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Conductivity, Dielectric And Modulus Studies of Methylcellulose-NH_4TF Polymer Electrolyte

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Abstract: Solid biopolymer electrolyte based on methylcellulose (MC) were prepared with different weight percentage of ammonium triflate (NH4TF) salt via solution casting technique. The film was characterized by impedance spectroscopy to measure its ionic conductivity. Samples with 45% of NH_4TF exhibit the highest conductivity of 1.14 x 10^{-4} S cm^{-1}at ambient. Dielectric data were analysed using complex permittivity and complex electrical modulus for the sample with highest conductivity. Dielectric data proved that the increase in conductivity is mainly due to the increase in number of charge carriers.

Keywords: Solid biopolymer electrolyte; Methyl Cellulose; salt; conductivity.

1. Introduction

Electrolyte is a substance concentrated with free ionic species, which behaves as an electrically conductive medium. It can be divided into a few categories based on its physical condition. However, there are a few obstacles that had been faced by liquid electrolytes which limit its performance. Such limitations are corrosion reactions between separator and electrodes, high tension during battery assembly operation, leakage of the harmful aqueous electrolytes that requires special sealing and packaging (Shanti, 2011). To overcome the problem associated with liquid electrolytes, scientist proposed a new electrolyte which is polymer electrolyte.

Polymer electrolyte basically is defined as solid ionic conductors formed by the dissolution of salts in suitable high molecular weight polymers (Vincent, 1987). It can be divided into few types which are gel, composites and solid. According to Buraidah and Arof (2011) polymer electrolytes have attracted much attention due to their potential applications in electrochemical devices such as rechargeable batteries, fuel cells, super capacitors and solar cells.

Since conductivity is the main focus for polymer electrolytes, many research have been conducted to study its conductivity. There are many ways to improve conductivity of polymer electrolytes such as polymer blending, plasticization, and mixed salts systems (Misenan et al., 2018; Buraidah & Arof, 2011; Kadir et al., 2009).

In the present work, methyl cellulose has been chosen as the host polymer. Methylcellulose is a chemical compound from cellulose. Generally, cellulose derivatives are polysaccharides composed of linear chains of (1-4) glucosidic units of methyl, hydroxypropyl or carboxyl substituents. Pinotti et al. (2007) stated that the advantages of using methylcellulose in producing polymer electrolyte is that it have efficient oxygen and lipid barrier properties. From literature, it is reported that, MC – ammonium fluoride (NH_4F) obtained the highest conductivity of 6.40×10^{-7} Scm^{-1} (Nik Aziz et al., 2010) and MC-ammonium nitrate (NH_4NO_3) obtained a room temperature conductivity of 2.10×10^{-6} S cm^{-1} (Suhaimi et al., 2010). Consequently, by doping ammonium iodide (NH_4I) with MC electrolyte give the highest conductivity at 5.08 x 10^{-4} Scm^{-1} (Salleh et al., 2016).

Additionally, earlier study was reported that, methyl cellulose/chitosan blend polymer doped with ammonium triflate (NH_4TF) has obtained optimum conductivity of 4.99 x 10^{-6} Scm^{-1} (Hamdan & Khiar, 2013). In this report methyl cellulose as single polymer host is dope with the NH_4TF salt to study the correlation between the concentration of salt doped in polymer electrolyte and its conductivity value.

2. Materials and Method

2.1. Sample Preparation

Methyl cellulose solution doped with various amount of ammonium triflate, NH4TF salt were prepared by solution casting technique. 0.5 g of methyl cellulose was dissolved in 50 mL distilled water. An amount of 10 w.t%, 15w.t%, 20w.t%, 25w.t%, 30w.t%, 35w.t%, 40w.t%, 45w.t% and 50w.t% of NH4TF was added into the solution. The solution was further stirred homogenously and then casted onto plastic petri dish and left to dry at room temperature before further analysis. The composition and their label is tabulated in table 1.

Table 1: Composition of biopolymer electrolyte with their tagging.

Ammonium triflate (NH_4TF), weightage	Label
10	10 SALT
15	15 SALT
20	20 SALT
25	25 SALT
30	30 SALT
35	35 SALT
40	40 SALT
45	45 SALT
50	50 SALT

2.2 Conductivity Measurement.

The conductivity of the sample was measured by using Impedance Spectroscopy via HIOKI 3532 LCR Hi Tester Bridge interfaced to a computer. The impedance values were measured within the frequency of 50Hz to 1MHz at ambient temperature. A negative imaginary impedance, *Zi* versus real impedance, *Zr* with same scale of horizontal and vertical axes were then plotted where the bulk resistance, *Rb* could be obtained. Hence, the conductivity of the sample in room temperature can be calculated by using equation (1):

$$\sigma = t / Rb\, A \quad (1)$$

Where *Rb* is bulk resistance, *t* is the thickness of the thin film and *A* is the surface area of contact. In order to measure the thickness of the thin film, a digital micro meter screw gauge was used. **3. Results and Discussion**

Figure 1 shows a typical cole-cole plot for methyl cellulose polymer doped with various concentration of NH_4TF. The complex impedance plot generated by impedance measurement basically consist of (i) a title spiked, (ii) a depressed semicircle or (iii) a combination of depressed semicircle and title spike (Kaith et al., 2014). From the plot, it can observed that for polymer electrolyte with lower concentration of salt mostly shows a combination of depressed semicircle and a spike. While for higher concentration of salt, the polymer electrolyte exhibits inclination of spike line with real impedance axis, Zr.

Additionally, the bulk electrical resistance (Rb) is interpreted from the intercept of semicircle curves and spike lines with the real impedance (Zr) axis. Ariffin and Khiar (2015) stated that the conduction of ions in the bulk of polymer electrolyte exhibits semicircles while the spike line is caused by the effect of electrode polarization which is a characteristic of diffusion process.

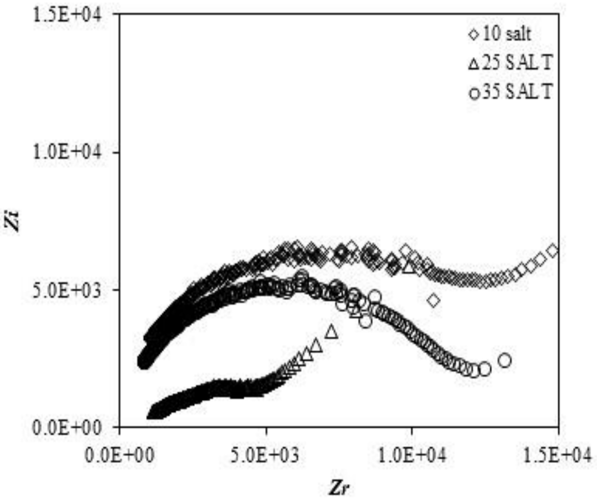


Figure 1. Impedance plot at ambient temperature. Onset Fig shows the impedance plot for the highest conducting sample.

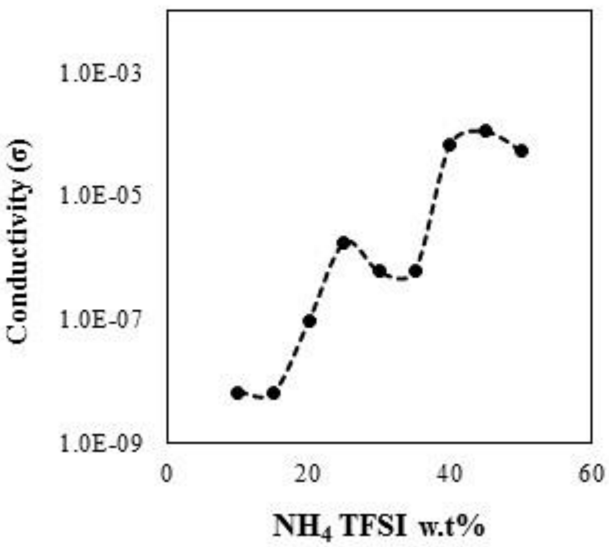


Figure 2. Variation of ionic conductivity as a function of NH4TF concentration

Figure 2. shows that the conductivity plot for methyl cellulose electrolyte with different amount of ammonium triflate.

The addition of NH_4TF doping introduces free ammonium cation (NH_4^+) and free triflate anion ($CF_3SO_3^-$) to be dissociated. The dissociated cation occurs when incorporation salt interact with functional group of polymer host. From the plot, it can be observed that the conductivity increases up to 1.14×10^{-4} Scm^{-1} with addition of 45 w.t% NH_4TF salt. This is due to the increase in the number of mobile ion in the polymer electrolyte system and also the amorphousness of the polymer is increase, hence reduces the energy barriers which enhance the mobility of the ion (Sahli & Ali, 2012). Nevertheless, the conductivity decreased beyond the 45 w.t% of NH_4TF doped polymer electrolyte due to the accumulation of ion cluster, which provide an overcrowded ions environment in the polymer salt system (Hafiza et al., 2017).

The dielectric studies can be the best way to describe the conductivity behaviour of polymer electrolytes. Dielectric constant εr charge carrier, n and the dissociation energy, *U* are related to the equation:

$$\eta = \eta_0 \exp(-U/(\varepsilon r\, kT)) \quad (2)$$

From this equation, it can be described that, when the dielectric constant, εr increases, the number of charge carriers increases. In polymer electrolytes, ions are the charge carriers where the dielectric constant represent the stored charge in material (Buraidah et al., 2009). The dielectric constant εr and its imaginary part of complex permitivity is given by:

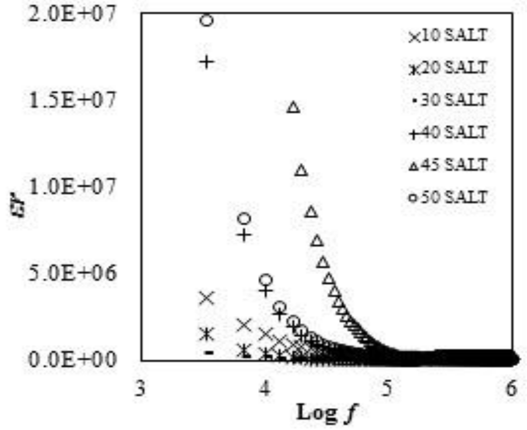
$$\varepsilon r = Zi / \omega C_0 (Zr^2 + Zi^2) \quad (3)$$

$$\varepsilon i = Zr / \omega C_0 (Zr^2 + Zi^2) \quad (4)$$

Where $Co = \varepsilon o A/t$ where εo is the permittivity of the free space, *A* is the area of the sample and t is the thickness of the sample and ω is equal to $2\pi f$, which *f* in frequency taken from the data in Hz.

Figure 3 (a) and (b) shows the real part, εr and imaginary part, εi of dielectric constant at selected w.t% of salt content. The observation from the graph shows that the real part of dielectric constant, εr increases with increasing salt content for respective frequencies until 45 w.t% where beyond that the εr value decreases. This is because of the increase in number density of mobile ions as when the composition of salt increases the stored charge of the sample increases (Buraidah and Arof, 2009). The dielectric constant decreases beyond 45 w.t% due to the re-association of ions. This also might be caused by the tendency of dipoles in the macromolecules to orient themselves in the direction of the applied field within low frequency range (Ibrahim et al., 2011).

(a)



(b)

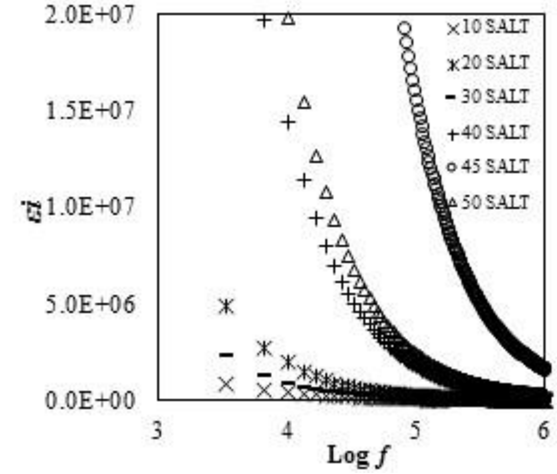


Figure 3: a) Real part of dielectric constant b) Imaginary part of dielectric constant, as a function of frequency for selected samples.

To further understand the dielectric behaviour dielectric moduli is needed which suppress the effects of electrode polarization. The equations for real electrical modulus *Mr* and imaginary modulus *Mi* can be expressed as follows:

$$Mr = \varepsilon r / (\varepsilon r^2 + \varepsilon i^2) \quad (5)$$

$$Mi = \varepsilon i / (\varepsilon r^2 + \varepsilon i^2) \quad (6)$$

Figure 4 (a) and (b) depicts the variation of real part, *Mr* and imaginary part, *Mi* of electric modulus respectively. As the frequencies increases, both of *Mr* and *Mi* also increases. At the low frequencies regions, both *Mr* and *Mi* tend towards zero values. The appearance of this long tail at low frequencies is highly attributed to the large capacitance associated with the electrodes which confirms a non-Debye behavior (Khiar at al., 2006).

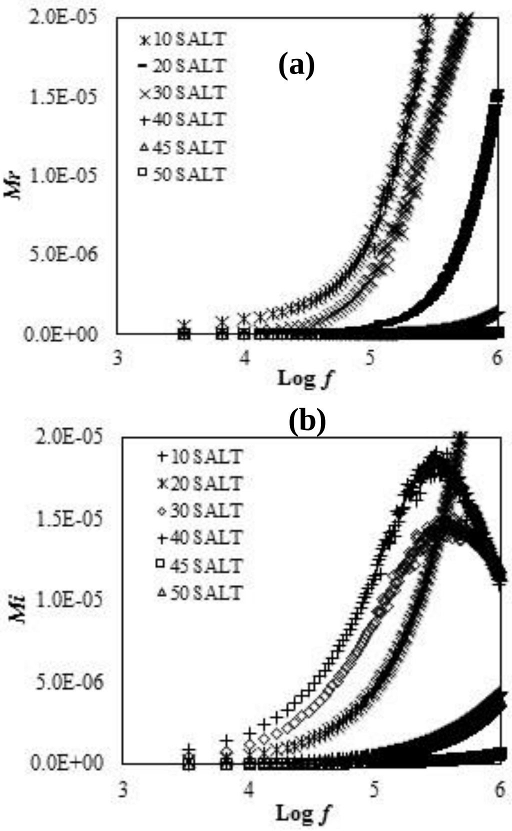


Figure 4: a) variation of real part, Mr and b) imaginary part, Mi of electric modulus as a function of frequency for 10 wt% to 50 wt% of salt content.

5. Conclusions

Solid polymer electrolyte from methyl cellulose with different weight percentage of NH_4TF (10 to 50 wt%) has been prepared via solution casting technique. The addition of NH_4TF gradually increases the ionic conductivity of polymer electrolyte with a maximum conductivity of 1.14 x 10^{-4} S cm^{-1} was achieved at 45 wt% of NH_4TF. The tendencies of dielectric constant, over the concentration of NH_4TF propose that the number of charge carriers strongly influences the increase in conductivity.

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