

Mixed ion and electronic conduction in polyethylene oxide based polymer electrolyte composites

M. KUMAR*

Department of Physics, D.A.V. College, Abohar-152 116, India

Polymer composites of polymer electrolyte (PEO/NH₄ClO₄) dispersed with organic polymer polyaniline or inorganic semiconductors Bi₂S₃/CuS in different weight ratios have been prepared and characterized. Preparation of composites is done by adding relevant amount of Bismuth nitrate or Copper sulphate in a viscous solution of polymer PEO/NH₄ClO₄ complex. On sulfuration by bubbling H₂S through it, the in situ formation and dispersal of Bi₂S₃ or CuS resulted. SEM/TEM studies showed the dispersal of particles from μm to nm sizes. Impedance plots have given the enhanced bulk conductivity of the composites than pristine polymer electrolyte. Wagner's polarization studies confirm the mixed ionic + electronic behaviour of composites with the contribution due to electrons/holes as 8-30 % to the total conductivity. The overall bulk conductivity is increased too. Maier's space charge model explains enhancement of dominating ionic conductivity behaviour with the addition of dispersed phase CuS, Bi₂S₃ or organic polyaniline in the pristine polymer electrolyte.

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1. Introduction

Polymer electrolytes or ion conducting polymer are extensively studied since their discovery by Fenton and Armand [1,2] due to their immense potential applications in solid state batteries fuel cell, supercapacitor, dye sensitized solar cell, sensors and electrochromic display devices [3-7]. The polymer electrolyte has much advantages over the liquid electrolyte such as like ease of preparation in thin film, good electrode-electrolyte contacts, wide range of composition and hence wider control of properties, mechanical stability and flexibility etc. Earlier most of the polymer electrolyte concern the salt in association with the polymers such as polyethylene oxide (PEO), polypropylene oxide (PPO), polyacrylic acid (PAA), polyethylene imine (PEI), polyethylene glycol (PEG) etc. [7-10]. PEO is the most popular in all above as it solvates large no of the salts possessing good electrochemical stability and the ionic conductivity of the order of 10⁻⁴-10⁻³ S cm⁻¹. However, this conductivity remains at these levels only above 70⁰C, typically in the 80-100⁰C range, where the PEO retains its amorphous state. Hence, the low value conductivity of polymer electrolytes at room temperature is a major problem associated with solvent free polymer electrolytes which restrict their use in solid state devices. To enhance the performance and utility of the PEO based polymer electrolytes in the electrochemical devices, various techniques had been employed such as changing polymer chain length, changing the nature of the complexing salt, mixing of the two polymers (copolymerisation), plasticization and the polymer electrolyte nanocomposites [11-15]. The polymer electrolyte nanocomposites involve dispersion of the nano sized ceramic and inorganic fillers. All of the above modification involve improving

conductivity while preserving the mechanical stability and good electrode electrolytes interface. Most of the above polymer electrolytes are purely ionic conductors with ionic transference no. $t_{ion} \sim 1$ and electronic contribution to the total conductivity is approximately nil. There is another class of the polymer electrolyte composites which deals with mixed ionic and electronic conducting. These polymer electrolytes are prepared by in-situ dispersal of semiconducting particles like Bi₂S₃, CuS in the pure polymer electrolyte which are termed as polymer crystal composites [16-19]. In another route the electronic conducting polymers like polyaniline, polypyrrole are incorporated in the purely ionic conducting matrix and termed as polymer-polymer composites [20]. The Bi₂S₃/CuS or Polyaniline being the semiconducting /electron conducting nature introduces the partially electronic conductivity with the ionic conductivity of pure polymer electrolyte and such composites are termed as mixed ion and electronic conductor (MIEC).

The present paper presents critical study of properties and application of these mixed ionic and electronic conducting polymer composites. The detailed properties are published elsewhere [17-20]. The motivation behind present work is many fold as under.

(a) The different chalcogenide or the semiconducting particles like PbS, CdS, CuS, Bi₂S₃, vary in the different sizes and have the wide range of the conductivity. The dispersal of these particles may result in the formation of polymer insulator to polymer semiconducting dispersed nanocomposites. Depending on the type and size, later may introduce the partial electronic conductivity in addition to enhanced ionic conductivity. Recent studies showed the application of the mixed ionic and electronic

conductor in the electrolyte magnetic shielding devices [21].

(b) Different chalcogenide particles have different band gap which is related to the optical absorption and colour of the nanocomposites. It is also interesting to note that there is variation of the bandgap with dispersal of chalcogenide particles of different sized ranging from micro to nanosized.

(c) Out of various techniques to enhance the bulk conductivity of the polymer composites, the dispersed phase materials had been taken as the excellent approach in the pure ion conducting polymer electrolyte. Addition of dispersoid/filler in the polymer electrolyte produces the access charge carrier at the interface and space charge layer. Maier explained such a conductivity enhancement by absorption model [22]. Also conductivity versus dispersed materials (wt.%) in the polycrystalline solid-solid is quite different and interesting from polymer solid composite electrolyte. Former show the one conductivity maxima which is found at much higher concentration (30-40 wt.% of the dispersoid) while later show two conductivity maxima which occur at 3-6 wt.% and 10-15 wt. %. Bunde et al. explained this conductivity peaking on the basis of the percolation model [23]. The dispersoid of various variety has been chosen for dispersed phase polymer composites and it is interesting to observe above stated aspect in these composites.

(d) Polymers like polyacetylene, polyaniline, polypyrrole, polythiophene etc. are electron conducting polymers. This is because of presence of conjugation (by aromatic, hetro aromatic and electron rich), which provide a great degree of delocalization of π - electrons in these molecules. The overlapping set of molecular orbitals gives a reasonable mobility to the charge carrier along the polymer chain. The electrical conductivity of these conjugated polymers can be controlled by the process of doping from insulator to semiconductor to metallic range. Due to the versatility in manipulation of their structure, conducting polymers have been focused as exciting materials for solid state technology.

2. Experimental

2.1. Material preparation

The Fig. 1 shows the methodology for the preparation of the polymer-crystal composites.

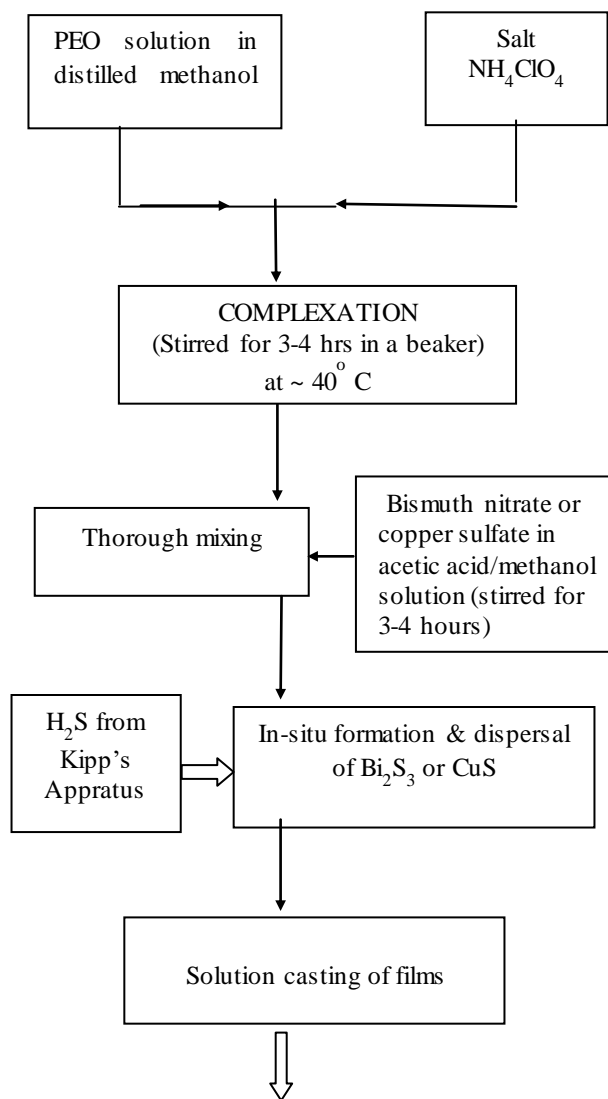
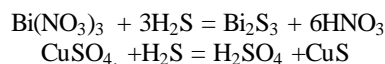


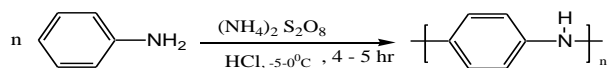
Fig. 1. Different steps involved in the preparation of polymer-crystal composite

In the first step, viscous solution of PEO:NH₄ClO₄ (96:4) complex is obtained by standard in situ method in the methonic solution in which bismuth nitrate or copper sulfate are added. Then, H₂S is bubbled through it which results in the “in-situ” formation of Bi₂S₃ or CuS particles which are dispersed in the polymeric solution. This is poured in polypropylene petridishes for casting of the films. The films are first dried in the ambient for about a week followed by drying in vacuum of $\sim 10^{-5}$ Torr. The material used is polyethylene oxide (Mol. Wt. $\sim 6 \times 10^5$, Aldrich), analytical reagent grade NH₄ClO₄ (Aldrich), bismuth nitrate, copper sulphate and methanol which was dehydrated before use. Dispersed semiconductor particles (Bi₂S₃/CuS) can be prepared by the conventional chemical method as follows:

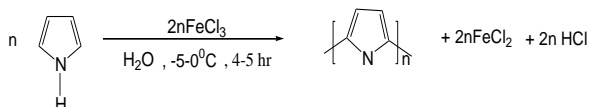


The synthesis of polymer-polymer composite was done first with the preparation of conducting polymer (PANI) which was synthesized with known template method as given below.

(i) Polyaniline (PANI):



(ii) Polypyrrole (PP):



To the above prepared conducting polymer, the polymer electrolyte (polymer matrix and salt) was mixed resulting in the formation of viscous solution. The composite so obtained was the polymer-polymer composite as shown below in the Fig. 2.

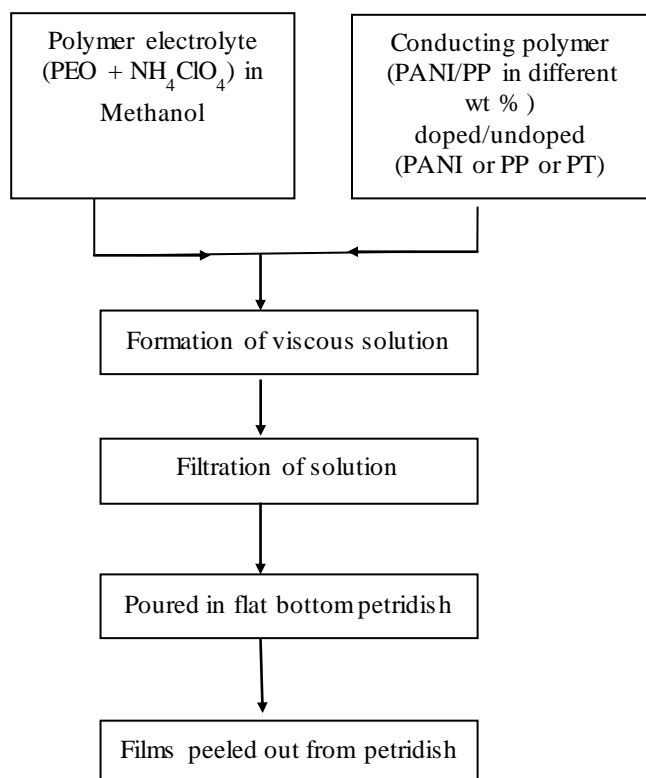


Fig. 2. Different steps involved in the preparation of polymer-polymer composite

2.2. Characterisation

Wagner's polarization method [24] has been used to measure the ionic and electronic transference number of various polymeric membrane. By applying a small dc voltage, current has been measured as a function of time.

The total initial current (I_T), corresponding to the unpolarized sample, is a result of both ionic + electronic currents while the final current (I_F) after complete polarization is due to the electron hole conduction only. The ionic and electronic transference numbers (t_{ion} & t_e) can be obtained from the relations:

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

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

The values of the ionic and electronic conductivities can be obtained from the following relations:

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

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

where, σ_T is the total measured conductivity.

For total bulk conductivity (σ_T) measurement of different composite films, the impedance plot (cole-cole plots) are drawn between the conductance G (S) and susceptance B (S) in the frequency range 40 Hz to 100 KHz. The cole-cole plots are the broadened semicircle and the intercept on the conductance (G) at the low frequency give to the bulk conductance of the composites films. Knowing the value of conductance G and the dimension of the sample, bulk conductivity can be calculated by using the relation given below.

$$\sigma = GL/A$$

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

3. Results and discussions

The nacent polymer electrolyte films PEO:NH₄ClO₄ are transparent and colourless but the films prepared by the polymer crystal composites PEO/NH₄ClO₄+xwt.% Bi₂S₃, PEO/NH₄ClO₄+xwt.% CuS are coloured because of the homogenous dispersal of the semiconducting particles Bi₂S₃/CuS in the polymer electrolyte. The colour of the various polymer composites with the composition are given the Table 1. The expected band gap is calculated from the optical absorption studies [18-19]. The film dispersed with Bi₂S₃ is brownish in colour because its band gap is 1.8 eV. Films dispersed with CuS are greenish blue in colour whose band gap is calculated to be 2.4 eV. From the Table 1, it is clear that colour and band gap of the composites films are related with the size of the dispersoid. The band gap of the composites films in both case increases as the size of the dispersoid becomes smaller from bulk to nano range (1.4 eV for bulk Bi₂S₃, and 2.2 eV for bulk CuS). This is due to well-known quantum effect. Also the Table 1 depicts that if the concentration of the salt increases, the band gap is also increased. It is due to formation of nano sized dispersed particles resulting increase of the band gap.

Table 1. Some of the features of PEO/NH₄ClO₄+x wt.% Bi₂S₃, PEO/NH₄ClO₄+x wt.% CuS polymer electrolyte composites

Amount of dispersed semiconductor (x wt.%)	H ₂ S bubbling rate	Colour of Memranes	Expected range of particles sizes)	Expected band gap from optical absorption	Experimental size from TEM (nm)
(A) Bi₂S₃					
1	30	Light brownish	Bulk + few nano	1.65	-
2	30	Light brownish	-	-	-
4	30	Light brownish	Bulk + nano	1.74	-
6	30	Dark brownish	-	-	50
8	30	Dark brownish	Bulk + more nano	1.76	20-50
10	30	Dark brownish	Bulk + more nano	1.80	20
(B) CuS					
1	30	Slight bluish	Bulk	2.2	-
2	30	Light bluish	Bulk + few nano	2.3	-
3	30	Greenish blue	Bulk +nano	2.36	200 and large
4	30	Greenish blue	-	-	-
5	30	Greenish blue	Bulk +nano	2.4	200

The TEM micrographs in Fig. 3 (a & b) for PEO:NH₄ClO₄+ x wt% Bi₂S₃, x =4 and x=6 show the percolation pathways for the charge carriers via the interconnected dispersed particles. The observed morphology of dispersoids shows their inherent chain type structure in the composites. Fig. 3 (c & d) show the scanning electron micrographs of [PEO:NH₄ClO₄+ x wt %

CuS, x=1 and x=4] films. It is seen that in some regions of the composite films, the dispersed particles tend to form large agglomerates. From the Fig. 3 (c & d), we see that isolated spherical shaped particles are well dispersed in the composite with particle size varying from ~ 20 nm to several hundred nm.

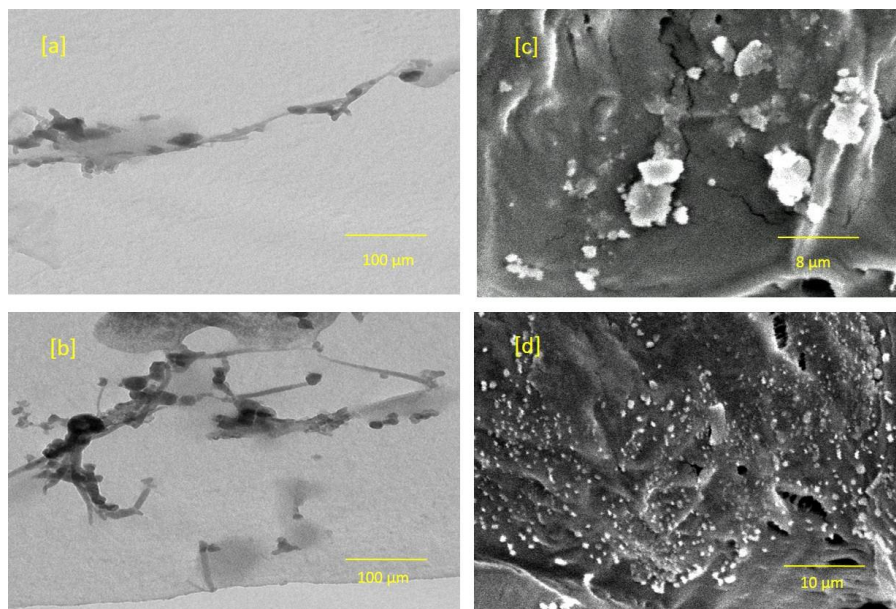


Fig. 3. TEM micrographs of PEO:NH₄ClO₄+ x wt% Bi₂S₃, [a] x=4 %, [b] x=6 % and SEM micrographs of PEO:NH₄ClO₄+ x wt% CuS [c] x=1 %, [d] x=4 %

The electrical bulk conductivity of the various composite films are shown in the table 3. From the table, the dispersal of the semiconducting particle in the composites has resulted in following two ways:

1. The dispersal of the semiconducting particles/electron conducting polymer have introduced the partial electronic conductivity than pure ionic conductivity of pure polymer electrolyte

2. The bulk conductivity is increased too.

Table 2. Ionic and electronic transference no. measurement of the different polymeric composites films (PEO:NH₄ClO₄+ x wt.% dispersoid)

Amount of dispersed semiconductor (x wt.%)	I _T (10 ⁻⁸ A)	I _F (10 ⁻⁸ A)	t _{ion} = (I _T - I _F) / I _T	t _e = 1 - t _{ion}
Bi ₂ S ₃				
3	31.99	1.5	0.96	0.040
4	32.98	1.6	0.9515	0.0485
6	30.82	1.8	0.9416	0.0584
8	36.30	2.2	0.9394	0.0606
10	47.5	3.8	0.92	0.080
CuS				
0.5	11	1.1	0.900	0.100
1	17.64	2.4	0.864	0.136
2	32.67	6.6	0.798	0.202
3	38.36	8.9	0.768	0.232
4	43.23	11.5	0.734	0.266
5	48.6	14.7	0.698	0.302

The total conductivity 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). The dispersion of Bi₂S₃/CuS/PANI in the ionic matrix can change the bulk conductivity behavior in the following ways:

(1) The Bi₂S₃/CuS/PANI dispersoid are the low conducting and their addition in the ionic matrix enhances the bulk conductivity. It is due to increase of the increase of the ion concentration and ionic conductivity. At the addition of low concentration of dispersoid, it decreases salt aggregation as it act as plasticizer. As a result the concentration of ions are increased and hence overall conductivity. It peaks at a certain concentration of dispersoid and then decreases. The decrease of bulk conductivity after maxima is probably due to immobilization or charge neutralization of ion concentration at higher concentration of dispersoid. This also confirms the dominating ionic conductivity of the MIEC.

As pointed out earlier in the section 1, in the dispersed phase composites, two peaks are expected in the conductivity vs dispersoid phase concentration. First peaks is found at low concentration approx. 3-6 wt.% while other is found at 10-15 wt.% of the dispersoid. In the our MIEC former is found and other could not be observed as the composite films at higher wt.% of dispersoid were brittle and not stable.

(2) From the Table 2, it is clear that as the amount of the dispersoid/conducting polymer increases, the electronic transference no. also increases due to increase of semiconducting constituents for electronic conduction ($\sigma = n\mu e$). In the case of polymer-polymer composites, with the addition of polyaniline in the polymer electrolyte

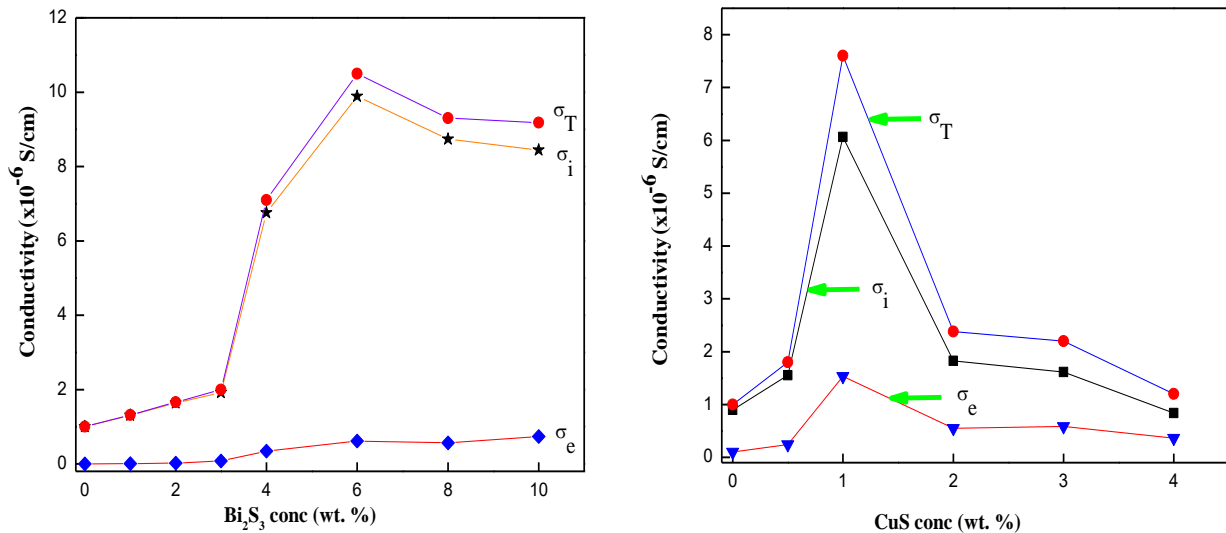
electronic conductivity increases due to delocalization of electronic conduction through the π back bone. It is also found the electronic conductivity initially increases and then decreases in both the cases. At the small concentration of the dispersoid/PANI, there is homogeneous distribution of it in the matrix. While at the higher concentration of dispersoid/PANI, there is contamination of it and formation of agglomerates.

(3) Table 3 and Fig. 4 shows the variation of maximum conductivity, ionic conductivity (σ_i) and electronic conductivity (σ_e) of composites with different dispersoid concentration. It can be seen that the peak conductivity with Bi₂S₃ dispersoid is higher than CuS. But the electronic conductivity of CuS is higher than Bi₂S₃ It could be concluded that total conductivity maxima depend on no. of access charge ion carrier generated on the addition of dispersoid in ionic matrix while the electronic conductivity depends on the no the dispersoid particles and its movability. The CuS being smaller in size and low molecular weight has largest mobility and more electronic conductivity.

(4) From the Fig. 4, it is clear that electronic conductivity is small as comparison with the ionic conductivity. Hence total conductivity is still ionic dominating. The present MIEC can be treated as polymer insulator composites with ionic dominating conductivity. The enhancement of ionic conductivity σ vs materials wt.% in such composites can be explained space charge model given by Maier and peaking in the plot can be explained by percolation threshold model.

Table 3. Conductivity measurement of the different polymeric composites films (PEO:NH₄ClO₄+ x wt.% dispersoid)

Amount of dispersed semiconductor (wt.%)	Ionic conductivity (σ_i) at 303 K [X 10 ⁻⁶ (S/cm)]	Electronic conductivity (σ_e) at 303 K [X 10 ⁻⁶ (S/cm)]	Total conductivity (σ_T) at 303 K [X 10 ⁻⁶ (S/cm)]
Bi₂S₃			
0	.999	.001	1
1	1.31	.01	1.32
2	1.61	.05	1.66
3	1.92	0.08	2
4	6.75565	0.34435	7.1
6	9.8868	0.6132	10.5
8	8.73642	0.56358	9.3
10	8.4456	0.7344	9.18
CuS			
0	0.9	0.1	1
0.5	1.5552	0.2448	1.8
1	6.0648	1.5352	7.6
2	1.82784	0.55216	2.38
3	1.6148	0.5852	2.2
4	0.8376	0.3624	1.2

Fig. 4. Variation of conductivity with the amount of PEO:NH₄ClO₄+ x wt% Bi₂S₃ and PEO:NH₄ClO₄+ x wt% CuS

4. Conclusion

Nano-composites of polymer electrolyte (PEO:NH₄ClO₄) have been prepared by dispersing nano sized Bi₂S₃ and CuS crystallites in it. Varying amount of Bi/Cu salt have been added to the viscous solution of polymer-salt (PEO:NH₄ClO₄) complex. On sulfuration by bubbling H₂S gas through it, the in-situ formation and dispersal of Bi₂S₃/CuS has resulted. Solution casting gives the “polymer crystal composites. Due to semiconducting nature of the dispersoid, it introduced partial electronic

conductivity in the otherwise pure ionic conductor. The composites films possess the mixed ionic and electronic conductivity (MIEC). In another route, the polymer-polymer composites are prepared by incorporating the electronic conducting polymers like polyaniline in the purely ionic conducting matrix. The electronic conducting polymer provide the substantial electronic conductivity with the major ionic conductivity. Electrical measurements have been done to calculate the total conductivity, ionic, electronic conductivity and electronic/ionic transference number of the composites. The films of PEO:NH₄ClO₄ are

translucent and colourless but PEO:NH₄ClO₄ + Bi₂S₃ and PEO:NH₄ClO₄+CuS films are of different colours (dark brown, greenish blue). The colour of films is directly linked with the optical absorption and band gap which could be determined by optical absorption studies. By varying the salt concentration and H₂S bubbling rate, different particle sizes could be obtained. The conductivity plot show the increase of electronic transference no. with the increase of concentration of the dispersoid and as high as 30 % for the CuS dispersed MIEC.

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*Corresponding author: mkverma782006@gmail.com