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The Development of Chitosan-Maltodextrin Polymer Electrolyte with the Addition of Ionic Liquid for Electrochemical Double Layer Capacitor (EDLC) Application

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In this paper, chitosan-maltodextrin based solid polymer electrolytes doped with ammonium chloride (NH₄Cl) as proton provider and 1-butyl-3-methylimidazolium chloride (BMIM-Cl) as plasticizer are prepared through solution casting method. The conductivity of salted electrolyte is increased to $(1.28 \pm 0.06) \times 10^{-3}$ S cm⁻¹ with the inclusion of 50 wt.% BMIM-Cl. The electrolytes are thermally assisted when the temperature is increased which obeys the Arrhenius rule. The complexation between polymers, salt, and plasticizer has been proven through the deconvolution of Fourier transference infrared (FTIR). The non-Debye behaviour is verified from the dielectric analysis. Deconvolution of X-ray diffraction (XRD) pattern presented the lowest degree of crystallinity for the highest ionic conducting electrolyte. The scanning electron microscope (SEM) and atomic force microscopy (AFM) analyses had been applied whereby the highest ionic conducting electrolyte exhibited a tunnel pattern on the surface which proved high amorphous characteristic. Transference number (TNM) analysis has confirmed that the ions are the dominant charge carriers in the electrolytes. Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) analysis had been carried out prior to the fabrication of EDLC. The highest value of specific capacitance is found at 56 F g⁻¹ where the range of energy density and power densities are between 2.5 to 9.0 Wh kg⁻¹ and 137 to 276 W kg⁻¹, respectively.

Keywords: Biopolymer electrolyte; chitosan-maltodextrin blend; ammonium chloride; ionic liquid; electrochemical double-layer capacitor

1. INTRODUCTION

Polymer electrolyte field a has high potential to be studied and expanded extensively as a separator in electrochemical devices such as low energy density battery applications and fuel cell [1,2]. In recent years, researchers have started to use renewable resources as an effort to minimize environmental problems related to fuel, coal, and natural gas growth [3]. There are many examples of natural polymers that have been studied in electrochemical devices such as gelatin, pectin, agar, chitosan, starch, and cellulose [4].

Chitosan (Ch) is a derivation from chitin which is a natural biopolymer extracted from shrimp shell waste. There are two main functional groups present in the structure of chitosan which are amine and hydroxyl groups [5,6]. Shukur et al. [7] reported the Ch as a polymer host in the chitosan-ammonium bromide (NH4Br) electrolyte system and gave a room temperature conductivity of $(4.38 \pm 1.26) \times 10^{-7}$ S cm⁻¹. Meanwhile, maltodextrin (Md) which comprises of amylose and amylopectin originates from starch which is produced through partial enzymatic hydrolysis. Two main chains which are α -(1, 4)-linked D-glucose; a linear group with helical shape, combined with α -(1, 6)-glucosidic linkage; which contains packing arrangement of double helices of high molecular weight groups [5]. Asnawi et al. [6] reported the application of Md as polymer host in the maltodextrin-methylcellulose-ammonium bromide (NH4Br) electrolyte system. This makes Md an interesting field to be further explored. Previous studies have shown that polymer blend based electrolyte is more conductive than single polymer based electrolyte [8,9]. For example, starch-chitosan-NH4Cl system has higher conductivity of 6.47×10^{-7} S cm⁻¹ than chitosan-NH4Cl at 6.54×10^{-8} S cm⁻¹ [10].

Recently, ionic liquid has been acknowledged as a type of plasticizer that is beneficial to enhance the polymer chains flexibility by breaking the temporary bonds between the polymer chains which will improve the migration of mobile charge carriers and increase the conductivity [11]. Besides, ionic liquid has several interesting properties such as low vapour pressure, low flammability and also has wide thermal and electrochemical windows [12]. According to Saroj et al. [8], the addition of ionic liquid is able to provide extra concentration of free ions that is significant to increase the conductivity. The incorporation of BMIM-NO₃ in chitosan-starch-NH4NO₃ has reported to achieve the highest conductivity of 2.26×10^{-4} S cm⁻¹ at room temperature [9]. Farah et al. [13] also found that the addition of 50 wt.% BMIM-Br in PVA-NaTf electrolyte has increased the room temperature conductivity from 4.87×10^{-6} S cm⁻¹ to 2.31×10^{-3} S cm⁻¹. BMIM-Cl is an alkylimidazolium-based ionic liquid whereby the molecular mobility of two imidazole molecules is re-oriented through the hydrogen bonds that leads to a strong plasticizing effect [14,15]. Therefore, the effect of BMIM-Cl ionic liquid in polymer electrolyte system in this work is further investigated along with the addition of NH4Cl salt for the improvement of polymer electrolyte properties.

The fabrication of electrochemical devices that are made of safe and non-toxic materials has received a great demand because of the concerns related to global warming and energy crisis [16,17]. Therefore, many researchers have started to explore the electrochemical double-layer capacitor (EDLC) with a solid-form electrolyte separator as a potential alternative for conventional batteries and fuel cells [18]. Numerous works reported the application of solid polymer electrolytes in the fabrication of EDLC [19–22]. The non-Faradaic process for the energy storage mechanism in EDLC is applied, where the

ions accumulate between the electrolyte and electrode to form a double-layer without any electrons transfer involved [23,24]. Based on several characterizations and analyses, the highest performance electrolyte in the plasticized system will be fabricated in the EDLC to explore the potential of Md-Ch blend to serve as the polymer host electrolyte.

2. EXPERIMENTAL METHOD

2.1 Electrolyte preparation

Polymer host (PB3) was prepared by using Md (food grade) and Ch (Sigma-Aldrich) whereby the preparation of Md solution was carried out by dissolving 0.3 g of Md in 100 ml of 1% acetic acid (SYSTERM) and stirred at 80 °C about 20 minutes. After the solution was cooled at room temperature, 0.7 g Ch was added and continuously stirred overnight until a homogenous solution was obtained. The salted system (S1-S6) was prepared by adding different amounts of NH₄Cl (R&M Chemicals) into the Ch-Md blend solution and stirred until fully dissolved. Then, 1-butyl-3-methylimidazolium chloride (BMIM-Cl) (Sigma-Aldrich) was purified before being introduced to the mixture of salted system. The plasticized system (IL1-IL6) was prepared by the inclusion of different amounts of BMIM-Cl to the Ch-Md-NH₄Cl solution and stirred until homogenous solutions were obtained. The plastic petri dish was used to cast the homogenous solution and left to dry at room temperature for several days. Then, a glass desiccator filled with silica gel was used to keep the samples for further drying before further characterization. Table 1 shows the designation and composition of electrolytes.

Designation	Chitosan: Maltodextrin (wt. %)	PB3: NH4Cl (wt. %)	S4: BMIM-Cl (wt. %)
 PB3	70:30	-	-
S 1	-	95 : 5	-
S2	-	90:10	-
S 3	-	85:15	-
S 4	-	80:20	-
S5	-	75:25	-
S 6	-	70:30	-
IL1	-	-	90:10
IL2	-	-	80:20
IL3	-	-	70:30
IL4	-	-	60:40
IL5	-	-	50:50
IL6	-	-	40:60

Table 1. The designation and composition of electrolytes

2.2 Carbon-based electrode preparation

The preparation of carbon-based solution was carried out by mixing 13 g of activated carbon (RP20, by Kuararay, Japan), 2 g of polyvinylidene fluoride (PVdF) and 1 g of carbon black (Super P). The compositions above were mixed and stirred in the 60 ml of N-methyl pyrrolidone (NMP) (EMPLURA) until the solution was fully dissolved. An aluminium foil which was used as the current collector was then coated with the solution (thickness of 0.25 mm) and dried at 60 °C.

2.3 Fourier Transform Infrared (FTIR) spectroscopy

The complexation between the polymers, salt, and plasticizer was studied using Fourier transform infrared (FTIR) spectroscopy. The wavenumber range of 400-4000 cm⁻¹ at a resolution of 4 cm⁻¹ was recorded using the Spotlight 400 Perkin-Elmer spectrometer. The deconvolution of FTIR spectra was constructed using Origin9 software to extract the peak positions and overlapping peaks of specific frequencies.

2.4 X-ray diffraction (XRD)

A good polymer blend host should contain a wide amorphous region, since the ions were easy to be conducted in amorphous phase. This purpose can be studied based on X-ray diffraction (XRD) analysis. Siemens D5000 X-ray diffractometer (1.5406 Å) was used with the resolution of 0.1° and the angle $2\Box$ varied from 5° to 80°. The deconvolution technique using Origin9 software was used to extract any overlapping of crystal and amorphous peaks in XRD pattern. The degree of crystallinity (X_c) values was determined using equation 1:

$$X_c = \frac{A_c}{A_T} \times 100 \tag{1}$$

where A_c is the area of crystalline peaks and A_T is the total area of crystalline and amorphous peaks.

2.5 Scanning electron microscopy (SEM) and Atomic force microscope (AFM)

The morphology of the electrolyte was studied using scanning electron microscopy (SEM) (Hitachi SU3500) at 1000× magnification. Prior to the SEM analysis, the electrolytes were coated with a thin layer of gold using mini sputter coater (Quorum) to prevent electrostatic charging on the films. The topography image of electrolyte was carried out using scanning probe spectroscopic method by atomic force microscope (AFM) in order to estimate the roughness of the electrolyte surface.

2.6 Electrochemical impedance spectroscopy (EIS)

HIOKI 3532-50 LCR HiTESTER was used for the impedance measurement at 298 K to 343 K in the frequency range of 50 Hz to 5MHz. Hence, the ionic conductivity of the electrolytes was calculated using equation 2:

$$\sigma = \frac{t}{A R_B} \tag{2}$$

where *t* is the thickness of the electrolyte film, the bulk resistance is referred as R_b and the electrode–electrolyte contact area is referred as *A*. The conductivity holder was built up with two stainless steel electrodes whereby the electrolyte film was sandwiched between the electrodes. The Cole-Cole plot from the impedance measurement was used to determine the value of R_b .

2.7 Transference number measurement (TNM) and Linear sweep voltammetry (LSV)

Transference number measurement (TNM) was carried out to study the effects of the transference numbers of ions (t_{ion}) towards the ionic conductivity behaviour of an electrolyte. The Dc polarization technique was applied to determine the ionic transference number. The highest conducting electrolyte was sandwiched in between two stainless steel electrodes to be polarizing using V&A Instrument DP3003 digital Dc power supply using 0.3 V operating voltage at room temperature. The values of t_{ion} and t_{el} can be calculated using the following equations [14,25]:

$$t_{ion} = \frac{I_i - I_{ss}}{I_i}$$

$$t_{el} = 1 - t_{ion}$$
(3)

where I_i is the initial current and I_{ss} is the currents at steady state.

The potential stability of the electrolyte was studied using linear sweep voltammetry (LSV) before being fabricated to any electrochemical devices. The relatively highest conducting electrolyte was placed between two stainless steels in Teflon conductivity holder in order to study the LSV measurements with scan rate of 5 mV s⁻¹ at room temperature by using Digi-IVY DY2300 potentiostat.

2.8 Fabrication and characterization of EDLC

An EDLC was fabricated by sandwiching the most conductive electrolyte with two identical carbon-based electrodes. Cyclic voltammetry (CV) measurements were conducted using Digi-IVY DY2300 potentiostat at a voltage range of 0.0 V to 0.9 V at different sweep rates.



Figure 1. Illustration of EDLC fabrication

The fabrication of EDLC was carried out by sandwiching the conductive electrolyte with two electrodes in the coin cells as shown in Fig. 1. In order to hold and clamp the EDLC tightly, Teflon cases with stainless steels were employed at the top and bottom of coin cells. The area of electrode was 2.01 cm^2 . Naware battery cycler was used to analyse the charge-discharger of the EDLC with a constant current density of 0.2 mA cm⁻² for 300 cycles. From the EDLC's charge-discharge cycling, the values of C_s , energy density (*E*), and power density (*P*) at selected cycles can be calculated.

3. RESULTS ANALYSIS AND DISCUSSION

3.1 Fourier Transform Infrared (FTIR) spectroscopy for salted and plasticized systems

FTIR analysis is carried out to prove the complexation between the polymers matrix, salt, and ionic liquid. Fig. 2 illustrates the deconvoluted FTIR spectra of salted and plasticized films at hydroxyl band region.

Fig. 2(a) shows the deconvolution FTIR spectra of salted films in hydroxyl band region. The additional of 5 wt. % NH₄Cl has exhibited the hydroxyl peak at 3397 cm⁻¹ in S1. As the concentration of NH₄Cl increases to 10 wt. %, the peak has shifted to a lower wavenumber at 3380 cm⁻¹ in S2. Kadir et al. [15] reported that the hydroxyl peak decreased from 3354 cm⁻¹ to 3350 cm⁻¹ when the salt concentration was increased from 5 wt.% to 10 wt.%. The hydroxyl peak is further moved to lower wavenumber at 3375 cm⁻¹ in S3 and 3370 cm⁻¹ in S4. As the concentration of salt is increased, the cations numbers also increased which proved the interaction between the cations and oxygen atom through the formation of hydrogen bonding [16]. Therefore, the conductivity is estimated to be higher at this situation which will be further discussed in the conductivity analysis. The hydroxyl peak has moved to higher wavenumber at 3397 cm⁻¹ for S5 and 3399 cm⁻¹ for S6 whereby more salt is added to the electrolyte. Excessive salt concentration leads to the decrement of charge carriers in the electrolyte, thus leading to ionic conductivity reduction [17].



Figure 2. Deconvolution of FTIR spectra for salted and plasticized electrolytes at hydroxyl band region

Besides hydroxyl peak, the interaction of polymer host with NH₄Cl can be proven by the presence of v_{as} (NH₄⁺) and v_s (NH₄⁺). The v_{as} (NH₄⁺) peak in S1 at 3231 cm⁻¹ has shifted to lower wavenumbers at 3230 cm⁻¹, 3225 cm⁻¹ and 3224 cm⁻¹ for S2, S3 and S4, respectively. Due to the increment of salt concentration up to 20 wt.%, the v_{as} (NH₄⁺) peaks slightly moved to lower wavenumber which attributed to ions dissociation and leads to conductivity value improvement [26]. The v_s (NH₄⁺) peak of S1 at 3109 cm⁻¹ also present a trend of shifting to lower wavenumber at 3104 cm⁻¹ for S2 and 3103 cm⁻¹ for S3. The v_s (NH₄⁺) peak in S4 however shifted to the highest wavenumber of 3125 cm⁻¹ which can be related to the interaction of free ions at the highest value of ionic conductivity. The addition of 25 wt. % and 30 wt. % of NH₄Cl however have shifted the wavenumber to 3062 cm⁻¹ for S5 and 3060 cm⁻¹ for S6. This situation is due to the association of ions when more than 20 wt. % of NH₄Cl is added hence leading to the decrement of ionic conductivity [27].

Fig. 2(b) shows the deconvolution FTIR spectra of plasticized films in hydroxyl band region. The location of hydroxyl band for IL1 is increased from 3370 cm⁻¹ in S4 to 3390 cm⁻¹. The hydroxyl band has further shifted to a higher wavenumber of 3394 cm⁻¹ in IL2 and 3396 cm⁻¹ in IL3, respectively. The hydroxyl band is further moved to a higher wavenumber at 3400 cm⁻¹ and 3402 cm⁻¹ in IL4 and IL5, respectively. This result shows that the presence of BMIM-Cl has promoted the dissociation of ions by improving the ions interaction which is proved by the shifting of hydroxyl band. This situation leads to the enhancement of conductivity which will be discussed in the conductivity section. In IL6 electrolyte spectrum, the hydroxyl band region is moved to a lower wavenumber of 3398 cm⁻¹. This phenomenon shows that the free ions have been associated back and this leads to the decrement of ionic conductivity. The FTIR result in this study is comparable as reported by Rayung et al. [19] whereby the hydroxyl band region moved to higher wavenumber as the concentration of plasticizer increased.

The v_{as} (NH₄⁺) peak of IL1 that is located at 3307 cm⁻¹ has gradually moved to a higher wavenumber of 3308 cm⁻¹ in IL2, 3318 cm⁻¹ in IL3, 3325 cm⁻¹ in IL4 and 3326 cm⁻¹ in IL5. This signifies the interaction of H⁺ with oxygen atom from hydroxyl, leading to the enhancement of ionic conductivity [16]. However, when the concentration of BMIM-Cl is more than 50 wt. %, the v_{as} (NH₄⁺) peak is shifted to a lower wavenumber of 3322 cm⁻¹ in IL6. The v_s (NH₄⁺) peak of IL1 is found at 3231 cm⁻¹ and has further moved to 3232 cm⁻¹ in IL2, 3238 cm⁻¹ in IL3, 3239 cm⁻¹ in IL4 and 3242 cm⁻¹ in IL5. This situation proves that the highest concentration of free ions found in the IL5 electrolyte leads to the highest conductivity value. However, the addition of 60 wt. % BMIM-Cl has caused the v_s (NH₄⁺) to shift to a lower wavenumber of 3237 cm⁻¹.

3.2 X-ray diffractograms (XRD) for salted and plasticized systems

Fig. 3 (a) and (b) illustrate the XRD patterns of electrolytes in salted system and plasticized system, respectively.



Figure 3. X-ray diffraction patterns for (a) salted system and (b) plasticized system

It can be seen that the S6 electrolyte in Fig. 3 (a) exhibits seven crystalline peaks located at $2\theta = 8.1^{\circ}$, 22.7° , 32.5° , 40.2° , 46.7° , 52.7° , and 58.2° which refer to the NH₄Cl salt peaks. These peaks are comparable to Shukur et al. [10] which reported the starch-Ch doped with NH₄Cl electrolyte system. The addition of BMIM-Cl is observed to minimize the crystalline area of the salted electrolyte as depicted in Fig. 3 (b).

Fig. 4 shows the deconvolution of XRD patterns for PB3 and salted electrolytes. Based on the shape and location of crystalline peaks in S1 which are located at $2\theta = 8.4^{\circ}$, 15.0°, and 22.9° are retained from the polymer blend host (PB3). Other crystalline peaks are observed in S1 which are located at $2\theta = 11.1^{\circ}$ and 18.2° due to the interaction between polymer blend with the NH₄Cl while amorphous peaks are retained from polymer blend host (PB3).



Figure 4. Deconvolution of XRD pattern for selected salted electrolytes

The location of crystalline peaks is slightly changed to $2\theta = 8.8^{\circ}$, 11.4° , 15.1° , 18.5° , and 22.8° in S2. As visible in S3, the intensity of crystalline peak at $2\theta = 11.2^{\circ}$ is higher than S2. It can be seen that four crystalline peaks of S3 which are located at $2\theta = 8.0^{\circ}$, 11.2° , 18.2° , and 22.7° show high intensity compared to the crystalline peaks of S4 which are located at $2\theta = 8.1^{\circ}$, 11.2° , 18.1° , and 22.7° . The amorphous peaks of S3 are located at $2\theta = 23.5^{\circ}$ and 35.9° which slightly moved to $2\theta = 23.2^{\circ}$ and 36.0° in S4. Ions can move freely in the amorphous regions as proven by the suppressed crystalline peaks [19]. The crystalline peaks in S4 remain at $2\theta = 22.7^{\circ}$, 32.5° , and 52.7° in S5 and S6. As the concentration of salt increases, the intensity of crystalline peaks of $2\theta = 22.7^{\circ}$, 32.5° , and 52.7° in S5 and S6 also increases. At this salt concentration, the ions associated back in the polymer matrix because the polymer host is unable to accommodate the excessive salt content. Table 2 presents that degree of crystallinity for salted electrolytes whereby the highest value attained by S1 is aligned with the lowest ionic conductivity which will be discussed in the next section. This result is comparable with Shukur et al. [10], who reported that the increment of crystalline peaks intensity is associated with the recrystallization of salt. The degree of crystallinity values interrelated to the ionic conductivity will be further discussed.

Electrolytes	Degree of crystallinity (x_c)		
PB3	21.6		
S 1	23.1		
S2	22.5		
S 3	19.3		
S 4	18.7		
S 5	19.1		
S 6	19.9		
IL1	13.4		
IL2	12.9		
IL3	12.4		
IL4	11.2		
IL5	10.5		
IL6	10.7		

Table 2. Degree of crystallinity for salted and plasticized electrolytes

Fig. 5 shows the deconvolution of XRD patterns in the plasticized system. Three amorphous peaks are noticed when BMIM-Cl is incorporated into the S4 electrolyte. It is also observed that the addition of BMIM-Cl has reduced the crystalline structure of the electrolytes containing BMIM-Cl as compared to salted electrolyte. Yusof et al. [20] reported that the addition of glycerol as plasticizer in the electrolyte system provided a hydroxyl group (OH) which contributed to the enhancement of conductivity when the oxygen atom from OH group was attracted to H⁺ and NH₄⁺. Based on Fig. 5, three crystalline peaks originated from S4 appear at $2\theta = 8.1^{\circ}$, 11.1° , and 17.0° in IL1, are shifted to $2\theta = 8.0^{\circ}$, 11.0° , and 18.8° in IL2 and $2\theta = 7.9^{\circ}$, 11.0° , and 16.0° in IL3.



Figure 5. Deconvolution of XRD pattern for plasticized electrolytes

The crystalline peaks at $2\theta = 7.7^{\circ}$, 11.2°, and 16.3° in IL4 then slightly moved to $2\theta = 7.6^{\circ}$, 11.0°, and 15.3° and $2\theta = 7.4^{\circ}$, 11.0°, and 15.2°, in the IL5 and IL6, respectively. From these observations, the intensity of the crystalline peaks is decreased with the increase of BMIM-Cl concentration. Tang et al. [21] reported that the incorporation of EMIM-BF₄ in the salted electrolyte would disrupt the crystalline structure due to the interaction between polymers, salt, and ionic liquid. A new amorphous peak appears at $2\theta = 58.9^{\circ}$ in IL1 before it moves to 45.0° in IL2, 58.0° in IL3, 60.4° in IL4. 58.7° in IL5. and 57.9° in IL6. respectively which provides the evidence that salted electrolyte has a good interaction with the BMIM-Cl. The other two amorphous peaks located at $2\theta = 24.0^{\circ}$ and 36.3° in IL1 moved to $2\theta = 24.8^{\circ}$ and 34.1° in IL2 and $2\theta = 25.1^{\circ}$ and 36.6° in IL3, respectively. The intensity of amorphous peaks increased when the concentration of BMIM-Cl is increased. This result verifies the interaction between polymer blend (PB3) with NH₄Cl and BMIM-Cl which contributes to the enhancement of the amorphousness of the electrolyte. IL5 electrolyte shows that the film has the highest amorphous properties due to the highest intensity of the amorphous peaks. The intensity of amorphous peaks in IL6 started to decrease due to the excessive concentration of BMIM-Cl in the system. Table 2 shows the degree of the crystallinity for the plasticized electrolytes. As the concentration of BMIM-Cl is increased, the degree of crystallinity is reduced from 18.7 % for IL0 to 10.5 % for IL5.

3.3 Morphology analysis

The scanning electron microscope (SEM) is one of the most versatile instruments available for the examination and analysis of the morphology of the conducting surfaces. Fig. 6 shows SEM images for selected electrolytes. Fig. 6(a) clearly shows a smooth and uniform surface morphology of PB3. It is observed that the surface is homogeneous without phase separation, suggesting that Md and Ch are miscible to each other. This smooth morphology suggests the complete amorphous nature of the polymers, which also coincides with the XRD result. The observation in this work is similar to a report by Shukur et al. [10] for polymer blend of 80 wt.% corn starch with 20 wt.% chitosan. A matching observation was also reported by Salman et al. [22] for polymer blend of 75 wt.% chitosan with 25 wt.% methyl cellulose. The S1 micrograph can be observed in Fig. 6(b). The film contains small grains without any phase separation, showing the presence of salt in the polymer [28]. There is also a change in colour of the surface when salt is added to the electrolyte.



Figure 6. SEM image of (a) PB3, (b) S1, (c) S4, (d) S6, (e) IL1, (f) IL5, and (g) IL6

A surface containing small grains can also be observed in the S4 electrolyte as shown in Fig. 6(c). The electrolyte smoother surface proves that the polymers and salt used in this study are compatible. The presence of pores in S4 is due to the improvement in amorphous region which leads to the enhancement of conductivity value [28]. This observation will be further supported by conductivity studies which will be discussed in conductivity section. Fig. 6(d) depicts the morphology for the S6 electrolyte. When the electrolyte contains more than 30 wt.% of NH₄Cl salt, there will be presence of solid structures which suspend out from the surface of the electrolyte film [29]. The solid structures are due to the crystallization of NH₄Cl which is revealed from the XRD analysis. This phenomenon is due to the inability of the NH₄Cl to be incorporated in the polymer host resulting on recrystallization of salt [22]. The recombination of ions will decrease the number of mobile ions which leads to the decrement of conductivity. The same observation is also reported by Johan et al. [30] for PEO-based electrolyte doped with LiCF₃SO₃.

The inclusion of BMIM-Cl is found to alter the morphology of the electrolytes. Fig. 6(e) shows the SEM micrograph of IL1 electrolyte. It can be seen that cross linking grains appear due to the interaction of S4 with BMIM-Cl. This outcome is comparable with Shukur el at. [10] for starch-Ch-NH4Cl doped with glycerol which also reported the appearance of linkages in their SEM micrograph. The micrograph of IL5 electrolyte in Fig. 6(f) shows the wrinkled surface when the concentration of BMIM-Cl is increased to 50 wt. %. The plasticizer has developed alternative pathways which appear as tunnel pattern on the surface, for ions conduction that can increase the conductivity [31]. This result indicates the high amorphous phase of IL5 electrolyte can be seen in Fig. 6(g). White particles appear on the surface potentially due to the recrystallization of the salt thus decrease the conductivity [17].

In the present study, the scanning probe spectroscopic method of AFM is used to determine the roughness factor of the sample.





Figure 7. AFM image of PB3, S4, and IL5

Two-dimensional and three-dimensional topography images of PB3, S4, and IL5 are shown in Fig. 7. The surface roughness of PB3 over the scanned area is found of the order of 18.69 nm. The rough surface exhibited by 3D view shows highly crystalline nature of the polymer blend. However, the polymers interaction between Ch and Md destroys the regular crystallized network present from the polymers nature [32].

The images of S4 clearly show the presence of numerous pores which are responsible for ions hopping and leads to the enhancement of conductivity value [33]. The surface roughness of S4 electrolyte has been estimated at 12.39 nm which is lower compared to PB3. A report by Selvakumar et al. [33] showed a lower surface roughness value for electrolyte system of PVdF-HFP doped with NH₄SCN compared to the polymer blend host. This result significantly proved the enhancement of amorphousness in the polymer matrix.

The plasticizing effect of BMIM-Cl on the polymer matrix is further studied using the AFM analysis. The images of IL5 in Fig. 7 reveal a smoother surface compared to S4, which is probably due to the reduction in crystallinity affected by the presence of BMIM-Cl [34]. The surface of IL5 obviously reveals the tunnel pattern which coincides with the SEM result. The surface roughness of IL5 electrolyte

has been estimated at 9.86 nm which is lower than S4. This result is proven by the enhancement of amorphousness phase that affects the conductivity value which agrees with the XRD result. Pramod et al. [35] reported that by doping EMIM-DCN ionic liquid into the electrolyte, the surface roughness had reduced and become more homogenous compared to electrolyte without ionic liquid.

3.4 Conductivity analysis

The conductivity of electrolytes is highly affected by the charge carrier concentration. Therefore, when the salt concentration varies, the conductivity is also expected to change. The conductivity enhancement is also due to the increase in the number of complexation sites in polymer electrolytes [36]. The room temperature conductivity of the electrolyte with different NH₄Cl concentration is presented in Fig. 8(a). The addition of 5 wt. % NH₄Cl (S1) has increased the ionic conductivity of PB3 film from $(3.85 \pm 1.48) \times 10^{-10}$ S cm⁻¹ to $(2.27 \pm 1.36) \times 10^{-9}$ S cm⁻¹.



Figure 8. (a) Effect of NH₄Cl concentration on conductivity at room temperature. (b) Effect of BMIM-Cl concentration on conductivity at room temperature. Effect of temperature on conductivity behaviour of (c) salted system and (d) plasticized system

When the concentration of NH₄Cl is increased to 10 wt. % (S2) and 15 wt. % (S3), the conductivity also increases up to $(1.12 \pm 0.40) \times 10^{-8}$ S cm⁻¹ and $(2.17 \pm 0.82) \times 10^{-7}$ S cm⁻¹, respectively. The ionic conductivity is further increased to $(2.12 \pm 0.87) \times 10^{-6}$ S cm⁻¹ for S4 as the salt concentration reaches 20 wt.%, which is related to the improvement in the number of mobile charge carriers [37]. This

result can also be proven from XRD result which shows a low degree of crystallinity at this salt concentration. Du et al. [38] reported the highest ionic conductivity of 6.54×10^{-8} S cm⁻¹ for Ch-NH₄Cl system. A higher ionic conductivity value obtained in this system shows that the ionic conductivity of an electrolyte can be enhanced by using polymer blend as the host. Besides, more complexation sites can be provided by blending two polymers which allow ions migration and exchange to happen frequently, leading to an increment in ionic conductivity. The ionic conductivity of S5 decreased to (4.49 \pm 0.90) \times 10⁻⁷ S cm⁻¹ which then further decreased to (5.20 \pm 2.10) \times 10⁻⁸ S cm⁻¹ for S6. The distance between dissociated ions become closer at higher salt concentration whereby they tend to recombine and form neutral ion pairs that lessen the contribution towards the ionic conductivity [39].

Fig. 8(b) depicts the conductivity of the plasticized system at room temperature. The ionic conductivity of IL1 increased to $(4.05 \pm 0.96) \times 10^{-6}$ S cm⁻¹ with 10 wt. % of BMIM-Cl. The ionic conductivity of the electrolytes is observed to gradually increase $(1.52 \pm 0.06) \times 10^{-5}$ S cm⁻¹ (IL2), $(4.42 \pm 0.01) \times 10^{-5}$ S cm⁻¹ (IL3) and $(1.78 \pm 0.07) \times 10^{-4}$ S cm⁻¹ (IL4). These increments are affected by the enhancement of the number of mobile charge carriers provided by the ionic liquid [40]. IL5 exhibits the highest conductivity of $(1.28 \pm 0.06) \times 10^{-3}$ S cm⁻¹ with 50 wt. % BMIM-Cl. However, the ionic conductivity starts to decrease to $(4.68 \pm 0.04) \times 10^{-4}$ S cm⁻¹ when 60 wt. % of BMIM-Cl is added. Subban et al. [41] reported the PEMA-NH₄CF₃SO₃ system incorporated with BMATFSI ionic liquid obtained the highest ionic conductivity of 8.35×10^{-4} S cm⁻¹. In the work done by Deraman et al. [42] showed that the PVC-NH₄CF₃SO₃ electrolyte system with the addition of BATS ionic liquid optimized the highest ionic conductivity of 1.56×10^{-4} S cm⁻¹. This describes that BMIM-Cl is a suitable plasticizer to be applied in the electrolyte film and has the potential to be a good charge carrier as other ionic liquids.

Electrolytes	E_a (eV)	Conductivity, σ (S cm ⁻¹)
S1	0.50	$(2.27 \pm 1.36) \times 10^{-9}$
S2	0.48	$(1.12\pm0.40) imes10^{-8}$
S 3	0.44	$(2.17\pm0.82) imes10^{-7}$
S 4	0.42	$(2.12 \pm 0.87) imes 10^{-6}$
S5	0.43	$(4.49 \pm 0.90) imes 10^{-7}$
S 6	0.47	$(5.20 \pm 2.10) imes 10^{-8}$
IL1	0.31	$(4.05\pm0.96) imes10^{-6}$
IL2	0.24	$(1.52\pm0.06) imes10^{-5}$
IL3	0.22	$(4.42\pm0.01) imes10^{-5}$
IL4	0.19	$(1.78\pm0.07) imes10^{-4}$
IL5	0.15	$(1.28 \pm 0.06) \times 10^{-3}$
II 6	0.18	$(4.68 \pm 0.04) \times 10^{-4}$

Table 3. The activation energy, E_a and conductivity values, σ for salted and plasticized electrolytes

Fig. 8(c) shows the conductivity behaviour for Ch-Md blend doped with NH₄Cl at elevated temperatures. From the observation, the ionic conductivity has increased with the increment of temperature from 298 K to 343 K. Therefore, this situation confirms the Arrhenius behaviour of the electrolyte film with regression value being close to unity, $R^2 \sim 1.00$. This outcome is comparable with

the previous study reported by Hambali et al. [43]. The Arrhenius equation as expressed in equation 5 can be used based on the temperature relation with the conductivity.

$$\sigma = \sigma_o \, \exp \frac{E_a}{k \, T} \tag{5}$$

where σ_o stands for the pre-exponential factor, the activation energy is referred to as E_a , the Boltzmann constant is referred to as k and the absolute temperature is referred to as T. The values of E_a and conductivity for salted electrolytes are calculated and tabulated in Table 3. It is found that the S4 electrolyte has the lowest E_a of 0.42 eV in salted system. This result is comparable with the work reported by Vanitha et al. [44] where the E_a value for the PVA-PVP doped with NaCl system was at 0.58 eV. Low E_a shows that the ions require low energy to be free from the coordinating site to move to another coordinating site [45].

The conductivity behaviour at high temperature for the plasticized electrolytes is also illustrated in Fig. 8(d). It is observed that the ionic conductivity is highly correlated to the temperature. This situation shows that a high temperature will cause the ions to move faster due to the enhancement of bond rotations [46]. The almost straight line with R^2 value of ~ 1.00, explained that the electrolytes follow the Arrhenius behaviour. This outcome is comparable with the previous studies as reported by Liew et al. [47] for the system of PVA-CH₃COONH₄ blended with BMIM-Tf, and Farhana et al. [48] for the system of PPC-NaI-BMIM-I. The values of E_a and conductivity for electrolytes in plasticized system are also tabulated in Table 3. It shows that IL5 has the lowest E_a value of 0.15 eV. This result is comparable with Bose et al. [49] and Vo et al. [50] which reported E_a values of 0.041 eV and 0.019 eV for their respective plasticized electrolyte systems. Bandara et al. [51] also reported the electrolyte with the highest ionic conductivity value showing the lowest activation energy value which indicates that the ions need less energy to be free from one allocation site to another.

3.5 Dielectric analysis

Dielectric study is analyzed from the impedance plots to support the trend of ionic conductivity. Dielectric constant, ε_r represents the charge in a material whereas dielectric loss, ε_i represents the value of the energy losses to move ions [52]. Equation 6 and 7 below are used to calculate the values of ε_r and ε_i .

$$\varepsilon_r = \frac{Z_i}{(Z_r^2 + Z_i^2) \,\omega C_o} \tag{6}$$

$$\varepsilon_i = \frac{Z_r}{(Z_r^2 + Z_i^2)\,\omega\mathcal{C}_o}\tag{7}$$

where C_o is vacuum capacitance, $\omega \Box$ is angular frequency, Z_r and Z_i is the real and imaginary parts of impedance, respectively.



Figure 9. The dependence of (a) ε_r and (b) ε_i on NH₄Cl at room temperature for different frequencies. The dependence of (c) ε_r and (d) ε_i on BMIM-Cl at room temperature for different frequencies

Fig. 9 portrays the dependence of (a) ε_r and (b) ε_i on the concentration of NH₄Cl at room temperature at different frequencies. Fig. 9 also shows the dependence of (c) ε_r and (d) ε_i on BMIM-Cl concentration for different frequencies at room temperature. The dielectric constant gives the highest value at low frequency region because the charges are able to accumulate between electrolyte-electrode boundaries caused by the electrode polarization. This phenomenon is due to the ability of the mobile ions to follow the direction of electric field where the ions tend to assemble [53,54]. High frequency region exhibits the decrement of dielectric constant values of electrolytes due to the fast rate of periodic reversal of the electric field. The increase of NH₄Cl and BMIM-Cl to the electrolyte will increase the values of ε_r and ε_i due to the increment of charge carriers. Nevertheless, the values of ε_r and ε_i start to decrease when the concentration of NH₄Cl and BMIM-Cl exceeds 20 wt. % and 50 wt. %, respectively. Higher concentration of salt leads to the decrement of ionic conductivity due to the ions aggregation which reduces the mobility of the ions by blocking the migration pathways [55,56]. These results are found similar with the conductivity trend of salted and plasticized electrolytes.

3.6 Transference number measurement (TNM)

The dominance of electrons and ions in the electrolyte contributes to the conduction process [57]. TNM technique is used to determine which charge carrier is dominant within the electrolytes. Fig. 10(a) and (b) shows the polarization current versus time for the highest conducting electrolyte in salted and plasticized systems which are S4 and IL5, respectively. The DC polarization procedure is applied to the working electrode with a potential of 0.3 V. The current is measured until the ionic transference number reaches a steady state. It can be observed that the initial currents are 11.6 μ A and 54.7 μ A for S4 and IL5 electrolytes, respectively. These results are due to the polarization process for both electron and ion at early stage. The currents are then dropped and become constant approximately at 0.8 μ A for S4 when the time beyond 1000 s and 0.4 μ A for IL5 when the time is beyond 3600 s for IL5. The significant decrease may be due to the blockage of ions on the electrode surfaces, which result in a constant current flow since the drifting ions are similar to the diffusion of ions and enable the electrons to be the only species to migrate through [58].



Figure 10. TNM plots for (a) S4 and (b) IL5 electrolytes and (c) LSV plots for S4 and IL5 electrolytes

For the salted system, the calculated values of t_{ion} and t_{el} are at 0.931 and 0.069, respectively. This values are comparable with a report from Aziz et al. [25] for system of Ch-methylcellulose doped with NH₄I where the value of t_{ion} and t_{el} were 0.934 and 0.036, respectively. Besides, Marf et al. [31] also reported the value of t_{ion} and t_{el} of 0.890 and 0.110, respectively for the electrolyte system of PVA-Ch incorporated with NH₄I. For the plasticized system, it is observed that the values of t_{ion} and t_{el} are at 0.993 and 0.007, respectively. This outcome is comparable as reported by Ghani et al. [59] whereby the carrageenan based electrolyte plasticized with BMIM-Cl system achieved the t_{ion} and t_{el} values of 0.980 and 0.020, respectively. Moreover, Hafiza et al. [60] reported the values of both t_{ion} and t_{el} for the plasticized system in this work is ionic conductor along with electron transfer is a unique characteristic [25]. The values of t_{ion} indicate that the charge carrier is exclusively ion in the polymer matrix for both salted system and plasticized system.

3.7 Linear sweep voltammetry (LSV)

A linear sweep voltammetry (LSV) technique can be applied to study the electrochemical stability of the electrolytes. The LSV response of the S4 and IL5 electrolytes at 5 mV/s sweep rate at room temperature are shown in Fig. 10(c). The decomposition voltage of S4 can be seen at 1.27 V. When the ionic liquid is added to the electrolyte, the value of the decomposition voltage has been extended to 1.81 V. Previously, Marf et al. [31], reported the value of decomposition voltage of PVA-Ch-NH₄I was at 1.33 V. Kadir et al. [61] also reported a decomposition voltage of 1.53 V obtained by the glycerolized system of methyl cellulose doped with NH₄Br. This phenomenon proves that the inclusion of plasticizer can impact the electrochemical stability of an electrolyte [62]. In this work, the electrolytes are observed to be appropriate for future application as most of the energy devices demanded a minimum breakdown voltage of 1.0 V [63,64].

3.8 Cyclic voltammetry (CV)

The performance of EDLC using the highest conducting electrolyte, IL5 is analyzed using CV prior to EDLC fabrication. The CV plot and the calculated specific capacitance values at different scan rates are illustrated in Fig. 11(a). It can be observed that the absence of any peak in the plot is a proof that redox reaction does not occur in the potential range of 0.0 V to 0.9 V. This situation signifies that there is a presence of electrochemical double-layer formation and also indicates that the electrolyte is stabilized with no decomposition takes place in this working voltage range [65,66]. The CV plots in this work are comparable with the literature [67–69]. High scan rate causes an inconsistency of the CV shape from a perfect rectangular shape which is caused by the carbon porosity and the internal resistance, thus creating a current dependence of voltage [70].



Figure 11. The plot of (a) cyclic voltammetry of EDLC at different scan rates (b) charge-discharge of EDLC at selected cycles (c) specific capacitance versus cycle number and (d) energy density and power density versus cycle number.

The values of specific capacitance, C_s from the CV plot can be determined using the following equation:

$$C_{s} = \int_{V_{1}}^{V_{2}} \frac{I(V)dV}{2(V_{2} - V_{1})mv}$$
(8)

where I(V) is the current-dependent potential, $(V_2 - V_1)$ is potential different, *m* is the mass of active materials and *v* is the scan rate. The values of C_s that have been calculated are tabulated in Table 4. When the scan rates increased, the values of C_s are decreased. This phenomenon is due to the movement of free ions to all vacant sites on the electrodes. The shorter time of interaction between ions and electrodes to complete the process of charging and discharging at higher scan rates leads to the reduced amount of stored energy. There is a different scenario at lower scan rates where the ions have enough time to be absorbed on the electrolyte surface, thus the amount of stored energy becomes higher

[71,72]. The lower energy loss at lower scan rates contributes to a high amount of stored charge [73]. Thus, double-layer charge will be formed on the surface of electrodes, which contributes to the enhancement of potential energy [74].

Scan rates (mV s ⁻¹)	Specific capacitance, <i>C</i> _s (F g ⁻¹) 15.67 9.66	
10		
20		
50	6.96	
100	5.65	

Table 4. The values of specific capacitance, C_s from CV plot

3.9 Charge-discharge characteristic

Fig. 11(b) shows the charge-discharge performance plot of EDLC at selected cycles. The current density for charge-discharge is applied at 0.2 mA cm⁻² with the working voltage is between 0.0 V to 0.9 V. The value of C_s is determined by using the equation below [75]:

$$C_{s} = \frac{2i}{m} \left(\frac{\int_{t_{i}}^{t_{f}} V(t) dt}{V^{2} |_{V_{i}}^{V_{f}}} \right)$$

$$(9)$$

where *i* is the constant current, V_f and V_i is the final and initial potential values, and $\int V(t)dt$ is the area under discharge curve. The plot of C_s against number of cycles is illustrated in Fig. 11(c). The highest value of C_s is obtained at 56 F g⁻¹ before dropped to 14 F g⁻¹ at the 50th cycle and further dropped to 7 F g⁻¹ during the 100th cycle. When the cycle number is beyond 200th, the value of C_s is remained constant approximately at ~ 4 F g⁻¹ to 3 F g⁻¹ due to ions aggregation at the electrode-electrolyte interface. The value of C_s from the charge-discharge measurement at ~50th cycles is comparable with the C_s value from the CV analysis at a scan rate of 10 mV s⁻¹. Liew et al., [47] reported that the C_s value from the CV plot of PVA-CH₃COONH₄-BMIMI was 2.02 F g⁻¹ at a scan rate of 10 mV s⁻¹, which was comparable with the C_s obtained from charge-discharge measurement at the 5th cycles. Hamsan et al., [65] reported that the C_s value obtained from the charge-discharge analysis was between ~21 to 22 F g⁻¹ beyond the 200th cycles. The C_s value from the CV analysis obtained was 20.48 F g⁻¹ at a scan rate of 2 mV s⁻¹ which in a good agreement with the C_s value resulted from the charge-discharged measurement. Therefore, the results presented in this work prove that the value of C_s attained from the EDLC is reliable. The comparison results of C_s values with other works are listed in Table 5.

Electrolyte system	C_{s} (F g ⁻¹)	Cycles	Reference
PVA- CH ₃ COONH ₄ - BMIM-Tf	3.36	5	[47]
Starch-cellulose-NH4NO3-glycerol	31.0	1000	[65]
PVA-CH ₃ COONH ₄ - BMIM-Br	45.3	500	[76]
PVdf-TEABF4- BMIM-Cl	61.7	300	[79]
PVA-CH ₃ COONH ₄ - BMIM-I	56.2	500	[80]
Ch-Md-NH ₄ Cl- BMIM-Cl	56.0	300	This work

Table 5. Comparison of specific capacitance, C_s values from charge-discharge of EDLC with other
works

The values of energy density, E and power density, P of the EDLC can be determined via the equations below:

$$E = \frac{1}{2} C_s V^2$$

$$P = \frac{V^2}{4m(ESR)}$$
(11)
(12)

The plot of the energy density against number of cycles can be observed in Fig. 11(d). The highest value of *E* is obtained at 9.0 Wh kg⁻¹. The value then decreased to 4.7 Wh kg⁻¹ at the 50th cycle and further decreased to 3.9 Wh kg⁻¹ during 100th cycle. When the *E* value decreased over the cycle number, it is ascribed to the increment of the internal resistance which leads to the increase of energy loss during the charge-discharge process [76]. The *E* values stabilized around 2.9 Wh kg⁻¹ to 2.5 Wh kg⁻¹ from the 200th to 300th cycle which harmonized with the pattern of *C_s* plot as shown in Fig. 11(c). This phenomenon shows that the ions experienced the same energy barrier during the ions migration towards the surfaces of electrodes [77]. The *E* achieved at 300th cycle for this EDLC is higher compared to the report by Hamsan et al. [65] who obtained the *E* value of 2.2 Wh kg⁻¹. The value of power density against number of cycles is also demonstrated in Fig. 11(d). From the observation, the *P* value dropped from 276 W kg⁻¹ to 137 W kg⁻¹ at the 300th cycle. This result has the same pattern as reported by Francis et al. [76] and Aziz et al. [78]. The decrement value of *P* is due to the depletion of electrolyte. This is because the aggregation of ions after the rapid charge-discharge processes will block the ions transportation towards the surface of electrode, hence leading to the decrement of ions adsorption at the electrolyte-electrode interface [79].

4. CONCLUSION

The chitosan-maltodextrin based electrolytes infused with NH₄Cl salt and plasticized with BMIM-Cl ionic liquid have been successfully prepared via the solution-casting method. IL5 electrolyte

shows the lowest degree of crystallinity based on the deconvolution of XRD pattern which is 10.5%. The linkages on the surface of IL5 prove that this electrolyte contains high amorphous characteristics as identified from the SEM study. The highest room temperature conductivity is achieved at $(1.28 \pm 0.06) \times 10^{-3}$ S cm⁻¹ for IL5. Results from the dielectric analysis show a non-Debye characteristic. The values of t_{ion} and t_{el} for IL5 electrolyte are found at 0.993 and 0.007 respectively which indicates that the electrolyte is an ionic conductor. The IL5 electrolyte is electrochemically stable up to 1.81 V, which was verified through the LSV analysis and confirms the suitability for the EDLC application. The charge-discharge plots have confirmed the capacitive behaviour of the EDLC where the highest specific capacitance value is achieved at 56 F g⁻¹. Energy and power density are stabilized at 2.5 to 9.0 Wh kg⁻¹ and 137 to 276 W kg⁻¹, respectively, as the EDLC completes the cycles.

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