Improving Ionic Conductivity of Carboxymethyl Cellulose Solid Biopolymer Electrolyte with Assist from Dimethyl Carbonate

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Abstract

Ionic conductivity is one of the important properties for an electrolyte to be considered before it can be used as practical application in energy storage. Therefore, this study aims to improve the ionic conductivity of solid biopolymer electrolyte (SBE) based on carboxymethyl cellulose (CMC) doped with ammonium acetate (AA) by incorporating plasticizer, namely, dimethyl carbonate (DMC). The SBEs were prepared using solution casting technique. Fourier Transform Infrared (FTIR) was used to ascertain the complexation among CMC, AA and DMC. From FTIR analysis, DMC is believed to have created new pathways for ionic conduction. The electrical properties of SBEs were investigated using Electrical Impedance Spectroscopy (EIS). The highest conducting value achieved for the plasticized system was 4.27×10⁻⁵ S cm⁻¹ for sample containing 10 wt% DMC. Dielectric analysis revealed that frequency and plasticizer content affect the dielectric constant value. By employing Transference Number Measurement (TNM), the charge transport in the SBE system proved to be predominantly ions where DMC 10 has the highest t⁺/⁻ (0.95). Overall, addition of 10 wt% of DMC has the best electrical properties.

Keywords: Solid biopolymer electrolytes, Carboxymethyl cellulose, Ammonium acetate, Plasticizer, Transference number, Dimethyl carbonate

Introduction

Nowadays, energy storage is becoming important due to the growth of mobile technologies. Among existing energy storage technologies, battery is one of the most established means of storing electricity in the form of chemical energy [1]. Battery is an electrochemical energy storage which converts stored chemical energy where the ions convert at anode and move to cathode via a conductive electrolyte to form electrical energy [2].

Since the last few decades, due to high demand of electrochemical energy storage such as batteries, fuel cells, sensors and super capacitors, electrolyte is gaining a lot of attention in order to increase the battery efficiency and improve safety [3]. The battery electrolyte is the first component that needs to be improved in order to create safer battery system since the nature of conventional electrolyte (i.e. liquid electrolyte) is the main cause of the problems faced by commercial batteries today [4]. Solid-state electrolyte is marked as the best alternative to overcome the problems faced by liquid electrolyte [4]. One technique to develop solid-state electrolyte is by using solid biopolymer electrolyte (SBE). SBE have several advantages over liquid or gel-based electrolytes, such as excellent mechanical stability, leakage free, lightweight, flexibility in design and ease of production [5]. Biopolymers or natural polymers are much cheaper to manufacture and have environmentally friendly properties. Due to these advantages, SBEs based on natural polymers such as starch, chitosan and cellulose has been developed throughout the years [5-10].

In this research, Carboxymethyl cellulose (CMC) was chosen as the core material for the biopolymer electrolyte development. CMC has several remarkable properties as an electrolyte material such as highly hydrophilic, adequate mechanical properties, non-toxic, biodegradable, biocompatible
The presence of the carboxyl group (COO\(^{-}\)) in CMC is beneficial in electrolyte application as it allows mobile charge carrier to form hydrogen bonds, consequently facilitating the migration of ions [12]. CMC itself is not conductive and according to reports, polymers-salts combination technique is an effective technique to provide ions as the charge carriers [13]. Thus, in this work is based on the work by [14], where CMC biopolymer is doped with ammonium acetate (AA) as charge carrier source since ammonium salts is a good candidate as ionic dopant [14,15]. However, the CMC-AA SBE system reported by can be further improved. There are numerous reports on improving polymer electrolyte conductivity by using plasticization technique [16-18]. Plasticizing the polymer-salt complex was said to improve the ionic conductivity by improving salt dissociation into free cations and anions and creating new pathways for ion migration [17].

This paper investigates the effect of plasticizer on the ionic conductivity of CMC-AA SBEs. The plasticizer selected for this study is dimethyl carbonate (DMC) since it has excellent features such as non-toxic production, environmentally friendly, non-corrosive, and safe handling [19]. Moreover, to the best of author knowledge, CMC-AA SBE plasticized with DMC has not been reported previously.

**Materials and methods**

**Sample preparation**

The CMC-AA SBEs were prepared using solution casting method following [14]. 2 g of CMC (DS = 0.7) procured from Across Organics/Thermo Fischer (CAS 9004-32-4, Geel, Belgium) was dissolved in 100 mL of distilled water using magnetic stirrer until the solution homogenous. Then, 0.5 g of AA (MM = 60.052 g/mol) was added and stirred until completely dissolved. For plasticize SBEs, DMC was added to the CMC-AA solution and stirred until homogenous solution was obtained. Different amount of DMC were added to prepare several samples to find the best DMC composition. Finally, the CMC-AA-DMC solution was poured into petri dishes and left to dry at room temperature. Table 1 shows the sample designations, DMC weight and film thickness. Figure 1 shows the physical appearance of the CMC-AA-DMC SBE where translucent and no phase separation thin film was observed.

![Figure 1 The CMC-AA-DMC solid biopolymer electrolytes.](image)

**Table 1** CMC-AA-DMC SBEs designation, plasticizer weight and thickness.

<table>
<thead>
<tr>
<th>Designation</th>
<th>Weight percentage of DMC (wt%)</th>
<th>Weight (g)</th>
<th>Thickness (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMC 0</td>
<td>0</td>
<td>0.00</td>
<td>0.0068</td>
</tr>
<tr>
<td>DMC 5</td>
<td>5</td>
<td>0.13</td>
<td>0.0085</td>
</tr>
<tr>
<td>DMC 10</td>
<td>10</td>
<td>0.28</td>
<td>0.0128</td>
</tr>
<tr>
<td>DMC 15</td>
<td>15</td>
<td>0.44</td>
<td>0.0076</td>
</tr>
<tr>
<td>DMC 20</td>
<td>20</td>
<td>0.63</td>
<td>0.0070</td>
</tr>
<tr>
<td>DMC 25</td>
<td>25</td>
<td>0.83</td>
<td>0.0051</td>
</tr>
</tbody>
</table>
Characterization

Electrical Impedance Spectroscopy (EIS)

This research utilized HIOKI 3532-50 LCR Hi-Tester for impedance testing to determine the ionic conductivity of CMC-AA-DMC SBE. The SBE was sandwiched between 2 stainless steel electrodes under spring pressure and impedance data was collected between 50 Hz and 1 MHz. The impedance spectroscopy data is presented as Cole-Cole plot. In the Cole-Cole plot, the negative imaginary impedance, $-Z_i$ is plotted against the real impedance component, $Z_r$.

Ionic Transference Number Measurement (TNM)

TNM was used to investigate the relationship between ion diffusion and the conductivity behavior of CMC-AA-DMC SBE. This research used direct current (dc) polarization technique where the samples were sandwiched between 2 stainless steel electrodes and later subjected to dc voltage (~1.0 V) to induced electric current. Then the electric current was monitored as a function of time until it is saturated.

Fourier Transform Infrared Spectrometer (FTIR)

FTIR was used to study the functional group of the SBE. Varian 3100 Excalibur FT-IR spectrometer model was coupled with Attenuated Total Reflection (ATR) accessory and a germanium crystal. The SBEs were tested in the range of 700 to 4000 cm$^{-1}$ with spectra resolution of 4 cm$^{-1}$.

Results and discussion

Impedance study of CMC-AA-DMC SBE

Figure 2 shows the Cole-Cole plot of CMC-AA-DMC SBE. The plot was divided into 2 regions of 1) low frequency and 2) high frequency. The Cole-Cole shows slanted line at low frequency while semi-circle at high frequency region where both related to ionic conduction in the bulk of the samples [20]. The semicircle is a parallel combination of resistor, which referred to charge carriers migration through the polymer matrix and capacitor represents a polarized immobile polymer chain [10,20]. While the slanted line at low frequency region is due to double layer capacitance of blocking electrode and roughness of the electrode/electrolyte interface [20]. From the figure, the semi-circle sizes diminished for DMC 5 up to DMC 20. This shows that, the addition of DMC has reduced charge carrier resistance due to formation of space charge in the CMC-AA-DMC SBE [21]. According to Ahmed et al. [16], the reduction of semi-circle shows that the samples is mainly ionic. The semi-circle later appears for DMC 25 indicating large resistance for charge carriers’ conduction.

From the Cole-Cole plot, the values of bulk resistance, $R_b$ was determined from the intercept of semicircle with the slanted line at x-axis. For the plot without semi-circle, the value was taken from the intercept of slanted line at x-axis and inserted into Eq. (1) to calculate the ionic conductivity of the CMC-AA-DMC SBE where $t$ is film thickness and $A$ is the electrode/electrolyte contact area. The calculated conductivity values were plotted and shown in Figure 3.

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

Figure 2 Cole-Cole plot of DMC-AA-DMC SBE (a) DMC 0, DMC 25 and DMC 30 (b) DMC 5, DMC 10, DMC 15 and DMC 20.
Figure 3 shows the ionic conductivity of the SBE increase from $1.28 \times 10^{-7}$ S cm$^{-1}$ (DMC 0) up to $4.26 \times 10^{-5}$ S cm$^{-1}$ for DMC 10. The increase of ionic conductivity for DMC 0 up to DMC 10 can be explained by 2 reasons. The first reason is due to new ionic pathways for the migration of free ions through the plasticizer [1]. The other reason is believed due to the increased number of charge carriers where introduction of DMC has increased the ionic dissociation thus increase the effective free ions. DMC increase dissociation of AA due to the presence of C = O from DMC structure (polar molecule) which able to attract cations from ion-pair or aggregates [22]. This led to increased ionic conductivity of the DMC-AA-DMC SBE [23]. The decreasing ionic conductivity value for DMC 15 up to DMC 25 is due to increased viscosity within the polymer matrix with increased plasticizer content which decreased ionic mobility [24-26]. The increased viscosity affected the mobility of charge carriers to conduct from one complexation site to another site. This can be supported through FTIR analysis in the next section.

Dielectric analysis

The study of dielectric constant, $\varepsilon_r$, can be used to measure stored charge in SBE where the ions act as charge carriers [17]. Equation (2) was used to calculate $\varepsilon_r$, where $C_0 = (\varepsilon_0 A)/\ell$ and $\omega = 2\pi f$. $\varepsilon_0$ is permittivity of free space, $Z_i$ and $Z_r$ are the imaginary and real parts of the complex permittivity, respectively, and $f$ is frequency. The calculated $\varepsilon_r$ is plotted and shown in Figure 4.

$$\varepsilon_r = \frac{Z_i}{\omega C_0 (Z_i^2 + Z_r^2)}$$  

(2)

From the figure, $\varepsilon_r$ value found to be independent at high frequency where it declines exponentially with increasing frequency and then become constant at very high frequency. The sharp increase of $\varepsilon_r$ at low frequencies is due to the increase in the ion conduction related polarization effects. Charge carrier has ample time to accumulate at the electrode/electrolyte boundary thus increase the dielectric value [27-29]. As the frequency increases, the rate of reversal of the electric field also increases, the charge carriers only localized to their potential well. As such, limiting polarization effect subsequently no charge builds up at the interface [13,28]. Figure 5 illustrates the dielectric value for each CMC-AA-DMC SBE sample at selected frequency. The dielectric value found to follow the ionic conductivity trend (Figure 2) where the value increase from DMC 0 and reach maximum value at DMC 10 and dropped afterwards until DMC 25. This supports the previous assumption in conductivity study that, the addition of DMC into SBE increase the number of charge carrier by increase AA ionic pair/aggregates dissociation into free ions.
Figure 4 The frequency dependence of $\varepsilon_r$ for CMC-AA-DMC SBEs at room temperature.

Figure 5 Dielectric constant value at selected frequency for CMC-AA-DMC SBEs.

Molecular interaction of CMC, AA and DMC

Figure 6 represents FTIR spectra of CMC-AA-DMC SBEs between wavenumber of 2100 to 700 cm$^{-1}$ with few obvious peaks observed. Peak at $\sim$1583 cm$^{-1}$ corresponds to asymmetric stretching vibration of COO$^-$ of CMC. The bending vibration mode of OH in CMC was detected at $\sim$1412 cm$^{-1}$. Peak at $\sim$1323 and 1053 cm$^{-1}$ can be assigned to symmetric stretching vibration of CH and the bending mode of CO, respectively. There is no significant shifting occurred when DMC was added into the SBE. The vibration modes observed in this work is in agreement to other cellulose based SBE system found in the literatures as tabulated in Table 2.
Figure 6 FTIR spectra of CMC-AA-DMC SBE (a) DMC 0 (b) DMC 5, (c) DMC 10, (d) DMC 15, (e) DMC 20 and (f) DMC 25.

Table 2 Comparison of vibrational mode for CMC-AA-DMC and other cellulose-based SBE reported in the literatures.

<table>
<thead>
<tr>
<th>Vibrational mode</th>
<th>Wavenumber (cm(^{-1}))</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Present study</td>
<td>Literature</td>
</tr>
<tr>
<td>(\nu_{\text{as}}(\text{COO}^-))</td>
<td>1583</td>
<td>1594</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1593</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1605</td>
</tr>
<tr>
<td>(\delta(\text{O-H}))</td>
<td>1412</td>
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<tr>
<td></td>
<td></td>
<td>1419</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1417</td>
</tr>
<tr>
<td>(\nu_{\text{s}}(\text{C-H}))</td>
<td>1323</td>
<td>1322</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1317</td>
</tr>
<tr>
<td>(\delta(\text{C-O}))</td>
<td>1053</td>
<td>1057</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1056</td>
</tr>
</tbody>
</table>

The characteristic transmission band of carboxylic group of CMC (1583 and 1053 cm\(^{-1}\)) was of importance since it is the most likely functional group for complexation to occur and thus selected for further analyze the effect of DMC towards the CMC based SBE. Figure 7 shows the overlap spectra for DMC 0, DMC 10 and DMC 25. From the figure, the DMC 10 peak increase compared to DMC 0. This signify that the functional group able to stretch further compared to DMC 0. This show that DMC has increase the free volume between the polymeric networks. This interaction proved that the presence of plasticizer (DMC) has create a new pathway for charge carriers to move from one complexation sites to another. The peak intensity for DMC 25 was lesser compared to DMC 10 but insignificant. This is believed due to increasing amount of DMC, which started to “clog” the polymeric network and affect the ionic conductivity as observed in the ionic conductivity analysis in previous section.
Transference number determination

Transference measurement helps to determine the ionic species contribution to the overall ionic conductivity of an electrolyte. Higher transference number is preferable for an electrolyte to avoid battery failure [31,32]. Figure 8 shows the normalized polarization current for DMC 0, DMC 10 and DMC 25. From the figure, the current decrease and become constant after a certain period. The reduction of current over time is the effect of mobile ions that was trapped at the blocking electrode [33]. Since the type of electrode used in the testing is not reactive with the mobile ions, the induced ions are therefore accumulated at the electrolyte/electrode contact and reduced the effective electric current. While the residue current observed is due to electronic current. Based on the result, the $t_{ion}$ appears to follow ionic conductivity trend where $t_{ion}$ is 0.95 for DMC 10 which is the highest conducting SBE is higher than DMC 0 (0.73) and DMC 25 (0.64). Higher $t_{ion}$ indicates that the DMC 10 is highly ionic compared to other 2 samples. The value obtained from this study is comparable to other studies reported in the literatures (Table 3). This further supported previous assumption that DMC has helped to increase the number of charge carriers and improve the ionic conduction and ionic conductivity value.

Figure 7 The overlap spectra of CMC-AA-DMC SBE for DMC 0, DMC 10 and DMC 25.

Figure 8 Transference number of (a) DMC 0, (b) DMC 10 and (c) DMC 25.
Conclusions

In this study, CMC-AA-DMC SBEs system was successfully prepared using solution casting technique. The ionic conductivity increased from $1.28 \times 10^{-7}$ S cm$^{-1}$ (DMC 0) to the highest value of $4.26 \times 10^{-5}$ S cm$^{-1}$ for DMC 10. The ionic conductivity improvement can be related to two factors, first, the plasticizer presence in the polymer matrix help to create new or easier path for ionic conduction as proven from carboxylic group stretching vibration via FTIR analysis. The second factor is the increased number of mobile ions as observed from highest dielectric value and ionic transference number analysis which corresponds to the highest conducting sample. These factors consequently improved the ionic conductivity properties of the SBEs. However, further study need to be done to increase the ionic conductivity to at least in the vicinity of $10^{-4}$ S cm$^{-1}$ as proposed by other researchers for any practical electrochemical application.

Acknowledgements

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References


Table 3 Comparison of current work $t_{\text{ion}}$ to other works.

<table>
<thead>
<tr>
<th>Electrolyte system</th>
<th>Transference number, $t_{\text{ion}}$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA-PVdF-NH$_3$SCN</td>
<td>0.96</td>
<td>[34]</td>
</tr>
<tr>
<td>PVA-NH$_4$Br</td>
<td>0.96</td>
<td>[35]</td>
</tr>
<tr>
<td>CMC-AA-DMC</td>
<td>0.95</td>
<td>Current work</td>
</tr>
</tbody>
</table>


[31] X Wu, K Chen, Z Yao, J Hu, M Huang, J Meng, S Ma, T Wu, Y Cui and C Li. Metal organic framework reinforced polymer electrolyte with high cation transference number to enable dendrite-free solid state Li metal conversion batteries. *J. Power Sources* 2021; 501, 229946.


