes from 1.65 eV to 1.8 eV as the particle size changes from micro to nano range. Similarly $\text{PEO}:\text{NH}_4\text{ClO}_4 + x$ wt.% CuS composite films are light bluish and greenish blue coloured with band gap 2.2 eV to 2.4 eV. Due to dispersal of semiconducting nature dispersoid bismuth sulfide/coppers sulfide in the composites, films are mixed ion and electron conductor. (MIEC) The ionic conductivity is dominating and electronic conductivity is the small part of bulk conductivity. SEM micrographs showed the non-homogenous dispersal of the dispersoid bismuth sulfide/coppers sulfide in the composite ranging from micro to nano-sizes. TEM micrographs shows the chain type structure and interconnected percolation pathways for the dispersoid.

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