Structural, morphological and electrical properties of chitosan/methylcellulose blend polymer doped with different concentrations of NH$_4$NO$_3$

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Abstract

Polymer blend electrolytes based on chitosan: methylcellulose loaded with ammonium nitrate (NH$_4$NO$_3$) were fabricated by solution cast method and characterized by XRD, FTIR, EIS, FESEM, and TNM techniques. XRD is used to show the decrease of the crystalline structure. FTIR method is used to confirm the interaction between electrolyte elements. The maximum room temperature DC conductivity of 3.54 $\times$ $10^{-4}$ S cm$^{-1}$ is provided by the highest conducting system using EIS data. The FESEM method showed that the morphology of the film has a uniform smooth surface at the highest salt concentration. This is in good agreement with the XRD, FTIR, and EIS results. The dielectric constant is high at the low frequency region due to electrode polarization. Transference number measurement (TNM) is used to show the dominant charge carriers. The values of the transference number of electron ($t_{\text{electron}}$) and ion ($t_{\text{ion}}$) showed that the ions are dominant. The TNM measurement shows the compatibility of the system for electrochemical energy storage device application.

1. Introduction

Electrochemical energy storage devices (ESDs) have drawn more attention by researchers as a replacement of energy sources as a result of their compatibility and eco-friendly nature [1]. During recent decades, the ESDs such as supercapacitors, fuel cells, and batteries were more studied using liquid electrolytes (LEs) due to its relatively high ionic conductivity. However, LEs have some undesired properties, such as safety problem, discharging harmful gas, and corrosivity [2]. Polymer electrolytes (PEs) show more advantages over the traditional LEs due to their remarkable properties such as flexibility, solvent free, transparency, light in weight, good ability of film forming, easy processability, good conductivity, and good electrochemical windows [3–5]. PEs improve safety as it avoids some issues for example use of corrosive solvent, internal shorting, electrolyte leakage, making of harmful gas, and existence of noncombustible reaction product on the surface of the electrodes [3, 6–8].

Biodegradable polymers (BPs) are more focused currently instead of non-BPs because of their eco-friendly and harmless. The effort of using BPs can decrease the environmental waste as they are recyclable and reusable. It is attractive to note that the existence of electronegative atoms such as nitrogen and oxygen through the monomers of polymer chains improves the property of the solvent to dissolve salt and thus providing ions. Interestingly, the oxygen and nitrogen in chitosan (C) encourage researchers to concentrate on C polymers [9–11] as its structure is enrichment with polar groups of OH and NH$_3$. These groups act as a conjunction site to provide association with the transition metal ions [12, 13]. Methylcellulose (M) is also another BP with enormous potential which is used in the application of PEs. M is extracted by alkali-based cellulose when treated with methyl chloride and its structural unit is joined by /β-(1 → 4) glycosidic bond [14, 15].

Through the various techniques, polymer blending is the mainly viable method [16]. In this research, polymer blend method is used with doping salt to get a unique property which is not easy to be obtained with a
single polymer. The blend of C and M is established to be a promising blending process. Both materials are enriched with oxygen and nitrogen containing functional group, which is viable for ionic conduction [9–11]. To develop the PE with ions, NH₄NO₃ is used in this work as it has low lattice energy (642 kJ mol⁻¹), meaning a high degree of dissociation [17]. Masao et al [18] documented a direct current (DC) conductivity of 2.98 × 10⁻³ S cm⁻¹ at ambient temperature for k-carrageenan/NH₄NO₃ for application in solar cell. The conductivity of 2.39 × 10⁻⁴ S cm⁻¹ has been documented by Shuhaimi et al for C/carrageenan/NH₄NO₃ [19].

This research is aimed to study C/M loaded with various concentration of NH₄NO₃ tested with x-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), electrochemical impedance spectroscopy (EIS), field emission scanning electron microscopy (FESEM), and transference number measurement (TNM). This research is crucial to understand the relation between DC conductivity and dielectric property. On the other hand, the electrochemical examination of TNM shows the appropriateness of the systems for application in energy storage devices when their conductivity is increased with different approaches for example the polymer blending and addition of fillers.

2. Materials and methods

2.1. Materials

Chitosan (C) (310000–375000 g mol⁻¹), methylcellulose (M) (4000 cP), NH₄NO₃ (80.043 g mol⁻¹) were purchased from Sigma-Adrich.

2.2. Electrolyte preparation

0.3 g M and 0.7 g of C were dissolved separately in 40 ml of 1% acetic acid for 3 h at room temperature to synthesize C: M polymer blend. Both of the solutions were blended and stirred for 2 h more to get a homogeneous mixture. NH₄NO₃ with concentrations of 0, 10, 20, and 30 wt% were loaded to the C: M and the samples were coded as CMN_0, CMN_10, CMN_20, and CMN_30, respectively. The Petri dishes were used to keep the electrolyte solutions and then the films dried at room temperature. The synthesized electrolyte films were put in a desiccator with silica gel for more drying the films and maintaining the condition of room temperature at 25 °C and relative humidity of ~50% for the films. Table 1 shows the electrolyte components.

Table 1. Components of the polymer blend electrolytes.

| Sample code | C/M (0.7/0.3) g | NH₄NO₃ wt% (g) |
|-------------|----------------|----------------|
| CMN_10      | 1              | 10 (0.111)     |
| CMN_20      | 1              | 20 (0.250)     |
| CMN_30      | 1              | 30 (0.428)     |

2.3. Structural, impedance, and morphological characterization

X-Ray Diffraction (XRD) spectra were measured with Empyrean x-ray diffractometer (Netherlands/ PANalytical) at 40 KV working voltage and 40 mA operating current. The electrolyte systems were scanned with x-ray beam (1.5406 Å) and the glancing angles (2θ) was run between 10° and 80° with 0.1° step size. To examine the interaction between electrolyte elements, Fourier Transform Infrared (FTIR) spectrophotometer (Thermo Scientific, Nicolet iS10) was used between 4000 and 450 cm⁻¹ with a resolution of 2 cm⁻¹. The impedance data was measured with HIOKI 3531 Z Hi-tester between 50 Hz and 5000 kHz. The synthesized films with varied thickness between 0.029 and 0.031 cm were cut with small discs (2 cm) in diameter and then put between two stainless steel electrodes with spring pressure. The cell was connected to a computer and a software was used to measure the imaginary (Z_l) and real (Z_r) parts of the complex impedance (Z'). Field emission scanning electron microscopy (FESEM) was carried out by a Hitachi SU8220 at magnification of ×2.00 k to study the surface morphology of the electrolyte films.

2.4. Electrochemical characterization

Transference number measurement (TNM) for ions and electrons [(t_ion) and (t_electron)] were measured when the cell system of [stainless steel (highest conducting system) stainless steel] polarized at operating voltage of 0.2 V using V&A Instrument DC power supply DP3003 at ambient temperature. The values of t_ion and t_electron were measured using equations (1) and (2):

\[
I_{\text{ion}} = \frac{I_i - I_o}{I_i} \quad (1)
\]
where, $I_i$ and $I_s$ stand for the initial current and steady state current.

3. Result and discussion

3.1. XRD study

Figures 1(a)–(c) reveals the XRD spectra for C: M polymer blend and the electrolyte films. According to literature, C has crystalline peaks at $2\theta = 15.2^\circ$, $17.9^\circ$, and $21^\circ$ because of intra molecular and inter molecular hydrogen bonding among the functional groups of the monomers [12, 20]. Literature showed that M has semicrystalline phase and one hollow at $2\theta$ from $18.5^\circ$ to $21.5^\circ$ which is due to inter-molecular hydrogen bonding along with a short distance order in the M chains [21–24]. As seen in figure 1(a)–(c) the intensity of the hollow is decreased and broadened when the NH$_4$NO$_3$ salt is added to the C: M polymer blend. From the figure a broad hump is only seen at the XRD spectra of C: M systems. This broad hump reveals that the C: M blend is nearly amorphous structure [25, 26]. Thus, the polymer blending is useful to fabricate materials with low degree of crystallinity and thus increasing conductivity. Polymer blending is a mixture of blending at least two polymers with different structure by secondary forces without the formation of covalent bond [27, 28]. When 10 wt% NH$_4$NO$_3$ is loaded into C: M polymer blend, the intensity of the hallow is decreased as seen in figure 1(b) and this is an evidence of reducing the crystalline structure in the C polymer [20]. While 30 wt% NH$_4$NO$_3$ is loaded to C: M, the intensity of the hollow is more decreased and broadened (figure 1(c)), meaning that the amorphous structure within the C: M blend is dominant. XRD test is also used to anticipate the trend of conductivity of the electrolyte [29]. The decrease of crystallinity through the C: M system by loading the inorganic salts is due to the interaction between the cations of the salt and the functional groups of the polymer by disrupting hydrogen bonding [20]. According to Hodge et al [30], the peak intensity is correlated with the degree of crystallinity. The authors stated that the intensity decrease and broadening in the XRD spectra are a strong evidence of amorphous dominated through the samples.

3.2. FTIR study

Figure 2 reveals the FTIR spectra of C: M blend and electrolyte films at a wavenumber between 450 and 4000 cm$^{-1}$. The absorption band owing to $\text{–OH}$ stretching is found at (region 1) 3626–3132 cm$^{-1}$ in a wide peak form which resulting from the salt incorporation to the system. The absorption bands owing to $\text{–OH}$ bending is

$$ t_{\text{electron}} = 1 - t_{\text{ion}} \quad (2) $$
found at (region 4) 1200–1480 cm$^{-1}$ in the form of a sharp peak which resulting from the salt addition to the system [31, 32]. Several peaks are seen in-band (region 4) where the one focused at 1312 cm$^{-1}$ is due to $\text{–OH}$ bending. Additionally, the $\text{–OH}$ bending peak ascribed to the $\text{NH}_4^+$ asymmetry reveals more tendency of distortion of the $\text{NH}_4^+$ to lose $\text{H}^+$ ions [33]. In addition, the $\text{–CH}$ asymmetrical and $\text{–CH}$ symmetrical stretching are seen through the region (2) 3005 to 2840 cm$^{-1}$ [34, 35]. While the $\text{–CH}$ bands intensity was increased and slightly shifted toward the lower wavenumber as the salt concentration increased, meaning that the interaction and complexation was developed between the C: M polymer blend and the salt [28]. The position of amine and carboxamide bands for the systems are positioned at (region 3) 1710–1517 cm$^{-1}$ where a small shift was observed when the salt concentration increased. This shift indicates the influence of the salt amount to provide extra ions to interact with the nitrogen and oxygen atoms in the polymer blend [36]. Shukur et al [37] documented the same range of amine band and carboxamide band for their PE samples. Finally, the sharp peak positioned at (region 5) 907–1190 cm$^{-1}$ is associated to the C-O stretching which is similar to the results documented by Mejenom et al [38] and Poy et al [39]. As the salt concentration increased into the C: M polymer blend, this peak became sharper and caused a tiny shoulder peak to emerge which also shows the complexation and interaction between the $\text{NH}_4\text{NO}_3$ and C: M blend.

### 3.3. EIS study

Cole–Cole plot consists of a low frequency straight line followed by a high frequency semicircle. The high frequency semicircle shows the bulk conductivity, which is owing to the parallel connection of bulk capacitance and bulk resistance ($R_b$) of the PEs. In this research, the Cole–Cole plot shows a semicircle and a tail for the CMN_10 and CMN_20 systems (figures 3(a), (b)) while the high frequency semicircle portion disappeared for the CMN_30 system (figure 3(c)) which means that the current carriers are due to ions and thus the total conductivity is mostly by ion conduction.

It is observed that with an increase in concentration of salt, the $R_b$ decreased as seen in table 2. As seen from the figure two distinct regions are emerged which are high-frequency semicircle and low-frequency tail due to the electrolyte’s bulk effect and electrode polarization (accumulation of charge) at the blocking electrodes, respectively. The formation of electric double layer capacitor (EDLC) is formed as a result of the accumulation of charge at the electrodes/electrolytes interfacial region [40].

From the impedance analysis, The $R_b$ has been measured by the intercept of the spike line on the $Z_r$ axis for the CMN_30 system and the $R_b$ for the CMN_10 and CMN_20 systems is measured from the intercept of the semicircle with the $Z_r$ axis. For the measurement of DC conductivity of each sample, equation (3) was used based on both sample dimension and $R_b$ value:

$$\sigma_{dc} = \left(\frac{1}{R_b}\right) \times \left(\frac{t}{A}\right)$$

where, $A$ and $t$ stand for the area of the film and thickness, respectively. The measured conductivity for each electrolyte film is shown in table 2. It is vital to describe that one of the requirements for using the electrolyte for EDLC device is a high DC conductivity. Rudhziah et al [41] documented a conductivity of $5.77 \times 10^{-4}$ S cm$^{-1}$ at
Figure 3. EIS plots for (a) CMN_10, (b) CMN_20, and (c) CMN_30 films.
ambient temperature for ammonium acetate/carboxymethyl cellulose. A conductivity of $5.62 \times 10^{-6}$ S cm$^{-1}$ for PVA/CH$_3$COONH$_4$ was documented by Hirankumar et al [42]. The EIS results are in good agreement with the XRD results as the CMN_30 has the highest amorphous phase and DC conductivity value.

3.4. FESEM study

The FESEM images are used to support the XRD and conductivity results as shown in figures 4(a)–(c). Based on literature in order to get a high value of conductivity, the surface morphology of the sample must be smooth which is associated to the amorphous structure of the film [43]. Indeed, the interaction and complex development between the C: M blends and the NH$_4$NO$_3$ can be evidenced by the smoothness of the surface morphology of the film (see figure 4(c)). It is seen that the surface morphology of the film loaded with 30 wt% NH$_4$NO$_3$ is smooth without emerging the protruded salts (see figure 4(c)) in comparison with the CMN_10 and CMN_20 systems in figures 3(a), (b). This result is in good agreement with the XRD, FTIR, and EIS results. According to literature, from the surface morphology, one can get information regarding the interaction and complexation between polymers and salts [44–47]. It has been reported that the smooth surface morphology of the electrolyte film reveals the transfer of ions across the electrolyte membrane is more freely and hence increasing conductivity [48]. The CMN_30 system shows the smoothest surface morphology and is more amorphous and also has the highest value of DC conductivity. Arof et al [49] prepared 36 wt% PVA and 24 wt% C polymer blend loaded with 40 wt% NH$_4$NO$_3$ salt with the conductivity value of $2.07 \times 10^{-5}$ S cm$^{-1}$. The authors added 70 wt% ethylene carbonate (EC) plasticizer to the 60 wt% PVA:40 wt% C:40 wt% NH$_4$NO$_3$ to improve the conductivity. They obtained the conductivity value of $1.60 \times 10^{-5}$ S cm$^{-1}$ for the plasticized system. The authors also showed the relation between conductivity and surface morphology of the electrolyte membrane. However they have seen a decrease in the conductivity value in their research at the 50 wt% and 60 wt% NH$_4$NO$_3$ for the non-plasticized systems and also at the 80 wt% EC for the plasticized system.

3.5. Dielectric analysis

Using the dielectric spectroscopy, one can show information on the phenomenon of ion transport, charge distribution, types and nature of molecular movement (as they robustly depends on the molecular structure), structural morphology, and chemical compositions of the polymers. The investigation of dielectric permittivity is divided into two parts, one of them is real part ($\varepsilon_r$) which represents the stored energy and another part is imaginary ($\varepsilon_i$) which corresponds to the loss of energy. Hence, the dielectric permittivity can be represented as a complex function using the following relations:

$$\varepsilon^* = \varepsilon_r - j\varepsilon_i$$

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

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

The frequency dependence dielectric constant and loss of PE systems is revealed in figures 5 and 6 at room temperature. Upon external field application, the dipole oscillation lags behind the applied field frequency owing to the incapability of the dipole to rotate along with the applied field frequency. Consequently, the values of dielectric loss ($\varepsilon_i$) and dielectric constant ($\varepsilon_r$) parameters decrease with increasing frequency. The high values of the both parameters at low frequency are due to the accumulation of charge occurrence at the interface of electrolyte and electrode which results in polarization. Additional, such polarization reduces with increasing frequency, and then a constant value of dielectric is obtained [50–52]. At low-frequency, dielectric constant has maximum value or is very high; this is due to the total polarization is influencing the dielectric constant for example space charge, orientation, atomic, electric, and dipole polarization. At high-frequency, only electric and atomic polarizations are responsible for dielectric constant with the low value.
The conductivity and dielectric constant relation is shown using equation (7).

\[
\sigma = n \times q \times \mu
\]  

(7)

Where \( q, \mu, \) and \( n \) are the electron charge, mobility, and number density of ions. When the concentration of salt increased, number density and mobility increase. The number density is related to the dissociation energy \( (\mathcal{U}) \) and dielectric constant due to the relation \( (\mu = n \exp(-\mathcal{U}/\mathcal{e}, k_B T)) \), where \( k_B \) and \( T \) stand for the Boltzmann constant and temperature, respectively. For instance, the loading of salts into polymer materials causes a dielectric constant to increase due to increasing the number density of ions [53].
3.6. Modulus analysis

Modulus investigation is one of the imperative methods which is helpful to get phenomena such as conductivity relaxation time and effect of electrode polarization (EP). The most benefit of this method is that this technique can distinguish the effects of interfacial with that of other effects of EP in the PE system. The complex electric modulus is measure using equations (8)–(10):

\[ M^* = M_r - jM_i \]  

(8)

\[ M_r = \frac{\varepsilon_r}{(\varepsilon_r^2 + \varepsilon_i^2)} = \omega C_o Z_i \]  

(9)
where $M_i$ and $M_r$ are imaginary part and real part of electric modulus, respectively. Figures 7 and 8 show the real part and imaginary part of modulus versus frequency curve for (C:M:NH$_4$NO$_3$) PE at room temperatures. From figures 7 and 8, it is seen that the negligible contribution of the effect of EP results in the lower values of modulus at the low frequency. The existence of the long tail at the low frequency shows towards the higher value of capacitance related with the both electrodes.

3.7. TNM study
Transference number measurement (TNM) test is useful to decide on the suitability of a PE for application in EDLC [28]. In this research, it was shown that the ions are the dominant charge carries while the electrons are minority carriers in the highest conducting electrolyte membrane system, meaning that the ions have the highest contribution in conductivity. The transference number of electrons and ions $t_{\text{electron}}$ and $t_{\text{ion}}$ were measured using equations (1) and (2). In this method, a DC potential is applied and provides the relation between current and time (see figure 9) [54]. An operating voltage of 0.2 V is applied to the fabricated cell, and thus the initial high value of current ($I_0$) of 12.5 $\mu$A at the beginning was measured which is by the contribution of both electrons and ions. This current value gets decrease as time passed and then it becomes constant at 0.5 $\mu$A. The stain less steel electrodes are used for this test as the stainless steel electrodes can block of ions while it allows the electrons to pass through it. Thus, the current gradually decreases till becomes constant at 0.5 $\mu$A and the electrolyte is polarized at the steady state current [55]. Kufian et al [56] documented that when the cell is polarized, the transfer of current is only by electrons. The values of $t_{\text{electron}}$ and $t_{\text{ion}}$ in this research were measured as 0.04 and 0.96, respectively and the high value of $t_{\text{ion}}$ which is close to the ideal value of one, shows the ionic nature of the mechanism of charge transport within the electrolyte membranes [54, 57, 58].

4. Conclusion
In conclusion, in this research polymer blend electrolytes based on C: M were fabricated and characterized. The electrochemical test of TNM was shown the appropriateness of the highest conducting membrane for application in electrochemical energy storage device. The XRD test showed the structural change by loading NH$_4$NO$_3$ salt. As the concentration of the NH$_4$NO$_3$ increased to 30 wt%, the amorphous structure of the electrolyte membrane was more increased. FTIR method confirmed the occurrence of interaction and complexation between the electrolyte elements. The optimal salt content is 30 wt% of NH$_4$NO$_3$ to get the highest DC conductivity ($3.54 \times 10^{-4}$ S cm$^{-1}$). The most amorphous electrolyte membrane showed the highest conductivity. The CMN_30 has the smoothest surface morphology and it is more amorphous. The XRD, FTIR, EIS, and FESEM results supported each other. The conductivity measurements of the electrolyte membranes and their dielectric properties were correlated. At the low frequency, the high values of dielectric constant and dielectric loss were observed due to the electrode polarization. From the TNM test, both $t_{\text{ion}}$ and $t_{\text{electron}}$ were measure. It was shown in this research that the $t_{\text{ion}}$ value for CMN_30 sample was 0.96 which is close to its ideal value. This allowed us to conclude that the C: M blend membrane in this research is suitable for application in electrical double-layer capacitor (EDLC) device.

Data availability statement
The data that support the findings of this study are available upon reasonable request from the authors.
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