AC Conductivity and Spectroscopic Studies of Copper Oxide Nanoparticles Doped HPMC/PVA Polymer Electrolytes

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Abstract: hydroxypropyl methylcellulose (HPMC) / poly vinylalcohol (PVA) blends doped with different ratio of copper oxide (CuO) nanoparticles were prepared using solution cast technique. The prepared samples were analyzed for AC conductivity using LCR meter (ZM2376) with in the frequency range 50 Hz to 1 MHz at room temperature. Jonschers power law holds good for the plots of AC conductivity in the high frequency region. DC conductivity is calculated from the plateau region of ac conductivity plots. We observe that the obtained dc conductivity values matches with the calculated conductivity value from bulk resistance. The presence of non-debye type conductivity relaxation is observed in this reported polymer electrolytes by analysing complex electrical modulus.

Keywords: Polymer electrolytes, AC conductivity, complex electrical modulus.

1. INTRODUCTION

In recent years, polymer blends doped with suitable nanoparticles are the specially focused materials for exhibiting unique chemical and physical properties and finds wide applications in the fields of nano-electronic devices, super capacitors etc. [1-3]. Electrolytes used in electronic gadgets and batteries might show high conductivity, but they are non-biodegradable and not safe to our environment. Hence in our reported work, we have concentrated on the preparation of bio-polymer blends of hydroxypropyl methylcellulose (HPMC) and Polyvinyl alcohol (PVA) doped with copper oxide (CuO) nanoparticles. HPMC polymer is chosen as it is more thermally stable when compared with other cellulose derivatives like methylcellulose (MC) and carboxymethylcellulose (CMC). Polyvinyl alcohol (PVA) is also a water-dissolvable biopolymer with good chemical resistance, thermal stability and mechanical strength [4-5]. Copper Oxide (CuO) is a low cost non-toxic p-type semiconductor material and is used in the preparation of electrochemical cells, gas sensors, solar cells, optical switches etc. [6-8]. The HPMC/PVA polymer blends are used as the host material to synthesize different nanocomposites by doping with different ratios of CuO nanoparticles. Incorporating CuO nanoparticles into the polymer blend matrix may bring remarkable changes in conductivity and electrochemical stability.

2. EXPERIMENTAL WORK

Sample Preparation

Polyvinyl alcohol (PVA) and Hydroxypropyl methylcellulose (HPMC E15LV) was purchased from Loba Chemicals India, CuO nanoparticles were purchased from S. D. Fine Chemicals India. Test samples were synthesized using solution cast technique. HPMC/PVA blends were prepared by using double distilled water as solvent. Different wt.% (1% - 4%) of CuO nanoparticles was slowly added into the blends and stirred for hours in magnetic stirrer to obtain clear homogeneous solution. This solution was then put inside the clean and leveled glass plates and allowed to evaporate at room temperature for few days. The peeled of thin films of polymer electrolytes were kept in desiccators for further data characterization.
Instrumentation

The AC conductivity measurements were carried out on these test samples within frequency range of 50Hz to 1MHz using LCR meter (ZM2376). The disc samples painted with air drying silver paste is kept between the stainless steel electrodes sample holder for the measurements.

3. RESULTS AND DISCUSSION

Complex Impedance Spectroscopy Studies

The complex impedance ($Z'$) is given by the following equation [9]

\[
Z' = Z' + j Z'' \quad \text{----------------------} (1)
\]

Where $Z'$ the real part and $Z''$ is the imaginary part of the impedance modulus given by

\[
Z' = \frac{1}{2\pi f C_0 \left[\varepsilon''/\varepsilon'' + j\varepsilon''/\varepsilon''\right]} \quad Z'' = \frac{1}{2\pi f C_0 \left[\varepsilon'/\varepsilon'' + j\varepsilon'/\varepsilon''\right]} \quad \text{----------------------} (2)
\]

Where ' f ' is frequency, ' $C_0$ ' is the capacitance of vacuum. $\varepsilon'$ and $\varepsilon''$ are the real and imaginary parts of dielectric permittivity.

Fig. 1 displays the complex impedance plots of $Z'$ (Cole-Cole plots) for HPMC/PVA - CuO polymer electrolytes. The different relaxation time of the charge carriers is revealed as the Argand plots with incomplete semicircular arc is seen with a diameter below the real impedance ($Z'$) axis [10]. It is clearly visible that the second semi-circle is absent which is evident for the negligible contribution of the electrode-material towards impedance. The decentralization of the semicircle shows the non-Debye sort of relaxation which obeys Cole – Cole's formalism. The bulk resistance ($R_b$) of the polymer electrolytes can be estimated from the intercepting point of the high-frequency semicircular arc with the real axis of the complex impedance. Fig. 1 clearly indicates that the $R_b$ value decreases with increasing dopant ratio of CuOnano particles. It can be observed clearly that the polymer blend electrolyte doped with 3Wt.% of CuO nanoparticle exhibits the least $R_b$ value of $0.49 \times 10^6$ Ω, Hence its ionic conductivity is high. The addition of CuO nanoparticles (4wt.%) increased the $R_b$ value indicating decrease in the ionic conductivity. This is because at high dopant concentration, more copper ions get accumulated into polymer host matrix which hinders the ion movement [11].
3.2 AC Conductivity Analysis

The AC conductivity \(\sigma_{ac}\) of the reported polymer-electrolyte films were calculated using real \((Z')\) and imaginary \((Z'')\) parts of complex impedance \((Z^*)\) using the following equation [12].

\[
\sigma_{ac} = \frac{Z_r}{(Z_r^2 + Z_i^2)} \left( \frac{1}{\lambda} \right) \quad (3)
\]

Fig. 2a and 2b displays room temperature AC conductivity for HPMC/PVA hosted polymer samples. It can be seen from figure 2b that the value of \(\sigma_{ac}\) increase sharply as the frequency increases. The increase in AC conductivity is due to the small values of capacitive reactance \((X_c = \frac{1}{2\pi fC})\) at high frequencies. The dc conductivity \((\sigma_{dc})\) values can be achieved by extrapolating the plateau region to the y-axis of the curve as shown in the plots of Fig. 2b. The extracted values of \(\sigma_{dc}\) from the plots of Fig. 2b are in good agreement with the bulk resistance values obtained from plots in figure 1, that is, the system HPMC/PVA – CuO (5:5:3 wt.%) with low bulk resistance \((R_b)\) value exhibits a high DC ionic conductivity of \(3.6 \times 10^{-5}\) S/cm. The frequency-dependent electrical conductivity for the present nanocomposite polymer-electrolyte system follows the Jonscher’s universal power law [13].

\[
\sigma (\omega) = \sigma_{dc} + A\omega^s \quad (4)
\]

Where ‘S’, ‘A’ and ‘\(\sigma_{dc}\)’ are the frequency-exponent, pre-exponential factor and dc conductivity respectively. The contribution of dc conductivity at lower frequency is due to the jumping of ions from one available site to another neighboring vacant site in the host polymer matrix. This successful ion hopping takes place for the frequency lower than that of hopping frequency. A successful hop occurs when the frequency is lower than the hopping frequency. The bulk conductivity of solid polymer electrolytes for all temperature signifies the frequency-independent region of the AC conductivity spectra [14]. More dispersive conductivity is observed at higher frequencies is because of the forward and backward hopping movement of ions [15].
3.3 Electrical Modulus Analysis at Room Temperature

FIGURE 3. Complex electrical modulus spectrum ($M'$ vs. $M''$)

The electrical modulus analysis is convenient in understanding the relaxation behavior of ionic materials. The complex electrical modulus ($M'$) can be calculated by using the following relationship [16].

$$M' = M + iM''$$  

Where

$$M' = \left[ \frac{\epsilon'}{\epsilon'' + \epsilon'''} \right]$$  

$$M'' = \left[ \frac{\epsilon''}{\epsilon'' + \epsilon'''} \right]$$  

Fig. 3 displays the room temperature spectrum of complex electrical modulus ($M'$ vs $M''$) for HPMC/PVA – CuO nanocomposite samples. The appearance of only one semicircular arc in the argand plots ($M'$ vs $M''$) shows the existence of ionic conductivity relaxation in these polymer-electrolytes (17). The smallest semicircle of the plots corresponds to the highest capacitance value (HPMC/PVA – CuO 3wt.% sample). An exact semicircle is not seen instead, a deformed shape of semicircle whose center is positioned below the x-axis is seen, which is the clear evidence for the presence of the spread of relaxation with different time constants. Therefore it can be concluded that non-debye type of relaxation process is present in these nanocomposite polymer electrolyte systems. The non-existence of semicircular arcs with single relaxation time reveals that ion transport is associated with the segmental motion of polymer chains. Consequently, copper ion transport through HPMC/PVA blend polymer chain occurs through the viscoelastic relaxation processes [18]. It is also evident from the plots that the sample HPMC/PVA – CuO 3wt.% which exhibits high value of $\sigma_{dc}$ (Fig. 3) shifts more towards the origin. This is related to the low resistance value of that sample ($M'' = \omega C_{0}Z_{r}$) (32).

4. CONCLUSION

Copper ion conducting thin films of HPMC/PVA hosted solid nanocomposite biopolymer electrolytes were prepared successfully by adopting Solution casting technique. The AC conductivity spectra at high frequency region obey Jonschers power law with two distinct regions. It is observed that, as the CuO dopant concentration increases, the ionic conductivity increases and becomes maximum for CuO 3wt.% doped HPMC/PVA biopolymer nanocomposite films. This shows the increase in the number of charge carriers is responsible for the high ionic conductivity. The dc conductivity obtained from the plateau region of ac conductivity plots closely matches with the calculated conductivity value from the bulk resistance. The polymer electrolyte thin film with CuO 3wt.% dopant concentration is more stable with high ionic conductivity and suitable for electrochemical device applications.

5. ACKNOWLEDGMENTS

I thank department of engineering Physics, VVCE, for providing LCR meter facilities for the reported study.
6. REFERENCES

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