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Conduction mechanism of enhanced CMC–NH$_4$Br biopolymer electrolytes

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Abstract. This study deals with the ionic conduction mechanism of carboxymethyl cellulose (CMC) – NH$_4$Br biopolymer electrolytes (BPEs) plasticized with ethylene carbonate (EC) prepared via solution-casting technique. The ionic conductivity of BPEs system was characterized by using impedance spectroscopy and shows the highest conductivity at ambient temperature for CMC– NH$_4$Br BPEs is 1.12×10^{-4} S/cm and enhanced to 3.31×10^{-3} S/cm with the addition of 8 wt. % EC. The conductivity–temperature plot of the BPEs system obeys Arrhenius law where $R^2 \sim 1$. The dielectric values were found to increase with increasing temperature thus divulged that the BPEs system to be non-Debye type. The temperature dependence of the power law exponent shows the CMC–NH$_4$Br–EC BPEs system follows the quantum mechanical tunneling (QMT) model of conduction mechanism, where the enhanced protonation of NH$_4$Br with addition of EC makes the charge transfer (polarons) able to tunnel through the potential barrier that exists between the lone pair electrons in carboxyl group of CMC and NH$_4$Br.

Introduction

Solid polymer electrolytes (SPEs) based on biopolymer materials have received great interests recently for applications in electrochemical devices due to their advantages such as thermally and mechanically stable [1]. Researchers tried to come out with new idea in order to prepare good polymer electrolytes with high ionic conductivity and good mechanical properties. Thus, there are several techniques that had been chosen such as copolymerization, blending, addition of ceramic filler and plasticization. One of the best and effective technique is the addition of plasticizers where could enhance the conductivity and better contact between the electrolyte/electrode. A high value of dielectric constant of plasticizer could solvate more salt, thus increases the number of free mobile ions that contribute towards the conductivity of the biopolymer electrolyte [2, 3]. From the polymerist point of view, the term plasticizer refers to a species, which will decrease the glass transition temperature of the biopolymer electrolyte and hence increase the segmental mobility [3]. Therefore in this work, we present the effect of plasticizer which is ethylene carbonate (EC) on ionic conduction for biopolymer electrolytes (BPEs) based on CMC- NH$_4$Br. The observed frequency and temperature dependence of complex impedance are analyzed using the existing theoretical models proposed to interpret the conduction process in BPEs system.

Methodology

Sample preparation. 2 g of CMC (Acros Organic Co.) was dissolved in distilled water. Then, the solution was added with 25 wt. % of NH$_4$Br (due to the highest ionic conductivity from the previous report) [4] and mixture was stirred continuously until complete dissolution become homogenous. Varied amount of EC were added with different amount in wt. %. The solution was then poured into several Petri dishes and left to dry at room temperature for the films to form. The films were kept in

desiccators for further drying. The composition of the samples and their designation are tabulated in Table 1.

Table 1. Designation for CMC- NH_4Br-EC based BPEs system.

EC composition (wt. %)	Designation
0	AE0
2	AE1
4	AE2
6	AE3
8	AE4
10	AE5
12	AE6

Characterization. For the impedance measurements, the BPEs film was sandwiched between two stainless steel electrodes and HIOKI 3532-50 LCR Hi-Tester impedance spectroscopy was using for the measurement in the temperature range of 303 K to 383 K. The effect of EC composition on the ionic conductivity σ was analyzed based on the frequency dependent electrical properties using the equation explained in [5, 6]. Various dielectric data such as complex dielectric, ε^* is evaluated from the recorded complex impedance data, for each temperature. Both constant, ε_r and loss parts, ε_i of complex dielectric permittivity are related to the measured of Z_r and Z_i for sample as follows:

$$\varepsilon_r = \frac{z_i}{\omega C_o\left(z_r{}^2 + z_i{}^2\right)} \tag{1}$$

$$\varepsilon_i = \frac{Z_r}{\omega C_o\left(Z_r{}^2 + Z_i{}^2\right)} \tag{2}$$

Here $C_0 = \varepsilon_o A/t$, ε_o is the permittivity of the free space, A is the sample-electrode contact area and t is the thickness of the sample. $\omega = 2\pi, f$ being the frequency in Hz.

Results and Discussion

Ionic conductivity studies. Fig. 1 shows the variation of ionic conductivity with EC composition at ambient temperature (303K) for BPEs system.
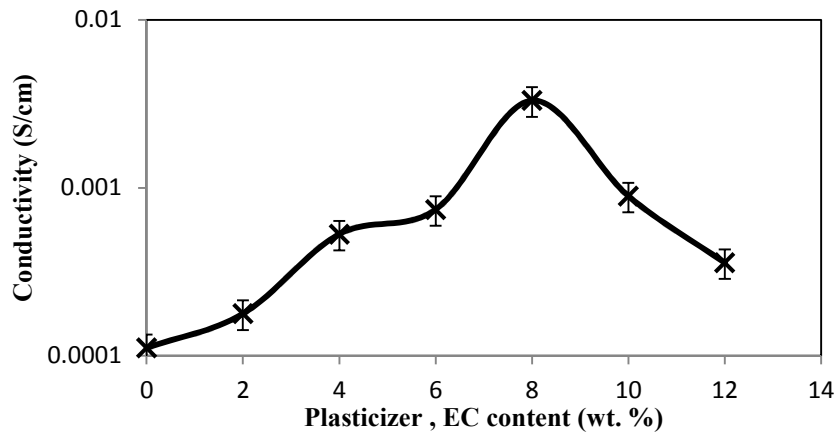

Fig. 1. Ionic conductivity for PEs system at ambient temperature.

From the previous report [4], the highest conductivity for unplasticized BPEs system containing with CMC-NH_4Br was identified at 1.12×10^{-4} S/cm for sample with 25 wt. % NH_4Br (sample AE0) and in the case of plasticized electrolytes, the conductivity increased to a maximum value at 3.31 x

10^{-3} S/cm when 8 wt. % EC was added as revealed for sample AE4. This means that the conductivity increased by four order of magnitude when EC was added in BPEs system. As more EC are added into the CMC-NH$_4$Br complexes, the number of transit sites for the H$^+$ ions to hop increases. It is believed that the function of EC in this BPEs system was provides new pathways of ions to hop and this permit more free volume to be present between the polymer chains and permits a large number of H$^+$ ions to move, thus increase in ionic conductivity. As the composition of EC is increased (greater than 8 wt. %), the ionic conductivity decreases gradually when it reaches 12 wt%. Beyond 8 wt. % of EC, addition of more plasticizer caused aggregation of ions which impedes the movement of mobile ions consequently reducing conductivity [7].

Fig. 2 shows the variation of log ionic conductivity as a function of reciprocal temperature for plasticized BPEs with various samples. The relationship between log conductivity and $10^3/T$ is almost linear where the regression values (R^2) lie close to unity. The increasing ionic conductivity for BPEs system with temperature may be due to the availability and mobility of ions through the EC-rich phase which entraps the residual solvents ensuing ion mobility and this was also due to the increment of thermal stability of film. Thus, favors inter or intra-chain ion hopping and accordingly, the ionic conductivity of the biopolymer electrolytes will be improved with the rise in temperature from 303 to 383 K. From the observation, it can be verified that these plasticized BPEs system obey Arrhenius law where the conductivity mechanism is thermally assisted [8].
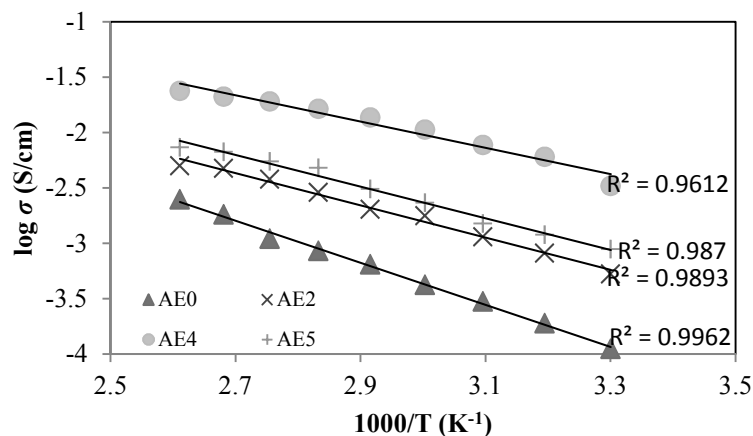

Fig. 2. Temperature dependence of ionic conductivity for PEs system.

Conduction mechanism studies. In this present work, sample AE4 was used for further studies on conduction mechanism due to the highest ionic conducting for plasticized BPEs system. The frequency dependence of the constant part of dielectric (ε_r) at various temperature for sample AE4 are shown in Fig. 3.
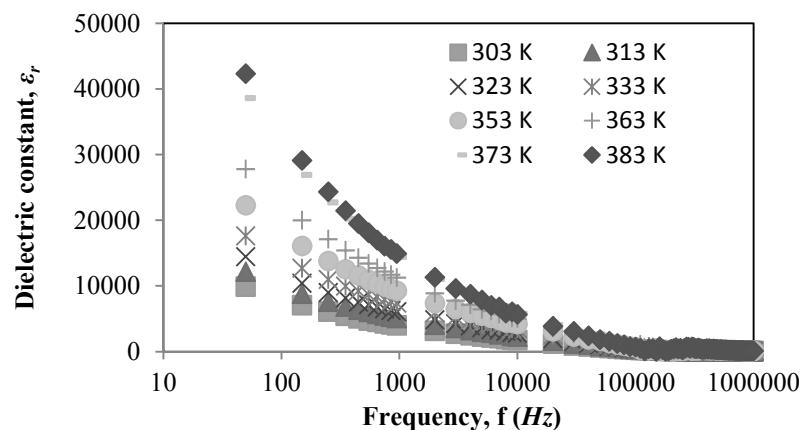

Fig. 3. Dielectric part of constant for sample AE4.

It is clear that ε_r shows the same pattern where all the plots rise towards high temperature but it decreases with the increase in frequency. The high value of ε_r at low frequencies is due to the enhanced charge carrier density at the electrolyte–electrode interface, i.e., due to the accumulation of charged species at the electrode-electrolyte interface [9, 10]. This indicates that as temperature increases, the degree of NH_4Br dissociation increases when EC was added which causes the increase in the number of free ions and in turn enhanced the conductivity of the sample with. Besides, it can be due to the electrode polarization effects which observed increase in the value of ε_r when temperature is applied. No relaxation peaks are observed suggesting that ε_r values may be used as the indicator thus it shows the increasing conductivity is mainly attributed to the increasing free mobile ions [11].
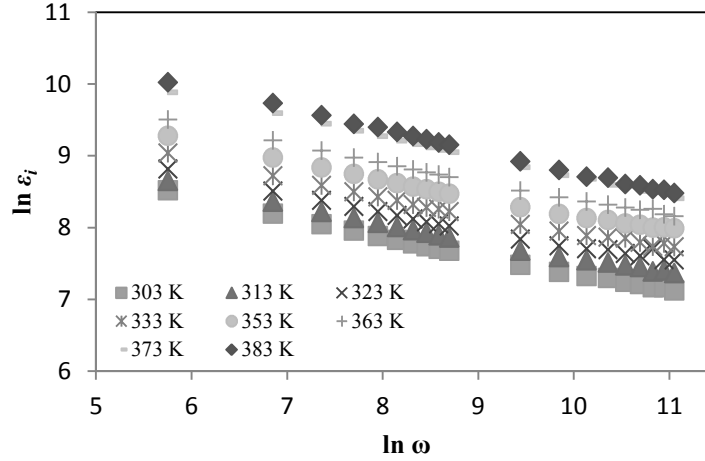

Fig. 4. Plot of ln ε_i vs ln ω for sample AE4.

Fig. 4 shows the plots of ln ε_i as a function of frequency for sample AE4 based BPEs system at various temperatures. It was observed that the ε_i exhibits high values at low frequencies attributable to charge accumulation. As temperature increases, the value of ε_i increases due to the fact that the number of mobile ions increases with introduce of EC in BPEs system. This would generate heat through internal friction and thus causes energy loss. Its shows non-Debye characteristic, which cannot be expressed by a single relaxation equation, has been accounted for by Jonscher's universal power law model (UPL) [12]. The Jonscher's power law model widely has been observed in disordered materials like ionically conducting glasses, conducting biopolymers and also doped crystalline solids [13]. According to UPL, at lower frequencies, an ion can jump from one site to its neighboring vacant site successfully contributing to the dc conductivity of plasticized BPEs as shown in sample AE4. Meanwhile at higher frequencies, the probability for the ion to go back again to its initial site increases due to the short time periods available. Therefore, the ε_i as shown in Fig.4 is obtained only in the electrode polarization region and the acceptable frequency range is 50Hz to 10 kHz. The ε_i is a measure of energy lost due to ionic movement when the polarity of electric field reverses rapidly.

The ac conductivity can be obtained from dielectric loss, ε_i at every frequency according to

$$\sigma_{ac} = \varepsilon_0\varepsilon_i\omega \tag{3}$$

$$\sigma(\omega) = \sigma_{dc} + A\omega^s \tag{4}$$

$$\sigma_{ac} = A\omega^s \tag{5}$$

Here $\sigma(\omega)$ is the total dc and ac conductivity. The dc conductivity, σ_{dc} is the frequency independent component, A is a parameter dependent on temperature and s is the power law exponent with value in the range between 0 and 1. From Eq. 3 and 5,

$$\ln \varepsilon_i = \ln \frac{A}{\varepsilon_0} + (s\text{-}1) \ln \omega \qquad\qquad (6)$$

where σ_{dc} is the d.c. limit of conductivity, A is a parameter dependent on temperature, and s is the power-law exponent with values in the range $0<s<1$ [4, 12]. The values of exponent s can be evaluated from the slope of the plots at higher frequency region where there is no or minimal space charge obtained in plasticized BPEs system. The variation of s with temperature suggests the conduction mechanism of the mobile species. The variation of s with temperature for biopolymer electrolytes system (sample AE4) is plotted in Fig. 5.
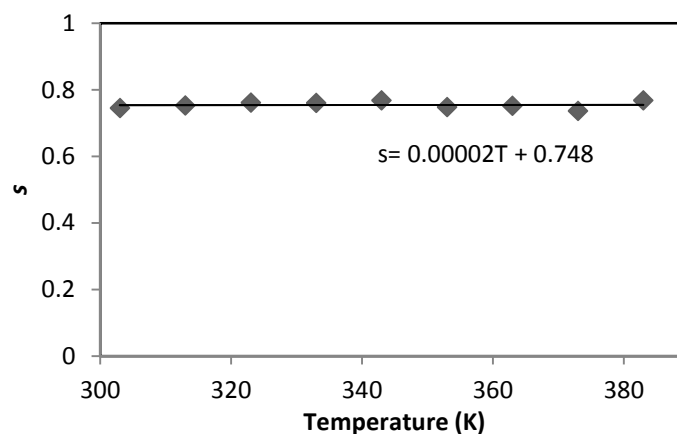

Fig. 5. Variation of exponent s versus temperature.

From Fig. 5, it is observed that exponent s value is found to be constant with increasing temperature and the plot can be best represented by the equation $s = 0.00002T + 0.748$. The small gradient of 0.00002 indicates that s is almost independent of T. Since the exponent s is almost proportional to 0.7 and temperature independent, thus the frequency dependence of BPEs system for sample AE4 is more applicable in explaining the conduction mechanism in terms of QMT model due to the variation of the exponent s with temperature [7, 14]. The conduction modeling obtained is disagreeing with highest conducting unplasticized CMC-NH_4Br sample [4] as previously reported where the conduction model follow SPH model. It can be explained, the QMT model which was fitted in plasticized BPEs system due to the ions (H^+) hopping mechanism. The addition of EC in BPEs system will offer the new pathways for ions to hop therefore; the enhanced protonation of NH_4Br by EC would makes the charge transfer (polarons) able to tunnel through the potential barrier that exists between the lone pair electrons in carboxyl group of CMC and NH_4Br. This conduction model of BPEs system is found to be similar with [8] work in plasticized biopolymer–ammonium salt system where the conduction modeling of their system was performed by QMT model as EC was introduced.

Conclusion

In this present work, CMC - NH_4Br based biopolymer electrolytes (BPEs) plasticized with ethylene carbonate (EC) was successfully prepared via solution-casting technique. The highest conductivity at ambient temperature for CMC–NH_4Br BPEs system is 1.12×10^{-4} S/cm and enhanced to maximum value at 3.31×10^{-3} S/cm with the addition of 8 wt. % EC. The conductivity-temperature of BPEs system obeys the Arrhenius law where the regression values (R^2) was found close to unity. The dielectric values were observed to increase with increasing temperature thus divulged that the BPEs system is non-Debye type. The temperature dependence of the power law exponent shows the CMC–NH_4Br–EC BPEs system follows the quantum mechanical tunneling (QMT) model of conduction mechanism.

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