Electrical Properties of Carboxymethyl Cellulose-Ammonium Sulphate Solid Biopolymer Electrolytes

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(Received: 22.7.21 ; Published: 14.8.22)

Abstract. Carboxymethyl cellulose-ammonium sulphate (CMC-$(NH_4)_2SO_4$) solid biopolymer electrolytes (SBEs) were prepared by using solution-casting method. The ionic conductivity of CMC-$(NH_4)_2SO_4$ SBEs were measured at ambient temperature from 303 K to 373 K using Electrical Impedance Spectroscopy (EIS). The highest ionic conductivity is $(5.085 \pm 0.001) \times 10^{-6}$ Scm^{-1} containing 10 wt.% of $(NH_4)_2SO_4$ with the lowest activation energy, E_a values which is (0.125 ± 0.001) eV. The temperature dependence plot shows that CMC-$(NH_4)_2SO_4$ SBEs are thermally activated and the regression value for 10 wt.% of $(NH_4)_2SO_4$ is 0.95 which obey the Arrhenius behavior, $R^2 \approx 1$. The frequency dependence of dielectric constant (ε_r), dielectric loss (ε_i), real part of electrical modulus (M_r) and the imaginary part of electrical modulus (M_i) were showed the SBE unfollowed non-Debye behavior.

Keywords: Carboxymethyl cellulose; ammonium sulphate; ionic conductivity; activation energy, frequency dependence

INTRODUCTION

The rechargeable battery has attracted much attention from researchers as a portable power sources that have been widely used in laptops, smartphones, cameras and watches. Currently, lithium-ion (Li-ion) battery is used in most portable electronic devices and considered as one of the most advanced rechargeable battery (Costa et al., 2020). This rechargeable battery is divided into four components; anode, cathode and electrolyte.

Presently, the electrolyte has been chosen to identify its electrical properties in the battery as it acts as a barrier that function by allowing the flow of ions from cathode to anode in order to perform a great potential in electrical and electrochemical properties (Sohaimy & Isa, 2020). It can be prepared in a variety of physical states and compositions, such as liquid electrolytes, gel polymer electrolytes and solid biopolymer electrolytes. In comparison to liquid and gel electrolytes, solid biopolymer electrolytes (SBEs) is the most intriguing electrolyte formation because they are flexible, robust, light-weight, safe and stable as an electrochemical medium (Dueramae et al., 2020).

Mostly, SBEs is made from bio-based polymer due to their excellent mechanical and electrical properties which contain higher energy density also improved in safety hazards (Samsudin et al., 2014). Additionally, Mindemark et al., (2018) has reported that the AC current were available to identify the type of charges either anion or cation that attached to the polymer backbone on the biopolymer host. Thus, in this work, carboxymethyl cellulose (CMC) is used as a biopolymer host due to its characteristics included non-toxic, biodegradable, easy in film formation and light weight (Chai & Isa, 2017). CMC is one of the modified cellulose which contains a polysaccharide backbone in substitution of carboxylic acid ($-CH_2COOH$) group bounded with hydroxyl groups of the glucopyranose monomers from cellulose (Sohaimy & Isa, 2017).

Furthermore, by dissolving inorganic ammonium salts in the polymer host, it can lead to enhance the conductivity of SBEs. Hassan et al., (2010) showed the potential of ammonium sulphate, $(NH_4)_2SO_4$

as an ionic dopant because of its unique characteristics with water-solubility also acts as a charge carrier to transport the cation and anion to perform the conductivity (Hemalatha et al, 2019).

The aim of this present study is to determine of ionic conductivity, temperature dependence plot, activation energy as well as its electrical properties including dielectric and modulus studies of CMC-$(NH_4)_2SO_4$ SBEs using Electrical Impedance Spectroscopy (EIS) at elevated temperature (303 K to 373 K).

MATERIALS AND METHODS

Sample preparation

2 g of CMC from Acros Organic Co. was dissolved in distilled water and added with different amount of $(NH_4)_2SO_4$ from Sigma Aldrich at room temperature. The CMC solution and different amount of $(NH_4)_2SO_4$ (0, 5, 10, 15, 20 and 25 wt.%) were designated as C0, C5, C10, C15, C20 and C25, respectively. The mixed solution was stirred until it completely dissolved and cast into several petri dishes. Then, it dried in the furnace (~50°C) for 24 h. For further drying, the samples were left at room temperature about 48 h and the formation of film was completed after the film was separated with petri dish.

Electrical Impedance Spectroscopy

CMC-$(NH_4)_2SO_4$ SBEs was measured by using HIOKI IM3536 LCR Meter for its ionic conductivity. The frequency was used in the range of 50 Hz to 1 MHz at 303-373 K. SBE was placed between two electrodes stainless steel. Its connected to a computer to get the Cole-Cole plot of the SBEs. Equation (1) was used to calculate the ionic conductivity, σ where t is the thickness of the sample (cm), R_b is the bulk resistance and A is the electrode-electrolyte contact area (cm^2) (Mazuki et al., 2018; Rasali et al., 2020).

$$\sigma = \frac{t}{R_b A} \tag{1}$$

The activation energy, E_a is calculated by using equation (2) where σ_0 is pre-exponential factor, k is Boltzmann's constant ($k = 8.617 \times 10^{-5}$eV K^{-1}) and T is the temperature (K). Based on equation (2), the temperature dependence graph was plotted to determine the behavior of CMC-$(NH_4)_2SO_4$ SBEs (Rani et al., 2021).

$$E_a = -\left[\ln\left(\frac{\sigma}{\sigma_0}\right).kT\right] \tag{2}$$

The dielectric properties of CMC-$(NH_4)_2SO_4$ SBEs were measured from the impedance data and known as dielectric constant (ε_r) and dielectric loss (ε_i). The dielectric constant is used to measure the storage charge while for the dielectric loss is used to measure the energy losses when the polarity of electric field for ion moves reverses (Fuzlin et al., 2018). The ε_r and ε_i were calculated by using equation below,

$$\varepsilon_r = \frac{Z_i}{\omega C_0\left({Z_r}^2 + {Z_i}^2\right)} \tag{3}$$

$$\varepsilon_i = \frac{Z_r}{\omega C_0\left({Z_r}^2 + {Z_i}^2\right)} \tag{4}$$

where C_0 is the capacitance ($C_0 = \frac{\varepsilon_0 A}{t}$, ε_0 is permittivity of free space), ω is the angular frequency ($\omega = 2\pi f$, f is frequency), Z_r is the real part of impedance, and Z_i is the imaginary part of impedance.

Thus, the dielectric behavior can be more effective by using the formulation of electrical modulus, *M*. The electrical modulus was studied in advance to determine the ionic transport dynamics in CMC-$(NH_4)_2SO_4$ SBEs. The real part of electrical modulus, M_r and the imaginary part of electrical modulus,

M_i were calculated by using equation below,

$$M_r = \frac{\varepsilon_r}{(\varepsilon_r{}^2 + \varepsilon_i{}^2)} \tag{5}$$

$$M_i = \frac{\varepsilon_i}{(\varepsilon_r{}^2 + \varepsilon_i{}^2)} \tag{6}$$

where ε_r is dielectric constant and ε_i is dielectric loss.

RESULTS AND DISCUSSION

Ionic conductivity study

Figure 1 showed the negative imaginary impedance, $-Z_i$ versus real impedance, Z_r of CMC-AS SBEs. In this figure, the bulk resistance, R_b is determined from the intercept of semicircle at high frequency and inclined spike at low frequency where all the value can be seen in Table 1. The appearance of semicircle is related to a charge transfer process in range at high frequency while the inclined spike is related to bulk conduction processes (Samsudin et al., 2012).

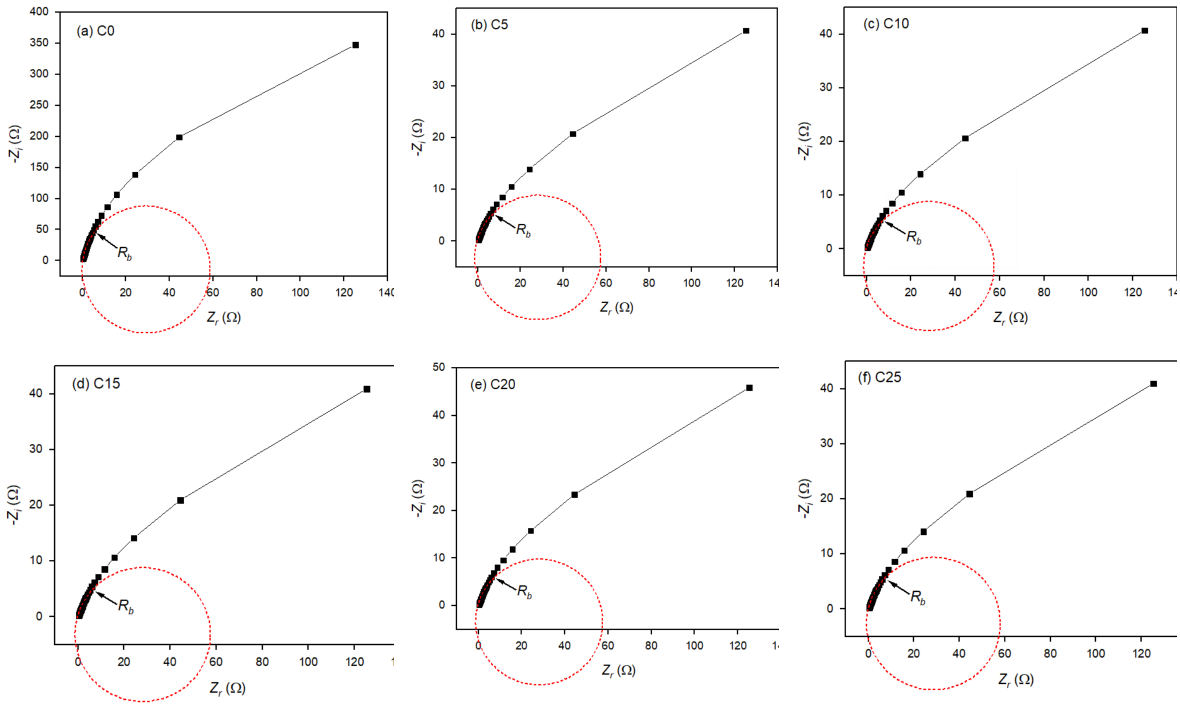


FIGURE 1. The impedance plot for SBEs of (a) CMC, (b) CMC + 5 wt.% $(NH_4)_2SO_4$, (c) CMC + 10 wt.% $(NH_4)_2SO_4$, (d) CMC + 15 wt.% $(NH_4)_2SO_4$, (e) CMC + 20 wt.% $(NH_4)_2SO_4$, and (f) CMC + 25 wt.% $(NH_4)_2SO_4$.

TABLE 1 Bulk resistance of CMC-AS SBEs.

Designation	Bulk resistance (Ω)
C0	1.57×10^5
C5	1.26×10^4
C10	2.42×10^2
C15	8.72×10^3
C20	9.31×10^3
C25	6.53×10^3

Figure 2 depicted the ambient temperature of the ionic conductivity for CMC-$(NH_4)_2SO_4$ SBEs.

Figure 2 showed that the sharp peak in the middle of graph. It represented the highest value of ionic conductivity was (5.085 ± 0.001) × 10^{-6} Scm^{-1} at 10 wt.% of $(NH_4)_2SO_4$ and the lowest value of ionic conductivity was (1.528 ± 0.001) × 10^{-8} Scm^{-1} 0 wt.% of $(NH_4)_2SO_4$. The increment of ionic conductivity with the addition of $(NH_4)_2SO_4$ can be attributed with the dissociation of ion hydrogen (H^+) between CMC and $(NH_4)_2SO_4$ (Fuzlin et al., 2021). The ionic conductivity decreases as $(NH_4)_2SO_4$ increases due to the overcrowded of ions which lead to the ion aggregation (Aniskari et al., 2017).

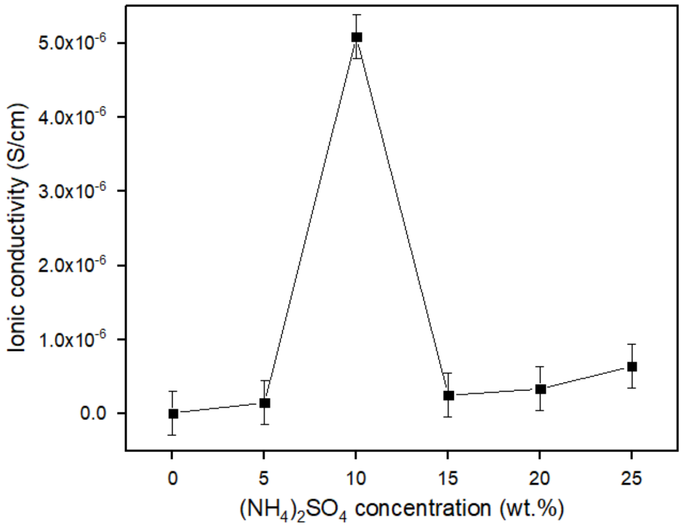
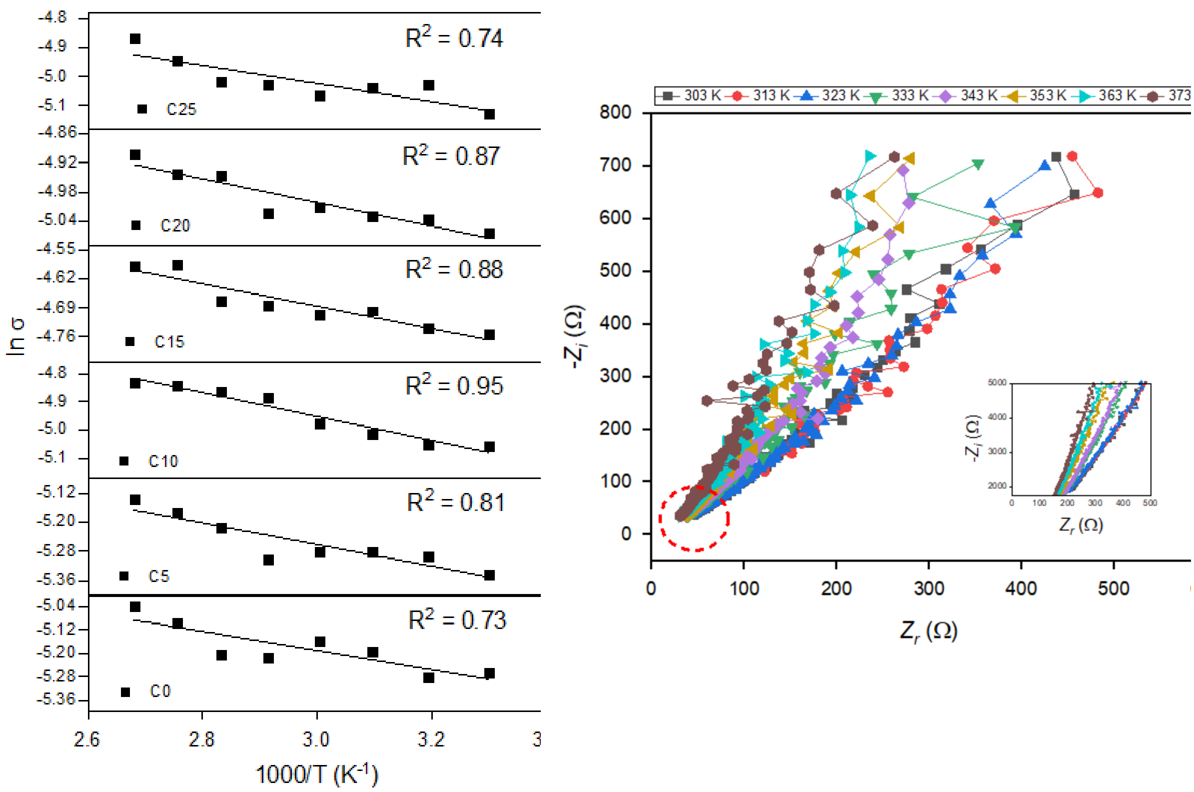


FIGURE 2. The ambient temperature of the ionic conductivity for CMC-$(NH_4)_2SO_4$ SBEs.

Figure 3(i) showed the temperature dependence plot of CMC-AS SBEs and Figure 3 (ii) showed the Cole-Cole plot of C10 from 303 K to 373 K. In Figure 3 (ii), the inset figure is plotted by referring the red circle at low frequency. It is observed that the temperature dependence plot is thermally activated as the conductivity increasing with temperature. The ionic conductivity increases because of thermal expansion that creates more free volume for the movement of charge carriers in the sample. Besides, the temperature increases make the charge move freely thus increasing the conductivity which suggests the CMC-AS SBEs is obeyed Arrhenius behavior. These SBE is confirmed that it acts as ionic conductor (Ramlli et al., 2014; Shukur et al., 2015). The regression value (R^2) for all the sample is showed in this figure and its gradient is tabulated in Table 2. The highest R^2 is 0.95 which represented for C10 where its bulk resistance is observed at low frequency spike (Figure 3 (ii)) and it was concluded that the total conductivity is the result of ionic conduction of SBEs (Rani et al., 2015).

The activation energy, E_a is the combination of energy of charge carrier creation and required energy to provide a conductive condition for the ion migration (Zainuddin et al., 2017). It can be calculated using Equation (2). Figure 4 illustrated the activation energy, E_a graph for CMC-$(NH_4)_2SO_4$ SBEs at ambient temperature. It was observed that the E_a value to be gradually decreased as the concentration of $(NH_4)_2SO_4$ increased. The highest ionic conductivity of CMC-$(NH_4)_2SO_4$ SBEs need the lowest energy to migrate with the charge carriers between CMC and $(NH_4)_2SO_4$. In this work, the lowest E_a value was (0.125 ± 0.001) eV (Rasali et al., 2018). As for increased E_a, it is due to ion overcrowding between CMC and $(NH_4)_2SO_4$ causing the energy barrier to be at maximum condition. The behavior of CMC-$(NH_4)_2SO_4$ SBEs was further investigated by dielectric studies.



(i) (ii)

FIGURE 3. (i) The ln σ vs 1000/T graph of CMC-AS SBEs and (ii) Cole-Cole plot of C10 at 303-373 K.

TABLE 2. Gradient value for CMC-AS SBEs.

Sample	Gradient
C0	-0.328 ± 0.082
C5	-0.297 ± 0.058
C10	-0.421 ± 0.040
C15	-0.270 ± 0.041
C20	-0.244 ± 0.039
C25	-0.309 ± 0.074

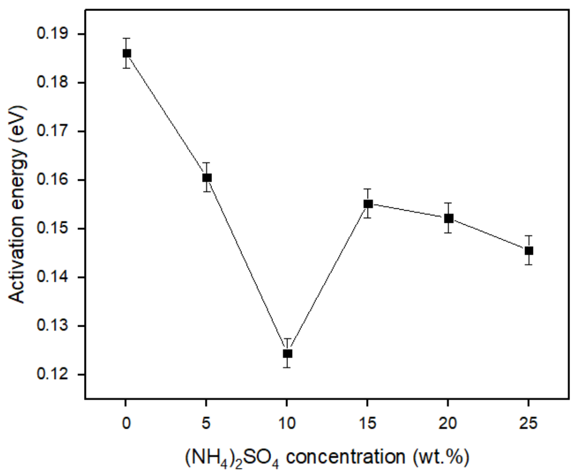


FIGURE 4. The activation energy graph for CMC-$(NH_4)_2SO_4$ SBEs at ambient temperature.

Dielectric studies

The dielectric behavior of SBEs was performed by using equation (3) and (4). ε_r and ε_i can be calculated and plotted as shown in Figure 5. Figure 5(i) illustrated the graph of log ε_r versus log ω and Figure 5(ii) showed the graph of log ε_i versus log ω for CMC-$(NH_4)_2SO_4$ SBEs at ambient temperature. Dielectric constant, ε_r is known as stored charge in a material and dielectric loss, ε_i is known as a measure of energy losses to move ions when the polarity of electric field turns rapidly (Selvin et al., 2018).

In this work, there is no relaxation peaks observed in the frequency range in Figure 5(i) and Figure 5(ii). The ε_r values for C10 was higher at lower frequency region due to the presence of blocking electrodes as the transfer of ion mobility in the external circuit could not be allowed. This would lead to a drop and constant ε_r values with increasing frequency. However, the ε_i values also higher at lower frequencies, which is explained by the motion of free charge ion between the materials and the electrodes (Hegde et al., 2020).

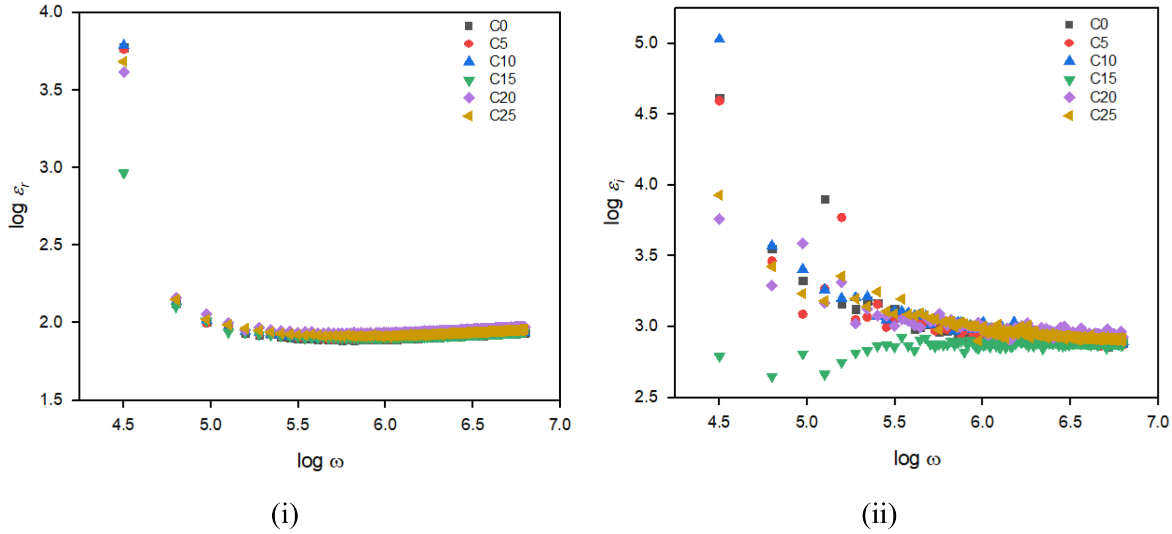


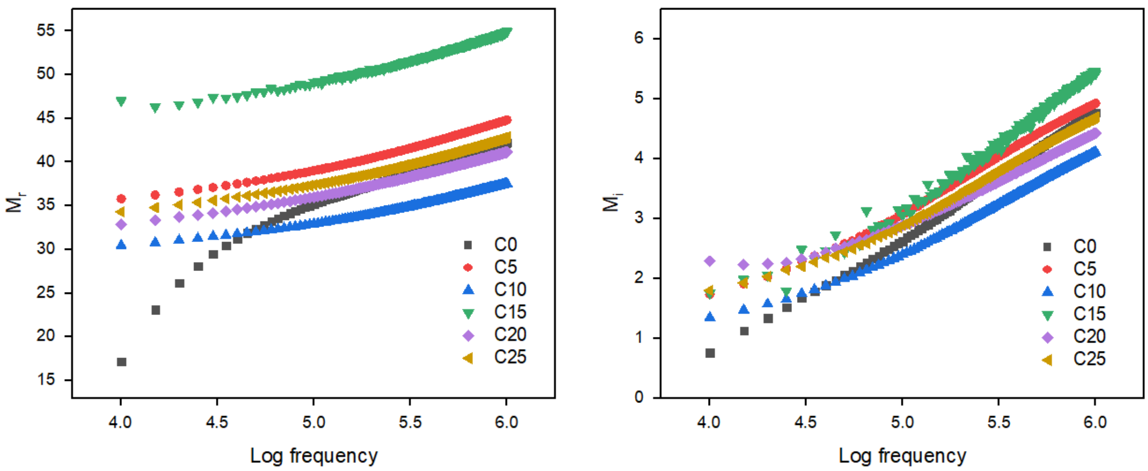
FIGURE 5. The graph of (i) dielectric constant and (ii) dielectric loss for CMC-$(NH_4)_2SO_4$ SBEs at ambient temperature.

In both figures, it can be observed that the ε_r and ε_i values increase because of the migration polarization of the mobile ions with higher ionic conductivity of the SBEs and could be confirmed as non-Debye dependence (Perumal et al., 2019). Furthermore, the dielectric behavior could be suppressing with the effect of electrode polarization using the electrical modulus formulation.

Modulus studies

The other behavior of electrical properties was modulus studies which suppresses the effect of electrode polarization by using equation (5) and (6). The graph of modulus studies was plotted in Figure 6 which illustrated as real modulus (M_r) and imaginary modulus (M_i) graph for CMC-$(NH_4)_2SO_4$ SBEs at ambient temperature.

In Figure 6(i), the log M_r for CMC-$(NH_4)_2SO_4$ SBEs have higher values at lower frequency while Figure 6 (ii), the log M_i is approaches to zero at lower frequency. Figure 6 (i) and (ii) showed that the value of log M_r and M_i is started to increase with increasing frequency. However, in both figures, there is no long tail appeared in the graph because of the lowest capacitive material (Ramlli et al., 2013). Hence, based on Othman et al., (2012), the lower M_i is attributed to the large capacitance within the electrodes. As for C10, the highest conductivity has the lowest value of M_r and M_i at higher frequency (Fuzlin et al., 2018). The presence of peaks at 1 kHz showed that the CMC-$(NH_4)_2SO_4$ SBEs are ionic conductors but the SBE is unfollowed non-Debye behavior (Zainuddin et al., 2017).



(i) (ii)

FIGURE 6. The graph of (i) real modulus and (ii) imaginary modulus for CMC-$(NH_4)_2SO_4$ SBEs at ambient temperature.

CONCLUSION

The solid biopolymer electrolytes (SBEs) of carboxymethyl cellulose doped with ammonium sulphate (CMC-$(NH_4)_2SO_4$) were successfully prepared via solution-casting technique. The CMC-$(NH_4)_2SO_4$ SBEs had been measured using Electrical Impedance Spectroscopy (EIS) at elevated temperature. Thus, the highest ionic conductivity was (5.085 ± 0.001) $\times 10^{-6}$ Scm^{-1} and the activation energy, E_a value was (0.125 ± 0.001) eV which is the lowest energy for CMC doped with 10 wt.% of $(NH_4)_2SO_4$. However, the temperature dependence was plotted and noticeably, the highest conductivity obtained the higher regression value which is 0.95. The frequency dependence of dielectric constant and dielectric loss has been measured and it was concluded that the CMC-$(NH_4)_2SO_4$ SBEs was in non-Debye dependence. However, the modulus studies were showed the imaginary modulus of CMC-$(NH_4)_2SO_4$ SBEs contained large capacitance associated with the electrodes but the real modulus was confirmed the CMC-$(NH_4)_2SO_4$ SBEs is unfollowed non-Debye behavior.

ACKNOWLEDGEMENT

We gratefully acknowledge the support from Advanced of Material Research Group (AOMRG) members and the experimental assistance from Faculty of Science, also financial support from Ministry of Higher Education (MoHE) through grant Q.J130000.3854.19J62 (Reference No. PY/2020/04000), UTMER Vot. 19J62 and Q.J130000.2654.17J86 (Reference No. PY/2019/01641), UTMER Vot. 17J86 of Universiti Teknologi Malaysia.

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