

Conductivity study of Carboxyl methyl cellulose Solid biopolymer electrolytes (SBE) doped with Ammonium Fluoride

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Abstract

Carboxyl methyl cellulose (CMC) doped with ammonium fluoride (NH_4F) solid biopolymer electrolyte (SBE) was prepared via solution cast technique. The ionic conductivity of CMC- NH_4F was measured using electrical impedance spectroscopy in temperature range from 303K to 333K. The highest conductivity observed is $2.68 \times 10^{-7} \text{ Scm}^{-1}$ for sample containing 9 wt. % NH_4F at 303K. The ionic conductivity of the samples increases proportionally with temperature which implies that these samples obey Arrhenius behavior. Activation energy graph plotted shows highest conductive sample attain lowest activation energy value. The dielectric analysis of the CMC- CN_4F SBE as ascertained from electrical impedance spectroscopy reveals that the highest conductivity sample has the highest dielectric constant at ambient temperature. These samples appear to be ionic conductor of non-Debye type.

Keywords: Solid biopolymer electrolyte, carboxyl methylcellulose, ammonium fluoride, ionic conductivity, dielectric analysis.

Introduction

In the past few decades, the study on developing solid biopolymer (SBE) electrolyte has caught the attention of many researchers¹⁻⁷ due to the high potential of the solid biopolymer electrolytes to be used as an electrolyte in battery system. Since the environmental conditions at present is seriously polluted makes finding devices with green materials much more desired⁸. Furthermore, with the electricity price is hiking up day by day makes low cost electrical devices more popular⁹. SBEs have the advantages of good contact surface with the electrodes, low self-discharge in batteries and less problems in leakage or pressure distortion; furthermore it is easy to produce and very affordable^{2,3,10}.

The bio-derived polymer such as Carboxyl methylcellulose^{1,2,5,6,11}, methylcellulose^{3,12}, cellulose acetate¹³ and chitosan were made from natural materials and it is most abundant materials on earth respectively^{2,4}. Carboxyl methylcellulose or CMC in short, is one of cellulose derivatives materials made from plants. In the other hand, CMC SBE thin films have good mechanical and electrical properties; furthermore it is non-toxic material, biodegradable and good film formability^{1,2,5,6,11,14}. Generally, the ionic conductivity of CMC is not that impressive but it can be enhanced with the addition of proper dopant^{5,6,14}. Hence in this work, ammonium fluoride was chosen to form CMC- NH_4F SBE system. Commercially, ammonium fluoride (NH_4F) is a white crystalline solid and it is highly soluble in water. The dielectric properties of the CMC- NH_4F SBEs films were analyzed via

electrochemical impedance spectroscopy at ambient to elevated temperatures in this present work.

Methodology

Sample Preparation: All the CMC- NH_4F SBE films were prepared using solution cast technique at room temperature⁹. CMC (Acros Organics Co, average molecular weight 90000, D.S. 0.7) was dissolved in distilled water. Then 3 wt. % of NH_4F (R&M Co) was added and was stirred continuously until homogenous solution was obtained. The obtained solution was cast into several petri dishes and dried at 50°C for films to form. Similar method was used for different wt. % NH_4F (5-13 wt %). A sample of CMC without dopant was also prepared as control sample. Table-1 shows the composition of the CMC- NH_4F SBE.

Table-1
Composition of electrolytes

Sample	CMC(g)	NH_4F (wt. %)
CMC-0	2	0
CMC-3	2	3
CMC-5	2	5
CMC-7	2	7
CMC-9	2	9
CMC-11	2	11
CMC-13	2	13

Ionic Conductivity Analysis: The ionic conductivity of CMC-NH₄F SBE was determined by using HIOKI 3532-50 LCR Hi-Tester and calculated using equation-1¹⁻⁷.

$$\sigma = \frac{t}{AR_b} \quad (1)$$

where t is the thickness of the SBE thin film, R_b is the bulk resistance of the sample and A is the area of contact of the SBE with the electrodes. All samples were tested in the range from 303K to 333K and the temperature dependence graph was plotted to inspect the behavior of the samples with temperatures. The conductivity-temperature correlation of SBEs usually obeys Arrhenius behavior with the regression value is almost unity ($R \approx 1$). This can be determined by using equation-2.

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{kT}\right) \quad (2)$$

Where σ_0 is the pre-exponential factor, E_a is the activation energy and k is Boltzmann constant. The relative permittivity of an ionic system is a dimensionless ratio of permittivity, ϵ to the permittivity of space, ϵ_0 and can be described as real and imaginary component in which has 90° out of phase between these two components¹⁰. These were represented in equation below.

$$\epsilon_r(\omega) = \frac{\epsilon^*(\omega)}{\epsilon_0} = \epsilon_r(\omega) - j \epsilon_i(\omega) \quad (3)$$

Here ϵ_r is the dielectric constant, $\epsilon_0 = 8.8541817 \times 10^{-12} \text{ F m}^{-1}$, ϵ_i is the dielectric loss and $j = \sqrt{-1}$ respectively¹⁰. The dielectric constant and loss was calculated using equation-4 and equation-5⁵.

$$\epsilon_r = \frac{Z_i}{\omega C_0(Z_r^2 + Z_i^2)} \quad (4)$$

$$\epsilon_i = \frac{Z_r}{\omega C_0(Z_r^2 + Z_i^2)} \quad (5)$$

Here $C_0 = \epsilon_0 A/t$ (ϵ_0 is permittivity of free space), $\omega = 2\pi f$ (f is frequency), Z_i is the imaginary part of the complex permittivity and Z_r is the real part of the complex permittivity¹¹. The use of electric modulus analysis to study ionic transport dynamics is debatable since its inception in the 80's. Never the less, function of electric modulus is generally successful at low frequencies¹⁰. The real part and imaginary part of electrical modulus were calculated using the equation-6 and equation-7.

$$M_r(\omega) = \frac{\epsilon_r}{(\epsilon_r^2 + \epsilon_i^2)} \quad (6)$$

$$M_i(\omega) = \frac{\epsilon_i}{(\epsilon_r^2 + \epsilon_i^2)} \quad (7)$$

Here ϵ_r is the dielectric constant and ϵ_i is the dielectric loss⁶.

Results and Discussion

Ionic Conductivity analysis: The ionic conductivity, σ of the CMC-NH₄F SBEs at room temperature is illustrated in figure-1. It can be observed from figure-1 that the ionic conductivity of the CMC-NH₄F SBE best explained into two regions. In region-1, the ionic conductivity increases with the increase in concentration of NH₄F. The highest ionic conductivity reached was $2.68 \times 10^{-7} \text{ Scm}^{-1}$ for sample containing 9 wt. % NH₄F.

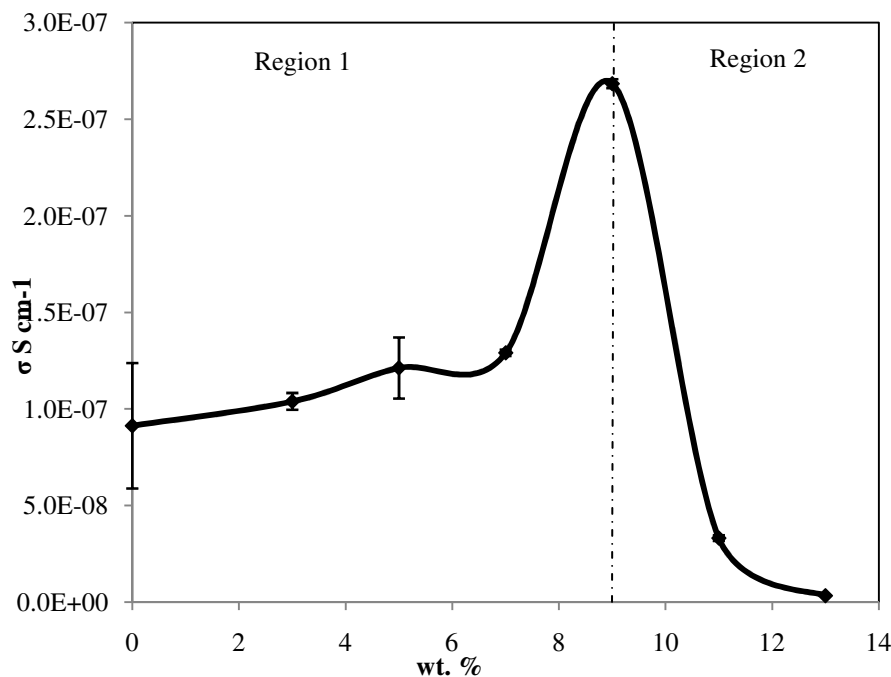


Figure-1
Ionic conductivity of CMC-NH₄F biopolymer electrolyte at 303K

The increasing in ionic conductivity of the CMC-NH₄F SBE can be explained as the increasing in number of mobile charge carriers and also may due to the interactions between CMC and NH₄F brings to high dispersion of proton, H⁺, thus enhance the ionic conductivity¹². In region-2, the ionic conductivity was decreases to such a degree with the addition of NH₄F. It is believed that the ionic mobility decreases due to the overcrowded of the mobile ions from the ionic dopant as a result from too many ions disperse throughout the CMC-NH₄F system^{1, 14}.

The activation energy of CMC-NH₄F was determined using equation-2 and depicted in figure-2. Theoretically, activation energy, E_a is the minimum energy required by an ion to escape from its bond by jumping to another region^{15,16}. However, the ionic conductivity of sample CMC-3 and CMC-5 increases with increasing E_a . The increased in ionic conductivity of the samples are believed to be influenced by the diffusion

coefficient and mobility of mobile ions besides the number of mobile ions⁵, despite having high activation energy. On the other hand, the value of E_a for other samples is inversely proportional to the ionic conductivity value.

Figure-3 shows the temperature dependence plot for selected samples of CMC-NH₄F biopolymer electrolytes in the range from 303K to 333K. From the plot, it is observed that these samples are thermally activated where the conductivity increases with temperature. The increase in conductivity was due to the thermal expansion of the sample which creates more free volume for the charge carriers to move¹⁶. With increase in temperature, there are more free volume making the ions to move more freely thus increasing the ionic conductivity in return¹⁷. This suggests that the CMC-NH₄F system obeys Arrhenius behavior further confirming that these SBE are ionic conductor¹⁸.

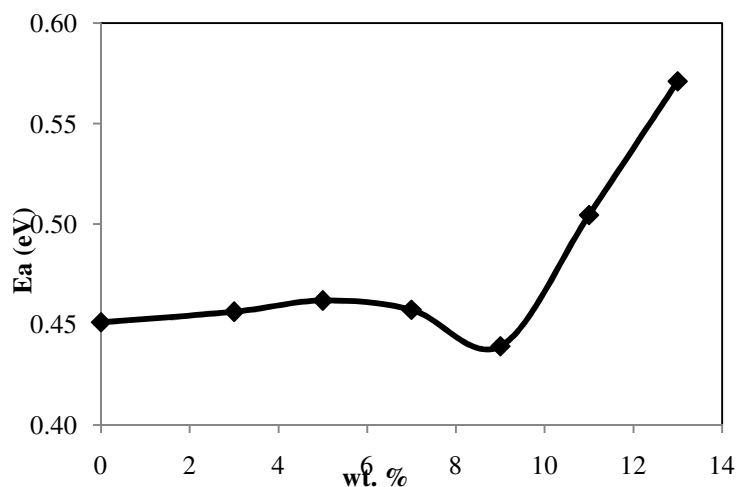


Figure-2

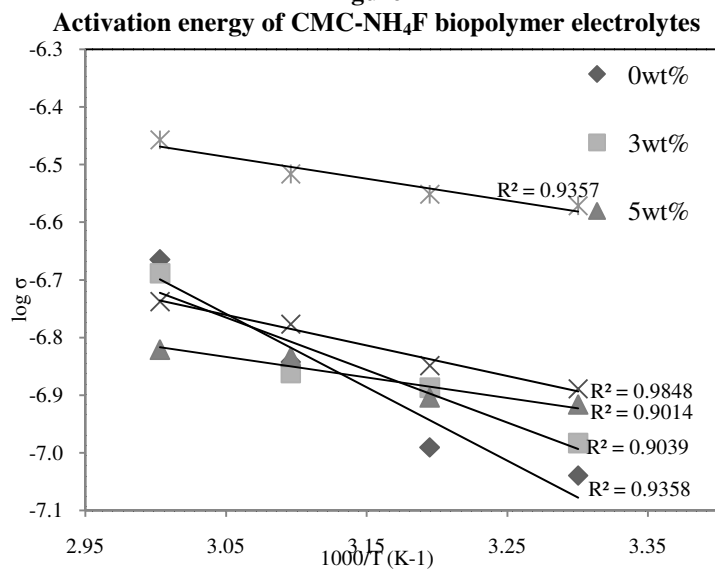


Figure-3

Temperature dependence of selected samples

The analysis of dielectric for biopolymer electrolytes system is a reliable approach for obtaining information regarding the characteristics of the ionic and molecular interactions¹⁸. Figure-4 represents the frequency dependence of dielectric constant,

ϵ_r with different composition of NH_4F with frequency. Meanwhile figure-5 and figure-6 represents the dielectric constant and loss for sample CMC-9 respectively.

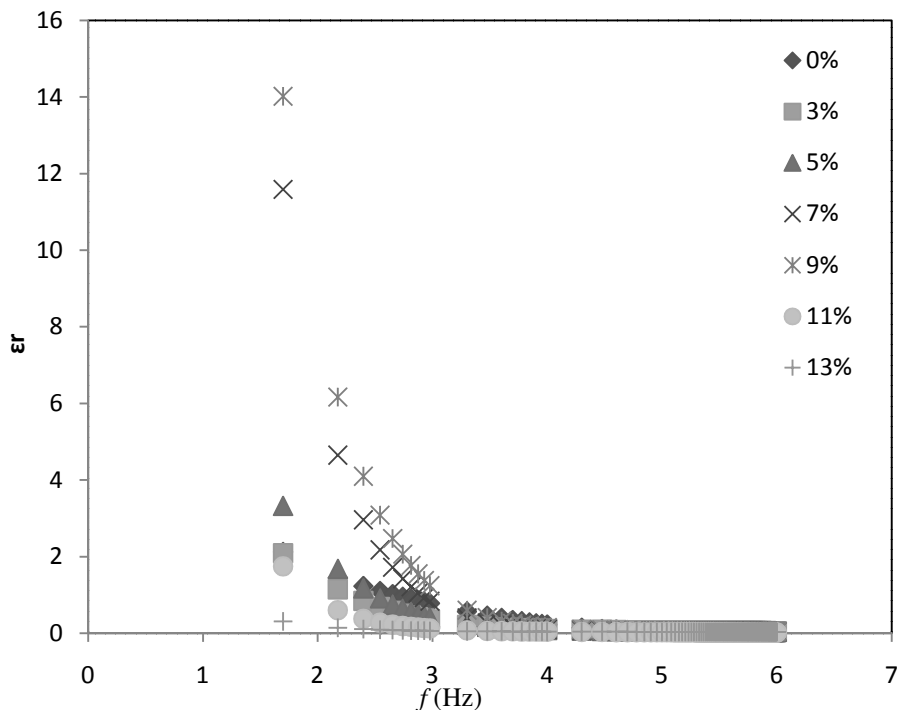


Figure-4
Dielectric constant for every sample with log frequency at 303K

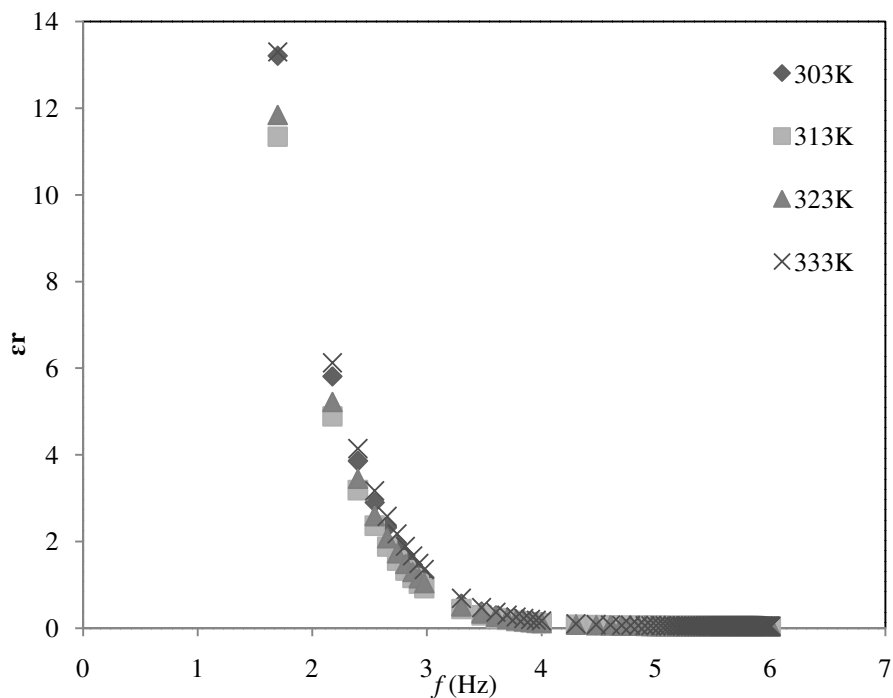


Figure-5
Dielectric constant for sample CMC-9 with log frequency

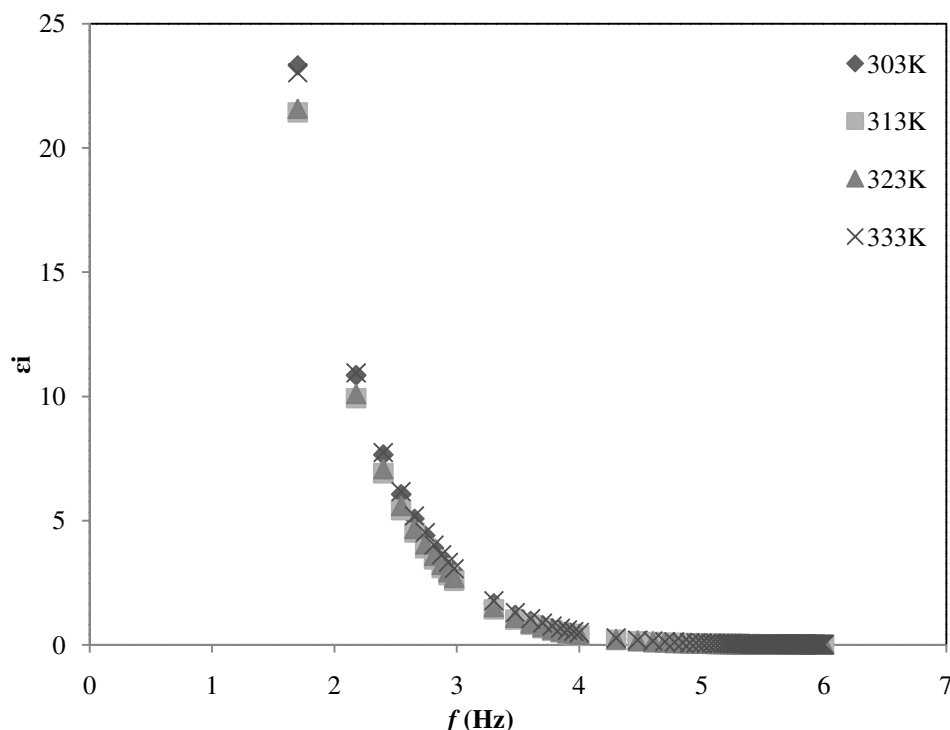


Figure-6
Dielectric loss for sample CMC-9 with log frequency

From figure-4, it is observed that with the addition of NH_4F the value of dielectric constant was increased. This trend clearly follows the conductivity analysis as described earlier with sample CMC-9 has the highest ionic conductivity and has the highest value of dielectric constant as well. The highest dielectric constant for the highest conductive sample was due to the increased number of charge carriers which resulted from the salt dissociation in the polymer matrix¹⁰. Figure-4 and figure-5 shows that the dielectric constant, ϵ_r , raise sharply at low frequencies and gradually dropped at higher frequencies. The sharp rise at low frequency was probably acted by a number or more of different types of contribution polarization factors whether electronic, atomic, ionic, and interfacial but the dielectric constant at high frequency was depends on the ionic movement, ion-ion orientation, and space charge effects^{16, 20-22}. The sharp rise at low frequencies signified that electrode polarization and space charge effects have occurred, confirming the non-Debye dependence for this samples^{13,20}. Meanwhile, as the frequency increases, the ϵ_r decreases and this may be due to the electrical relaxation process which the ionic and orientation source of polarization start to decrease at higher frequency and finally disappears as a result from the inertia of mobile ions²³.

Dielectric loss ϵ_i is the direct measure of dissipated energy and generally contributes in the ionic transport and the polarization of the charge²⁰. From figure-6, the ϵ_i shows the same pattern with ϵ_r (figure-5). The high value of ϵ_i at low frequency was observed and this event can be explained in which due to the

enhancement in mobility of charge carrier and can be related to the free charge motion within the electrolytes. The value of ϵ_i decreases at higher frequencies may due to the lesser ions that can pile up at the interface which have faster rate in direction of the electric field change²³.

By using dielectric modulus, a successful analysis of dielectric behavior of CMC- NH_4F SBE was achieved which suppressed the effect of electrode polarization²⁰. Figure-7 and Figure 8 shows the real, M_r and imaginary, M_i part of the modulus of sample CMC-9 respectively. Based on figure-7, the value of M_r is low and approaching zero at lower frequencies region. With frequency increases, the value of M_r start to increase as well for all temperatures. From these observation, it may be related to a lack of restoring force leading the mobility of charge carriers under the action of an induced electric field. This behaviour supports the conduction occurrences because of the long-range of charge carriers. Both figures, the dispersion of real and imaginay part of the electrical modulus, shows sharp rise at higher frequencies^{20,24}. From figure-8, it is observed that well defined peak are present and this demonstrates that this sample is an ionic conductor. This event has been reported in almost in every polymer electrolytes systems, the possible peak at higher frequencies represents that it is an ionic conductors^{20, 25}. At lower frequencies, both M_r and M_i move towards zero implying that there is large association between the values of capacitance with the electrodes²³.

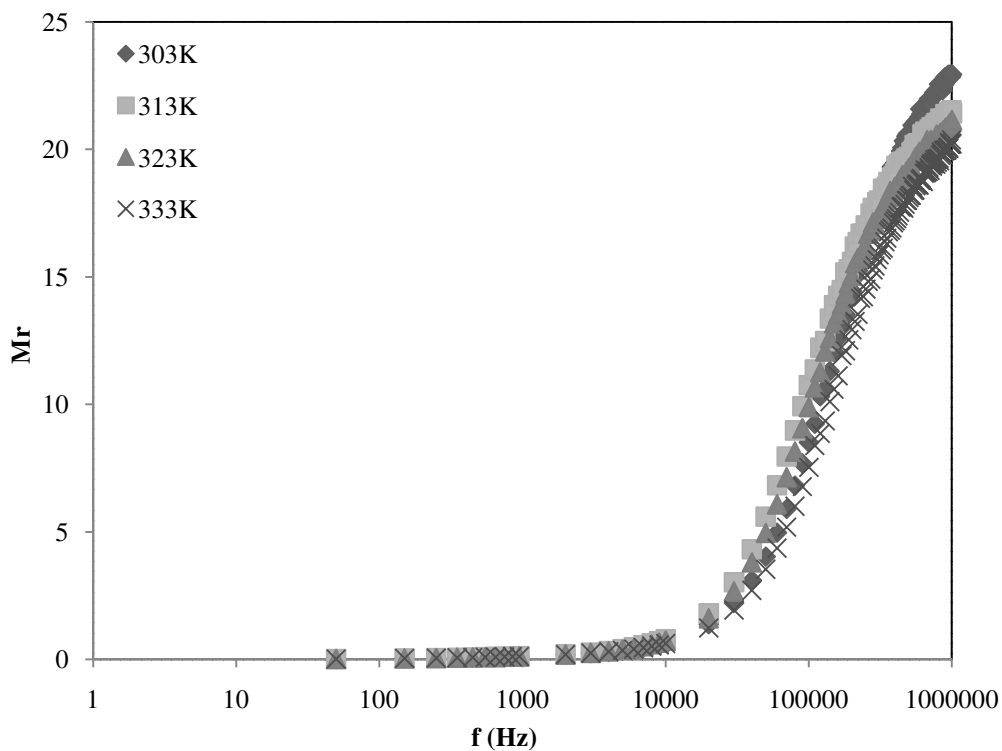


Figure-7
Dispersion of real part of the electrical modulus for sample CMC- 9 with log frequency

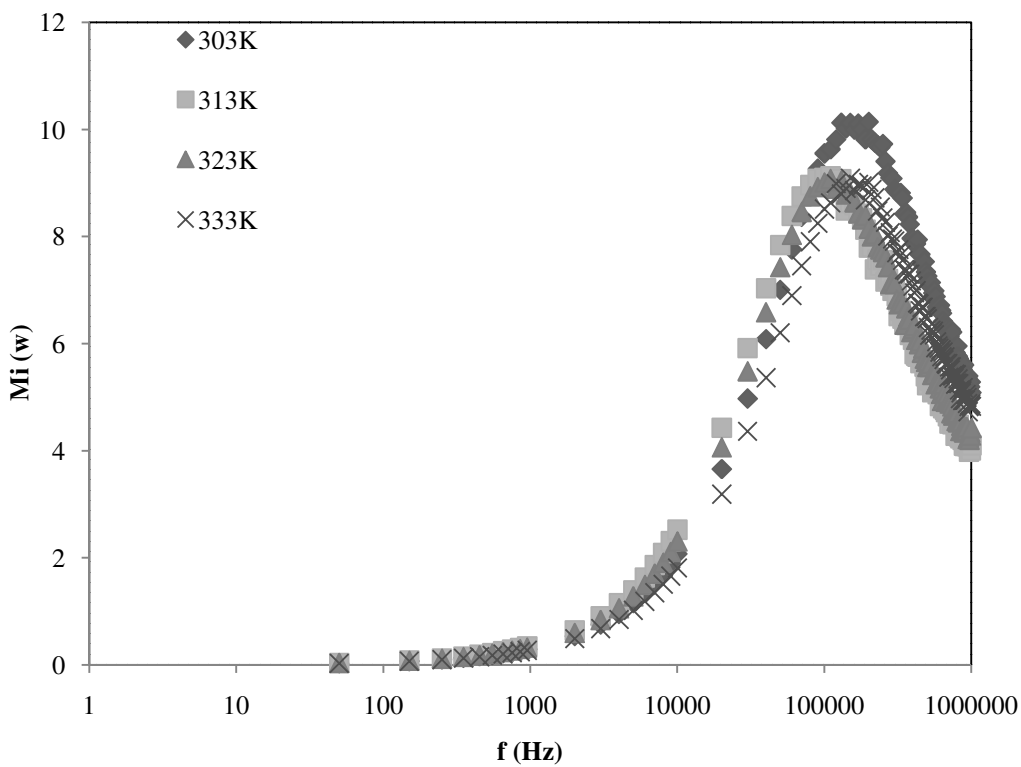


Figure-8
Dispersion of imaginary part of the electrical modulus for sample CMC- 9 with log frequency

Conclusion

Solid biopolymer electrolyte based on Carboxyl methyl cellulose (CMC) as host and doped with NH_4F ranged from 0 to 13 wt. % was successfully formed via solution cast technique. The highest ionic conductivity obtained is $2.68 \times 10^{-7} \text{ S cm}^{-1}$ for sample containing 9 wt. % NH_4F at 303K. The value of activation energy of the highest conductive sample was found to be the lowest. The samples show Arrhenius behavior where the conductivity is thermally activated. The dielectric analysis shows that this sample follows the non-Debye dependence and the samples are ionic conductor since the ionic conductivity increases at higher temperature.

Acknowledgements

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