Ionic Conductivity and Structural Properties for CMC - AN in Propylene Carbonate as Plasticizer in Solid Biopolymer Electrolytes

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Abstract. The present study aims to investigate the structural and ionic conductivity of carboxymethyl cellulose (CMC) - ammonium nitrate (AN) – propylene carbonate (PC) as proton conducting polymer electrolytes. The CMC-AN-PC were prepared via solution casting technique. The complexion of polymer electrolyte films has been confirmed via FTIR studies. Fourier transform infrared (FTIR) spectra showed the occurrence of complexation between the polymer electrolyte components. Impedance studies reveals that the highest ionic conductivity of CMC-AN-5wt% PC 6.5 x 10^{-3} Scm^{-1} was observed in polymer electrolyte system obtained at ambient temperature.

Keyword. polymer electrolyte, solution casting technique, ionic conductivity, Fourier transform infrared, Impedance

1. INTRODUCTION

Ionically conductive polymer electrolytes have potential applications in electrochemical devices such as batteries [1, 3], sensors [2], electrochromic windows [3], supercapacitors [4] and etc. Due to their capability and versatility, solid polymer electrolytes (SBEs) have been introduced in this system to improve the conductive of polymer electrolytes. SBE plays an important role in solid state ionics due to their distinctive properties, such as ease of fabrication, good electrode–electrolyte contact and good dimensional, thermal stability, able to accommodate a wide range of ionic salt doping compositions and high ionic conductivity [5].

CMC is a cellulose derivative and appears as a white or slightly yellow flocculent fiber powder or white powder. It is odourless, tasteless, non-toxic, and is soluble in cold water or hot water to form a certain stick degree of the transparent solution. CMC is a natural organic polymer, the most abundant bio-macromolecule, biocompatible and biodegradable [3, 6]. It contains a hydrophobic polysaccharide backbone and many hydrophilic carboxyl groups and shows an amphiphilic characteristic [3]. CMC is produced by etherification of the hydroxyl groups with sodium monochloroacetate (SMCA) in the presence of aqueous alkali as shown in Figure 1.
Figure1 Structure of pure CMC from GaussView 5.0 (red – oxygen, dark grey – carbon, white – hydrogen, purple - sodium).

The addition of ionic dopant to the polymer was reported to increase the ionic conductivity of SBEs by increasing the number of free mobile ions [7]. Thus, the choice of a suitable doping material is essential to ensure the SBE is able to dissociate well in a non-aqueous medium and also provide the pathway for proton to travel with high mobility between electrodes.

In addition, the main purpose of using plasticization methods in polymer-ionic dopant is to enhance the ionic conductivity [7]. A good plasticizer should possess several properties, such as low viscosity, low volatility, high molecular weight, good miscibility between polymer-salt complexes and a high dielectric constant [8].

A variety of plasticizers has been used in polymer electrolytes, such as polyethylene glycol, PEG, imethylformamide, DMF, ethylene carbonate, EC, dibutyl phthalate, DBP, glycerol, dimethyl sulfoxide, DMSO. These plasticizers have been chosen due to their good properties such as, high dielectric constant, help to enhance the ionic dissociation, low viscosity, decrease the glass transition and increase the amorphous content [9]. In this research, propylene carbonate (PC) has been chosen as the plasticizer since it has high dielectric constant, $\varepsilon = 64.4$ [10]. In addition, PC is highly soluble with CMC and AN.

The present work aimed to investigate the electrical and structural of the SBEs system by using electrical impedance spectroscopy (EIS) and Fourier Transform Infrared (FTIR) Spectroscopy, respectively. These experiment combination techniques give in deep understanding on the SBE behavior.
2. Experimental

2.0 g of carboxymethyl cellulose (CMC) from Acros Organic Co. was added into distilled water and stirred until it was completely dissolved. The varied amount of ammonium nitrate (AN) was added to the CMC solution and stirred again until the solutions became homogeneous. The mixture was cast into petri dish and heated onto the oven at constant temperature of 50°C for almost 14 hours. Then, the solutions were left to dry at room temperature (28°C) for film formation. For the plasticized sample, the highest conductivity of CMC-AN SBE was chosen to be added with plasticizer. The same method was used to produce CMC-AN-PC SBEs by adding different amount of propylene carbonate (PC) as plasticizer into CMC-AN mixture as captured in Table 1.

Table 1 Designation of CMC-AN-PC SBEs.

| Designation | Formulation |
|-------------|-------------|
|             | CMC (g)     | AN (wt.%) | AN (g) | PC (wt.%) | PC (g) |
| 0P          | 2           | 45        | 1.64   | 0         | 0.00   |
| 5P          | 2           | 45        | 1.64   | 5         | 0.16   |
| 10P         | 2           | 45        | 1.64   | 10        | 0.34   |
| 15P         | 2           | 45        | 1.64   | 15        | 0.53   |
| 20P         | 2           | 45        | 1.64   | 20        | 0.76   |
| 25P         | 2           | 45        | 1.64   | 25        | 1.10   |

2.1 Electrical Impedance Spectroscopy

Electrical impedance spectroscopy (EIS) was utilized to determine the ionic conductivity of SBEs in the frequency range of 50 Hz to 1MHz. The range of the frequency has been used because of the bulk resistance, $R_b$ exists at that range. Electrical measurements were performed on a HIOKI 3532-50 LCR Hi-Tester by ambient temperature at 303K. SBE was placed between the blocking stainless steel electrodes of a sample cell holder connected EIS. The bulk resistance ($R_b$) of SBE was obtained from the plot of imaginary part (-$Z_i$) versus real part ($Z_r$) of impedance.

2.2 Fourier Transform Infrared Spectroscopy

The complexation of SBEs can be determined by using Fourier Transform Infrared spectroscopy. A Thermo Nicolet 380 FTIR spectrometer equipped with an Attenuated Total Reflection (ATR) accessory utilizing a germanium crystal. The spectrum was recorded in the frequency ranging between 4000 and 700 cm$^{-1}$ with a resolution of 4 cm$^{-1}$.
3. Discussion

3.1 Cole-Cole plot

Figure 2 showed the Cole-Cole plot of CMC-AN-PC SBEs at ambient temperature. From the Cole-Cole plot, the value of bulk resistance, $R_b$ was determined. The $R_b$ can be established by measuring the intercept of the tilted line with the x-axis. The Cole-Cole plot of the SBEs containing 0, 5, 10, 15, 20 and 25 wt% of PC showed straight line trend. This straight-line graph or spike represent formation of double layer capacitance at the blocking electrode-electrolyte interface which causes the inclination and is better known as the polarization effect due to migration of ions [11].

![Figure 2 Cole-Cole plot of CMC-AN-PC SBEs at room temperature.](image-url)
3.2 Ionic conductivity at room temperature

The value of the bulk resistance, $R_b$ from the Cole-Cole plot in Figure 2 can be substituted into the ionic conductivity ($\sigma$) equation below,

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

where, $t$ is the thickness, $R_b$ is the bulk resistance, $A$ (cm$^2$) is the electrode-electrolyte contact area of SBEs.

The ionic conductivity of this system was divided into three regions (Figure 3), where Region I is between 0 – 5 wt.%, Region II between 5 – 20 wt.% and Region III 20 – 25 wt.%. In Region I, the ionic conductivity of unplasticized SBE is $(2.11 \pm 0.03) \times 10^{-3}$ Scm$^{-1}$ and increases to $(6.53 \pm 0.01) \times 10^{-3}$ Scm$^{-1}$ for CMC-AN-5 wt.% PC. After 5 wt.% PC, the ionic conductivity starts to decrease until it reaches the minimum ionic conductivity value of Region II, 20 wt.% PC $(2.63 \pm 0.01) \times 10^{-3}$ Scm$^{-1}$. Beyond 20wt.% PC, the ionic conductivity increases to $(3.63 \pm 0.01) \times 10^{-3}$ Scm$^{-1}$.

As reported by previous work [10], the addition of plasticizer with high dielectric constant such as PC can assist the dissociation of ion / aggregate of salt and producing more free H$^+$ ion to facilitate in the conduction process. However, the insufficient of PC added into CMC-AN SBE may not assist in salt dissociation and causes a reduction in ionic conductivity (Region II in Figure 2). In Region III, the addition of sufficient PC concentration is believed to introduce a shorter pathway between H$^+$ ion and PC, causing more ion dissociation. The number of free ion and ionic mobility are expected to increase and thus improves in ionic conductivity. This result is similar to the work reported by [7] in their plasticized polymer-salt system. Based on these results, it can be said that the addition of AN and EC has influenced the ionic conductivity variation in this system.

![Figure 3 Ionic conductivity plot of PC concentration in SBEs.](image-url)
3.3 FTIR analysis

In order to study the interaction between CMC-AN-PC, Figure 4 is plotted as (a) pure PC; (b) pure AN and (c) pure CMC. Figure 5 represents the FTIR spectra of CMC-AN-PC between wavenumber of 4000 and 700 cm\(^{-1}\). A broad absorption peak of O-H stretching at 3680 cm\(^{-1}\) to 2680 cm\(^{-1}\). Pure CMC shows a strong peak of symmetric stretching mode of carboxylic group, \(\nu_a (\text{C}=\text{O})\) at 1591 cm\(^{-1}\). The bands located at 1417 cm\(^{-1}\) and 1321 cm\(^{-1}\) corresponds to CH\(_2\) scissoring, \(\delta (\text{C}-\text{H})\) and bending mode of C-OH bonding, \(\delta (\text{C}-\text{OH})\), respectively. The doubled stretching mode of C-O-C were observed at 1105 cm\(^{-1}\) and 1057 cm\(^{-1}\). This result is agreement as reported by several researchers [12-13].

Pure AN exhibits intense vibration bands in the range of 4000 cm\(^{-1}\) to 900 cm\(^{-1}\) as showed in Figure 4. As compare to Figure 5, at wavenumber of 3250 cm\(^{-1}\), 3074 cm\(^{-1}\) and 2351 cm\(^{-1}\) corresponds to stretching mode of ammonium (NH\(_4^+\)) ion. The mixture of CMC-AN-PC SBEs were observed the asymmetric stretching and deformation modes of both \(\nu(NH_4^+)\) and \(\nu(NO_3^-)\) to appear between 1800 cm\(^{-1}\) to 1500 cm\(^{-1}\)[7]. Zhao et al (2008) reported the asymmetric deformation mode of ammonium ions, \(\nu(NH_4^+)\) occurs at 1470 cm\(^{-1}\). The others of the vibration bands from pure AN at the lower wavenumber belongs to the stretching \(\nu(NO_3^-)\) and bending \(\delta(NO_3^-)\) modes of nitrate ions [15-17].

In Figure 5, a peak corresponds to C=O stretching of PC was appeared at 1770 cm\(^{-1}\) at 5P to the lower wavenumber of 1750 cm\(^{-1}\) upon the addition of 5wt.% of PC in CMC-AN SBE. The peaks were prominent and the intensity increased as PC composition increased. The increase in peak intensity at C=O is believed due to increase of PC supplied in the polymer matrix and proving the interaction between CMC and PC. At the peaks for C-H bending deformation at 1422 cm\(^{-1}\) at 5P seems decreased to the lower wavenumber to 1405 cm\(^{-1}\) at 25P. It can be summarized that, there is no obvious increment of intensity changes between CMC-AN and PC concentration from the IR spectrum. That is the reason, the ionic conductivity in not increase upon the addition of 10wt.% until 20wt.% of PC concentration from the IR spectrum.
**Figure 4** (a) Pure PC (b) pure AN and (c) pure CMC.

**Figure 5** IR spectra of 0P, 5P, 10P, 15P, 20P and 25P SBEs.
4. Conclusion

The CMC-AN-PC SBEs have been successfully prepared by solution casting technique. The highest ionic conductivity obtained at $6.5 \times 10^{-3}$ Scm$^{-1}$ at 5 wt. % of PC at ambient temperature. FTIR studies confirmed that the complexation of CMC-AN-PC SBEs. The changes of wavenumber showed that the interaction was completely occurred when 5wt.% of PC was added to CMC-AN system. The IR spectrum shows the amount of PC in the CMC-AN is not sufficient enough to increase the ionic conductivity and to dissociate in this system.

Acknowledgement

We gratefully acknowledge the financial support from Ministry of Higher Education (MoHE) through grant UTMER Vot. 19J62 of Universiti Teknologi Malaysia and the experimental assistance from Faculty of Science.

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