Optical, Structural and Electrical Studies of Biopolymer Electrolytes Based on Methylcellulose Doped with Ca(NO₃)₂

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Abstract. The intention of this research is to study effect of the different weight percent (wt%) of calcium nitrate, Ca(NO₃)₂ (CN) salt into biopolymer of Methylcellulose (MC). MC-CN solid biopolymer electrolyte was prepared by using casting technique. The concentrations of CN salt were prepared between 5 to 25 wt%. The optical and electrical characteristics of the samples were study by using Fourier Transform-Infrared (FTIR) spectroscopy, X-ray Diffraction (XRD) and Electrical Impedance Spectroscopy (EIS). The highest conductivity of the samples was containing 25 wt% of CN is 2.21X10⁻⁷ S cm⁻¹. The optical study by using FTIR shows that the CN salt act as the conducting ions devoid of effect the molecular structure of the polymer. Additionally, the data of XRD revealed that MC-CN an amorphous phase.

1. Introduction

The dependency of science and technology according by study of materials and application stand of ionically conducting solid known as “Solid-State Ionics”. Besides, solid states ionic are dividing into liquid electrolyte and solid electrolyte. The liquid electrolyte gives a major weakness such as poor electrochemical stability, leakage and reaction with electrode indirectly not suitable to apply in electrochemical devices [1]. To overcome this weakness, the potential application in various technological areas focuses on solid polymer electrolytes which act as an authority over liquid electrolytes because of being strong [2]. Polymer electrolyte are one of the significant part in solid state ionic based on several properties which are good electrode-electrolyte contact [3], high ionic conductivity with wide surface area to operate high energy density while ease fabrication into thin film and capable to accommodate a large range of doping salt compositions [4].

Furthermore, technology nowadays emphasize of “green materials” aspect to avoid the all profanation environment and energy disaster. Besides, the new biopolymer electrolytes (BPE) product be found by many researchers help to lower the cost and being environmentally green compare synthetic polymer electrolytes [5]. The polymer electrolyte could unfold as solid electrolytes comparable perfectly intercalation electrodes. The polymer are also the most crucial categorization of conjugated polymers appropriate in a various type of applications such as light emitting diodes, conducting polymers and field effect transistors because of their great optical and electrical properties [6]. However, common polymer
without blend with other polymer not guaranteed good chemical or physical characteristic to meet extensive variety of electrochemical devices [7]. The blend polymers have better conductivity compare with common polymer. While the conductivity for common polymer can increase by mix with salt materials involving dissimilar types of transporting ions [8].

Meanwhile, biopolymer are make more intention among researcher due to their properties which are biodegradable polymer and known as environmentally friendly products [9]. Biopolymer is also inexpensive of cost materials and abundance in nature which act as the main reason to choose Methylcellulose (MC) as the biopolymer electrolyte in this research. MC is one of the simplest cellulose derivatives [10]. Besides, MC is also good solubility in water with low temperature while act as biodegradable cellulose ether [11]. MC present large-strength films that are transparent, water soluble, oil and grease resistant and low oxygen with transmission rates of moisture vapour [12]. In addition, with this research, the biopolymer of MC as the host polymer are mix with CN salt to increase the conductivity and achieve the standard characterize of electrolyte which help in the system of application such as solar cell, battery and others.

2. Methodology/Materials
2.1 Preparation of Biopolymer Electrolyte Films
Solid biopolymer electrolyte thin films were prepared by using cast technique. 2 g of MC from Sigma Aldrich were dissolved in distilled water then different amount of wt% of CN salt from Merck KGaA was added and stirred continuously until the salt was dissolved completely. Then, make sure the salt and polymer complex were homogenously mixed and were placed into different polystyrene petri dishes and bare to evaporate the mixtures under room atmosphere.

2.2 Fourier transform-infrared (FTIR) spectroscopy
Fourier transform-infrared (FTIR) spectroscopy, model of Thermo Nicolet Avatar 380 FT-IR spectrometer are functionate to study the synergy of the biopolymer provide and the doping salts. While, it is also to investigate the complex nature and functional groups present in complex electrolyte. The sample was analyzed by used spectrophotometer helmeted with an Attenuated Total Reflection accessory with a germanium crystal. On the surface of germanium, crystal placed of the sample and infrared light passed through the sample, which used range of wavenumber at 4000 to 400 cm$^{-1}$ and a resolution at 1 cm$^{-1}$.

2.3 X-ray Diffraction (XRD) Study
The sample was analysed by using X-ray Diffraction (XRD). It was also investigated the XRD patterns at room temperature and the amorphosity structure of the sample by used a MiniFlex II diffractometer equipped with an X’celerator, using Cu K$_\alpha$ radiation based on scale of 2$\theta$ from 5° to 80°.

2.4 Electrical Impedance Spectroscopy (EIS)
The biopolymer electrolytes were sandwiched in the middle blocking stainless steel electrode that was connected to a computer in the form of small circle with 2 cm diameter of electrolyte. The sample were measured the conductivities of MC-Ca(NO$_3$)$_2$ by using a Hioki 3532-50 LCR Hi-Tester interfaced to a computer with used a frequency range between 50Hz to 1MHz. The Nyquist/Cole-Cole plots obtain negative imaginary impedance ($-Z_i$) versus real impedance ($Z_r$) values. While can measure the bulk resistance, $R_b$ from the plot and conductivity was calculated using equation follows:

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

Where, $t$ is the thickness of sample (cm) and $A$ is the contact area (cm$^2$) between the samples and the electrode.
3. Results and Discussion

3.1 FTIR Analysis

FTIR analysis has been operated to investigate the compositional, structural and interaction bonding between MC and CN in BPE system [5]. Besides, the FTIR spectra of MC-CN biopolymer electrolytes shown in Fig.1 with wavenumbers between 4000 to 500 cm$^{-1}$. From the figure, the peak at 1055 cm$^{-1}$ is described as the antisymmetric stretching of asymmetric oxygen bridge in the cyclohexane ring with range between 1150 to 1000 cm$^{-1}$ which is C-O-C bond [13]. The increment with the 25 wt% of CN, the peak is observed shifted to lower wavenumber show the complexation between MC and CN in the system. Consequent to addition of CN salt, Ca$^{2+}$ will provide as cation which will attract at the oxygen atom at C-O-C bond of the ether group in the identical polymer to form polymer salt complexes [14]. However, from the Fig.1 show 1055 cm$^{-1}$ and 1049 cm$^{-1}$ peaks are raise in the percent of transmittance as the weight percent of salt is increased. The changes in this system augmented due to the coordination interaction of C-O-C in MC with Ca$^{2+}$ of CN salt [15].

![Figure 1. Fourier transform-infrared (FTIR) spectroscopy analysis.](image)

3.2 XRD Analysis

The amorphous on crystallinity of the polymer film with respect to pure MC and CN complex have been examine by x-ray diffraction. XRD is a multi-purpose tool to monitor the transition in structural properties to both crystalline and amorphous region of BPEs system. The pattern of six different samples which are 0, 5, 10, 15, 20, and 25 wt% with pure MC based on an x-ray diffraction at room atmosphere from $2\theta = 5^\circ$ to $80^\circ$ are shown in Fig.2. Based that figure, the broad diffused band at $2\theta = 21^\circ$ while the starter peak at $2\theta = 8^\circ$. The two peaks, at $2\theta = 8^\circ$ with $21^\circ$ was appeared and showed as pure MC pattern [16]. The existence based on peak at $8^\circ$ is declaration with cellulose adaptation [9]. The increment of the width peaks of MC at $2\theta = 8^\circ$, $21^\circ$ due to addition of CN salt and proportionate intensity decrease. While the strongest cellulose peak at $21^\circ$ with MC:CN(25%). However, the Fig.2 below can be observed that at 25 wt% CN salt to pure MC relative intensity of broad peak at $2\theta = 21^\circ$ increase prove the increment of the conductivity.
3.3 **EIS Analysis**

The conductivity of MC without salt is $\approx 10^{-10}$ S cm$^{-1}$ and it increase distinctly to $\approx 10^{-7}$ S cm$^{-1}$ on complexing the MC with CN. However, the conductivity of BPEs relies on diverse determinant, which are ionic conducting types, the temperature and variety of charge carriers (cationic or anionic). In prevalent, the higher frequency semicircle depict of complex impedance plot as bulk resistance of polymer electrolytes, while the low frequency is because of the capacitance of the double-layer formed at the electrode/electrolyte interface [17].

Besides, based on Fig.3 show that the decrease in the high frequency semi-circular part consequent to doping CN from 0 to 25 wt%. In this case can relate that the current carriers are ions and the total conductivity mostly the result of ion conduction [18]. Furthermore, the value of conductivity occur escalation correlative with inclusion of the CN and achieve maximum value of $2.21 \times 10^{-7}$ S cm$^{-1}$ for sample with 25 wt%.

Moreover, increment of the conductivity continuously with increasing of wt% CN configuration while it claimed to the FTIR analysis supported by the ion association. In MC-CN, the Ca$^{2+}$ interacted with the O at C-O-C bond of the ether group of the MC host. The increment of salt may have increase the number of ions or developed new conducting pathway which increase the movement of the protons [19]. While, the more salt added to the host polymer endorse a decline in conductivity because of the complexation between MC and CN reduces the movement of the charge carriers [20].
Figure 3. Electrical Impedance Spectroscopy (EIS) analysis of conductivity (Scm$^{-1}$).

4. Conclusion
The discovery of new BPE has been consummate in this work by incorporating different concentrations (0-25 wt%) of CN with biopolymer materials MC via solution casting technique. The conductivity biopolymer electrolyte of MC-CN increases due to function of 0-25 wt% of CN. The highest conductivity obtained of this polymer-salt complex was 2.9 × 10$^{-7}$ Scm$^{-1}$, for sample 25 wt% CN. The increment in movement of proton ions and malleable structure are accountable for the augmentation of conductivity. Its evidence that effect of complexation of CN in MC polymer common, influenced by the charge carrier concentration due to the shifted of the peak at 1055 cm$^{-1}$ of wavenumber and confirms composite nature of electrolyte with intensity of broad peak at 2θ = 21° increase show the increment of the conductivity from FTIR analysis and as well as XRD analysis.

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