Carboxymethyl Cellulose Doped Ammonium Iodide Solid Biopolymer Electrolytes: Electrical and Structural Analysis

N.H. Ahmad
Department of Physics, Faculty of Science, Universiti Teknologi Malaysia

M.N.H. Mahmud
Department of Physics, Faculty of Science, Universiti Teknologi Malaysia

Nurhafizah, H.
Department of Physics, Faculty of Science, Universiti Teknologi Malaysia

F.E. Zainuddin
Department of Physics, Faculty of Science, Universiti Teknologi Malaysia

https://doi.org/10.5109/7395637

出版情報：Proceedings of International Exchange and Innovation Conference on Engineering & Sciences (IEICES). 11, pp.1014-1020, 2025-10-30. International Exchange and Innovation Conference on Engineering & Sciences
バージョン：

Carboxymethyl Cellulose Doped Ammonium Iodide Solid Biopolymer Electrolytes: Electrical and Structural Analysis

N.H. Ahmad[1*], M.N.H. Mahmud[1], Nurhafizah, H.[1], F.E. Zainuddin[1]
[1]Department of Physics, Faculty of Science, Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia
*nurhidayahahmad@utm.my

Abstract: *Solid biopolymer electrolytes (SBEs) are prepared by solution-casting technique using carboxymethyl cellulose (CMC) doped with various concentrations of ammonium iodide (AI) (0-50 wt.%). Electrical impedance spectroscopy (EIS) is used to determine its ionic conductivity. At room temperature, the highest ionic conductivity is AI3 (30wt.% of AI) which is 7.21 × 10^{-6} S cm^{-1}. X-ray diffraction (XRD) and Fourier-transform infrared (FTIR) were used to determine its structural properties. XRD revealed that CMC-AI SBEs having an amorphous nature and discovered that AI3 is the most amorphous. The dispersed hump centered at 2θ = 18.36° (AI0) and peaks observed to be broadened and move to a greater Bragg angle when AI salt is added. The complexation of CMC-AI SBEs was discovered using FTIR based on the peak which is observed from the coordinating site in CMC (COO−, C–O–C, and –OH). The interactions between CMC and AI occur at the bending mode of CMC at 1019 cm^{-1}. The shifting of the wavenumber showed that the interaction had completely occurred when AI was added. From this, CMC-AI is thought to be a potential SBEs for application in proton batteries due to its advantageous properties.*

Keywords: Solid biopolymer electrolyte, carboxymethyl cellulose, ammonium iodide, electrical properties, structural properties

1. INTRODUCTION

Batteries are one of the most well-established methods of storing electricity [1]. Nowadays, the world is confronted with significant issues related to energy use. Excessive use of fossil fuels has resulted in rapid global warming and an increase in the frequency of extreme climate events [2]. Organic batteries could be made from renewable resources and provide competitive electrochemical properties while being safer and easier to recycle [3]. Lithium-ion batteries have found success in a widely applications because of their high energy density and stable performance but somehow, they are facing the lack of supply of lithium reserves on Earth [4]. Proton batteries have become a good alternative as they are low cost, have no safety issues and could store more energy [5].

Solid polymer electrolytes (SPEs) which are synthetic polymers have several advantages over both liquid and gel electrolytes make it the best choice among others due to their higher energy density, flexibility, higher operating temperatures and safety, no electrolyte leakage and ease of application [6]. The research about SPEs has advanced dramatically since it was found out would be useful in solid-state batteries. As the result, researchers have focused on SPEs to utilise it in electrochemical devices. However, other issues arise when the world started to realise that the used of synthetic polymer which are nonbiodegradable has posing environmental risks. Despite most of the synthetic polymer are insoluble in solvent [7], other issues such as global warming, price fluctuations, shortage of petroleum resources, pollution, and other economic and ecological issues have made synthetic polymer no longer the best choice [8].

Researchers come out with new approach by introducing biodegradable polymer as the replacement to synthetic polymer due to their advantageous properties. Solid biopolymer electrolytes (SBEs) which comes from natural polymer have been employed as the better choices in electrolytes because of their broad availability, leave no harmful residues, low cost and ease of fabrication [9]. It also has high ionic conductivity, high energy density, wide electrochemical stability window, solvent-free, leak-proof and all-important criteria for any type of electrochemical device such as fuel cells, supercapacitors, batteries and dye sensitised solar cells (DSSCs) [10]. Furthermore, these biopolymers leave no harmful residues and may even improve soil quality as they degrade [9]. To date, many researchers have been interested in the properties of natural polymers and decided to make use of it as polymer hosts in solid biopolymer electrolytes (SBEs) [11].

In this work, carboxymethyl cellulose (CMC) is the interest. CMC is one of the plant-based cellulose derivatives and potential option for serving as a solid electrolyte polymer host. On the other hand, CMC was chosen for this study because it also has good mechanical, electrical properties and has good film formability [12]. In addition, CMC also does not cause any issues to the environment as it is non-toxic, abundant, biodegradable and non-hazardous. This is mainly due to the presence of a hydrophilic carboxyl group (–CH_2COONa) in the biopolymer, which permits the biopolymer to dissolve in a solvent. Furthermore, CMC has a significant degree of amorphous phase by nature. Conducting ions such as can now be transported more easily [13]. CMC is a form of cellulose polymer that has a wide range of applications, including paper, food additives, textile fibers, adhesives, paints, pharmaceuticals, cosmetics, and medical supplies. According to the research by [14], biopolymer electrolytes made of CMC doped with ammonium chloride NH_4Cl polymer have been successfully

manufactured. At ambient temperature, they were managed to obtain the highest ionic conductivity of 1.43 x 10^{-3} S cm^{-1} for a SBE containing 16 wt.% NH_4Cl.

2. EXPERIMENTAL

2.1 Materials

The polymer host – carboxymethyl cellulose (CMC) and the salt – ammonium iodide (AI) was obtained from Sigma-Aldrich. Distilled water was used as a solvent throughout the experiment.

2.2 Preparation of solid biopolymer electrolytes (SBEs)

The technique to prepare the CMC-based SBEs in this work is via solution-casting techniques. 2.0 g of CMC and weight percentage of AI was varied, which the concentration of ionic dopant increased to achieve the highest conducting SBEs. The designation and composition of CMC-based SBEs were summarized in Table 1. CMC was added into 100 ml distilled water with constant stirring until homogenous. After the CMC was fully dissolved, AI salt was added into the mixture and continuously stirred until the salt was fully dissolved. The solution was poured into a petri dish. The solution was then kept inside a desiccator until the sample was fully dry. The samples undergo further characterization.

Table 1. Designation of CMC-AI SBEs

Sample	CMC (g)	AI (wt.%)
AI0	2.0	0
AI1		10
AI2		20
AI3		30
AI4		40
AI5		50

2.3 Characterization of solid biopolymer electrolytes (SBEs)

Electrical impedance spectroscopy (EIS) was used for electrical studies for this work. EIS was done using HIOKI LCR-Hi Tester 3532-50. The analyzer was paired with drying oven for temperature-dependent conductivity analysis. The temperature-dependent conductivity analysis was conducted from 30°C to 80°C with 5 °C intervals. The SBEs were sandwiched between two stainless steel electrodes, and the frequency range was set from 50 Hz to 1 MHz. The interaction of CMC and AI was observed using Fourier transform infrared (FTIR) spectroscopy. The FTIR analysis was performed using Thermo Nicolet 380 FTIR spectrometer equipped with attenuated total reflection (ATR) accessory. The spectrum was obtained with range of 800 – 4000 cm^{-1} with resolution of 4 cm^{-1}.The structure of SBEs samples were further analyzed with X-ray diffraction (XRD) spectroscopy using XRD-Rigaku MiniFlex II in 2θ angle from 5° to 90°.

3. RESULTS AND DISCUSSION

3.1 Conductivity analysis

The bulk resistance (R_b) can be obtained by plotting the imaginary impedance (Z_i) versus the real impedance (Z_r) in Nyquist plot. Figure 1 shows the Nyquist plot of CMC-based SBEs samples with various concentrations of AI. The value of R_b was determined by identifying the intersection of semicircular arc and the spike at lower frequency. The ionic conductivity (σ) was determined by using Eq. 1 as shown below

$$\sigma = \frac{t}{R_b A} \tag{1}$$

where t is the thickness of the sample, R_b is bulk resistance, and A is area of electrode-electrolyte contact area. The ionic conductivity of CMC-based SBEs at room temperature was presented in Fig. 1. It is observed that the ionic conductivity increases when the concentration of AI increases up to 30 wt.% with value of 7.21×10^{-6} S cm^{-1}. The increment of ionic conductivity can be contributed from the increased number of mobile ions in SBEs polymer matrix [15]. But, for 40wt.% of AI, the ionic conductivity dropped. This is due to the excessive number of mobile ions, causing the formation of ion pairs and ion aggregations within the polymer matrix [16].

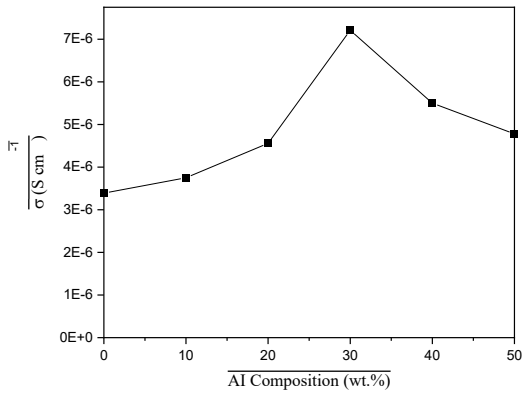

Fig. 1. Ionic conductivity of CMC-based SBEs at room temperature

3.2 Temperature-dependent analysis

A study was done to analyze the temperature-dependance ionic conductivity to identify the activation energy of the SBEs sample. Based on Fig. 2, the CMC-based SBEs experienced increased ionic conductivity as temperature increases. As the temperature increases, the flexibility of polymer matrix was enhanced, promoting a higher ion migration. External thermal energy provides more energy for charge carriers to facilitate ion migration [17]. From the Arrhenius plot, the activation energy (E_a) can be calculated using Eqn. 2 as shown below

$$ln\left[\frac{\sigma}{\sigma_0}\right] = \left[\frac{-E_a}{k}\right]\left[\frac{1}{T}\right] \tag{2}$$

where σ_o is an exponential factor, E_a is activation energy, k is Boltzmann constant and T is temperature in Kelvin. Activation energy is defined as the minimum energy required for charge carriers to migrate through the electrolyte [18]. The regression value that is close to unity ($R^2 \approx 1$) is considered following the Arrhenius theory. From the Arrhenius plot, it is shown that the regression value is close to unity which confirms the CMC-based SBEs obeys the Arrhenius rule. The activation energy was calculated and tabulated in Table

2. It can be observed that the activation energy for AI3 exhibits the lowest value of 0.0047 eV. This indicates that the ions have a well-balanced interaction with polymer host. Many reports say that the decrease of activation energy is due to efficient movement of ions throughout amorphous structure of polymer whereas the increase of temperature assists the ion hopping . At AI4, the activation energy start to increase. This is due to the formation of ion pairs that retards the mobile ions by increasing the viscosity of polymer chain [19].

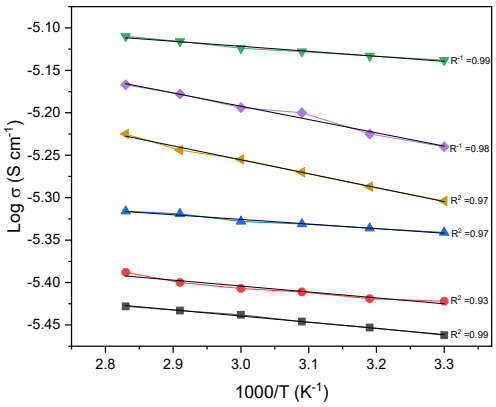

Fig. 2. Arrhenius plot of CMC-based SBEs

Table 2. Activation energy of CMC-based SBEs at room temperature

Sample	Activation energy, (eV)
AI0	0.0063
AI1	0.0060
AI2	0.0051
AI3	0.0047
AI4	0.0134
AI5	0.0141

3.3 Dielectric analysis

The study of relative permittivity in SBEs provides the comprehension of the polarization effect that occurs at the electrode-electrolyte interface. Complex dielectric is composed of real and imaginary part of dielectric loss. Real dielectric or known as dielectric constant (ε_r) is quantitative measure of material polarization. Dielectric constant also represents the ability of the material to store or retain electric charge. Imaginary dielectric also represented as dielectric loss (ε_i) indicating the energy dissipation from the alignment of dipoles in response to the external electric field. Dielectric constant and dielectric loss can be determined using the Eqn. 3 and Eqn. 4 respectively

$$\epsilon_r = \frac{Z_i}{\omega\left[\frac{\epsilon_0 A}{t}\right][Z_r^2 + Z_i^2]} \tag{3}$$

$$\epsilon_i = \frac{Z_r}{\omega\left[\frac{\epsilon_0 A}{t}\right][Z_r^2 + Z_i^2]} \tag{4}$$

where ω is angular frequency and ε_o is permittivity of free space. Fig. 3 and Fig. 4 represent the dielectric constant and dielectric loss respectively versus log frequency. It can be observed that, at low frequency region AI3 exhibits the highest dielectric constant in trend with conductivity study. A high value of dielectric constant signifies the enhanced dissociation characteristic whereas reduces the formation of ion-pair formation [20]. At higher concentration of AI, the dielectric constant decreases due to the reformation of ion-pairs. This causes the number of charge density decreases, leading to weaker mobility [21]. Similar pattern of dielectric loss compared to dielectric constant, aligning with the conductivity trend. As the salt content increases, the number of charge carriers increases, resulting in higher energy dissipation. The drop of dielectric loss occurs at AI4 due to the recombination of ions [22].

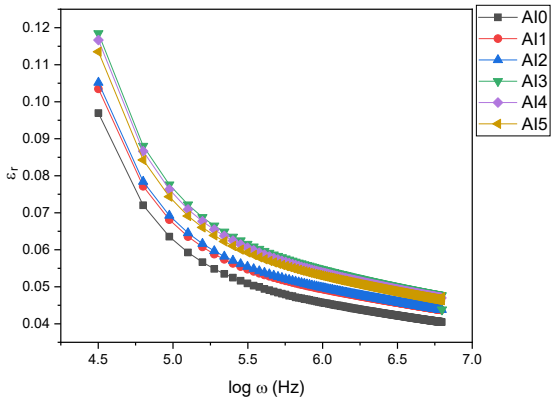

Fig. 3. Dielectric constant of CMC-based SBEs at room temperature

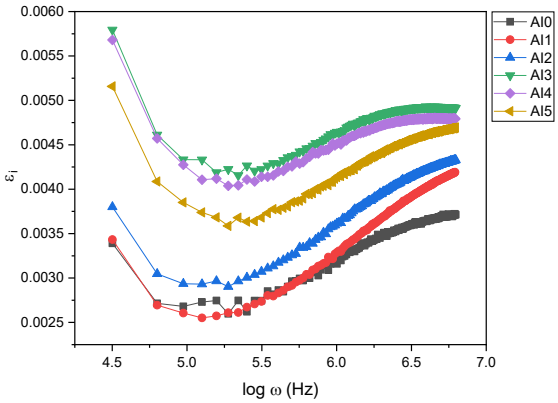

Fig. 4. Dielectric loss of CMC-based SBEs at room temperature

3.4 Modulus analysis

When exposed to an external electric field, the electric modulus of polymer electrolytes provides a quantitative measure of the material's ability to store and release charge. It provides crucial information on the mechanisms controlling electrical relaxation and charge transfer by characterizing the dynamic behavior of the polymer electrolyte system in response to changes in the electric field's frequency [23]. Real and imaginary modulus can be expressed as shown in Eqn. 5 and Eqn. 6 respectively.

$$M_r = \frac{\epsilon_r}{\epsilon_r^2 + \epsilon_i^2} \tag{5}$$

$$M_i = \frac{\epsilon_i}{\epsilon_r^2 + \epsilon_i^2} \quad (6)$$

Fig. 5 and Fig. 6 shows the real and imaginary modulus respectively. Electrode polarization decreases at low frequencies for real and imaginary modulus. This is due to the significant capacitance value linked with the electrodes. The dispersion moves to higher frequencies when the value of M_r and M_i rises from a low frequency. At high frequency, the possible presence of peaks in the modulus formalism for all SBE samples indicates that the SBE films are ionic conductors. The plot exhibits low value at lower frequencies which might be due to the large value of capacitance associated with the electrodes. This further confirm the non-Debye behavior in the samples [24].

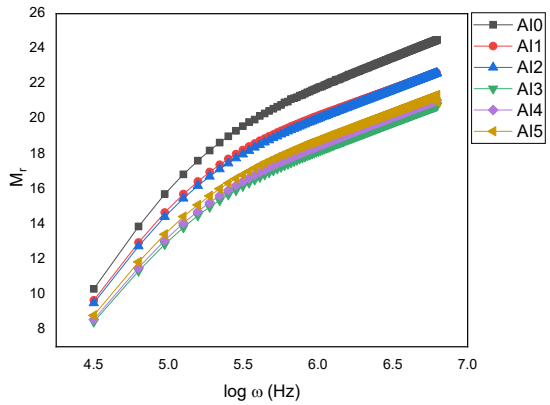

Fig. 5. Real modulus of CMC-based SBEs at room temperature

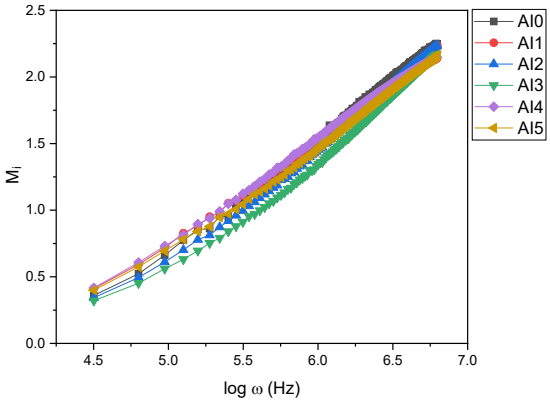

Fig. 6. Imaginary modulus of CMC-based SBEs at room temperature

3.5 XRD analysis

The degree of crystallinity of the polymer complex was investigated using X-ray diffraction (XRD) [25]. Figure 7 shows XRD patterns obtained from CMC-AI SBEs. The XRD spectrum for AI0 shows a dispersed hump centered at 2θ = 18.36°. As seen in Fig. 7, the broad peaks broaden and move to a greater Bragg angle when AI salt is added, from 2θ = 18.36° (AI0) to 22.28° (AI5). When AI was introduced into the current system, the diffraction peak became less intense and broader. The broadening of the peak illustrates the amorphous nature that increases as the AI content increases [26]. The amorphous phase leads to an increase in protonation of (H^+) in CMC which enhances conductivity as measured by the conductivity analysis [27]. The findings are consistent with observation that the conductivity of polymer electrolytes is thought to be changed when the amorphousness of the polymer electrolytes system changes [28].

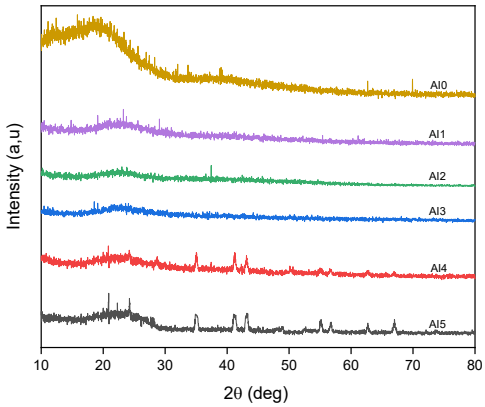

Fig. 7. XRD spectrum of CMC-AI system with varied amount of AI concentration

The XRD spectra revealed the amorphous phase of CMC-AI SBEs. The degree of crystallinity (X_c) of each CMC-AI SBEs were calculated using Eqn. 7 where Ac is the area of crystalline peaks and Aa is the area of amorphous peaks. The degree of crystallinity, X_c for the CMC-AI SBEs is in between 20.53 % to 37.20 %. Table 3 demonstrates that the degree of crystallinity of the CMC-AI SBEs decreases with the addition of ionic dopant. The degree of crystallinity is inversely proportional to the amorphousness of SBEs. AI3 with the highest ionic conductivity and has the lowest degree of crystallinity [26]. This is explained by the amorphous form of the SBEs, which helps in ion diffusion and lowers the energy barrier to the segmental motion of the polymer system, allowing for easier movement of free ions and hence an increase in ionic conductivity [11].

$$\chi_c = \frac{A_c}{A_c + A_a} \times 100\% \quad (7)$$

Table 3. Degree of crystallinity of CMC-AI SBEs

Sample	Degree of crystallinity, X_c (%)
AI0	26.19
AI1	22.40
AI2	21.27
AI3	20.53
AI4	35.69
AI5	37.20

However, the rise in crystallinity in AI4 and AI5 is related to the amount of residual crystallinity provided by the AI, which was discovered to reduce the ionic conductivity [26]. This might be attributed to the ion trapped in CMC-AI SBEs when 40wt.% and 50wt.% AI were added. The crystallinity nature of the two highest salt concentration samples, AI4 and AI5, is increased due to the formation of several crystalline peaks at 35.04°, 41.24°, 43.12° and 34.88°, 41.04°, 43.2° respectively, which implies the existence of a new crystalline phase in CMC-AI SBEs as a result of re-association of the cation

NH_4^+ and anion I^- on the sample surface because the distance between NH_4^+ and anion I^- are very small, so they can recombine to form AI salt again. As a result, the existence of these peaks indicates that the polymer is no longer capable of solving salt [29].

3.6 FTIR analysis

The structural, compositional, and bonding information for the biopolymer electrolyte system was obtained via FTIR analysis. The FTIR spectra was analyzed to determine the bands associated with any functional groups [14]. This analysis is important for better understanding the proposed SBE system's conduction process. Fig. 8 depicts the IR spectra of pure CMC and AI, while Table 4 lists their functional groups.

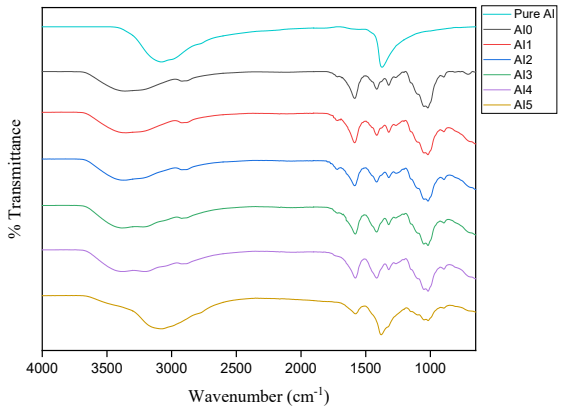

Fig. 8. FTIR spectrum for pure AI and CMC-based SBEs

Table 4. Vibrational modes and wavenumbers of pure CMC and pure AI

Band assignment	CMC Wavenumber (cm^{-1})	AI Wavenumber (cm^{-1})
C-O-C bending	1019	-
O-H bending	1322	-
CH_2 scissoring	1415	-
COO^- asymmetric	1586	-
CH asymmetric	2913	-
OH stretching	3326	-
N-H bending	-	1374
N-H stretching	-	3078

The signature peaks of the CMC are five absorption bands that emerge in the region of 1019 cm^{-1}, 1322 cm^{-1}, 1415 cm^{-1}, 1586 cm^{-1} and 3326 cm^{-1} corresponding to bending C-O-C, bending OH, scissoring CH_2 asymmetric COO^- and stretching OH respectively which are considered as the signature peaks of the CMC. These are carbohydrate characteristic peaks that proved the carboxymethyl substituent at the CMC backbone [30]. These bands are shown to be significant and are emphasized if the peaks in these functional groups shift. The ranges of 650 to 4000 cm^{-1} are responsible for the vibration of CMC carboxyl group which is the likely site of CMC-AI interaction [31]. In the case of AI, vibration bands have been found out at the range of 1000 to 3500 cm^{-1}. The complexation between CMC and AI can be clearly seen in Table 5.

Table 5. Vibrational modes and wavenumbers of CMC-MAI SBEs

Functional group (cm^{-1})	Sample					
	AI0	AI1	AI2	AI3	AI4	AI5
C-O-C bending	1019	1019	1018	1018	1018	1017
O-H bending	1322	1321	1321	1322	1322	1323
CH_2 scissoring	1415	1414	1416	1416	1416	1377
COO^- asymmetric	1586	1586	1586	1582	1581	1579
CH asymmetric	2913	2909	2907	2921	2913	2833
OH stretching	3326	3325	3348	3378	3377	3078
N-H bending	-	1374	1374	1374	1374	1374
N-H stretching	-	-	-	3323	3208	3121

Complexation between the polymer host and salt has been linked to spectral alterations such as band shifts, the formation of new bands, or the elimination of bands [31]. Figure 8 depicts that adding a range of AI concentrations to CMC-AI SBEs resulted in the emergence of complexation bands in the range of 896 cm^{-1} to 1915 cm^{-1}. The COO- stretching band of CMC shifts to the lower wavenumber from 1586 cm^{-1} to 1579 cm^{-1} because of AI molecules interacting with lone pair electrons. Accordingly, more ions are inhibited towards the CMC via (COO^-) to form hydrogen bonding, and this phenomenon is demonstrated through the shifting of peak to the lower wavenumber [31]. This phenomenon has also been reported in previous studies by [11] where the authors believed that the H^+ ion that originated from the ammonium salts acts as a conducting

ion which migrates towards the anion group in polymer electrolyte system.

Strong absorption peak at 2913 cm^{-1} and 3326 cm^{-1} assigned to -CH stretching and O-H stretching of CMC respectively have shifted to 2833 cm^{-1} and 3078 cm^{-1}. The increase in NH_4I concentration led the hydroxyl band to expand, confirming that complexation occurs between NH_4^+ and host polymer chains [29]. The broad band at 3000 to 3600 cm^{-1} corresponds to the stretching mode of the O-H hydroxyl group of CMC which contributes to the formation of intermolecular and intramolecular hydrogen bonds and has been shifted from 3326 to 3078 cm^{-1} [25]. The slightly altered broadness of the peak at 2913 cm^{-1} is easily seen. When the AI is enhanced to 50 wt.%, the broadness tends to decrease. In this work, the exchange of H^+ between NH_4^+ and the carbonyl group of CMC produces variations in these band vibrations. It is assumed that the addition of salt increased the number of H^+ ions in the SBEs, producing a change in band vibrations and intensities. This is seen in the current investigation, where the addition of ammonium salt extended the peaks for CMC [31].

For higher salt concentration, the CH_2 scissoring band at 1415 cm^{-1} for the AI0 was pushed toward lower wavenumber at 1415 cm^{-1}. The decrease in wavenumber causes an increase in bond length, and then complexation occurs between cations and the functional groups of host polymers chains [29]. The strength of the COO^- peak declines as the AI salt's composition increases, showing that the AI salt interacts with the COO^- only weak interaction. The existence of a single free electron invites free ions to interact during COO^- stretching. A peak generated for AI salt indicates the separation of the bond between the NH_4^+ and I^- ions. This allows protonation between the NH_4^+ structure's weakly bound H^+ and the complex site [29]. The protonated H^+ can then migrate to the conduction point (COO^-), increasing the ionic conductivity of the SBE [29]. The study shows that protonation has happened in the current polymer-salt complexes and that interactions between CMC and AI have been formed.

4. CONCLUSION

In conclusion, CMC-Al Solid biopolymer electrolytes (SBEs) were prepared using the solution casting method and analyzed through EIS, XRD, FTIR, and Gaussian software. The study found that adding AI increased the ionic conductivity of the CMC film from 3.39×10^{-6} to 7.21×10^{-6} S cm^{-1} at room temperature. The system displayed Arrhenius behavior with strong thermal activation ($R^2 = 0.99$) and frequency-dependent properties characteristic of non-Debye behavior. XRD analysis showed that AI increased the amorphous nature of the SBEs, decreasing crystallinity and shifting the broad peak centered at $2\theta = 18.36°$ (AI0). FTIR and Gaussian analysis confirmed complex formation between CMC and AI, with bonding interactions involving COO^-, C–O–C, and OH groups. The H^+ ions from NH_4^+ groups were likely responsible for improved conductivity by enhancing ion transport. The interaction between CMC and AI was confirmed, suggesting strong compatibility. Although the current conductivity values are still below the typical threshold (~10^{-4} S cm^{-1}) for electrochemical applications, the CMC-AI SBEs show promise for use in proton batteries due to their low cost, good ionic conductivity, and environmental friendliness.

5. REFERENCES

[1] C. M. N. (M.N. Chai) and M. I. N. Mohamad Isa, "SOLID BIOPOLYMER ELECTROLYTES BASED ON CARBOXYMETHYL CELLULOSE FOR USE IN COIN CELL PROTON BATTERIES," *J Sustain Sci Manag*, Jan. 2017.

[2] Y. Xu, X. Wu, and X. Ji, "The Renaissance of Proton Batteries," *Small Struct*, vol. 2, no. 5, p. 2000113, 2021, doi: https://doi.org/10.1002/sstr.202000113.

[3] R. Emanuelsson, M. Sterby, M. Strømme, and M. Sjödin, "An All-Organic Proton Battery," *J Am Chem Soc*, vol. 139, no. 13, pp. 4828–4834, Apr. 2017, doi: 10.1021/jacs.7b00159.

[4] Y. Xu, X. Wu, and X. Ji, "The Renaissance of Proton Batteries," *Small Structures*, vol. 2, no. 5, p. 2000113, May 2021, doi: 10.1002/sstr.202000113.

[5] K. Mishra, S. Pundir, and D. K. Rai, "All-Solid-State Proton Battery Using Gel Polymer Electrolyte," *AIP Conf Proc*, vol. 1591, Mar. 2014, doi: 10.1063/1.4872700.

[6] R. Singh, A. R. Polu, B. Bhattacharya, H. W. Rhee, C. Varlikli, and P. K. Singh, "Perspectives for solid biopolymer electrolytes in dye sensitized solar cell and battery application," Nov. 01, 2016, *Elsevier Ltd*. doi: 10.1016/j.rser.2016.06.026.

[7] M. Abd. Shukur and M. Kadir, "Electrical and transport properties of NH4Br-doped cornstarch-based solid biopolymer electrolyte," *Ionics (Kiel)*, vol. 21, pp. 111–124, May 2014, doi: 10.1007/s11581-014-1157-5.

[8] M. Rayung *et al.*, "Bio-Based Polymer Electrolytes for Electrochemical Devices: Insight into the Ionic Conductivity Performance," *Materials*, vol. 13, p. 838, Feb. 2020, doi: 10.3390/ma13040838.

[9] P. R. Kasturi, H. Ramasamy, D. Meyrick, Y. Sung Lee, and R. Kalai Selvan, "Preparation of starch-based porous carbon electrode and biopolymer electrolyte for all solid-state electric double layer capacitor," *J Colloid Interface Sci*, vol. 554, pp. 142–156, 2019, doi: https://doi.org/10.1016/j.jcis.2019.06.081.

[10] R. Singh, A. R. Polu, B. Bhattacharya, H.-W. Rhee, C. Varlikli, and P. K. Singh, "Perspectives for solid biopolymer electrolytes in dye sensitized solar cell and battery application," *Renewable and Sustainable Energy Reviews*, vol. 65, pp. 1098–1117, 2016, doi: https://doi.org/10.1016/j.rser.2016.06.026.

[11] M. A. Ramlli and M. I. N. Isa, "Structural and Ionic Transport Properties of Protonic Conducting Solid Biopolymer Electrolytes Based on Carboxymethyl Cellulose Doped with Ammonium Fluoride," *J Phys Chem B*, vol.

120, no. 44, pp. 11567–11573, Nov. 2016, doi: 10.1021/acs.jpcb.6b06068.

[12] M. Ramlli and M. I. N. Mohamad Isa, "Solid Biopolymer Electrolytes Based Carboxymethyl Cellulose Doped With Ammonium Fluoride: Ionic Transport and Conduction Mechanism," *Polymers from Renewable Resources*, vol. 6, pp. 55–63, May 2015, doi: 10.1177/204124791500600202.

[13] M. I. H. A. Sohaimy and M. I. N. M. Isa, "Natural Inspired Carboxymethyl Cellulose (CMC) Doped with Ammonium Carbonate (AC) as Biopolymer Electrolyte," *Polymers (Basel)*, vol. 12, no. 11, 2020, doi: 10.3390/polym12112487.

[14] N. H. Ahmad and M. I. N. Isa, "Characterization of un-plasticized and propylene carbonate plasticized carboxymethyl cellulose doped ammonium chloride solid biopolymer electrolytes," *Carbohydr Polym*, vol. 137, pp. 426–432, 2016, doi: https://doi.org/10.1016/j.carbpol.2015.10.092.

[15] P. Sj, A. Arya, and A. Sharma, "Selection of Best Composition of Na+ ion Conducting PEO-PEI Blend Solid Polymer Electrolyte Based on Structural, Electrical, and Dielectric Spectroscopic Analysis," *Ionics (Kiel)*, vol. 26, Feb. 2020, doi: 10.1007/s11581-019-03245-5.

[16] M. H. Hamsan, M. Abd. Shukur, S. B. Aziz, Y. Yusof, and M. Kadir, "Influence of $$¥hbox {NH}_{4}$$NH4Br as an ionic source on the structural/electrical properties of dextran-based biopolymer electrolytes and EDLC application," *Bulletin of Materials Science*, vol. 43, Dec. 2020, doi: 10.1007/s12034-019-2008-9.

[17] A. Arya and A. Sharma, "Investigation on enhancement of electrical, dielectric and ion transport properties of nanoclay-based blend polymer nanocomposites," *Polymer Bulletin*, vol. 77, Jun. 2020, doi: 10.1007/s00289-019-02893-x.

[18] K. Kondamareddy, R. Muchakayala, Y. Pavani, S. Bhavani, A. K. Sharma, and V. Rao, "Investigations on the effect of complexation of NaF salt with polymer blend (PEO/PVP) electrolytes on ionic conductivity and optical energy band gaps," *Physica B Condens Matter*, vol. 406, pp. 1706–1712, Apr. 2011, doi: 10.1016/j.physb.2011.02.010.

[19] M. A. M. Saeed and O. Gh. Abdullah, "Effect of High Ammonium Salt Concentration and Temperature on the Structure, Morphology, and Ionic Conductivity of Proton-Conductor Solid Polymer Electrolytes Based PVA," *Membranes (Basel)*, vol. 10, no. 10, 2020, doi: 10.3390/membranes10100262.

[20] H. Gudla, Y. Shao, S. Phunnarungsi, D. Brandell, and C. Zhang, "Importance of the Ion-Pair Lifetime in Polymer Electrolytes," *J Phys Chem Lett*, vol. 12, no. 35, pp. 8460–8464, Sep. 2021, doi: 10.1021/acs.jpclett.1c02474.

[21] S. Selvalakshmi, T. Mathavan, S. Selvasekarapandian, and M. Premalatha, "Study on NH4I composition effect in agar–agar-based biopolymer electrolyte," *Ionics (Kiel)*, vol. 23, no. 10, pp. 2791–2797, 2017, doi: 10.1007/s11581-016-1952-2.

[22] M. G. McLin and C. A. Angell, "Ion-pairing effects on viscosity/conductance relations in Raman-characterized polymer electrolytes: lithium perchlorate and sodium triflate in PPG(4000)," *J Phys Chem*, vol. 95, no. 23, pp. 9464–9469, Nov. 1991, doi: 10.1021/j100176a079.

[23] J. Yong, Y.-C. Chen, S. B. Aziz, M. U. Khandaker, and H. J. Woo, "Correlated barrier hopping dynamics of Na+ ions in poly(vinyl alcohol) biopolymer-based solid polymer electrolytes: Electrical and structural analysis," *Electrochim Acta*, vol. 513, p. 145610, 2025, doi: https://doi.org/10.1016/j.electacta.2024.145610.

[24] M. L. H. Rozali and M. I. N. Mohamad Isa, "Electrical Behaviour of Carboxy Methyl Cellulose Doped Adipic Acid Solid Biopolymer Electrolyte," *International Journal of Material Sciences*, vol. 4, p. 59, Jan. 2014, doi: 10.14355/ijmsci.2014.0402.03.

[25] P. Manavalan and M. T., "Study on NH4I composition effect in agar–agar-based biopolymer electrolyte," *Ionics (Kiel)*, vol. 23, pp. 1–7, Oct. 2017, doi: 10.1007/s11581-016-1952-2.

[26] N. Zainuddin, N. Rasali, and A. S. Samsudin, "Study on the effect of PEG in ionic transport for CMC-NH4Br-based solid polymer electrolyte," *Ionics (Kiel)*, vol. 24, Oct. 2018, doi: 10.1007/s11581-018-2505-7.

[27] N. Rasali, Y. Nagao, and A. S. Samsudin, "Enhancement on amorphous phase in solid biopolymer electrolyte based alginate doped NH4NO3," *Ionics (Kiel)*, vol. 25, Feb. 2019, doi: 10.1007/s11581-018-2667-3.

[28] H. T. Ahmed and O. Gh. Abdullah, "Structural and ionic conductivity characterization of PEO:MC-NH4I proton-conducting polymer blend electrolytes based films," *Results Phys*, vol. 16, p. 102861, 2020, doi: https://doi.org/10.1016/j.rinp.2019.102861.

[29] H. T. Ahmed and O. Gh. Abdullah, "Structural and ionic conductivity characterization of PEO:MC-NH4I proton-conducting polymer blend electrolytes based films," *Results Phys*, vol. 16, p. 102861, 2020, doi: https://doi.org/10.1016/j.rinp.2019.102861.

[30] M. A. Saadiah, D. Zhang, Y. Nagao, S. K. Muzakir, and A. S. Samsudin, "Reducing crystallinity on thin film based CMC/PVA hybrid polymer for application as a host in polymer electrolytes," *J Non Cryst Solids*, vol. 511, pp. 201–211, 2019, doi: https://doi.org/10.1016/j.jnoncrysol.2018.11.032.

[31] K. Kamarudin and M. I. N. Mohamad Isa, "Structural and DC ionic conductivity studies of carboxymethylcellulose doped with ammonium nitrate as solid polymer electrolytes," vol. 8, pp. 1581–1587, Aug. 2013.