

Effect of Ammonium Carbonate Salt Concentration on Structural and Ionic Conductivity of Cellulose Based Solid Polymer Electrolytes

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Abstract: The cellulose based solid polymer electrolytes (SPEs) containing carboxymethyl cellulose doped with ammonium carbonate (AC) have been prepared via solution casting techniques. The XRD analysis shows that the SPE films are amorphous in nature. FTIR spectroscopy shows that the occurrence of interaction between AC salt and the polymer matrix at wavenumber range of 800-1800 cm^{-1} . Impedance measurement shows that the highest ionic conductivity was achieved at $7.71 \times 10^{-6} \text{ S cm}^{-1}$ (7 wt% AC) obtained at 303 K. The ionic conductivity of SPE films at different salt concentration were revealed to follow Arrhenius law and thermally assisted.

Keywords: Solid polymer electrolytes, Carboxymethyl cellulose, Ammonium carbonate, Structural, Ionic conductivity

Introduction

With the ever worrying problem of pollution and depleted fossil fuels throughout the world, research community at this time is engaging an intense research for alternative energy sources [1]. Solid polymer electrolytes (SPE) is viewed as a good alternative in secondary batteries electrolytes since it possess good dimensional and thermal stability, no leakage, flexibility and ease to fabricate and good electrode-electrolyte contact [2]. Several types of SPE have been previously reported such as poly(ethylene oxide) (PEO) [3], polymethyl methacrylate (PMMA) [4], Chitosan (CS) [5], polyacrylonitrile (PAN) [6] and polyvinyl chloride (PVC) [7].

Amongst those types of SPE, carboxymethyl cellulose (CMC), a natural anionic polysaccharide, which is widely used in many industrial sectors including food, textiles, paper, adhesives, paints, pharmaceuticals, cosmetics and mineral processing. CMC is an abundant natural product which has a white- to cream-colored, tasteless, odorless and free-flowing powder [8,9]. Due to its biodegradable properties and good film forming abilities, CMC is chosen as the polymer host in this work [10,11].

The polymer host will need to be complexes with an ionic dopant in order to enhance the ionic conductivity. Since ammonium salts have been considered as a good proton donor, ammonium carbonate (AC) has been chosen as the ionic dopant in this SPE system [12]. On top of that, AC contains high weight percentage of hydrogen since it has 2 ammonium group (NH_4) [13]. The present work aims to investigate the structural and ionic conductivity of SPEs based carboxymethyl cellulose incorporating with ammonium carbonate. SPE films were characterized using XRD, FTIR and EIS.

Experimental

SPE Films Preparation

2 g of CMC was stirred in distilled water until homogenous. Once homogenous, different amount of AC (1-11 wt.% AC) was added into the CMC solution. The mixture solution was then stirred continuously until completely dissolved. Then, the mixture solution was casted into petri dishes for drying process at room temperature (303 K). The final dried film was placed in desiccator to further eliminate water presence in the film for another one week. The SPE film was cut into suitable sizes for sample characterization.

Characterization Techniques

X-ray diffraction Rigaku Miniflex II diffractometer was used to determine the nature of the SPE films. A suitable size of SPE film was cut and placed onto a glass slide sample holder. The measurement was conducted at scanning angle, 2θ between 5° and 80° using $\text{CuK}\alpha$ radiation.

Fourier Transform Infrared (FTIR) spectroscopy Thermo Nicolet 380 FTIR equipped with an attenuated total reflection (ATR) accessory with germanium crystal. The sample was placed on germanium crystal and infrared light was passed through the sample within the frequency ranging from 4000 cm^{-1} to 675 cm^{-1} at spectra resolution of 4 cm^{-1} .

The electrical impedance spectroscopy (EIS) HIOKI 3532-50 LCR Hi-Tester interfaced to a computer with frequency of 50 Hz to 1 MHz was used to investigate the ionic conductivity of SPE films. The films was cut into a suitable size and placed between the stainless steel blocking electrodes of the sample holder.

Results and Discussion

XRD Analysis

Figure 1 represents the XRD patterns of SPE films at

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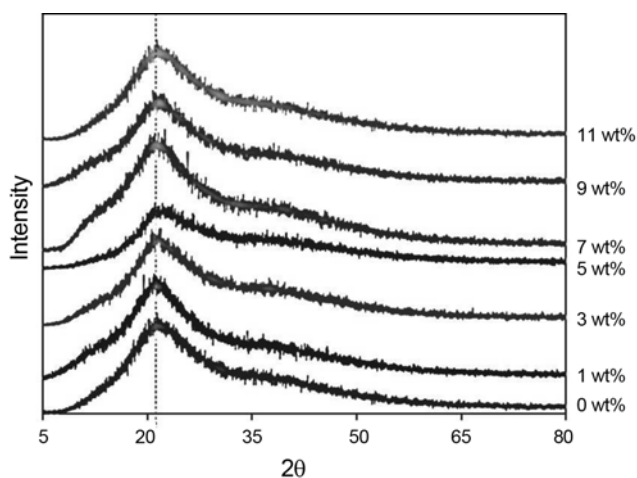


Figure 1. XRD pattern of SPE films containing different concentration of AC salt measured at room temperature.

different weight percentage of AC. From the figure, the broad peak centered at $10^{\circ} \leq 2\theta \leq 30^{\circ}$ was observed for every SPE films. The broad peak indicates that all SPE film is amorphous in nature. According to Shuhaimi *et al.* [14], changes in amorphous level in polymer system will affect its conductivity where increase in amorphous nature will result in increase of conductivity. As can be seen from the Figure 1, an increase of amorphousness can be seen with the decrease in broad peak at 20.24. These suggest that complete dissolution of AC occurred into the polymer host with every increment of ionic dopant. These observations explain that the polymer undergoes significant structural reorganization [15].

FTIR Analysis

Interaction between polymer host (CMC) and ionic dopant (AC salt) can be analyzed through FTIR the Shifting, disappearance/emergence of new bands in FTIR spectra. Figure 2 represents the spectra in the region of 800-1800 cm^{-1} for SPE films at different concentration (1-11 wt.%). From previous reports in CMC polymer [9,14,16], it is expected that the interaction occurs at the stretching of carboxylic group (COO^-) of CMC. In this reports the carboxyl band can be found at 1591 cm^{-1} and 1417 cm^{-1} for asymmetrical ($\text{C}=\text{O}$) stretching and symmetrical ($\text{C}-\text{O}$) stretching respectively.

It can be observed that when the AC concentration increase till 7 wt.%, the carboxyl group ($\text{C}=\text{O}$) band at 1591 cm^{-1} has weakened. This suggest interaction between $\text{C}=\text{O}$ moiety and H^+ from NH_4^+ substructure from AC. This phenomenon can be related to the lone pair electron that attracts the salt molecule of AC to the system [17]. In polymer-ammonium system, the conducting species is from H^+ of ammonium ion (NH_4^+). In tetrahedral structure of ammonium ion, one of the four hydrogen atom are loosely bound which makes it easy to dissociate and hop to

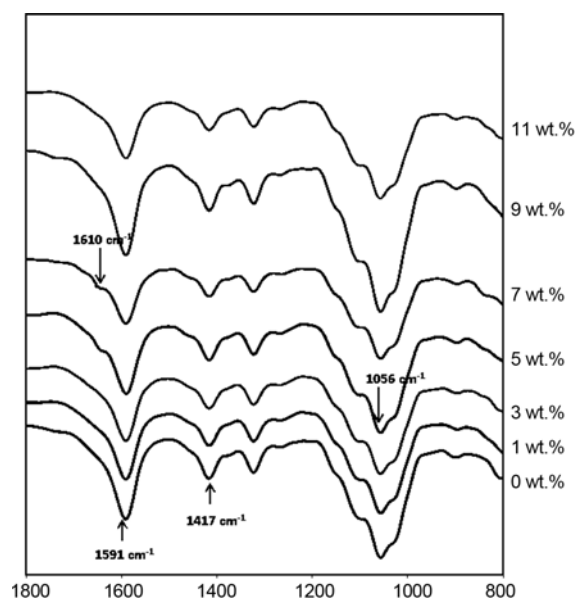


Figure 2. FTIR spectra of SPE films at wavenumber of 800-1800 cm^{-1} .

neighboring site causing conduction process [14,18,19]. As AC concentration increases, H^+ concentration also increases. Consequently, more hydrogen bonding were formed as electron are withdrawn toward $\text{C}=\text{O}$ which leads to the weakening of 1591 cm^{-1} band. However, the ionic conductivity value decreases when AC concentration go above 7 wt.%. This is believed due to the ions recombine to form neutral aggregates [20]. New band appeared at 1610 cm^{-1} is associated to H^+ from AC. The band at 1056 cm^{-1} indicates the $\text{C}-\text{O}$ stretching of the polysaccharides skeleton from CMC.

Ionic Conductivity Measurement

Ionic conductivity, σ of polymer-salt system depends on the type of charge carriers (cations/anions), number of mobile ions (η) and mobility of charge carriers (μ) [16] can be calculated from the equation below:

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

where t is the SPE film thickness, R_b is the bulk resistance and A is the surface contact area of electrode and electrolyte. The R_b for each SPE film was obtained from the Cole-cole plot of negative imaginary impedance, $-Z_i$ against real impedance, $-Z_r$. Figure 3 shows the plot of salt dependence of ionic conductivity at 303 K. The ionic conductivity appears to increase from $9.33 \times 10^{-9} \text{ S cm}^{-1}$ to $7.71 \times 10^{-6} \text{ S cm}^{-1}$ with the increment of salt concentration from 0 wt.% to 7 wt.% AC. This increment of ionic conductivity is believed due to the increasing number of mobile ions in the polymer-salt system. This can be explained by the ion association of AC into the CMC described in the FTIR analysis. As AC

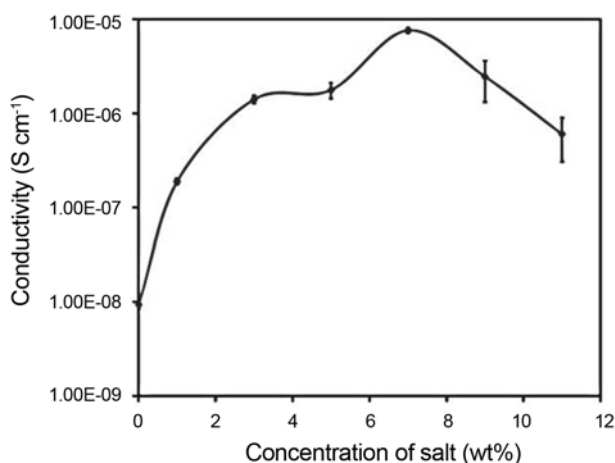


Figure 3. Ionic conductivity of SPE films obtained at 303 K.

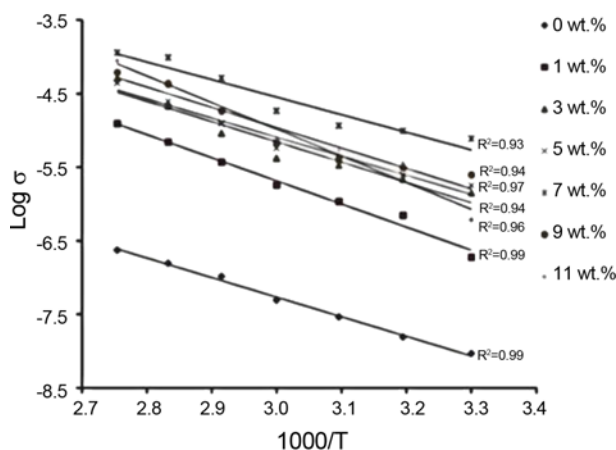


Figure 4. Temperature dependence of ionic conductivity at different AC concentration of SPE films measured at 303-363 K.

concentration increases, more protons are supplied into the polymer-salt system, leading to the increase of ionic conductivity. Further addition of AC (> 7 wt.% AC) into the polymer system seems to decrease the conductivity value to 6.04×10^{-6} S cm^{-1} . This behavior may due to the reducing of ionic mobility caused by the overcrowded of free mobile ions [21]. These are also due the dissociation of H^+ in the densely packed system and thus lower the ionic mobility.

Temperature dependence of ionic conductivity was obtained at temperature range of 303-363 K as shown in Figure 4. The plot of $\log \sigma$ versus $1000/T$ can be expressed through relation,

$$\sigma = \sigma_0 e^{-E_a/kT} \quad (2)$$

where σ_0 is the pre-exponential factor, E_a the activation energy, k is the Boltzman constant and T is the absolute temperature. The ionic conductivity of polymer-salt system shows an increasing trend with the increment of temperature.

The regression values, R^2 are found to be closed to unity for all SPE films and follow Arrhenius behavior. The increment of ionic conductivity with temperature can be explained by the free volume model. This model stated that the free volume increase as the temperature increase due to the lattice vibration which, in turn promotes ions mobility in inter- and intra-chain hopping, thus increase the ionic conductivity in the polymer-salt system [14,22].

The ionic conductivity value can also be affected by the amorphous nature of the system. According to Johan *et al.* and Sohaimy *et al.* [19,23], the amorphous nature will results in a greater ion diffusion and thus create a greater ionic conductivity where it make the SPE to be temperature dependent. Furthermore, it also causes a reduction in the energy barrier to the segmental motion of the polymer electrolyte [24].

Conclusion

The cellulose based solid polymer electrolytes doped with AC has been successfully prepared via solution casting technique. XRD analysis showed that SPE films are amorphous in nature while FTIR analysis confirmed that the interaction has existed in the polymer-salt system. The ionic conductivity was revealed to rise from 9.33×10^{-9} S cm^{-1} (0 wt.% AC) to 7.71×10^{-6} S cm^{-1} (7 wt.% AC). The polymer-salt system was found to follow Arrhenius behavior rule and thermally assisted. From the result obtained, CMC-AC solid polymer electrolyte films show a promising potential application in electrochemical devices such as in supercapacitors, fuel cells and batteries.

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