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Irregularities Trend in Electrical Conductivity of CMC/PVA-NH₄Cl Based Solid Biopolymer Electrolytes

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Abstract. In this present work, solid biopolymer electrolytes (SBEs) system consists of the blended polymer namely carboxymethyl cellulose (CMC) and polyvinyl alcohol (PVA) doped ammonium chloride (NH₄Cl) at different composition from 0 to 10 wt. % were successfully prepared by using casting technique. The electrical conductivity of solid biopolymer electrolytes (SBEs) system was investigated by using Electrical Impedance Spectroscopy (EIS). Electrical study shows the highest ionic conductivity in room temperature (303 K) was achieved at $8.86 \times 10^{-5} \text{ Scm}^{-1}$ for sample containing 6 wt. % of NH₄Cl. The present system shown unexpected drop after different amount of NH₄Cl (1-5 wt. %) were added into the CMC/PVA and its might attributed to the factor of composition of dopant. All SBEs systems were found to be obeys Arrhenius behaviour where the plots show close to unity ($R^2 \sim 1$) and thermally activated.

INTRODUCTION

In recent years, polymer electrolytes have attracted much attention to chemists and physicists due to their possible applications in advanced electrochemical devices such as batteries, capacitors, sensors, electrochromic displays, photo electrochemical solar cells and fuel cells [1]. Polymer electrolytes have advantages such as good electrode electrolyte contact, high in ionic conductivity and simple preparation in different form [2,3]. However, solid biopolymer electrolytes (SBEs) should exhibit high ionic mobility, ionic transport that is closely coupled to the high local flexibility and the segmental motion of the polymer chain in order to be industrialized [4]. Intensive research has focusing environmentally friendly material with profitable properties as an alternative solution in SBEs [5,6].

Understanding the interactions between the host polymer and salt dopant is essential to achieve a high ionic conductivity along with the needs of the chemical stability and mechanical strength [4]. In the present work, carboxymethyl cellulose (CMC) and polyvinyl alcohol (PVA) were used as host polymers because they have unique characteristics such as high viscosity, transparency, non-toxicity, biocompatibility, and biodegradability [7]. CMC contains two parts, which are hydrophilic carboxyl groups and hydrophobic polysaccharides which gives water-soluble properties [8,9]. Ammonium chloride (NH₄Cl) was used as dopant in this work due to its suitability in the application of low-energy density devices [10-12]. The samples of CMC/PVA-NH₄Cl SBEs system prepared was analyzed via the electrical impedance spectroscopy (EIS) for the evaluation of electrical conductivity.

MATERIALS AND METHODS

Sample preparation

CMC and PVA were obtained from Acros Organic Co. and Merck Co., respectively. CMC powder was dissolved in distilled water. The 80:20 ratio of CMC: PVA was used as biopolymer blended host due to their highest conducting sample [13] and was dissolved in distilled water. Then, varied amount of NH_4Cl is added into the solution in the range of 1 wt. % to 10 wt. % and stirred continuously until it become homogenous. The mixture solution was stirred constantly at 60 °C for 30 minutes. The mixture is then cast into several petri dishes and left to dry at room temperature for the film to form.

Electrical chemical Impedance Analysis (EIS)

The electrical properties of the bio-polymer blend CMC/PVA doped NH_4Cl electrolyte film with different composition were tested by using HIOKI 3532-50 LCR Hi-Tester over the frequency range from 50 Hz to 1 MHz at room temperature. The biopolymer electrolytes sample was cut into small size with diameter of sample is 2 cm and sandwiched between two stainless steel electrodes. The bulk resistance (R_b) value was obtained from the plot of imaginary impedance (Z_i) versus real impedance (Z_r) and the ionic conductivity, σ was determined using equation (1) below:

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

where t is a thickness of the sample and A (cm^2) the cross-sectional area of the biopolymer electrolytes film. The thickness of the bio-polymer electrolytes films was found to be in the range of 0.0116 to 0.0696 cm using a digital thickness gauge (DML3032).

RESULTS AND DISCUSSION

Physical appearance of CMC/PVA- NH_4Cl SBEs system

The physical appearance of the SBEs prepared with and without NH_4Cl dopant is presented in Figure 1. The prepared sample shows with flexible, transparent and self-standing behaviour as solid films.

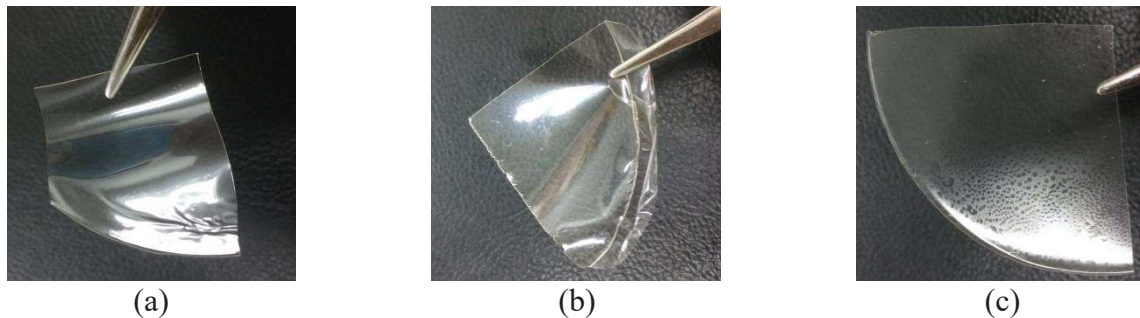


FIGURE 1. Appearance of SBEs thin films for (a) pure CMC/PVA (b) 1wt% and (c) 6wt%

Impedance studies

Figure 2 shows the Cole-Cole plot of various samples CMC/PVA- NH_4Cl based SBEs system at room temperature. Based on the figure, the Cole–Cole plot consists of a high-frequency semicircle and low-frequency spike. From the intercept of high frequency semicircle and low-frequency spike on the Z' axis, the bulk resistance, R_b can be determined [14]. It can be seen that there is formation of semicircle when NH_4Cl was added for sample containing with 1 to 5 wt. %. The semicircle is related to the relaxation process in the bulk polymer electrolyte which triggers the decrement of ionic conductance ability. This phenomenon is obvious for those samples added with 1 and 5 wt. % of NH_4Cl due to the motionless polymer chain [13] and hence increasing the R_b

value. However, the addition of 6 wt. % NH_4Cl , causes the semicircle to disappear and replaced by tilted spike. This phenomenon might be due to electrode polarizations which occur in the system containing 6 wt. % of NH_4Cl that gives lower R_b value and resulting in higher ionic conductivity [15]. On the other hand, the re-appearance of semicircle can be noticed as more NH_4Cl is added (7 and 9 wt. %). This may be explained by the dielectric polarization destruction that hindered the polymer motion which decreasing the R_b value hence increasing the conductivity of the SBEs system. In this present work, the semicircle can be represented as parallel combination of bulk resistance (R_b) that attributed to the movable ions inside the polymer matrix and capacitor (C_g) and the low-frequency spike can be represented with leak capacitor or constant phase element (CPE). The parallel combination circuit element can be explained with migration of protons (H^+) and bulk capacitance that happen due to immobile polymer chains cause the appearance of high frequency semi-circle [16]. Meanwhile, CPE was utilizing in a model to replace the capacitor to balance the heterogeneity in the SBEs system [17]. The impedance of CPE (Z_{CPE}) can be represented by the following equation:

$$Z_{CPE} = \frac{1}{k(j\omega)^\rho} \text{ where } 0 \leq \rho \leq 1 \quad (2)$$

Or

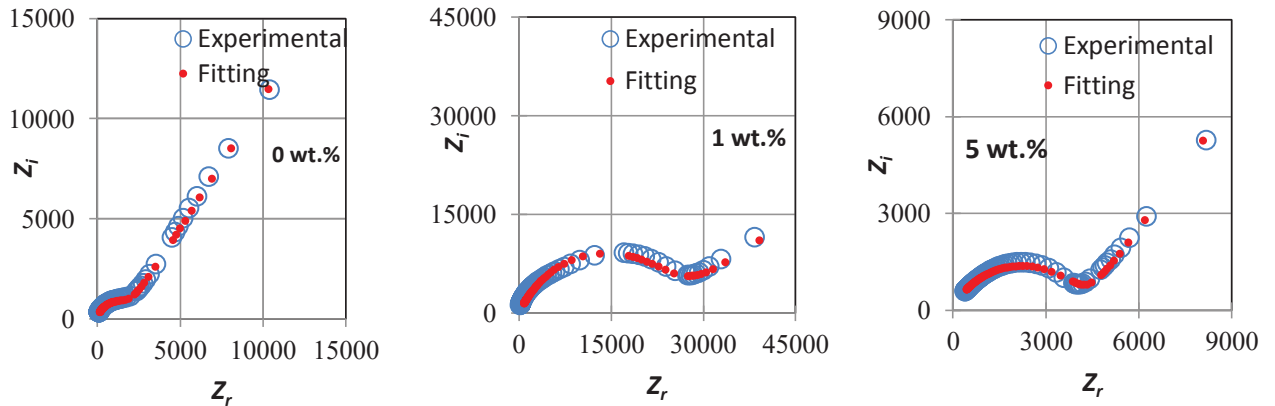
$$Z_{CPE} = k \left[\cos\left(\frac{\rho}{2}\right) - j \left(\frac{\rho}{2}\right) \right] / \omega^\rho \quad (3)$$

Where k^{-1} corresponds to the capacitance value of the CPE element, ω is angular frequency ($\omega = 2\pi f$ where f is frequency), and ρ is related to the deviation from the vertical axis in the Z_r versus Z_i plot. The values of Z_r and Z_i associated to the equivalent circuit can be termed as follows:

$$Z_r = \frac{R_b + R_b^2 k_1^{-1} \omega^{p_1} \cos\left(\frac{\pi p_1}{2}\right)}{1 + 2R_b k_1^{-1} \omega^{p_1} \cos\left(\frac{\pi p_1}{2}\right) + R_b^2 k_1^{-2} \omega^{2p_1}} + \frac{\cos(\pi p_2/2)}{k_2^{-1} \omega^{p_2}} \quad (4)$$

$$Z_i = \frac{R_b^2 k_1^{-1} \omega^{p_1} \sin\left(\frac{\pi p_1}{2}\right)}{1 + 2R_b k_1^{-1} \omega^{p_1} \cos\left(\frac{\pi p_1}{2}\right) + R_b^2 k_1^{-2} \omega^{2p_1}} + \frac{\sin \pi p_2/2}{k_2^{-1} \omega^{p_2}} \quad (5)$$

where p_1 is the deviation of the radius of the circle from the imaginary axis, and p_2 is the deviation of the inclined adjacent line to the semicircle from the real axis.



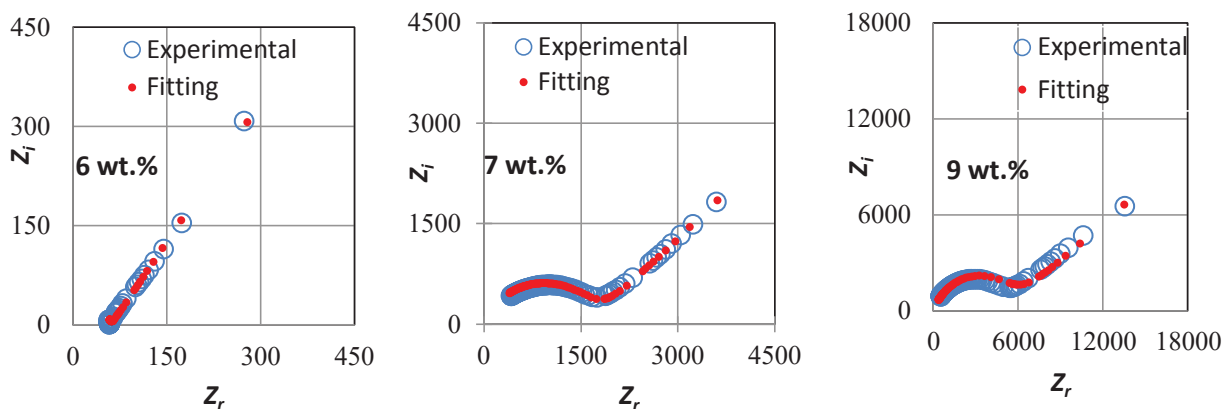


FIGURE 2. Cole-Cole plot of CMC/PVA doped NH_4Cl based solid biopolymer electrolytes systems

Table 1 shows the parameters of bulk resistance for SBEs system which calculated from the equation (4) and (5) based on the try and error fitting method as reported by Shuhaimi et al., [18]; Teo et al., [19]; Shukur et al., [20]. It shows that the R_b value is decreased and sample containing with 6 wt. % NH_4Cl gave the lowest and this due to the improvement of the polymer chain mobility and the thermal movement of the polymer chain [21]. Based on Table 1, it can be seen that theoretical fitting result give almost similar trend to the value obtained by experimental thus it proved that the try and error fitting is aligned with the experimental results.

TABLE 1. list of parameters of circuit elements for all biopolymer electrolytes system composition

Bulk resistance, R_b (Ω)	Sample (wt. %)					
	0	1	5	6	7	9
Fitting	1.64×10^3	2.30×10^4	4.19×10^3	6.24×10^1	1.12×10^3	5.21×10^3
Experimental	2.44×10^3	2.89×10^4	4.29×10^3	6.54×10^1	1.76×10^3	5.82×10^3

Conductivity studies

Figure 3 shows the variation of conductivity for each composition of NH_4Cl . The electrical conductivity of the samples was in the range of 10^{-5} to 10^{-7} Scm^{-1} . As observed in Figure 3, after the incorporation of 1 wt. % NH_4Cl the conductivity was found to decrease which lower than un-doped sample and this might be triggered to the dissociation of NH_4Cl . There are several factors that can influence the ionic conductivity in polymer electrolytes such as salt concentration, temperature, cation and anion types [22,23]. Kim et al. [24] report in their work where the abnormal drop in the electrical conductivity is actually triggered by the electronic structure which observed in polymer electrolytes system. We can speculate that meanwhile, the ionic conductivity predominates over the NH_4Cl composition, where a decreasing trend was observed from 1 wt. % until 5 wt. %. This indicates that segmental mobility has decreased and resulting in reduced chain mobility thus reduces in ionic conductivity at lower composition [25]. Moreover, both CMC and PVA possess hydroxyl group (-OH) which is able to interact with the cation and anion of the NH_4Cl . This interaction leads to a blocking pathway (percolative) of the ions and increasing the structural relaxation which appears to be case with the hydroxyl based polymers such as polyvinyl alcohol (PVA), polyhydroxymethylacrylate (PHM) and polyacrylonitrile (PAN) and other polymers as reported by Wei et al., 1998 [26].

In the present system, the highest conductivity obtained for CMC/PVA- NH_4Cl SBEs system at room temperature was $8.86 \times 10^{-5} \text{ Scm}^{-1}$ for sample containing with 6 wt. % of NH_4Cl . The increase in ionic conductivity at higher value can be related to the increasing in the number of mobile charge carriers with the improvement in the ionic conductivity with increasing dopant composition up to 6 wt. % [27-29]. However, at higher NH_4Cl composition above 6 wt. %, the saturation of ions causes the distance between ions become closer and causes ions association and forms neutral aggregate which lead to decreased again in ionic conductivity [30]. Decreased in conductivity maybe attributed to the presence of mobile ion that can be related due to the drop in density of mobile ion which

occurred from the overcrowded of ions when more (H^+) was dissociated from NH_4Cl and this also reported from the other similar works [20,31-33].

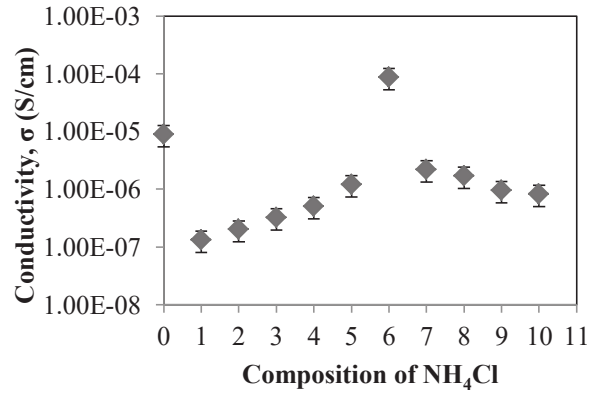


FIGURE 3. Variation of conductivity, σ with concentration of NH_4Cl at room temperature.

Temperature dependence studies

Figure 4 depicts the temperature dependence of proton conductivity for all compositions CMC/PVA doped NH_4Cl system based biopolymer electrolytes over the temperature range 303-353 K. The increase in temperature helps to increase the conductivity of electrolyte which is ascribed to the ionic mobility and the degree of salt dissociation [34]. From Figure 4, it can be observed that the conductivity value of all SBE systems do not show a sudden jump with temperature, indicating that there is no phase transition in the polymer electrolyte structure within the measured temperature range. This result is in good agreement with other similar research works [35,36] and the present SBEs system is considered as promising bio-polymer electrolyte with relatively higher conductivity at higher temperature. In this work, the temperature dependence of SBEs system was found to be thermally activated and follow the Arrhenius-behaviour which can be described by the following relation:

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{kT}\right) \quad (6)$$

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

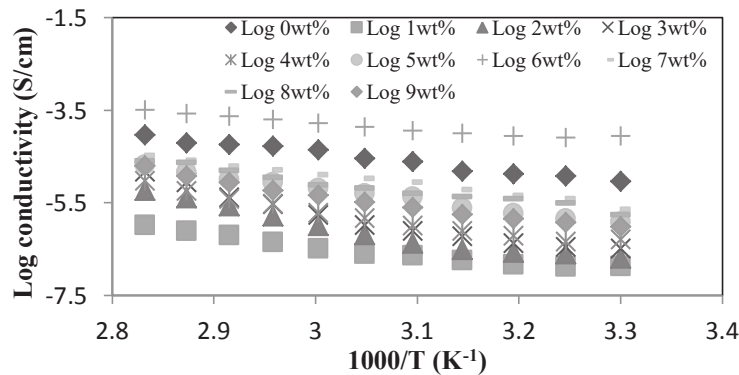


FIGURE 4. Temperature dependence of ionic conductivity for SBEs system.

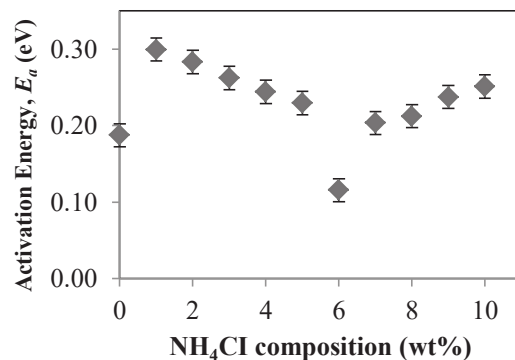


FIGURE 5. Variation of activation energy, E_a of SBEs system at room temperature.

Figure 5 presented the variation of activation energy, E_a which calculated from the slope of temperature dependence in Figure 4 previously. From Figure 5, it can be seen that E_a value trend are inversely proportional with ionic conductivity. It can be noted here, sample containing with 1 to 5 wt. % NH_4Cl gave higher value of E_a and this proved that as discussed in conductivity analysis where huge amount of E_a is needed for ion migration in the SBEs system. Due to the volume space is limited in CMC/PVA and also smaller amount of NH_4Cl which was added in the SBEs system lead to the formation of weak ions to migrate therefore, high E_a value is needed and this turn to the decreased in ionic conductivity. It shows that sample 6 wt. % NH_4Cl exhibit lower E_a value and sample with lower value of E_a has rapid ionic conduction and thus increasing ionic conductivity since the ion transfer is greatly affected by the polymer segmental motion [37,38].

CONCLUSIONS

In the present work, the development of blended CMC/PVA doped with NH_4Cl based solid biopolymer electrolytes (SBEs) system was successfully via casting technique. The prepared samples were tested for electrical characterization by using impedance spectroscopy technique. From the results, it can be concluded that an increase in NH_4Cl composition, causes the R_b value to decrease to a lower value. However, there is irregularities trend in ionic conductivity when 1 to 5 wt. % of NH_4Cl was added which was found lower than un-doped sample and this due to the decreasing in segmental mobility that observed in SBEs system. The CMC/PVA- NH_4Cl SBEs system exhibits the highest conductivity at room temperature with $8.86 \times 10^{-5} \text{ S cm}^{-1}$ and lowest activation energy, E_a for sample containing with 6 wt. % NH_4Cl . The temperature dependence of ionic conductivity demonstrates that the present SBEs system is thermally activated and follows the Arrhenius characteristics.

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