

# Electrical Behavior of Ethylene Carbonate-Plasticized Cellulose Biopolymer Electrolyte Films

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Energy security is becoming a major concern across the globe which has boosted development of battery technology. Electrolytes play a major part in any battery systems where they are usually in the form of liquid. Electrolytes are usually produced by dissolving ionic dopants in organic solvents. This paper reports the electrical behavior of a plasticized biopolymer film system. The biopolymer film showed good ionic conductivity enhancement when plasticized with ethylene carbonate where optimum value of  $7.41 \times 10^{-4}$  S/cm was obtained. The ionic conductivity improvement was aided by lower activation energy,  $E_a$  and the biopolymer film followed the Arrhenius behavior. Dielectric analysis was done to further analyze electrical properties of the biopolymer film.

**Key words:** Biopolymer electrolyte; carboxymethyl cellulose; ionic conductivity; ethylene carbonate

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Various efforts are being done globally in order to find the next form of energy to reduce and subsequently replace our dependency on polluting forms of energy sources such as coal, petroleum, and nuclear energy. Thanks to the Paris Agreement in 2016, almost the entire nations on the planet have agreed to reduce their polluting emissions from the aforementioned forms of energy sources to ensure the global temperature rises to be well below 2°C for this century. The effect can be seen from the increasing demand for electric vehicles globally [1] and is said to replace petrol vehicles in the foreseeable future [2]. The advantages of cleaner energy are what have propelled the energy storage advancement. One component of energy storage that currently being researched is the development of electrolytes.

Since the discovery of ionic conducting polymer electrolyte by Wright in 1973, many efforts have been done to improve the transport properties of polymer electrolytes for electrochemical application such as PEO, PVC, PMMA, PVDF and PAN [3, 4, 5, 6]. Polymer electrolytes have several advantages compared to the conventional liquid electrolytes, such as light weight, improve leakage problem, mechanically stable, flexible for packaging design, eliminate corrosive solvent and harmful gas formation, and wider electrochemical and thermal stability range, as well as

low volatility with easy handling [7, 8]. However, in the last few years, polymer electrolyte study focus has shifted to natural polymer/biopolymer such as agar-agar, starch, cellulose etc. [9]. This is due to the abundance, biodegradable, water soluble, and good mechanical properties.

Carboxymethyl cellulose (CMC) is one of the most used biopolymers in electrolyte study apart from other cellulose-based biopolymers such as methyl cellulose (MC) and hydroxyethyl cellulose (HEC) [10, 11, 12]. CMC has good film forming abilities due to the presence of hydrophilic carboxyl group ( $-\text{CH}_2\text{COONa}$ ) [13]. On top of that, CMC has high degree of amorphous phase [14]. These allow for easier ionic transport like lithium ( $\text{Li}^+$ ) and proton ( $\text{H}^+$ ). CMC biopolymer by itself is an insulator, but once it is mixed with ionic salts it can become a semiconductor. Previously, we have reported the effect of ammonium carbonate (AC) composition in CMC-based biopolymer electrolyte films and concluded that the highest ionic conductivity achieved of  $7.71 \times 10^{-6}$  S/cm was considered to be low for any possible electrochemical device applications and thus needed further improvements [15].

Several reports have shown that addition of plasticizer can improve biopolymer electrolyte films performance [10]. Thus, the addition of plasticizer is

used as the technique to increase the performance of CMC-based biopolymer films. As of to date, no study has reported on the enhanced performance of CMC-AC biopolymer electrolyte films. This study examined the electrical behavior of the proton conducting CMC-based biopolymer electrolyte films doped with AC as the ionic source and plasticized with ethylene carbonate (EC). The ionic conductivity at room and elevated temperature was examined and further electrical properties through dielectric analysis were investigated.

#### MATERIALS AND METHOD

Solution casting technique was utilized for biopolymer film formation. Carboxymethyl cellulose (CAS 9004-32-4), ammonium carbonate (CAS 12125-02-9), and ethylene carbonate (CAS 96-49-1) were obtained from Sigma-Aldrich and used as received. First, 2 g of CMC was dissolved in distilled water until the solution was homogenous. Then, 7 wt. % of AC was added into the CMC solution and left to stir until it completely dissolved. Once dissolved, different wt. % of EC (10 – 50 wt. %) was added into the CMC solution and left to stir for a few hours before continuing to the drying process (film forming). The drying process took place at room temperature.

HIOKI 3532-50 LCR Hi-Tester was utilized to investigate the impedance of the prepared electrolyte in the frequency ranges between 50 Hz to 1 MHz at different temperatures (30 to 100 °C). The impedance plot (negative imaginary impedance,  $-Z_i$  against real impedance,  $Z_r$  was analyzed to obtain the bulk resistance,  $R_b$  (refer to Table 1), and the value was used to calculate the ionic conductivity as shown in Equation 1, where  $t$  = thickness and  $A$  = contact area. The films thickness was measured using Mitutoyo digital micrometer.

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

The ionic conductivity-temperature relationship was plotted according to the Arrhenius relationship as

shown in Equation 2. Where,  $\sigma_o$  = pre-exponential factor,  $E_a$  = activation energy,  $k$  = Boltzmann constant, and  $T$  = temperature.

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

Further electrical analysis was done to investigate dielectric behavior by using Equations 3 and 4, where  $C_o = \epsilon_o A/t$  ( $\epsilon_o$  is the permittivity of free space),  $\omega = 2\pi f$  ( $f$  is frequency in Hz), and  $\epsilon_r$  and  $\epsilon_i$  represent dielectric constant and dielectric loss, respectively.

$$\epsilon_r = \frac{Z_i}{\omega C_o (Z_r^2 + Z_i^2)} \quad (3)$$

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

Real dielectric modulus,  $M_r$ , was calculated using Equation 5 to detect the relaxation peak in the biopolymer films.

$$M_r(\omega) = \frac{\epsilon_i}{(\epsilon_r^2 + \epsilon_i^2)} \quad (5)$$

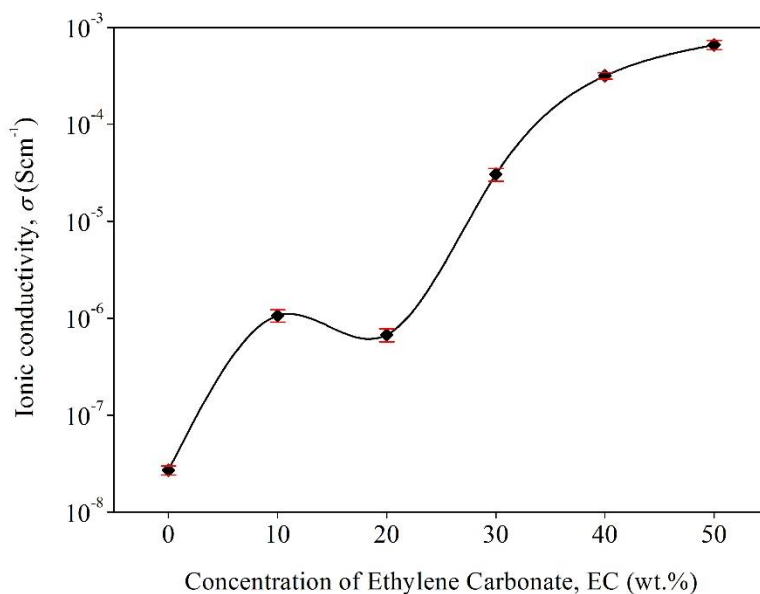
#### RESULTS AND DISCUSSION

##### Ionic Conductivity Analysis

The bulk resistance,  $R_b$  obtained (refer to Table 1) was used to calculate the ionic conductivity of the plasticized biopolymer films by using Equation 1 and is shown in Figure 1 as a plot of a function of ethylene carbonate composition.  $R_b$  for the plasticized biopolymer films was lower compared to  $R_b$  of the un-plasticized film with each increment of EC concentration. Low resistance is desirable for electrochemical applications as it allows for faster ionic movement across the biopolymer films. The optimum ionic conductivity achieved in this plasticized EC system was  $7.41 \times 10^{-4}$  S/cm for sample EC-50. This was a marked improvement compared to the previously reported value of  $7.71 \times 10^{-6}$  S/cm of CMC-based biopolymer films doped with AC [15].

**Table 1.** The biopolymer film compositions with respective analysis parameters

Sample	CMC (gram)	AC (gram)	EC (gram)	Bulk Resistance, $R_b$ (ohm)	Activation Energy, $E_a$ (eV)	Regression value, $R^2$
EC-0			0.000	$176353 \pm 19522$	0.12	0.94
EC-10			0.239	$4323 \pm 842$	0.18	0.95
EC-20	2.000	0.151	0.478	$4481 \pm 686$	0.21	0.94
EC-30			0.717	$124 \pm 20$	0.18	0.98
EC-40			0.956	$20 \pm 2$	0.09	0.97
EC-50			1.195	$11 \pm 2$	0.06	0.98



**Figure 1.** Ionic conductivity of plasticized biopolymer electrolytes by EC concentration at room temperature

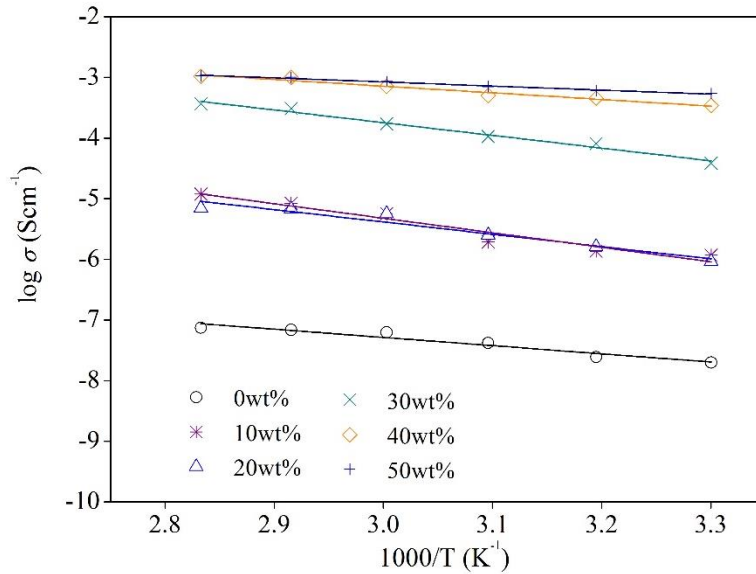
The initial increase in conductivity value was believed due to increased number of mobile ions. Incorporation of EC helped to dissociate ammonium ions to produce more  $H^+$  by disrupting the cohesive forces between polymer chains thus leading to increased ionic conductivity [16]. Further addition of EC (20 wt. %) led to slight decrease in ionic conductivity which implied that mobile ions were not formed parallel with EC addition. This behavior can be explained by the formation of ion pairs/aggregates. As more mobile ions were formed, the distance between ions became closer to form ion pairs/aggregates [17]. However, the ionic conductivity increased back at higher EC concentration (30-50 wt. %). It is believed that at higher concentration, EC not only eases mobile ions dissociation but it also starts to act as temporary/transit sites for the mobile ions ( $H^+$ ) before being transported to coordination sites from polymer chains once induced by electric field [18]. The temporary/transit sites allow the mobile ions to move across the biopolymer electrolyte and thus increase the ionic conductivity. It was noted that the highest

conducting electrolytes of this system were almost equivalent to other research, as presented in Table 2.

The temperature effect on the ionic conductivity of the plasticized biopolymer films was also investigated and the plot is shown in Figure 2. The temperature dependence was plotted following the Arrhenius equation (Equation 2). Temperature increase boosted the ionic conductivity of the plasticized biopolymer films up until 353 K. Further increase in temperature resulted in decrease of ionic conductivity. The heat subjected to the biopolymer films allowed for energy to be absorbed by the biopolymers which created free volume due to vibration [19]. This improved the polymer segmental motion hence facilitated ionic mobility and led to increased ionic conductivity at elevated temperatures. The activation energy (refer to Table 1) calculated from Equation 2 showed that the highest conducting sample had the lowest activation energy value which allowed for easier migration of mobile ions to the polymer backbones [20, 21].

**Table 2.** Comparison of ionic conductivity for current work to other research using plasticizer in polymer electrolyte systems

System	Ionic conductivity, $\sigma$ (S/cm)	References
Agar + $NH_4Br$ + EC	$\sim 10^{-3}$	[22]
Starch + LiOAc + glycerol	$\sim 10^{-5}$	[23]
2-HEC + $NH_4NO_3$ + EC	$\sim 10^{-3}$	[21]
CMC + $(NH_4)_2CO_3$ + EC	$7.41 \times 10^{-4}$	Current work

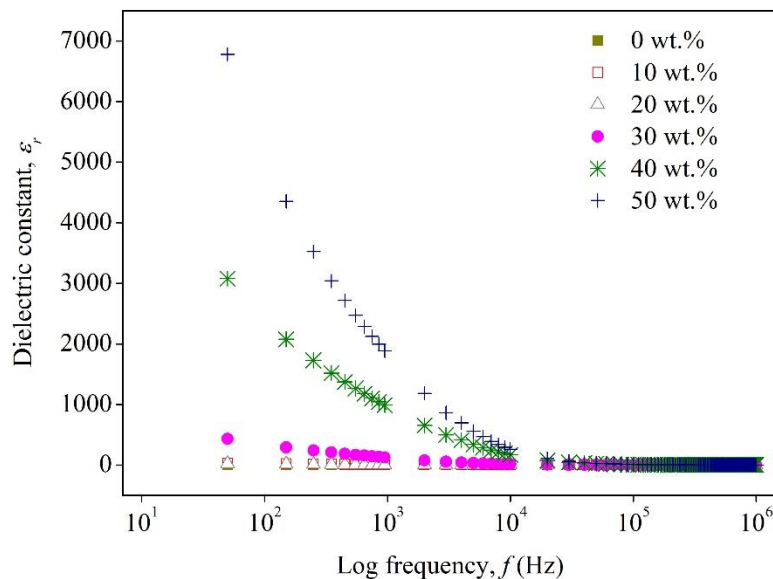


**Figure 2.** Ionic conductivity of plasticized biopolymer films with respect to temperature

### Dielectric Analysis of Plasticized Biopolymer Films

Dielectric analysis helps researchers to understand the conductive characteristics of ionic and molecular interactions through polarization effect [24, 25]. Figure 3 shows the dielectric constant,  $\epsilon_r$  at room temperature of the plasticized biopolymer films for each EC concentration. The dielectric plot can be divided into two frequencies of low and high frequencies. At low frequency range,  $\epsilon_r$  value was high, which was linked to the increase concentration of charge carriers at the electrode/electrolyte interface during polarization [26].

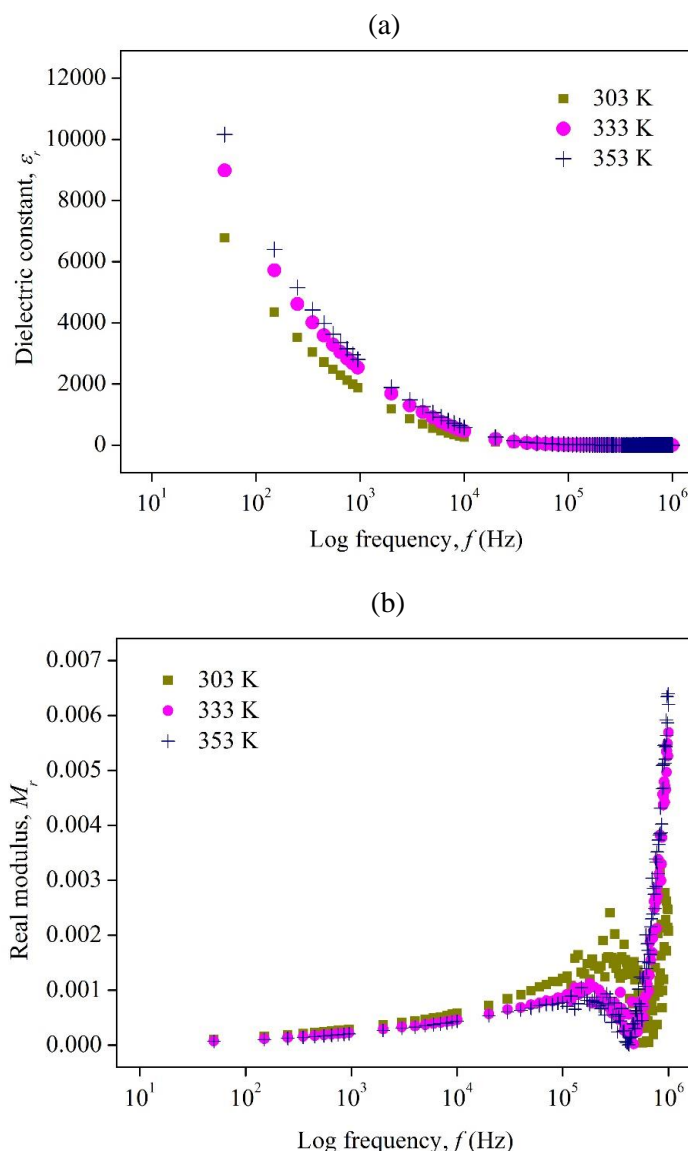
The slow electric field direction changes at low frequencies allowed the charge carriers to follow the changing electric field and subsequently built charges at the interface. The large  $\epsilon_r$  value gap between high and low EC concentrations is believed to be due to the pathway created by higher EC composition which eases charge carriers' hopping. At high frequency range, the charge carriers could not keep pace with the electric field changes, causing no charge build-up at the electrode/electrolyte interface and thus reduce the dielectric constant,  $\epsilon_r$  value [27, 9].



**Figure 3.** Dielectric constant of the biopolymer films for each EC composition at room temperature

Figure 4a shows the plot of  $\epsilon_r$  values at selected temperatures for the biopolymer film with 50 wt. % of EC, which was the highest conducting sample in the system. The plot showed a similar trend as stated previously where  $\epsilon_r$  value was the highest at low frequency and the lowest at high frequency. On top of that, at elevated temperatures,  $\epsilon_r$  value was higher. This was due to increased number of charge carriers. Higher temperature helps to increase salt dissociation which evidently increases  $\epsilon_r$  value. Higher temperature also softens the polymer backbones and increases the segmental motion of polymer chains and thus allows for greater ions mobility. The variation of real dielectric modulus,  $M_r$ , at selected temperatures is shown in Figure 4b. Dielectric modulus gives better understanding of the dielectric properties of the biopolymer films by suppressing the polarization effect [25]. From the figure,

it can be seen that there appears to be a relaxation peak at each temperature. These peaks can be interpreted as the relaxation process of mobile  $H^+$  ions due to electric field re-orientation. The relaxation process can be divided into two regions of (i) low frequency side and (ii) high frequency side where at low frequency side of the peaks means that the ions are capable of performing successful hopping from one site to the next one, whereas at high frequency side of the peak, the  $H^+$  ions are confined to its potential well and only able to perform local motion (reorientation). It was also noted that the relaxation peak decreased with increased temperature which suggested plurality of relaxation mechanism (non-Debye) [23]. This indicated that the plasticized biopolymer films were ionic conductors as suggested by Ramesh and Arof [28].



**Figure 4.** (a) The dielectric plot for sample plasticized with 50 wt. % of EC at elevated temperatures and (b) the dielectric modulus of 50 wt. % of EC at selected temperatures.

## CONCLUSION

Plasticized biopolymer films developed from CMC, AC, and EC had been prepared successfully. The highest conductivity film with the value of  $7.41 \times 10^{-4}$  S/cm was obtained when plasticized with 50 wt. % of EC. The activation energy for the highest conducting sample was 0.06 eV, which was lower than the rest of the films. Dielectric analysis has proved that the highest conducting films were ionic conductors and the overall enhancement of the biopolymer films was due to increased number of charge carriers. For future work, we would suggest techniques such as polymer blending and incorporation of inorganic fillers materials to further improve the ionic conductivity of the electrolytes.

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