The Pharma Innovation Journal 2018; 7(6): 665-669

www.ThePharmaJournal.com

The Pharma Innovation

ISSN (E): 2277- 7695
ISSN (P): 2349-8242
NAAS Rating: 5.03
TPI 2018; 7(6): 665-669
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www.thepharmajournal.com
Received: 19-04-2018
Accepted: 21-05-2018

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Frequency dependent studies of the copper sulfide dispersed polymer electrolyte composites

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Abstract

Polymer electrolyte composites based on the polyethylene oxide (PEO) and ammonium perchlorate dispersed with the cupper sulfide is successfully prepared and charz acterized with the electrical studies. The a.c. conductivity measurement of the polymer electrolyte composites is done by the complex impedance studies. Plots between the conductance (G) and susceptance (B) are the semicircles and the intercepts on the real axis gives the value of bulk conductance of various polymeric films. Bulk conductivity and dispersoid wt. % plot showed the conductivity enhancement with variation ~10^{-6} to 10^{-5} S/cm^{-1} with the peak value at 7.6 x 10^{-6} S/cm. The decrease in the overall conductivity after the peak value could be explained by Mayer's space charge model. The frequency dispersion plot showed the plateau region in the frequency range from 10 Hz to 10 KHz. Detailed I-V studies show p-type behavior of dispersoid in the composite.

Keywords: Polymer electrolyte composites, complex impedance spectroscopy, bulk electrical conductivity

Introduction

Introduction

Polymer electrolytes are continuing to receive a lot of attention from the last three decades due to their immense potential applications in solid state batteries, fuel cells, supercapacitors, dye sensitized solar cells, sensors and electro chromic display devices [1-6]. Polymer electrolytes concern the complexes of alkali metal salt with the polar polymer like polyethylene oxide, polypropylene oxide PEO, polypropylene oxide (PPO), polyacrylic acid (PAA), polyethylene imine (PEI), polyethylene glycol (PEG) etc. [7-9]. These materials have the advantage over the liquid electrolytes like flexibility, ease of preparation, good mechanical stability, and good electrode electrolyte contact. The conductivity in these polymer electrolytes is primarily due to the ionic motion in the dissociated forms between the electrodes. Out of the various polymers the polyethylene oxide (PEO) is the most popular polymer electrolyte which dissolve large number of the salts possessing good mechanical stability and conductivity. However high value of conductivity (10^{-4}-10^{-3} S/cm^{-1}) of polyethylene oxide based polymer electrolyte is achieved at high temperature typically in the 80-100^{0}C range, where the PEO retains its amorphous state. The low value of conductivity (~10^{-6} S/cm^{-1}) at room temperature, of polymer electrolyte are least desired for application point of view. To enhance the performance and conductivity of polymer electrolytes, many approaches have been employed which comprises as changing polymer chain length, changing the nature of the complexing salt, mixing of the two polymers (copolymerization), plasticization [10-14]. One of the most versatile technique to enhance its performance and conductivity is the preparation of the polymer electrolyte composites [15-18]. The present work is focused on the preparation of the composites in which third phase semiconductor copper sulfide is dispersed in pristine polymer electrolyte (PEO: NH_4ClO_4).

Materials and methods

The polymer electrolyte composites film are prepared by well-known in situ method [15]. The host polymer Polyethylene oxide (PEO) and the salt NH_4ClO_4 are mixed in the weight ratio of 96:4 (the composition of the maximum conductivity) in methanol and continuously stirred for the 3-4 hours. To above prepared solution, the copper sulfate salt is added with continuous stirring of solution. The H_2S gas is slowly bubbled through the viscous solution and resulted the formation of copper sulfide disperoid in the polymer matrix. The above prepared viscous solution is poured in the petridishes for casting of the films. The films are then dried to the ambient for ten days.

The dispersed bismuth sulfide particle in the composites are formed according to following reaction

$CuSO_4. + H_2S = H_2SO_4 + CuS$

For the electrical characterization of the films, the small piece of the films is cut and aluminum electrodes are vacuum evaporated for the electrical contacts having area of contact 0.50 cm^2.

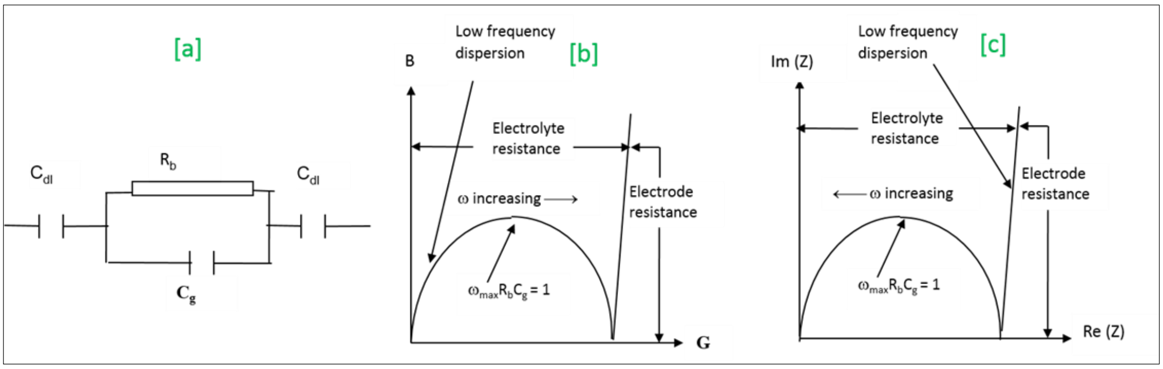

Fig 1: (a) The equivalent circuit of sample with blocking/irreversible electrodes (b) corresponding admittance plot and (c) corresponding Impedance plots.

The polymer composites films are prepared by varying the cupper sulfide salt with the different weight percentage (0-6 wt. %) to the pristine polymer electrolyte (PEO: NH_4ClO_4). Complex impedance spectroscopy technique or a. c. method is used to measure the electrical conductivity of different polymeric films in the frequency range from 10 Hz to 100 KHz. Complex impedance spectroscopy concerns to the measurement of real and imaginary part of impedance/admittance at different frequencies. Impedance (Z)/admittance (Y) being a complex quantity can be written as:

$$Z\,(w) = Z^{/}\,(w) - j\,Z^{//}\,(w)$$
$$Y\,(w) = G\,(w) + j\,B\,(w)$$

where $Z^{/}$ and $Z^{//}$ are real and imaginary parts of the impedance respectively. G and B are the conductance and susceptance respectively. The plots of $Z^{/}$ (= Z cosθ) and $Z^{//}$ (= Z sinθ) in the complex plane at various frequencies are known as impedance plots gives the frequency dispersion curves. These frequency dispersion curves provide information about the electrode-electrolyte interface, bulk resistance and grain boundary etc. Depending upon the relaxation time of the circuit present in the system, one or more than one arcs or semicircles are obtained. In the present sample with blocking/irreversible electrodes, we have an additional double layer capacitance (C_{dl}) is in series with the C_g-R_b combination for samples having blocking electrodes as shown in Figure. 1(a). So due to this there will be an additional low frequency dispersion region in admittance/impedance plots as shown in Figures 1(b) and 1(c). Polarization at electrode-electrolyte interface dominates over C_g at low frequencies. As in an ideal case, electrode-electrolyte interface are considered as perfectly smooth and flat, but it is not true in practical cases. In practical case, these impedance plots get modified and the intercept of the low frequency and high frequency dispersion curves on real axis (high frequency) gives a bulk resistance/conductance of the samples. In the present studies, we have used LCR Hioki 3522 meter working in the frequency range of 10 Hz to 100 KHz for the measurements of electrical conductivity. Impedance/admittance plots are drawn and the conductivity was calculated by using this relation:

$$\sigma = GL/A$$

where G is the conductance which is determined from the admittance plots, plots, L is the distance between the electrodes and A is the area of cross-section of each electrode.

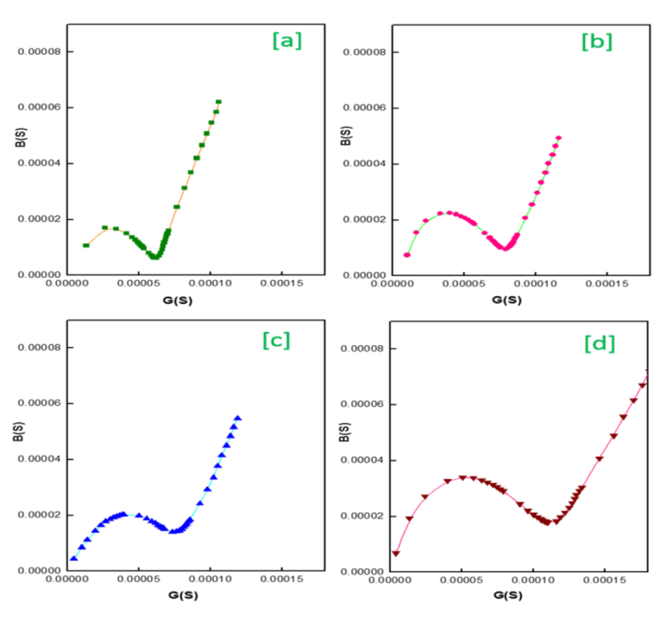

Fig 2: Complex impedance plots of polymer electrolyte PEO: NH_4ClO_4 with the dispersoid copper sulfide in different concentration (a) 1wt.% (b) 3 wt.% (c) 4 wt.% (d) 5 wt.%

Result and discussion

Figure 2 shows the complex impedance plot for the composite films having different amount of the dispersoid copper sulfide (wt. %). The plots are the broadened arc/semicircles and intercept on the real axis (horizontal axis) give the value of bulk conductance G. As stated in the section 2, the bulk conductivity is calculated by the relation

$$\sigma = GL/.A$$

Table 1 and figure 3 shows the variation of the bulk or overall conductivity of the different polymeric films. From the plot it can be seen that initial conductivity is the bulk conductivity of the pristine polymer electrolyte with no dispersal of dispersoid copper sulfide. But with the addition of the copper sulfide in the polymer electrolyte, there is first increase in the bulk conductivity, obtaining the peak value and then decreases. The peaking in the plot could be explained on the basis of Mayer's space charge model [19] as follows. Initial conductivity of the pristine polymer electrolyte is primarily due to ions which are in the dissociated forms. With the addition of the third phase dispersoid copper sulfide in the polymer electrolyte, the ion association in the composite decrease resulting generation of access numbers of ions. As result of which there is enhancement of the overall conductivity in the composites. The conductivity gets the maximum value 7.6 x 10^{-6} S/cm and decreases due again association of ion pairs.

Table 1: Conductivity measurement of the different composites films

Sample	CuS concentration (Wt. %)	Total conductivity (σ_T) at 303 K (X 10^{-6} S/cm)
PEO:NH_4ClO_4(96:4)	0	1.00
PEO:NH_4ClO_4(96:4)	1	1.80
PEO:NH_4ClO_4(96:4)	2	7.60
PEO:NH_4ClO_4(96:4)	3	2.38
PEO:NH_4ClO_4(96:4)	4	2.20
PEO:NH_4ClO_4(96:4)	5	1.29

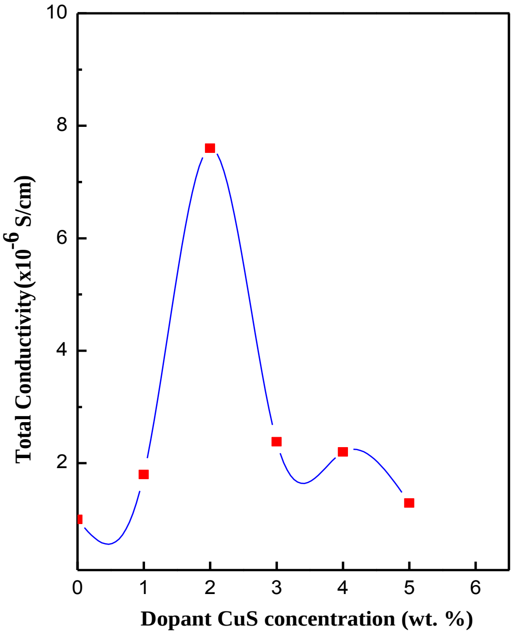

Fig 3: Variation of total conductivity with the weight percentage of dispersoid cupper sulfide

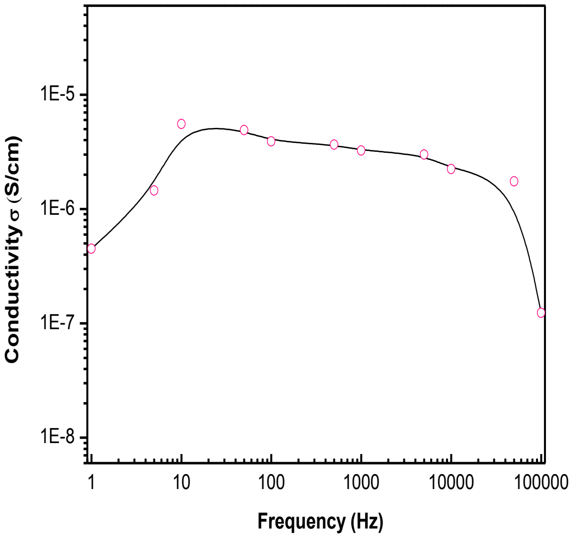

Fig 4: Total conductivity vs frequency plot for the polymer electrolyte PEO: NH_4ClO_4 with the 3 wt. % dispersoid cupper sulfide.

The frequency response for the conductivity of 3 wt.% copper sulfide in the composites is shown in the figure 4. From the plot it can be depicted that, there is a plateau region for the frequency range from 10 Hz to 50 KHz. The decreases in conductivity before and after plateau region could be explained as follows. The small value of the conductivity in the very low frequency region is due to polarization and resulting accumulation of ions to the respective electrodes. At low frequency the nonionic transport contribute to the total conductivity which could be electronic/hole conductivity which is very small portion in the ionic conductor. At the very high frequency the sample is considered as microscopic dipole which has to follow the polarization with the frequency of applied electric field with some delay. The value of the conductivity of the sample depends on the easiness of the translational motion of the ions through the sample with the minimum delay. As the very high frequency, the conductivity decrease due to increase of delay discussed above.

In the polymer electrolyte composites when the small potential is applied, there is polarization of ions to the electrode electrolyte interface and final current is due to electrons or hole. Depending on the access no of electrons or holes present in the sample, we can inference the nature of type of material (n type or p type). According to Wagner [20], the relation between applied voltage and current is given below

$$I_e = RT\frac{A}{LF}.\sigma_e[1-e^{(-\frac{VF}{RT})}] \qquad I_h = RT\frac{A}{LF}.\sigma_h[e^{(\frac{VF}{RT})}-1]$$

Where T is the temperature in (^{o} K), A area of the sample, L is the thickness of the sample, F is the Faraday constant and R is a gas constant. At room temperature (298 K) and at moderate voltages, the value of exp (VF/RT)>>1, then two equations becomes

$$I_e = RT\frac{A}{LF}\sigma_e \qquad I_h = RT\frac{A}{LF}\sigma_h\, e^{(\frac{VF}{RT})}$$

Hence from the above relation it is clear that the electronic conductivity or I_e is independent at moderate high voltage and however I_h it increases exponentially with applied voltage in the case of hole conductivity.

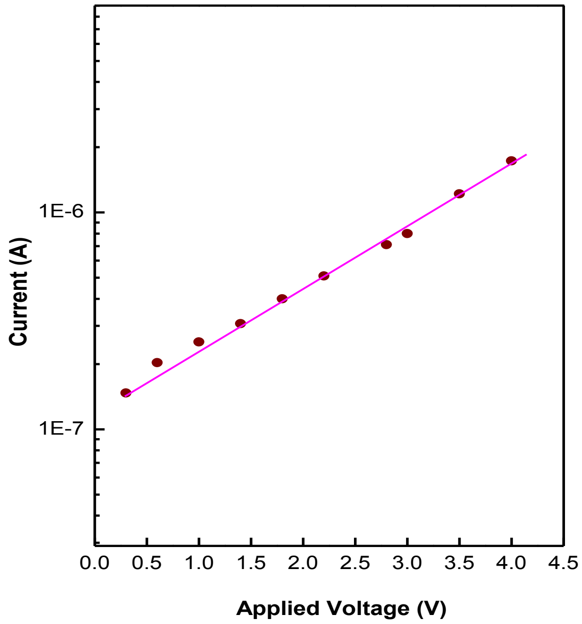

Fig 5: I-V Plot for the polymer electrolyte with the 3 wt. % cupper sulfide dispersoid

The variation of the final or residual current with polarizing applied voltage for the 3 (wt. %) of cupper sulfide is shown in the figure 5. From the plot, it is clear that the current increases with low voltage to moderate voltage (0-4.5 V). Hence from the plot it is concluded that holes act as the majority charge carriers in the composite and dispesoid copper sulfide in the sample is p type.

Conclusion

In summary, the composite polymer electrolytes of PEO: NH_4ClO_4 (96:4) with the dispersal of copper sulfide (0-6 wt.%) are successfully prepared by in situ method. The composites films are characterized with the various electrical studies. The bulk conductivity is calculated by the impedance plots and maximum conductivity is found to be 7.6 x 10^{-6} S/cm. The enhanced conductivity and decrease in conductivity after the peak value could be explained by Mayer's space charge model. Conductivity dispersion curve showed the plateau region from 10 Hz to 10 KHz. Wagner's polarization showed the p type nature of the copper sulfide dispersoid in the composites.

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