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Research Article

Ionic Conductivity and Structural Analysis of Carboxymethyl Cellulose Doped With Ammonium Fluoride as Solid Biopolymer Electrolytes

¹M.A. Ramlli, ¹K.H. Kamarudin and ^{1,2}M.I.N. Isa

¹Advanced Materials Research Group, School of Fundamental Science, Universiti Malaysia Terengganu, 21030 Kuala Terengganu, Terengganu, Malaysia.
²Research Management Centre, Universiti Malaysia Terengganu, 21030 Kuala Terengganu, Terengganu, Malaysia.

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ABSTRACT

In the present work, a series of solid biopolymer electrolytes (SBEs) from carboxymethyl cellulose (CMC) doped with ammonium fluoride (NH₄F) (0 - 13 wt. %) was successfully prepared by solution cast technique. SBE sample containing 9 wt.% NH₄F was found to exhibit the highest ionic conductivity of $2.68 \times 10^{-7} \text{ S cm}^{-1}$ at ambient temperature. XRD analysis revealed that the SBE samples containing NH₄F salt to be semi-crystalline in nature. FTIR spectra showed that the interaction between CMC and NH₄F has occurred in the polymer-salt system and the CMC-NH₄F SBE system was a proton conductor.

Keywords: Solid biopolymer electrolytes, carboxymethyl cellulose, ionic conductivity, ammonium fluoride, XRD, FTIR

INTRODUCTION

Nowadays, solid biopolymer electrolytes (SBEs) gain tremendous interest to researchers due to their potential application in electrochemical devices such as in batteries, fuel cells and supercapacitors [1]. Modern electronic devices like cell phones, remote controllers, laptops and tablets used batteries as their energy storage. However, today's commercial batteries contain hazardous and toxic chemicals such as lithium, cadmium, mercury and lead. These materials are harmful to the environment and human. Most of the batteries were thrown away when they were broken or drained which may cause environmental pollution. When burned, toxic chemicals will release hazardous gasses into the air.

To overcome this problem, an alternative solution based green materials can be employed into the battery system. This includes using polymer

based electrolyte as host polymer. Natural polymer such as starch and cellulose [2,3] and synthetic polymer such as polyvinyl alcohols and polyethylene oxide^{4,5} are the two types of polymers. Synthetic polymer was usually chosen because of their highly conductive properties, however they were very expensive. Although natural polymers not as conductive as synthetic polymers, they were very affordable and abundance in nature and they have good films formability [1,6].

In this research, carboxymethyl cellulose (CMC) was used as host polymer due to the superior characteristics such as non-toxic, biocompatible, renewable and biodegradable capabilities.⁷ In order to enhance the ionic conductivity, ammonium fluoride (NH₄F) salt was selected as proton donor to be doped into the polymer matrix. The SBE samples were further characterized using EIS, XRD and FTIR to investigate the ionic conductivity and structural

properties of the SBE system.

2. Experimental:

Preparation of SBE samples:

For SBE samples preparation, CMC (Argos Organic Co.) and NH_4F (R&M Chemicals) were

dissolved in distilled water until homogenous solutions were obtained. The mixture was casted into several Petri dishes, and left to dry in oven at 60°C until the films were formed. Table 1 lists the designation and NH_4F weight percentage for SBE samples.

Table 1: Designation and weight percentage of NH_4F salt for SBE samples.

Sample	CMC ($\pm 0.0001\text{g}$)	NH_4F (wt. %)
CMCAF-0	2.0000	0
CMCAF-3		3
CMCAF-5		5
CMCAF-7		7
CMCAF-9		9
CMCAF-11		11
CMCAF-13		13

Characterization techniques:

The ionic conductivity of the SBE samples was performed using electrical impedance spectroscopy (EIS) HIOKI 35320-50 LCR Hi Tester with 50-1M Hz frequency range. The SBE samples were cut into a suitable size and placed between two stainless steel electrodes. The complex impedance technique was used to determine the impedance of the SBE samples. The ionic conductivity was calculated using equation,

$$\sigma = t / (R_b * A) \quad (1)$$

where σ is the ionic conductivity, R_b is the bulk resistance, t is the thickness of the SBE and A is the area of contact between the SBE sample and electrodes.

The X-ray diffraction (XRD) was carried out using MiniFlex II Ringaku with CuK_α radiation scan angle, 2θ was varied from 5° to 80° . Fourier Transform Infrared (FTIR) were recorded using Thermo Nicolet 38 FTIR spectrometer equipped with an attenuated total reflection (ATR) accessory with a germanium crystal in wavenumber between 700 cm^{-1} - 4000 cm^{-1}

Results and Discussion

Ionic conductivity:

The plot of ionic conductivity against NH_4F salt concentration of the SBE samples was revealed in Figure 1. From the figure, the ionic conductivity of the SBE has increased with the addition of NH_4F concentration and dropped after adding more than 9 wt. % NH_4F . The highest ionic conductivity was achieved at $2.68 \times 10^{-7}\text{ Scm}^{-1}$ for CMCAF-9 SBE sample. The increasing in ionic conductivity with the addition of NH_4F concentration was due to the interaction between CMC and NH_4F which brings to the dispersion of proton, H^+ in the polymer salt systems. Thus, increase the number of mobile ions and enhance the ionic conductivity of SBE samples [8]. However, upon addition of more than 9 wt. % NH_4F , the ionic conductivity was found to decrease as a result of dispersion of free ions. These free ions forms clusters and restrict other free ion movement leading to the decrease in ionic conductivity in the SBE system [9].

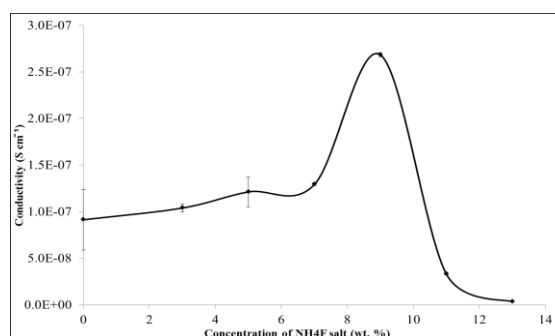


Fig. 1: Plot of ionic conductivity versus NH_4F salt concentration of SBE samples measured at ambient temperature.

XRD analysis:

Figure 2 represents the X-ray diffraction pattern of pure NH_4F salt and CMCAF-0 obtained at room temperature. XRD pattern for pure NH_4F salt showed intense poly-crystalline peaks at $2\theta = 23.66^\circ$, 43.22° and 62.06° . Amorphous peak centered at $\sim 20^\circ$ was observed for CMCAF-0 sample. This broad peak

was known as amorphous hump and it is a characteristic of an amorphous material [9,10].

Figure 3 depicts the X-ray diffraction pattern of SBE samples with different weight percentage of NH_4F . Upon addition of NH_4F salt into the SBE samples, the amorphous peak of polymer has broadened and three crystalline peaks originated

from NH_4F salt are clearly being seen. The broadened amorphous hump indicates the amorphous nature of the SBE samples [11]. From the XRD results in Figure 3, the SBE samples were revealed to exhibit semi-crystalline structure with the addition of NH_4F . The broadness of amorphous peaks and the

appearance of poly-crystalline peaks in the SBE samples indicated the complexation/interaction of CMC- NH_4F in the polymer-salt system. FTIR analysis has been carried out to further investigate the CMC- NH_4F interaction in the SBE system.

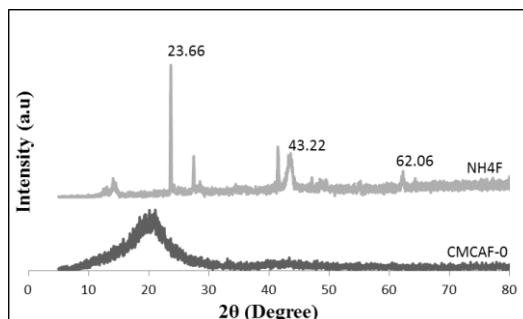


Fig. 2: X-ray diffraction patterns of pure NH_4F salt and CMCAF-0.

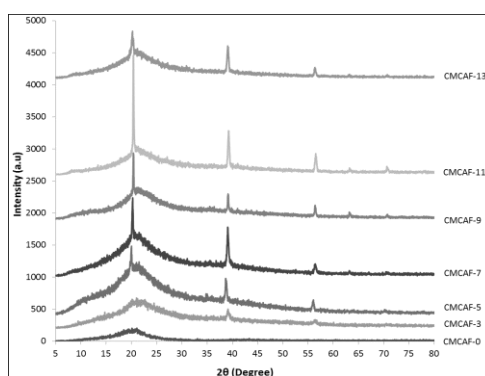


Fig. 3: X-ray diffraction pattern of all SBE samples.

FTIR analysis:

Figure 4 shows the FTIR spectra of CMCAF-0 sample and pure NH_4F measured in the range of 800 cm^{-1} to 4000 cm^{-1} at ambient temperature. The vibration modes of CMCAF-0 sample and pure NH_4F were listed in Table 2. For CMCAF-0, the broad peak centered at 3365 cm^{-1} is attributed to the stretching band of O-H hydrogen bonding. 3028 cm^{-1} band region can be associated to the N-H stretching of amine group in the NH_4F structure. The weak peak at 2895 cm^{-1} band is related to the stretching mode of C-H which associated with the ring methane hydrogen atom [12,13]. The sharp peak at 1585 cm^{-1} is referred to C=O stretching mode of carbonyl group from CMC main backbone [1,14]. A sharp peak at 1448 cm^{-1} band can be attributed to the N-H bending where the symmetric and asymmetric vibration band of NH_4^+ originating for NH_4F structure [15]. The O-H stretching and C-H bending modes can be seen at 1408 cm^{-1} and 1315 cm^{-1} band, respectively which denote the characteristic of polysaccharide skeleton. The 1084 cm^{-1} band represents the C-O stretching mode [16]. The bending mode of O-H was found at 1047 cm^{-1} .

According to Kamarudin and Isa [17], the

interaction of CMC and salts/acids occurred in the frequency range of $1800\text{--}800\text{ cm}^{-1}$. Figure 5 represents FTIR spectra of SBE samples with varied NH_4F salt concentration between 1700 cm^{-1} and 830 cm^{-1} wavenumber. From the figure, it was observed that the intensity of the peaks were decreased with the addition of NH_4F salt. A down shifted pattern of peaks was observed starting from SBE sample containing 3 wt. % NH_4F salt to 9 wt. % NH_4F salt and, at higher salt concentrations, the peaks shifted back to higher wavenumber. The changes of intensity of the peaks and, the shifted peaks were due to the interaction between the proton (H^+) ion from NH_4F salt with the polar group of CMC [15]. From the ionic conductivity analysis, the highest conductive sample was CMCAF-9, and the similarity was found in FTIR analysis. The increase of ionic conductivity until 9 wt. % NH_4F (CMCAF-9) was represented by the down shifted of peaks and, the decrease of ionic conductivity was represented by the shift of peaks to the higher wavenumber.

In the present work, the carbonyl group C=O (peak A) was found at 1585 cm^{-1} for 0 wt. % NH_4F . The peak has shifted to 1581 cm^{-1} with the addition of 3 wt. % NH_4F , and then shifted to 1579 cm^{-1} with

the presence of 5 wt. % NH_4F . An addition of 7 wt. % NH_4F has shifted the $\text{C}=\text{O}$ peak to 1578 cm^{-1} and further shifted to 1574 cm^{-1} with the addition of 9 wt. % NH_4F as shown in Figure 5. The intensity of the peaks was also decreased with the addition of NH_4F salt until 9 wt. % NH_4F . The changes of peak intensity and the shifting of band wavenumber are expected to occur in the present work because of the interaction between $\text{C}=\text{O}$ of carbonyl group in CMC and H^+ of NH_4^+ substructure in NH_4F salt [8]. The shifting of $\text{C}=\text{O}$ towards lower wavenumber with the increasing of NH_4F concentration in CMC was the results of higher concentration of H^+ in CMC. This

attracts more electrons to CMC through $\text{C}=\text{O}$ to form hydrogen bonding thus increasing the ionic conductivity of the SBE samples [1]. The addition of 11 wt. % NH_4F and 13 wt. % NH_4F concentration, the $\text{C}=\text{O}$ peak shifted to a higher wavenumber from 1574 cm^{-1} to 1576 cm^{-1} . It is believed that the upward shifted was due to the deprotonation occurred, where the ions recombine to form neutral ion pairs thus decreasing the ionic conductivity [18]. A similar effect was also reported by Kadir *et al.* [19] and Mason *et al.* [20] where the ion recombination creates neutral ion pairs at higher concentration salt.

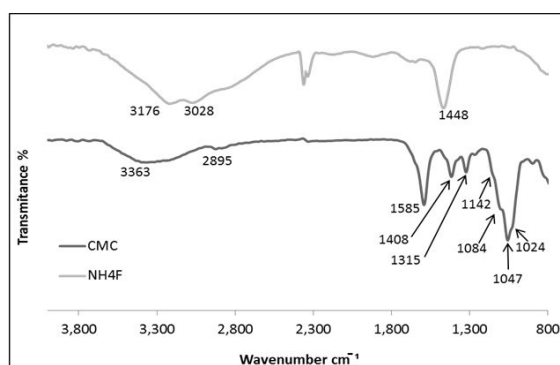


Fig. 4: FTIR spectra of pure CMC and NH_4F salt at ambient temperature.

Table 2: Vibration modes of pure CMC (CMCAF-0) and NH_4F salt.

Vibration modes	Wavenumber (cm^{-1})
<i>Pure CMC (CMCAF-0)</i>	
Stretching mode of O-H	3363
Stretching mode of C-H	2895
Stretching mode of C=O	1585
Stretching mode of O-H	1408
Bending mode of C-H	1315
Bending mode of C-O	1084
Bending mode of C-O	1047
Bending mode of C-O	1024
<i>NH_4F</i>	
Stretching mode N-H	3176
Stretching mode N-H	3028
Bending mode of N-H	1448

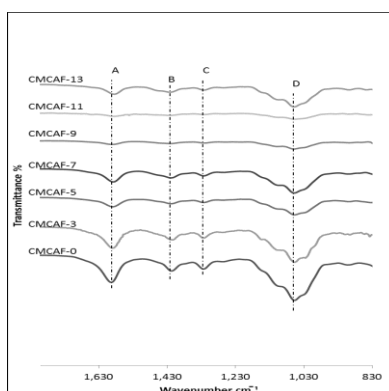


Fig. 5: FTIR spectrum of SBEs with varied NH_4F salt concentration at 830 cm^{-1} to 1700 cm^{-1} region.

Table 3 lists the peaks position and corresponding vibration modes of SBE samples

obtained from FTIR spectra. At higher salt concentration (> 9 wt. % NH_4F), the peaks position

have been shifted to the higher wavenumber. The N-H band originated from pure NH_4F salt has been deformed and overlapped via O-H band (peak B) in CMC thus proved the interactions have occurred between CMC and NH_4F salt in the SBE system.

The protonation and deprotonation in CMC- NH_4F SBE was depicted in Figure 6. Based on the figure, the conducting species in the SBE system was H^+ . Although there are two more possible conducting cation in the system NH_3^+ and NH_4^+ , conduction from H^+ ion is more likely to occur in polymer-ammonium salt system [18,19]. The interaction in the present SBE system occurs through the exchange

of ions between sites and can be explained by Grotthuss mechanism. Ammonium salt consists of four hydrogen atoms which two of them bound identically. The other two hydrogen atoms either strictly or weakly bound. The weakly bound H^+ ion can be easily dissociated and may hop from one site to another leaving a vacancy. This vacancy will be filled by another H^+ ion from a neighboring site [1.19]. Thus, the hydrogen of the NH_4^+ from the NH_4F is presumed to interact with the oxygen at the coordinating site of the host polymer (CMC) as proposed in Figure 6.

Table 3: Vibration modes of SBE samples.

Sample	Peak position / Wavenumber (cm^{-1})			
	A (C=O)	B (O-H)	C (C-H)	D (C-O)
CMCAF-3	1581	1406	1313	1047
CMCAF-5	1479	1406	1311	1047
CMCAF-7	1578	1404	1311	1045
CMCAF-9	1574	1402	1309	1043
CMCAF-11	1576	1408	1309	1045
CMCAF-13	1576	1410	1311	1049

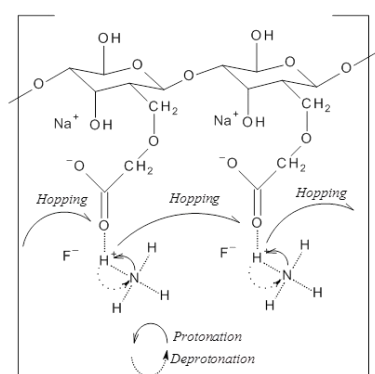


Fig. 6: Interaction between CMC and NH_4F salt (NH_4^+).

4. Conclusion:

A new type of solid biopolymer electrolytes based on CMC doped with NH_4F has been successfully utilized by solution cast method. The impedance analysis showed that the ionic conductivity was increased with the addition of NH_4F concentration to optimum salt concentration of 9 wt.% NH_4F (CMCAF-9). The highest conductive sample of $2.68 \times 10^{-7} \text{ Scm}^{-1}$ (CMCAF-9) was obtained at room temperature. XRD analysis revealed that the SBE samples are semi-crystalline in nature. The shifting and appearance/disappearance of bands revealed in FTIR analysis proved that the interactions have occurred in the polymer-salt system. The CMC- NH_4F SBE system was identified as a proton conductor based on the results obtained.

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Authors' Contribution

This research is a part of Master degree and was performed by M.A. Ramlli.

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There is no conflict of interest.

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