Characterization of Solid Polymer Electrolyte Based on Methylcellulose Doped Ammonium Bromide

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Abstract. A new biodegradable and low cost solid polymer electrolyte (SPE) membrane mainly from Methylcellulose (MC) blended with Ammonium Bromide (AB) to enhance the SPEs ionic conductivity. Casting method was used in this study in order to produce thin film. In this study, MC as a base doped with different weight percentage of AB (4\%, 9\%, 14\%, 19\%, 24\% and 29\%) to produce thin film for further study on polymer electrolytes. Two objectives were done in this study: prepare MC doped AB thin film via casting method and to determine and compare the conductivity of MC and AB with different weight percentage (wt.\%) of AB. The result shows that different weight percentage of salt resulting different result of conductivities as ion conductivities is the major part in the battery system. Sample MCAB19 was found to have the maximum ionic conductivity value of $1.42 \times 10^{-7}$ Scm\textsuperscript{-1} at room temperature. The samples’ conductivity is very low comparing to the commercial used nowadays. However, it is proven that the combination of MC and AB has the prospective to be an alternative to a SPE in the battery.

1. Introduction
Battery usually consists of electrolyte, anode and cathode. The main component of the battery is the electrolyte that contains free ions that acts as a medium of electrical conductor. Electrolytes are in general contain ions in the form of solution. They are identified as ionic solution either in liquid or solid types of electrolytes \cite{1}. A process named chemical dissociation which the individual atomic component is separated in the solution where the ions is hold apart by force applied. An electrolyte is form by adding salt into solvent such as water and then apply a force through it \cite{2}.

Ionic solution is also known as electrolytes. Polymer electrolytes (PEs) is said to be vastly used in the future as energy storage media \cite{3}. In order to powering our electronic devices and machines, energy storage medium is found almost universally in high energy consumption societies. Polymers in general are categorised into two main classes either synthetic or natural. It is found that majority of the electrochemical devices existing in market are liquid electrolyte based. Yet, SPEs give better performance in terms of higher energy density, flexible geometry, higher operating temperatures and no-leakage of electrolyte and ease of application \cite{4}.

On the other hand, PEs had its own advantages compared to the other types of electrolytes such as having good electrode-electrolyte contact, simple preparation, and good mechanical properties. Having good mechanical properties, make it easy to fabricate into a thin film where a wide range of composition allows better properties and able to build effective electrode-electrolyte contacts. The
listed advantages make PEs extensively investigated, especially chitosan-based SPE. Due to increase in popularity of chitosan, MC-based PEs have become surpassed even though MC-based PE having excellent film-making properties and compatible structure, besides it also relatively cheap and more abundant than chitosan. The abundance of MC is the main factor because it is easily available in unprocessed forms such as flour and starches [3].

The electricity price is hiking up day by day makes low cost electrical devices more popular and the challenge is to produce low cost conductive membrane with good stabilities in mechanical properties, good ionic conductivity and great dimensional. Methylcellulose has been showed as one of the potential polymer host for proton conducting electrolytes among all of the materials. The new development of PE-based on MC has been proficient by doping in AB salt into it which was used as proton donor [1].

MC was selected as a polymer host because it has good properties such as thermal, chemical, mechanical stability, as well as water absorption characteristics which is the main criteria to have good conductivity. AB was used as a dopant salt since it crystallizes into small prisms with a sharp saline taste and is exceptionally soluble in water [5].

Generally, ammonium salts are used because it is considered as a good proton donor to the polymer matrix [6-7]. This proton-conducting PE was made by the solution casting method. The polymer-salt complex formation and the polymer-proton interactions will be analysed through Electrochemical Impedance Spectroscopy (EIS).

2. Methodology
The silica gel was used to absorb the mixture from the thin film formed. The function of distilled water is to dissolve the MC and salt AB. The host of this polymer is that had been choose is MC because of its impressive properties in thermal, chemical, mechanical stability, and water absorption. The dopant salts used are AB because the chemical crystallizes in colorless prisms, possessing a saline taste, and easily soluble in water.

The petri dishes were used to cast 5ml of dilute solution for further drying. In order to get a complete dilute solution, it requires to stir about 2-3 hours with a magnetic stirrer. AB was poured into petri dish, the solution was kept in desiccator for further drying. Fourier Transform Infra-Red (FTIR) was functioning to obtain structural, composition and bonding information of PE. Besides, Electrochemical Impedance Spectroscopy (EIS) use to determine the ionic conductivity of MC-AB that was interfaced to a computer in frequency range 50 Hz to 1 MHz.

2 grams of MC is obtained from ACROS Organics was dissolved in 100 ml distilled water. The solution was stirred for a few hours until MC powder completely dissolve. For comparison result, the first sample prepare is only MC solution. The 2nd, 3rd, 4th, 5th, and 6th samples were added with difference wt.% of AB that obtained from Fisher Scientific Chemical. The solution was stirred with magnetic bar until completely dissolve. The mixture was poured into several different petri dishes and left dried at room temperature to allow the film to form. The films were kept in desiccators for about 1 month before being characterized to ensure no water present in the PEs system. The MC-ABs were cut into suitable dimensions and undergone various analysis.

| Table 1. Composition of electrolytes |
|---|---|---|
| Sample | MC (g) | Salt (%) | Salt (g) |
| MCAB | 2 | 0 | 0.0000 |
| MCAB3 | 2 | 3 | 0.0618 |
| MCAB8 | 2 | 8 | 0.1739 |
| MCAB13 | 2 | 13 | 0.2990 |
| MCAB18 | 2 | 18 | 0.4390 |
| MCAB23 | 2 | 23 | 0.5970 |
| MCAB28 | 2 | 28 | 0.7780 |
The PE samples were cut into 2 cm diameter discs. The disc was sandwiched between two stainless steel electrolytes under spring pressure. The samples were measured at room temperature using Electrical Impedance Spectroscopy (EIS) using HIOKI 353250 LCR Hi Tester interfaced to a computer in a frequency range between 50 Hz and 1 MHz. FTIR spectrometer Thermo Nicolet 380 was used for FTIR spectroscopy measurement. The samples were cut into 4 x 5 cm dimension to fit the place of infrared analysis. The background spectra was first collected then it is detracted from the test spectra in order to get only the actual sample to be analyzed. The sample was put on germanium crystal and then the IR light was passed through the sample with the frequency ranging from 4000 to 675 cm\(^{-1}\) with spectra resolution of 4 cm.

3. Results and Discussion

By physical observation, it can be concluded that every sample have their own surface structure, difference thickness and fragility. The thickness was measured by using digital vernier caliper and the fragility was test by pull out the thin film by hand.

### Table 2. Observation of thin film

| Sample | Surface structure           | Thickness | Fragility |
|--------|----------------------------|-----------|-----------|
| MCAB   | Smooth, no bubbles         | High      | No        |
| MCAB3  | Smooth, no bubbles         | Moderate  | No        |
| MCAB8  | Smooth, no bubbles         | Moderate  | No        |
| MCAB13 | Not smooth, have bubbles   | High      | No        |
| MCAB18 | Smooth, no bubbles         | Low       | Yes       |
| MCAB23 | Smooth, no bubbles         | Low       | Yes       |
| MCAB28 | Smooth, no bubbles         | Low       | Yes       |

The surface structure is smooth and have no bubbles but the thin film is quite thick and it is not fragile. The surface structure for MCAB3 and MCAB8 were same which is the surface structure were smooth and have no bubbles. The thickness were moderate but still hard to pull it out. Sample MCAB13 was not smooth and the surface contain bubbles. It happened during the casting because of the unwell stirred. Sample MCAB18, MCAB23 and MCAB28 have the same characteristics. The surface structures were smooth and have no bubbles while the thickness were low and they were easy to tear (high fragility).

In general, the increment weight percentage of AB in the MC solution gives the thin film lower of thickness and high of fragility which is easy to tear.

![Figure 1. Impedance plot for MC](image-url)
From the Figure 1, since the sample is only MC, the bulk resistance that obtained from graph is higher because the MC is not doped with AB yet. The value of bulk resistance is $7.3342 \times 10^6 \, \Omega$.

![Image](image1.png)

**Figure 2.** Impedance plot for MCAB3

Based on the graph plot in Figure 2, the value of bulk resistance is $2.8340 \times 10^5 \, \Omega$. The value is increase when the MC was doped with 3% of AB.

![Image](image2.png)

**Figure 3.** Impedance plot for MCAB8

Figure 3 shows the graph of MC doped with 8% of AB. The value of bulk resistance is increase consistently. The bulk resistance of MCAB8 is $3.2224 \times 10^5 \, \Omega$. 

In this graph, the value of bulk resistance still increases. The combination of MC doped 13% of AB gives the value of $5.3846 \times 10^5 \, \Omega$.

From the Figure 5, the value of bulk resistance is $1.000 \times 10^5 \, \Omega$. It is found that the obtained bulk resistance of MC doped 18% of AB is decreased.
Figure 6. Impedance plot for MCAB23

Figure 6 showed the bulk resistance of MC doped 23% of AB is $1.5556 \times 10^4 \, \Omega$. This value is increase since the value of weight percentage is increase.

Figure 7. Impedance plot for MCAB28

For the last sample in Figure 7, the bulk resistance value is highly increase to $5.2000 \times 10^4 \, \Omega$. AB getting the bulk resistance value from Nyquist plot, the conductivity of the sample thin film was calculated. The formula that had been used as below:

$$\text{Conductivity, } \sigma = \frac{t}{R_b A}$$

Where, $A$ is the area of the film and $t$ its thickness. $R_b$ is bulk resistance and was obtained from the complex impedance plot at the intersection of the plot and the real impedance axis. The ionic conductivity values obtained showed that the samples have ionic conductivities in the range of $10^{-9}$ to $10^{-7} \, \text{Scm}^{-1}$ at room temperature (298K) as presented in Table 3.
Table 3. Ionic conductivity of MC doped AB at room temperature

| Sample   | Bulk Resistance, Rb (Ω) | Conductivity (Scm⁻¹) |
|----------|-------------------------|----------------------|
| MCAB     | 7.3342 x 10⁶            | 1.1078 x 10⁹         |
| MCAB3    | 2.8340 x 10⁵            | 2.4259 x 10⁸         |
| MCAB8    | 3.2224 x 10⁵            | 1.7456 x 10⁸         |
| MCAB13   | 5.3846 x 10⁵            | 6.9643 x 10⁹         |
| MCAB18   | 1.0000 x 10⁵            | 5.0000 x 10⁸         |
| MCAB23   | 1.5556 x 10⁴            | 4.8213 x 10⁷         |
| MCAB28   | 5.2000 x 10⁴            | 1.6827 x 10⁷         |

Table 3 showed the ionic conductivity at room temperature increases with the increment of AB concentration. For MC concentration, the value of ionic conductivity is 1.1078 x 10⁹ Scm⁻¹. The ionic conductivity increases for samples MCAB3 and MCAB8 with value for each samples is 2.4259 x 10⁸ Scm⁻¹ and 1.7456 x 10⁸ Scm⁻¹. Sample MCAB13 showed the decrement value of ionic conductivity. The value decrease to 6.9643 x 10⁹ Scm⁻¹ and it is quite higher from the value of MCAB8. The decrement of the value probably because of the temperature during the casting method. Then, the sample of MCAB18, MCAB23 and MCAB28 are increase uniformly from 5.0000 x 10⁸ Scm⁻¹, 4.8213 x 10⁷ Scm⁻¹ and 1.6827 x 10⁷ Scm⁻¹ respectively. The conductivity varies with a wide range of factors, such as cation and anion types, salt concentration, temperature, and others [8].

So, in this ionic conductivity study, from the result obtained, we can conclude that the combination of MC doped 23% of AB has the highest value (1.6827 x 10⁷ Scm⁻¹) compared to MC doped 3% of AB (2.4259 x 10⁸ Scm⁻¹). It is found that as AB concentration increases, the ionic conductivity also increases which could be due to the increase in the number of mobile charge carriers. The interaction between AB and MC caused high dispersion of H⁺, therefore increase the ionic conductivity [1].

The composition and C-H bonding data in the PE system was analysed using the FTIR spectrometer. FTIR spectra as shown in Figure 8 were recorded in the range of 400 cm⁻¹ to 4000 cm⁻¹ which was represent the functional groups of interest that were believed the interaction of coordination in MC with AB has taken place. The values obtained by IR spectra are the measurement of the relative values of the degree of coordination upon the variation of AB concentration.

Figure 8 shows the wavelength for each sample are quite similar. From the graph, it can observe that there were interaction between MC and AB concentration. With the addition of AB in the system, this peak was expected to be affected due to the lone pair electrons that attracted the salt molecule of AB to it. The possible interaction between the MC and doping AB is highlighted in Figure 9 and 10. Hence, this was proven that the sample have contained the combination of MC doped AB.
The interaction between MC and AB can be confirmed by FTIR spectroscopic analysis. The proton conductor ionic species has been established as a conduction mechanism in the PE. The graph presented the interaction of all the samples is in between range 2800 – 3300 cm⁻¹. From the Table 1, we can see that between the range, the bonding that presented in the graph for all the samples is the alkane C-H stretching and the intensity of this peak is medium.

Figure 9. Interaction between the MC and doping AB

The formation of new proton conducting PE-based on MC doped AB were prepared by casting method and found to be in the form of transparent thin film. Sample MCAB28 was found to have the maximum ionic conductivity at room temperature which is $1.6827 \times 10^{-7}$ S cm⁻¹. If compared to the commercial conductivity based on polymer, the conductivity is still poor but to be used as SPE, the combination of MC and AB proved that it has its own potential. The concentration of ammonium salts also can be determined as the source of conductivity enhancement. The combination of this MC doped AB can be used as the PE for battery. It is proven since the result showed the higher the AB concentration, the higher the ionic conductivity produced. From FTIR analysis, it showed that there were bonding between the combination of MC doped AB. The possibility interaction between MC and AB was obtained by FTIR spectroscopy and this is supported by Grotthus mechanism and a proton conductor (H⁺) is the established ionic species in the PE [3].

Figure 10. Interaction between the MC and doping AB

4. Conclusions
The formation of new proton conducting PE-based on MC doped AB were prepared by casting method and found to be in the form of transparent thin film. Sample MCAB28 was found to have the maximum ionic conductivity at room temperature which is $1.6827 \times 10^{-7}$ S cm⁻¹. If compared to the commercial conductivity based on polymer, the conductivity is still poor but to be used as SPE, the combination of MC and AB proved that it has its own potential. The concentration of ammonium salts also can be determined as the source of conductivity enhancement. The combination of this MC doped AB can be used as the PE for battery. It is proven since the result showed the higher the AB concentration, the higher the ionic conductivity produced. From FTIR analysis, it showed that there were bonding between the combination of MC doped AB. The possibility interaction between MC and AB was obtained by FTIR spectroscopy and this is supported by Grotthus mechanism and a proton conductor (H⁺) is the established ionic species in the PE [3].

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