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Proton conducting polymer electrolytes of methylcellulose doped ammonium fluoride: Conductivity and ionic transport studies

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Methylcellulose (MC) was used as polymer host and Ammonium Fluoride (AF) salt was used as the proton donor. A proton-conducting solid polymer electrolytes (SPE) was prepared by the solution casting method. The highest ionic conductivity at room temperature is 6.4×10^{-7} Scm^{-1}. The ionic mobility and diffusion coefficient that was calculated in this work is in good agreement with the increment of weight percent (wt %) of acid concentration. The value of cation of diffusion coefficient and ionic mobility was higher than value of anion. Thus, the results proven that the present samples were proton conductor.

Key words: Methylcellulose, ammonium fluoride, polymer electrolyte, proton conductor, ionic transport.

INTRODUCTION

Batteries consists of three main components; anode, cathodes and electrolyte. Electrolyte is the key component to the battery and it is a substance that contains free ions which behaves as an electrically conductive medium. They generally consist of ions in solution. Electrolytes are also known as ionic solution but molten and solid electrolytes are also possible. To form an electrolyte, salt need to be added into solvent such as water and individual atomic component are separated by the force applied upon the solute molecule, in a process called chemical dissociation in which the solution applies force to hold the ions apart (Majid and Arof, 2005).

Studies on solid polymer electrolytes (SPE) have been progressing actively due to their potential application in solid state electrochemical cells, high energy density batteries, fuel cells, sensors and electrochromic devices (Bhargav et al., 2009; Baskaran et al., 2004). Polymer electrolytes have good mechanical properties, can be easily fabricated as thin film, can have a wide range of composition allowing control of properties and are able to

form effective electrode-electrolyte contacts. Compare to other types of polymer electrolyte, solid polymer electrolytes (SPEs) have a very limited or problem in leakage or pressure distortion, Avellaneda et al. (2007). Many types of polymer electrolytes have been studied in the pursuit to develop solid electrolyte system (Anantha and Hariharan 2005). These include PVA (Selvasekarapandian et al., 2005), PVC (Ramesh and Arof 2001; Subban and Arof, 2004; Ramesh and Ng, 2009) and PEO (Karan et al., 2008; Marzantowicz et al., 2008).

In this work, MC was chosen as a polymer host because it has good properties such as thermal, chemical, mechanical stability, as well as water absorption characteristics are of great importance to get the good conductivity. AF was used as a dopant salt because of it crystallizes as small prisms, having a sharp saline taste and is exceedingly soluble in water (Wells, 1984).

EXPERIMENTAL

Sample preparation

MC was obtained from Sigma Aldrich. 2 g of MC powder was then dissolved in 100 ml distilled water. This solution was stirred for a

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Table 1. Composition of the electrolytes.

Sample	Methylcellulose (g)	Salt (wt %)	Salt (g) x10^{-1}
AF-8	2	8	1.77
AF-11	2	11	2.50
AF-14	2	14	3.33
AF-18	2	18	4.29
AF-21	2	21	5.39
AF-25	2	25	6.67

few hours until the methylcellulose powder was completely dissolved. Then difference weight percent (wt %) of NH_4F, 99% (Sigma Aldrich) was added to the MC solution and stirred until it dissolved. The mixture was then cast into plastic Petri dishes and left to dry at room temperature. The film was then kept in desiccator (with silica gel desiccant) for further drying. The composition of the MC and NH_4F used is shown in Table 1.

Characterization of samples

Electrochemical impedance spectroscopy (EIS)

Conductivities of (MC-AF) were measured using the HIOKI 3532-50 LCR Hi-Tester that was interfaced to a computer in frequency range 50 to 1 MHz. When the films were formed they were cut into a suitable size and placed between the blocking stainless steel electrodes of a sample holder which are connected by leads to a computer. Negative imaginary impendence ($-Z_i$) versus real impedance (Z_r) were obtained from the plot and in order to get the bulk resistance, R_b, the horizontal and vertically axis must in the same scale. According to (Majid and Arof, 2007), the conductivity can be calculated as follow:

$$\sigma_{DC} = \frac{t}{R_b A} \tag{1}$$

where, t is the thickness of the sample and A is the electrode-electrolytes contact area.

Transference number measurements (TNM)

Transference number measurements (TNM) were performed to correlate the diffusion phenomena to the conductivity behavior of MC-AF polymer electrolytes. The cation transference numbers, t_+ in the electrolytes were determined by monitoring the current as a function of time on application of a fixed dc voltage (1.5 V) across the sample sandwiched between two stainless steel electrodes. According to Linford (1988), to obtain the cationic transference number of the material, TNM will carried out using the d.c polarization technique. The circuitry is as shown in Figure 1.

RESULTS AND DISCUSSION

Conductivity study

The electrical conductivity values obtained from the complex impedance plots showed that, samples have

electrical conductivities in the range of 10^{-10} to 10^{-7} Scm^{-1} at room temperature (298 K) and it is presented in Table 2.

The conductivity varies with a wide range of factors, such as cation and anion types, salt concentration, temperature, etc (Hirankumar et al., 2004). Table 2 shows that, the ionic conductivity at room temperature increases with the increment of AF concentration (AF-8 to AF-18). The increase in the ionic conductivity with increasing AF concentration can be related to the increase in the number of mobile charge carriers. This is because the interaction between AF and MC bring to high dispersion of H$^+$, so that, the conductivity will be increase.

The possible decrease in the ionic conductivity after sample AF-18 can be attributed to the formation of ion multiples. In addition of higher AF concentration (after AF-18) the conductivity found to decrease. According to Selvasekarapandian et al. (2005), the decrement of conductivity in addition of high concentration can be explained by association of ions at higher salt concentration, which leads to the formation of ion cluster and thus the number of charge carriers and their mobility are decreased. In addition, at higher salt concentrations the dipole interaction between the protons in the medium increases, which reduces the ion mobility and thus the conductivity.

The temperature dependence of conductivity for MC-AF polymer electrolytes is shown in Figure 2. Within the temperature range investigated, the conductivity–temperature relationship of the polymer electrolytes is characteristically Arrhenius behavior, suggesting that the conductivity is thermally assisted (Idris et al., 2009). The regression value, R^2 for temperature dependence is in the range of 0.95 – 0.99 and this show it obey the Arrhenius law ($R^2 \sim 1$).

From the Arrhenius plot of Log σ versus 1000/T, the activation energy, E_a can be obtained from the slope and the pre-exponential factor can be obtained from the intercept at the vertical axis. Thus, the number of mobile ions, n, can be calculated from the Rice and Roth equation as follow:

$$n = \frac{3\sigma k T m}{2Z e^2 E_a \tau \exp(-E_a / kT)} \tag{2}$$

Where, m is the mass of ionic charge carrier, E_a is the activation energy, k is the Boltzmann constant, T is temperature and τ is the transit time.

In using the Rice and Roth equation, the value of a transit time, τ must be known. According to (Rice and Roth, 1972), the transit time, τ is given by, $\tau = \dfrac{l}{v}$ and the velocity, v is $v = \left(\dfrac{2E_a}{l} \right)^{1/2}$. The value of mean free path,
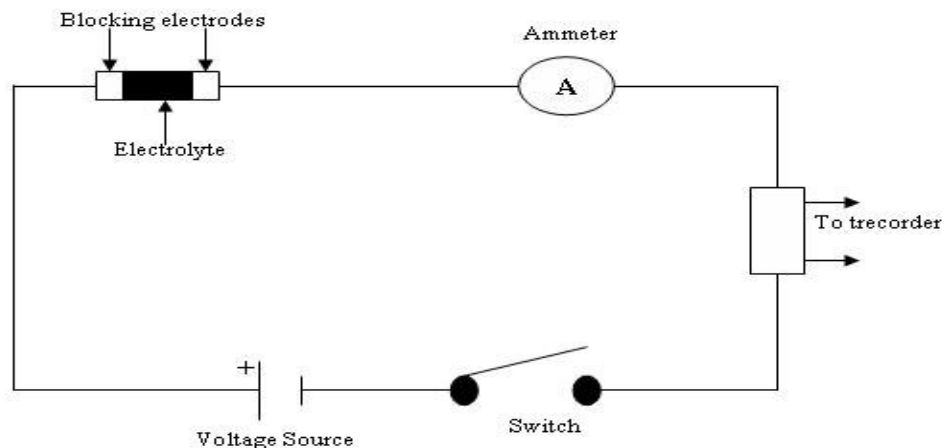
Figure 1. Experimental arrangement for measuring ionic transference number by d.c polarization technique.

Table 2. Room temperature ionic conductivity of MC doped with NH_4F salt

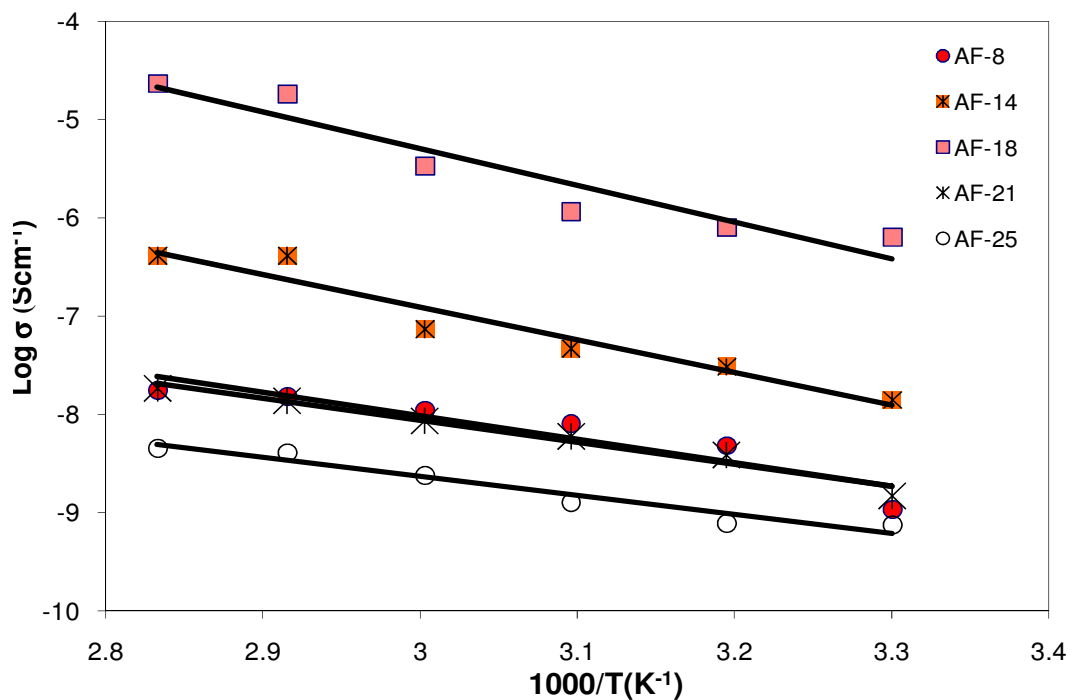| Sample	Bulk Resistance, R_b (Ohm)	Conductivity, σ (Scm^{-1})	Standard deviation, σ (Scm^{-1})
AF-8	1.33×10^6	1.09×10^{-9}	$\pm 7.42 \times 10^{-11}$
AF-11	3.00×10^5	6.55×10^{-9}	$\pm 7.45 \times 10^{-10}$
AF-14	9.15×10^4	1.40×10^{-8}	$\pm 1.53 \times 10^{-9}$
AF-18	2.82×10^6	6.40×10^{-7}	$\pm 1.64 \times 10^{-8}$
AF-21	1.30×10^6	1.48×10^{-9}	$\pm 1.34 \times 10^{-10}$
AF-25	2.72×10^6	7.52×10^{-10}	$\pm 1.94 \times 10^{-11}$

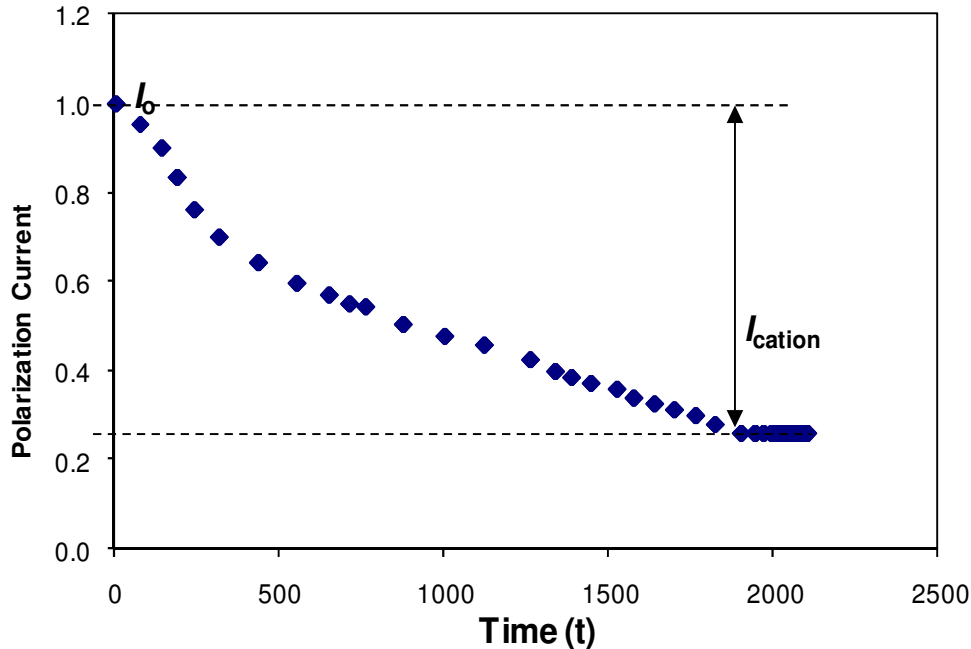**Figure 2.** The temperature dependence for conductivity of MC-AF electrolyte.

Figure 3. Normalized polarization current, I (A) versus Time, t (s) for sample AF-21.

is obtained from (Yokota et al., 2007). Generally the ionic conductivity in a polymer electrolyte is linked to the number of mobile ions and the mobility of conducting species, in the polymer complexes (Majid and Arof, 2005). Further proved of the effect by ionic mobility and diffusion coefficient will be done by performing TNM.

Ionic transport study

When a voltage V, which is below the decomposition potential of the electrolyte is applied to the cell, ionic migration will occur until steady state is achieved. At the steady state, the cell is polarized and any residual current flows because of electron migration across the electrolyte and interfaces. This is because the ionic currents through an ion-blocking electrode fall rapidly with time if the electrolyte is primarily ionic. The plot of polarized current versus time is shown in Figure. 3. The initial total current decreases with time due to the depletion of the ionic species in the electrolyte and becomes constant in the fully depleted situation.

The diffusion coefficients of cations and anions in each of the samples were calculated from the measured values of conductivity and cation transference number, t_+ according to the following equations (Winnie and Arof, 2006):

$$t_+ = \frac{I_{cation}}{I_0} \tag{3}$$

$$D = D_+ + D_- = \left(\frac{kT\sigma}{ne^2} \right) \tag{4}$$

$$t_+ = \frac{D_+}{D_+ + D_-} \tag{5}$$

Besides, the ionic mobility can be defined according to the following equation:

$$\mu = \mu_+ + \mu_- = \frac{\sigma}{nq} \tag{6}$$

$$t_+ = \frac{\mu_+}{\mu_+ + \mu_-} \tag{7}$$

Where, q is the charge of electron and μ_+ and μ_- is the ionic mobility of cation and anion. The calculated value of D_+, D_-, μ_+ and μ_- are listed in Table 3.

From the Table 2, the conductivity shows that the sample AF-18 has the highest conductivity followed by sample AF-14 > AF-11 > AF-21 > AF-8 > AF-25 and this trend also followed by the cations and anions of diffusion coefficient and the ionic mobility in Table 3. The value is increases with the increasing of the conductivity. From the calculation, μ_+ has the greater value than the μ_- and when the μ_+ decreases the conductivity also decreases, the same behavior also can be detected for D_+, so from the study of TNM it can be concluded that the conductivity was influenced by the μ_+ and the D_+. These

Table 3. Ionic mobility and diffusion coefficient of cations and anions

Sample	t_+	D_+ (cm^2s^{-1})	D_- (cm^2s^{-1})	μ_+ $(cm^2V^{-1}s^{-1})$	μ_- $(cm^2V^{-1}s^{-1})$
AF-8	8.46×10^{-01}	1.14×10^{-13}	2.07×10^{-14}	4.44×10^{-12}	8.07×10^{-13}
AF-11	6.40×10^{-01}	1.43×10^{-13}	8.05×10^{-14}	5.57×10^{-12}	3.13×10^{-12}
AF-14	6.67×10^{-01}	9.38×10^{-13}	4.69×10^{-13}	3.65×10^{-11}	1.82×10^{-11}
AF-18	6.88×10^{-01}	1.19×10^{-11}	5.42×10^{-12}	4.64×10^{-10}	2.11×10^{-10}
AF-21	7.42×10^{-01}	1.79×10^{-13}	6.25×10^{-14}	6.98×10^{-12}	2.43×10^{-12}
AF-25	8.66×10^{-01}	1.40×10^{-13}	2.17×10^{-14}	5.45×10^{-12}	8.43×10^{-13}

properties of mobility concrete that MC–AF electrolyte is a proton conductor

Conclusions

Proton conducting polymer electrolytes based on methylcellulose and Ammonium fluoride were prepared and found to be transparent thin film. Sample AF-18 was found to have the highest ionic conductivity at room temperature of 6.4×10^{-7} Scm^{-1}. The conductivity is still poor compare to the current conductivity based on polymer but the study is just to identify the potential of the methylcellulose to be used as solid polymer electrolytes. From the open sources literature it can be enhanced with addition of plasticizer or filler. The temperature dependence of MC-AF system obeys the Arrhenius behavior from the plot log σ versus 1,000/T. Conductivity enhancement in the MC–AF polymer electrolyte is caused not only by the increase in the concentration of free ions but also by the increase in mobility and diffusion coefficient of ions. From the TNM, it is proven that the sample is a proton conductor where the value of μ_+ and D_+ is found to be higher than the value of μ_- and D_-.

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