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To cite this article: M. I. N. Isa & A. S. Samsudin (2017) An enhancement on electrical properties of carboxymethyl cellulose-NH₄Br based biopolymer electrolytes through impedance characterization, International Journal of Polymer Analysis and Characterization, 22:5, 447-454, DOI: [10.1080/1023666X.2017.1316630](https://doi.org/10.1080/1023666X.2017.1316630)

To link to this article: <https://doi.org/10.1080/1023666X.2017.1316630>



Published online: 17 May 2017.



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An enhancement on electrical properties of carboxymethyl cellulose-NH₄Br based biopolymer electrolytes through impedance characterization

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ABSTRACT

In this work, the formulation of biopolymer electrolytes (BEs) system has been accomplished by incorporating various plasticizers with carboxymethyl cellulose-NH₄Br through solution casting technique. The ionic conductivity at room temperature of BEs system was achieved at $\sim 10^{-4}$ S cm⁻¹ with addition of 25 wt% NH₄Br and enhanced to $\sim 10^{-3}$ S cm⁻¹ when plasticizers were added. The temperature-dependence of the BEs system exhibits Arrhenius behavior. Jonschers power law was used to study the electrical properties and shows that the highest conducting BEs system can be represented by overlapping overlapping a large polaron tunneling model for poly(ethylene glycol) system a, small polaron hopping model for glycerol system, and a quantum mechanical tunneling model for ethylene carbonate system.

ARTICLE HISTORY

Submitted 15 March 2017
Accepted 4 April 2017



KEYWORDS

CMC; ionic conductivity; plasticizer; polymer electrolytes; universal power law

Introduction

Studies on solid polymer electrolytes (SPE) have been progressing actively due to their diversify potential application in solid state electrochemical cells, high energy density batteries, fuel cells, sensors, and electrochromic devices upon its discovery by Wright et al. in early 1970s.^[1–3] SPEs have good mechanical properties, can be easily fabricated as thin film, can have a wide range of composition, allowing control of properties, and are able to form effective electrode-electrolyte contacts. Compared to its contender, i.e., liquid electrolytes, SPEs have a very limited or no problem in leakage or pressure distortion.^[4] Currently, many types of polymers have been studied in the pursuit to develop a solid electrolyte system and these include PVA, PVC, and PEO.^[5–7]

In addition, natural polymer such as chitosan, starch, and cellulose were found to have potential to be applied as solid biopolymer electrolytes (SBEs). Recently, due to the good biocompatibility properties, carboxymethyl cellulose (CMC) attracts more attention as representative water-soluble polysaccharide in many research fields.^[8] CMC is particularly interested due to its unique properties, such as provide a good electrode-electrolyte contact, water—soluble materials, abundant in nature, low cost material, and most significant characteristic of CMC, it is biodegradable.^[3,9,10] Formerly, CMC has been utilized in wide applications, such as textile and food industry. It is well-known that CMC is a poor conductor of electricity because of its unavailability of large number of free electrons to participate in the conduction process, thus ionic dopant material can be doped into the SBE system to increase the number of free ions, hence elevate its conductivity.

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In 2014, our previous work had successfully developed and characterized the CMC doped NH_4BrSBEs system.^[11] However, it has limitation due to the instability of electrochemical properties thus gives an inherent problem of low conductivity and mobile ions which limit its applications. Nevertheless, this can be overcome by several techniques that have been developed by other researchers to modulate the ionic conductivity, such as random and comb-like copolymer of two polymers, polymer blending,^[12] mixed dopant system, and impregnation of additives, such as plasticizers and ceramic inorganic fillers.^[13] One of the effective method is the addition of plasticizers which could enhance the conductivity and better contact between the electrolyte/electrode.^[14] The term plasticizer refers to a species, which will decrease the glass transition temperature of the biopolymer electrolyte and hence increase the segmental mobility.^[10]

In this present work, the enhancement on electrical properties of CMC- NH_4Br -based biopolymer electrolytes (BEs) system was performed by introduction with different type plasticizer namely polyethylene glycol, glycerol, and ethylene carbonate (EC). The observed frequency and temperature dependence of complex impedance are analyzed using the universal power law (UPL) for the conduction process in BEs system and also to determine its potential to be used as conducting materials toward the advancement of energy materials.

Methodology

Sample preparation

The solution casting technique was used to obtain film with CMC (Acros Organic Co.) dissolved in distilled water. Then, the solution was added with 25 wt% of NH_4Br (due to the optimum composition CMC- NH_4Br that provide highest in ionic conductivity)^[11] and the mixture was stirred continuously until complete dissolution and becoming homogenous. Varied amount of plasticizers namely polyethylene glycol (PEG), glycerol, and EC were added with different weight percentage (interval of 2 wt%). The solution was then poured into different Petri dishes and left to dry at room temperature for the plasticized-CMC- NH_4Br films to form.

Characterization

For the impedance measurements, the BEs film was sandwiched between two stainless steel electrodes with diameter 2 cm, under spring pressure. Impedance of the films was taken using the HIOKI 3532-50 LCR Hi-Tester impedance spectroscopy in the temperature range of 303–373 K. The ionic conductivity, σ , was analyzed based on the frequency dependent electrical properties using the equation explained in Isa and Samsudin,^[10] Samsudin et al.,^[11] and Kumar et al.^[12]

Results and discussion

Transparent, clear with good mechanical stability of plasticized CMC- NH_4Br biopolymer electrolytes films were obtained as shown in Figure 1.

Conductivity study

The variation of conductivity as a function of the different plasticizers weight percentage in the CMC- NH_4Br BEs system is presented in Figure 2.

It can be observed that the ionic conductivity of CMC- NH_4Br BEs system was increased when plasticizer was added, except for sample containing 2 wt% of PEG. The decreasing of ionic conductivity at lower PEG content may be due to the inadequate energy barrier aided from PEG for ions (H^+) to detach from NH_4^+ moiety of NH_4Br . The addition of PEG at lower content could also cause the delaying of ions pathway to migrate toward polymer backbone thus the reduction in ionic

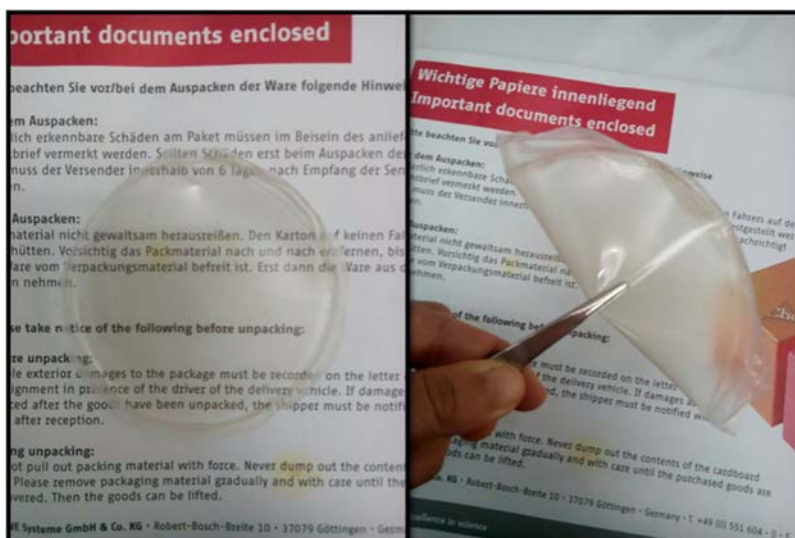


Figure 1. Clear, transparent and good mechanical properties of plasticized CMC-NH₄Br BEs film.

conductivity was observed. Furthermore, the slight amount of PEG can be explained where the PEG was not able to overcome the rate of ion association thus a decrease in conductivity.^[15]

The ionic conductivity of BEs system is increased by further addition of PEG, glycerol, and EC and achieved ideal value of 2.48×10^{-3} (8 wt% PEG), 1.91×10^{-3} (6 wt% glycerol), $3.31 \times 10^{-3} \text{ S cm}^{-1}$ (8 wt% EC), respectively. The higher value in ionic conductivity for PE system shows that the plasticized-CMC-NH₄Br is comparable with the electrolytes using synthetic polymer by doping with lithium salts. The increase of ionic conductivity can be explicated in the way that as the plasticizer content increases, alternative pathways will be formed in the presence of a huge number of liquid-filled microspores and there will be inferior viscosity in CMC-NH₄Br for superior transportation of ions and greater available capacity for better ion conduction.^[16] Besides, higher content of plasticizer would open up the narrow rivulets of plasticizer-rich phase for greater ionic transport and provide a large free volume of relatively superior conducting phase.^[9] These results are in similar agreement with those described in the literature.^[9,17] The higher ionic conductivity ($\sim 10^{-3} \text{ S cm}^{-1}$) of plasticized CMC-NH₄Br BEs system is comparable with other current polymer electrolytes system and also good candidate for application in electrochemical devices.^[18]

Figure 3 presents the temperature-dependence conductivity plot for various higher conducting sample of BEs system at different temperatures. It could be observed that the ionic conductivity for sample containing EC was higher as compared to unplasticized sample, and samples added with

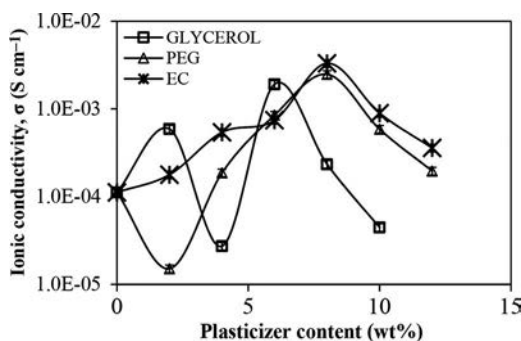


Figure 2. The variation of ionic conductivity for BEs system.

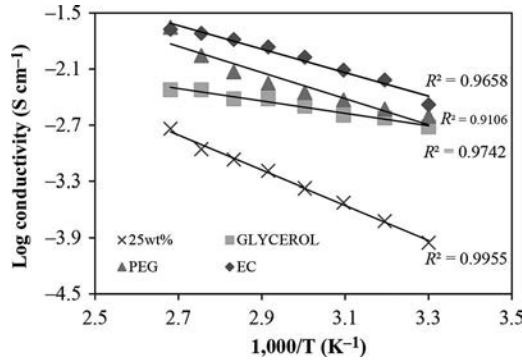


Figure 3. Temperature dependence of ionic conductivity for BEs system.

PEG and glycerol. Among the plasticizers used in the BEs system, EC exhibits a higher dielectric constant value^[17] and this was due to the function of EC in detaching NH₄⁺ in CMC complexes by lowering the Coulombic force between NH₄⁺ and Br⁻ ions, which produces more H⁺ conducting ions when the temperature was increased. According to Ratner and Shriver,^[19] the temperature-dependent conductivity of polymer electrolytes system follows many relationships. It shows that the relationship of conductivity and temperature in BEs system is almost linear, and thus obeys the Arrhenius rule, and is thermally assisted.^[13,14] The Arrhenius behavior can be expressed with the equation below:

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{kT}\right) \tag{1}$$

where σ_0 is the pre-exponential factor, E_a the activation energy, and k is the Boltzman constant.

The E_a are calculated for the higher conducting system from the straight lines of the Arrhenius plot, and are presented in Table 1. It can be found that that the E_a value decreases (≥ 0.1 eV) drastically by incorporating with plasticizer in CMC-NH₄Br BEs system. This may due to its high ionic conductivity in plasticizer system, which requires lesser energy to migrate the higher volume of number ions (H⁺) to associate with CMC backbone. From the results, it is remarkable that the polymer electrolyte system with lower values (below 1 eV) of E_a is sufficient for applications as the electrochemical devices.^[13,20]

Electrical properties study

The examination on electrical properties is a very important approach to understand the behavior of molecular interactions and conduction process in polymer electrolyte system. The imaginary and real portions of the dielectric permittivity, ϵ^* were calculated using the equation:

$$\epsilon^* = \epsilon_r - j\epsilon_i = \epsilon_r - j\left(\frac{\sigma_r}{\omega\epsilon_0}\right) = \frac{1}{j\omega CZ^*} \tag{2}$$

where loss (ϵ_i) and constant (ϵ_r) of dielectric properties refer to the loss and the stored energy of the applied electric field,^[21] respectively.

Table 1. The activation energy for higher conducting BEs system.

Sample	Activation energy, E_a (eV)
25 wt% NH ₄ Br	0.120
8 wt% PEG	0.072
6 wt% Glycerol	0.057
8 wt% EC	0.102

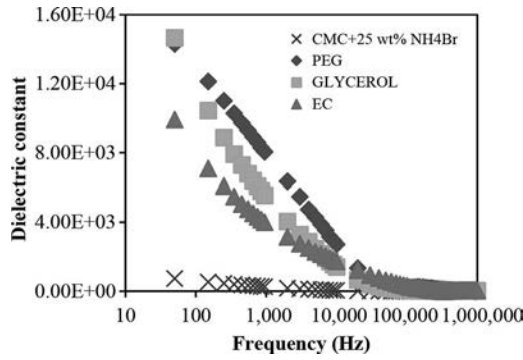


Figure 4. Dielectric permittivity at ambient temperature for BEs system.

Figure 4 represents the ϵ_r for CMC BEs system at ambient temperature and depicts the ϵ_r for CMC SBEs system at ambient temperature. Based on the plot, it could be observed that the ϵ_r values of plasticized system is higher, and increased significantly as compared to unplasticized sample. It could be explained that with the addition of plasticizer, the number of ions will be increased with the reduction of local viscosity around the charge-transporting ions.^[15] This phenomenon could be understood because the higher value of dielectric constant of plasticizer materials enables them to lower the cation–anion bond between NH_4^+ and Br^- , and thus improves the dissociation of CMC– NH_4Br complexes. The high ϵ_r value of plasticized BEs system helps to avoid ion-pair construction between cation (H^+) from NH_4Br and COO^- group from CMC, hence most ions are available to release by continuously protonation toward COO^- . Hence, this reveals that plasticizer is also acting as a variable to encourage for ion dissociation. Dissociation of NH_4Br into ions will result in an increase in free ion and lead to increase of ϵ_r of the system. The result from dielectric properties also shows that the non-Debye behavior was observed where no single relaxation was found in the BEs system.^[15,18]

Electrical modulus M^* can be presented with the relationships of dielectric permittivity:

$$M^* = \frac{1}{\epsilon^*} = M_r + iM_i \quad (3)$$

where M_r is the real and M_i is the imaginary part of modulus. Figure 5 depicts the frequency dependence on M_r and M_i , respectively, for the highest conducting BEs system at ambient temperature.

It can be observed that the M_r and M_i part of electric modulus for CMC BEs system in the present work shows small value or approaches to zero at low frequency region and becomes higher at the high frequency. The long tail at lower frequency could be attributed to the high capacitance associated with electrode polarization effects, and is found to be similar with other research systems which use a

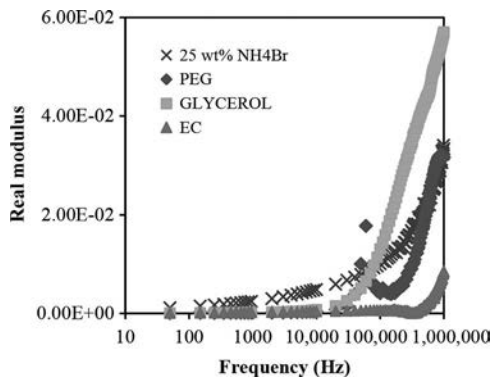


Figure 5. Electrical modulus (a) real and (b) imaginary part for highest conducting BMEs system at ambient temperature.

plasticizer in polymer electrolytes.^[9,16,22] This indicates that the plasticizer is very capacitive, which again suggests the enhancement of the dissociation for NH₄Br in CMC which accumulates at low frequency region. As plasticizer composition increased, the pattern of spectra are shifted to the higher frequencies, and the value for both electrical modulus increased beyond the frequency window of the present work.

By using UPL, the mechanism of AC conductivity can be examined.^[3,23,24] From ϵ_i , the ac conductivity can be attained by the following equations:

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

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

$$\sigma_{ac} = \epsilon_0 \epsilon_i \omega \tag{6}$$

where $\sigma(\omega)$ is the total DC and AC conductivity, A is a parameter which is temperature dependent, σ_{dc} is the frequency independent component or DC conductivity, and s is the exponent of power law (range between 0 and 1). Using Equations (5) and (6),

$$\ln \epsilon_i = \ln \frac{A}{\epsilon_0} + (s - 1) \ln \omega \tag{7}$$

where

$$\epsilon_i = \frac{Z_r}{\omega C_o (Z_r^2 + Z_i^2)} \tag{8}$$

Figure 6 depicts the dielectric loss, ϵ_i at ambient temperatures for higher conductivity BEs system. It is noted that ϵ_i initially fell off rapidly with frequency for entire plasticized samples, and stabilized at higher frequencies. The higher values of ϵ_i for all plasticized sample at lower frequency are attributed to the electrode polarization effect as mentioned earlier, where the charge accumulation at the electrode/electrolyte interfaces occurred when plasticizer was added into CMC–NH₄Br BEs system.

Based on plot in Figure 6, the s values can be obtained from the gradient at the high frequency region are due to no negligible space charge.^[14] The variation of s with temperature for high conducting system of plasticized CMC–NH₄Br BEs system were presented in Figure 7.

To verify the theoretical model conduction of polymer–salt complexes electrolytes system, different theories have been proposed such as overlapping large polaron tunneling (OLPT) model,^[15] correlated barrier hopping model,^[14] quantum mechanical tunneling (QMT) model,^[25] and small polaron hopping (SPH) model.^[26] From the observations shown in Figure 7, it can be concluded that the OLPT model is fitted for the highest conducting sample for PEG system, SPH model for glycerol

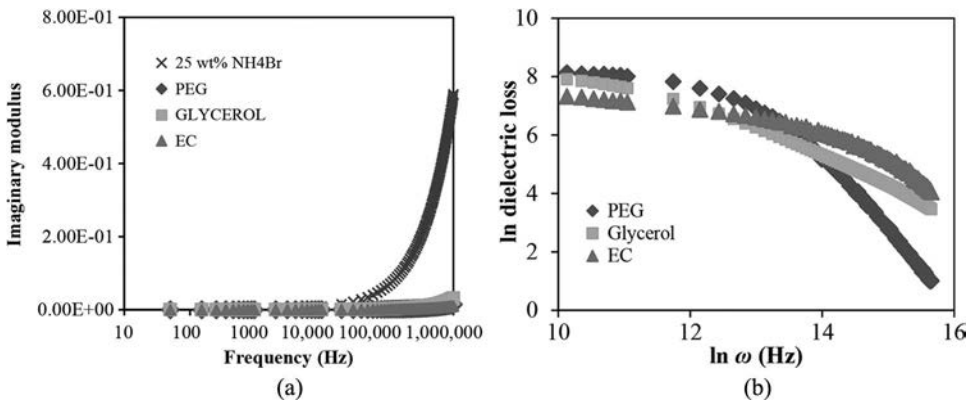


Figure 6. $\ln \epsilon_i$ versus $\ln \omega$ at ambient temperature for highest conducting BEs system.

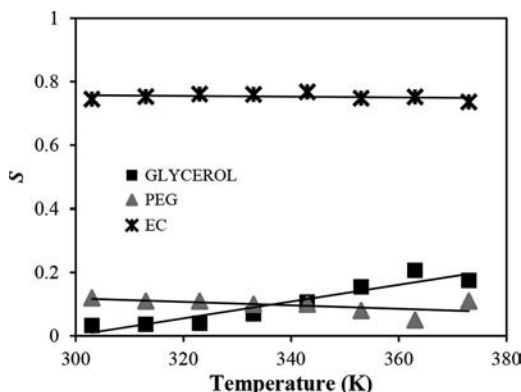


Figure 7. Variation of exponent s versus temperature for highest conducting BEs system.

system, and QMT model for EC system. The OLPT model suggests that with the addition of PEG into, CMC-NH₄Br complexes lead to the overlapping of the stress fields of the polarons (made up from H⁺), thus forming an alternative pathway for the ions (H⁺) to hop, which are capable to pass by the possible barrier that occurs between two potential interaction sites.^[15] Meanwhile, in SPH model, it can be inferred that CMC and glycerol did not interact chemically with each other, whereas some interaction occurred between NH₄Br and plasticizer. The QMT model which was presented in EC system can be explained due to the ions (H⁺) hopping mechanism. With the addition of EC in BEs system, it will compromise the alternative pathways for ions to move therefore increasing the dissociation of ions from NH₄Br. The introduction of EC would make the charge transfer able to tunnel through the potential barrier that exists between the ion pair electrons in carboxyl group of CMC and NH₄Br. This behavior was similarly observed in other research work done by Shukur et al.^[25] who stated that EC plays a main role in enhancing the ionic conductivity of their system.

Conclusion

The development of biopolymer electrolytes has been accomplished in this work by incorporating different types of plasticizer namely polyethylene glycol (PEG), glycerol, and ethylene carbonate with bio-materials CMC doped 25 wt% NH₄Br through solution casting technique. The BEs systems were successfully formed as solid films with good mechanical properties with no phase separation. The SBEs ionic conductivity was improved by the introduction of different plasticizers from $\sim 10^{-4}$ to $\sim 10^{-3}$ S cm⁻¹, with the highest conducting sample observed at $\sim 3 \times 10^{-3}$ S cm⁻¹ for 8 wt% EC. The temperature-conductivity plots of the SBE systems show the Arrhenius behavior and were found as thermally assisted. The electrical study shows that the addition of plasticizer enhanced the dielectric value, which contributes to higher dissociation of ions (H⁺), thus increasing the ionic conductivity, and was confirmed to be non-Debye. The Jonschers power law showed that the electrical conduction mechanism studies for the highest conducting CMC SBEs system could be explained by OLPT model (PEG), SPH model (glycerol), and QMT model (EC). All these results suggest that the superior properties of biopolymer material, namely CMC, has high potential as semiconducting materials for applications in electrochemical devices.

Acknowledgment

The authors would like to thank FIST, UMP for the technical and research support.

Funding

The authors would like to thank Universiti Malaysia Pahang for the UMP Grant RDU: 150324.

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