Cornstarch-based biopolymer electrolyte doped with Na$_3$PO$_4$

Syakirah Shahrudin and *Azizah Hanom Ahmad

Abstract—**In this work, polymer electrolytes have been prepared by doping starch with Sodium Phosphate (Na$_3$PO$_4$). The incorporation of 25% Na$_3$PO$_4$ optimizes the room temperature conductivity of the electrolyte at 7.27 x 10^{-6} Scm^{-1}. The temperature dependence of conductivity for the electrolyte is Arrhenius and the activation energy, E$_a$, of 75% corn starch-25% Na$_3$PO$_4$ electrolyte is 0.26eV. The dielectric studies reveal the non-Debye nature of the electrolyte. The complexation of Na$_3$PO$_4$ with the polymer host was studied using Fourier transform infrared (FTIR) spectroscopy.**

Index Terms—**Starch, conductivity, polymer electrolyte.**

I. Introduction

Advancement of technology for electronic gadget such as smart phones, laptops, computer and many more have driven research in energy storage and devices like batteries and solar cells. Research on solid polymer electrolytes (SPEs) has been attracting wide interest due to their potential as ionic conductors in energy devices [1]. Solid polymer electrolytes are one of the realistic alternatives way to replace the conventional liquid electrolytes. In contrast with liquid electrolyte, SPEs promising candidates for application in compact and light weight electrochemical devices of the modern age. SPEs offer a lot of advantages such as eliminate corrosive solvent and harmful gas formation, wider electrochemical and thermal stability range as well as low volatility with easy to fabricate [2].

Selecting the suitable polymer host is important in composite electrolytes. The polymer should have great characteristics such a high elasticity and good thermal and mechanical stability [3]. A lot of biopolymers-based polymer-salt composites have been studied but, starch-based materials are gaining much attention and many leading groups are working in the field [4,5]. Currently, researchers looking for alternative polymer host with improved conductivity and mechanical properties as well as cost effective and environmentally friendly. Corn starch is one of the natural polymers which are non-toxic, biodegradable, available in abundance and soluble in water. However, most of biodegradable materials such as corn starch formed very low thin film conductivity.

It has been suggested to enhance the conductivity was by adding salts in the electrolytes. There are lots of research reported the study of electrolytes using Lithium salts as the doping salts for application in lithium ion batteries [6,7].

However, there are concerns about the increase usage of lithium in electrochemical device applications. Therefore, to overcome this problem, sodium-based electrolytes have been selected for the present study. The selection of the salt because sodium salts are lower cost, ready availability, lower toxicity and low atomic mass, most abundant element on the earth, and exhibit similar chemical properties to lithium which is indicate that Na chemistry possible to be applied to same battery system [8,9].

Sodium Iodide (NaI) -Sodium Phosphate (Na$_3$PO$_4$) achieved maximum conductivity in the range of 10^{-3} Scm^{-1} [10]. The conductivity of ethyl methacrylate (90MMA-co-10EMA) and NaI electrolyte reported to be 5.19×10^{-6} Scm^{-1} [11]. Besides that, starch- Sodium thiocyanate (NaSCN) electrolyte achived 1.12×10^{-4} Scm^{-1} by Tiwari et.al [5]. Hence, this study focuses on the preparation and characterization of cornstarch and sodium salts which is sodium phosphate (Na$_3$PO$_4$). The samples will be characterized to understand their vibrational and conductivity behaviors.

II. Experiment

For sample preparation, Cornstarch (Sigma-Aldrich) was dissolved in distilled water and heated at 80°C for 20 minutes. After the solutions cooled to room temperature, different concentrations of Na$_3$PO$_4$ were added to the solutions to prepare the starch-Na$_3$PO$_4$ (salted) system. All solutions were stirred until they become homogenous. Then, the homogenous solutions were cast into different petri dish and left to dry at vacuum oven to form electrolyte films. The samples were kept in a desiccator filled with silica gel for further drying.

In order to study the complexation between the electrolyte components, FTIR spectroscopy was recorded in the wavenumber range of 500-4000Scm^{-1}.

Impedance measurements were conducted using HIOKI3531-01 LCR Hi-tester between the frequency ranges of 50 Hz to 1 MHz at room temperature and at various temperatures (287K–373K) were performed. The electrolytes were sandwiched between two stainless steel electrodes of a conductivity holder. The values of bulk resistance Rb of the electrolytes were determined from Nyquist plots obtained. Conductivity σ was calculated using:

$$\sigma = \left(\frac{t}{R_b} \right)\left(\frac{1}{A} \right). \tag{1}$$

where t is the thickness of the electrolyte and A is the electrode-electrolyte contact area. The impedance measurements on each electrolyte sample were done at least three times and the average value was considered for the calculation of the conductivity value.

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III. RESULTS AND DISCUSSION

Figure 1 shows the hydroxyl band in the spectrum of pure corn starch in the form of powder and film. The band for pure corn starch powder appears at 3296cm^{-1} while the band in the spectrum for film has shifted to 3276cm^{-1}. The results indicate the interactions between polymer and the distilled water solvent. The wide absorption in hydroxyl band region of pure cornstarch film due to several –OH groups in starch.

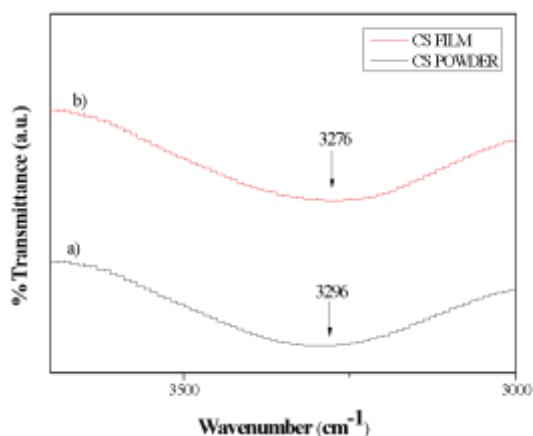Figure 1. FTIR spectra for a) pure cornstarch powder and b) pure starch film in the region of 3000-3600cm^{-1}

FTIR spectra of selected samples for salted system in the hydroxyl band region shown in figure 2. The band in the spectrum of pure starch film in figure 2(a) shifts from 3276 cm^{-1} to 3275 cm-1 when 5wt% of NH$_3$PO$_4$ was added to the system. Addition of 25 wt% NH$_3$PO$_4$, the hydroxyl band has shifted to 3248 cm^{-1} and further shifted to 3235 cm^{-1} when 35 wt% of salt added. It is reported that the increasing salt content in the polymer matrix has shifted the hydroxyl band of pure polymer film to lower wavenumbers [19, 25].

The peak selected in Figure 3 indicate entire anhydrglucose ring stretching in corn starch. The peak of 994 cm^{-1} for pure corn starch is shifted to lower frequencies of 981 cm^{-1} and 979 cm^{-1} for 25 wt% and 35 wt% of NH$_3$PO$_4$ respectively due to influence of the peak in NH$_3$PO$_4$ salt, which is evidence of complexation between corn starch polymer and NH$_3$PO$_4$ salt. [12] has been reported the peak in pure rice starch is shifted to lower frequencies expressing complexation with LiI salt.
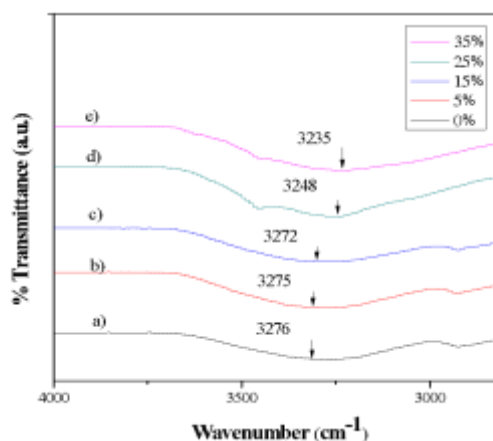

Figure 2. FTIR spectra for a) 0 wt% b) 5 wt% c) 15 wt% d) 25 wt% and e) 35 wt% of Na$_3$PO$_4$ in the region of 2500-4000cm^{-1}

From Figure 3(a), a peak appears at 1,078 cm^{-1} in the spectrum of pure starch film. Zaki et. al [4] reported a peak at 1,078 cm^{-1} in the spectrum of starch film which is attributed to C–O bond stretching of the C –O–C group in starch. Their result is similar with the present work. In Figure 3 (d), in addition of 25 wt% NH$_3$PO$_4$, the peak shifted to 1,049 cm^{-1}. Further shifting can be observed with increasing salt content. On addition of 35 wt% NH$_3$PO$_4$, the peak is located at 1,045 cm^{-1}. According to Ramesh et. al [13], cations interact with oxygen atoms in the C–O–C group. All these results conclude that starch has interacted with NH$_3$PO$_4$ salt in the present work.
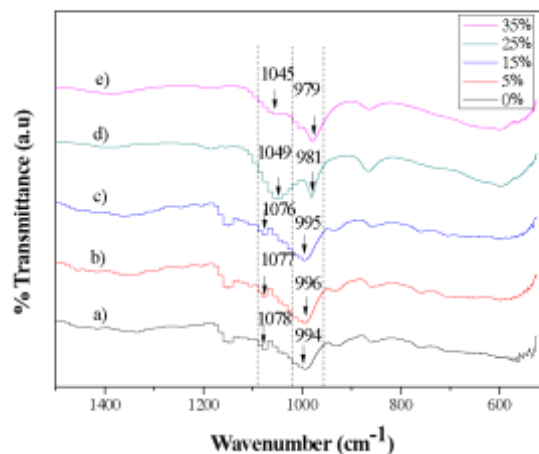

Figure 3. FTIR spectra for a) 0 wt% b) 5 wt% c) 15 wt% d) 25 wt% and e) 35 wt% of Na$_3$PO$_4$ in the region of 550-1500cm^{-1}

Figure 4 depicts the effect of ionic conductivity biopolrum electrolyte as function of NH$_3$PO$_4$ concentration at room temperature. As can be seen, the ionic conductivity increases with the amount of NH$_3$PO$_4$ up to maximum of 7.27E-6 Scm^{-1} for 25 wt. % of NH$_3$PO$_4$ with a subsequent decrease.

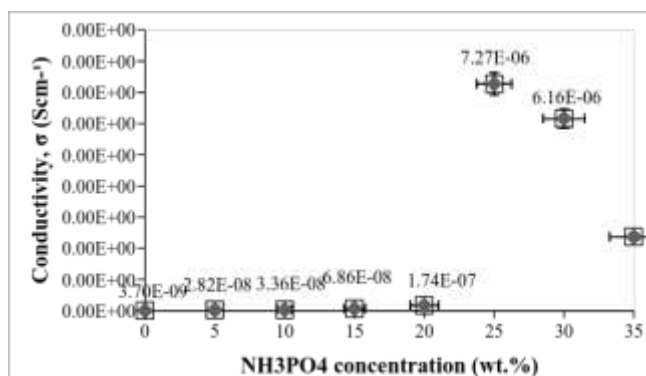Figure 4. Effect of NH$_3$PO$_4$ concentration on conductivity at room temperature

Figure 5. Effect of temperature on conductivity for 75 wt% cornstarch-25 wt% NH$_3$PO$_4$

The variation of conductivity with temperature for 75wt% starch–25wt% NH$_3$PO$_4$ is shown in figure 5. The conductivity of electrolyte is observed to be increased with an increase in temperature. This proves that cornstarch with NH$_3$PO$_4$ salt is thermally stable and can operate at high temperature. From the conductivity–temperature relationship, the electrolyte obeyed the Arrhenius rule [14]. The increase in conductivity with temperature is explained as a hopping mechanism between coordinate site, local structural relaxations, and segmental motion of the polymer. However, the polymer chain acquires faster internal modes in which bond rotations produce segmental motion. This in turn favors hopping interchain and intrachain ion movements, and conductivity of polymer electrolyte thus becomes high [15].

The conductivity-versus-temperature plots were observed in a number of other polymer electrolyte systems. The Arrhenian conductivity–temperature relationship has been reported for systems of starch–LiClO$_4$ [16], starch–NH$_4$I content [1] and starch–LiI-ionic liquid [17]. The activation energies, Ea, of 75 wt% starch–25 wt% NH$_3$PO$_4$ electrolyte are calculated from the relation,

$$\sigma = \sigma_0 \exp\left(\frac{-E_0}{KT}\right). \tag{2}$$

where σ_o is the pre-exponential factor, k is the Boltzmann constant and T is the temperature. Ea is the energy required for an ion to migrate from one site to another. From the Anderson–Stuart model [18], Ea is the sum of the binding energy of the ion to its site and the kinetic energy for migration. If the energy of the ion is only sufficient to overcome the binding energy, the ion will be dislocated from its site but will still remain at the same location. If it has more energy than the binding energy, the ion will be free to move. The 75 wt% starch–25 wt% NH$_3$PO$_4$ electrolyte has an Ea value of 0.26eV. This result indicates that the higher conducting electrolyte requires only a small amount of energy to start a migration process.
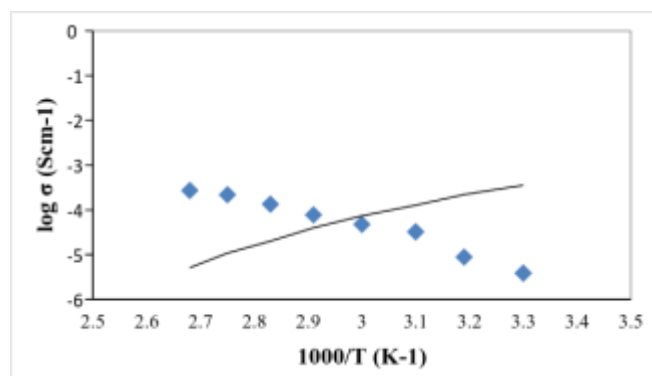
The complex dielectric ε∗ behavior of a polymer electrolyte system of a system is expressed as,

$$\varepsilon^* = \varepsilon_r - i\varepsilon_i \tag{3}$$

where ε_r is the dielectric constant and ε_i is the dielectric loss. From the impedance measurements, ε_r and ε_i were calculated using the following equations,

$$\varepsilon_r = \frac{Z_i}{\omega C_0 \left(Z_r^2 + Z_i^2\right)} \tag{4}$$

$$\varepsilon_i = \frac{Z_r}{\omega C_0 \left(Z_r^2 + Z_i^2\right)} \tag{5}$$

Here,

$$C_0 = \frac{\varepsilon_0 A}{t} \quad \text{and} \tag{6}$$

$$\omega = 2\pi f \tag{7}$$

ε_0 is the permittivity of free space, f is the frequency, Z_i is the imaginary part of impedance and Z_r is the real part of impedance. Study on the dielectric behavior of the polymer electrolyte helps to understand the polarization effect at the electrode–electrolyte interface. The value of ε_r is indicates the material's stored charge, while ε_i represents the amount of energy loss to move ions.
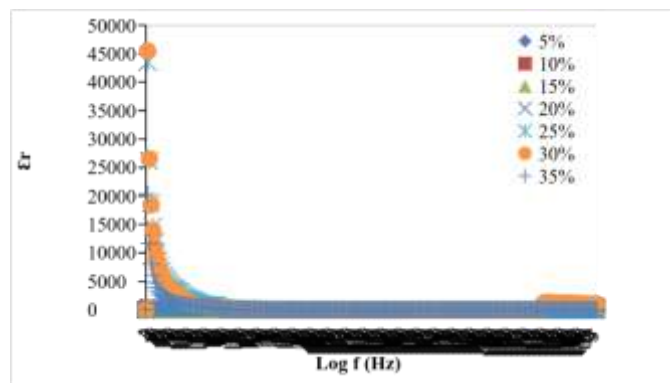
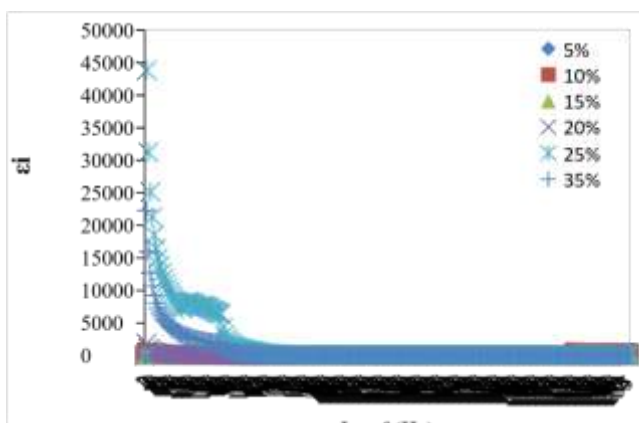Figure 6. Plots of ε_r versus frequency for different wt% of NH$_3$PO$_4$ in cornstarch-based polymer electrolyte

Figure 7. Plots of ε_i versus frequency for different wt% of NH_3PO_4 in cornstarch-based polymer electrolyte

Figure 8. Typical plot of the variation of complex dielectric permitivitty, ε_r with frequency for 25 wt% of NH_3PO_4 in the temperature range of 298K-373K

Figure 6 shows the real dielectric, ε_r results of different wt% of NH_3PO_4 in cornstarch-based polymer electrolyte. It shows that the sample of 75 wt% starch–25 wt% NH_3PO_4 electrolyte is the highest in the system, which indicates that the electrolyte contains more charges. The optimize value of conductivity is 25 wt% salt concentrations as shown in Figure 4. Liew et. al [19] reported the result of dielectric constant is in agreement with the increment of the conductivity for their Starch-PVA-LiBr electrolyte system. The values of dielectric constant are very high at low frequencies and relatively constant at higher frequencies. The high value of ε_r due to interfacial effects within the bulk of the biopolymer electrolyte [20]. The results in dielectric loss, ε_i as shown in Figure 7, is also similar to the results of dielectric permittivity, ε_r.

Figure 8 and 9 illustrate the real and imaginary parts of the dielectric constants as a function of frequency at different temperatures 298K- 373K for sample of 25 wt% of NH_3PO_4. There are few factors that affect the ionic conductivity; which are due to the number of charge carriers, the concentration of mobile ions and the availability of a connecting polar domain as the conduction pathway [21]. In this work, the increase in conductivity regarded to the increment of charge carriers, while the decrease in conductivity value can be explained by the formation of ion pairs producing neutral species, which reduces number offree ions [22].

At the low-frequency region, the high value of ε_r and εi is represents the dielectric polarization. Ions tend to diffuse and migrate along the electric field appropriately. Since ions are not transparent to the stainless steel electrodes, they accumulate at the electrode–electrolyte interface, becoming localized, and form a heterocharge layer [23,24]. Assume that the thickness of the electrolyte is greater than the heterocharge layer, the charge density increases rapidly leading to electrode polarization [21]. At high frequencies, the periodic reversal of the electric field occurs so fast that there is no excess ion diffusion in the direction of the field. The decrease in the value of ε_r and ε_i at high frequency due to the charge accumulation decreases at the electrode-electrolyte interface. The decrease in ε_r and ε_i with increasing frequency implies that the systems are non-Debye type.
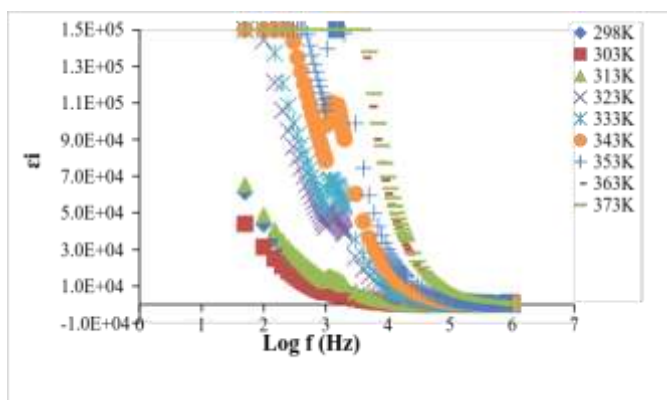

Figure 9. Typical plot of the variation of complex dielectric permitivitty, ε_i with frequency for 25 wt% of NH_3PO_4 in the temperature range of 298K-373K
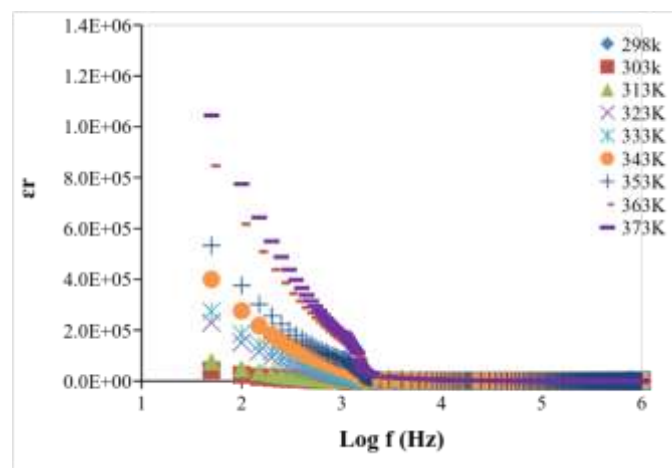
Figure 10 and 11 shows the variation of real part of dielectric modulus, M_r and complex dielectric modulus, M_i with respect to frequency in the temperature range between 298K- 373K respectively. Both M_r and M_i tend towards zero at low frequency regime which might be due to the large value of capacitance associated with the electrodes. The frequency range on the lower region of the peak frequency determine the charge carriers are mobile over a long distances [25].
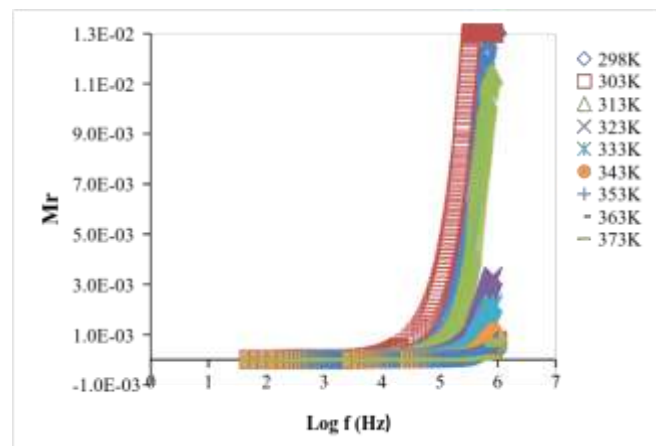

Figure 10. Variation of real part of dielectric modulus, M_r as a function of frequency for 25 wt% of NH_3PO_4 in the temperature range of 298K- 373K
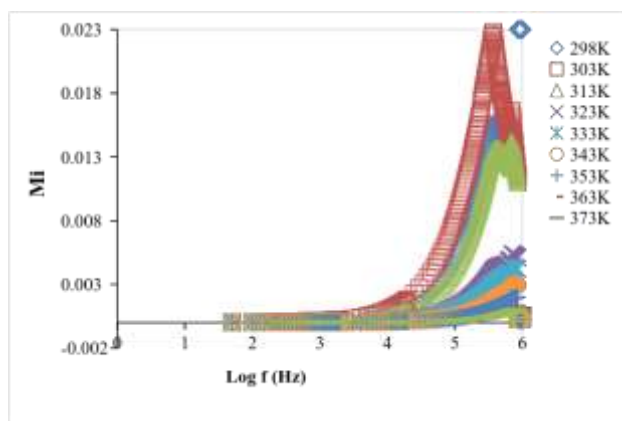
Figure 11. Variation of imaginary part of dielectric modulus, M_i as a function of frequency for 25 wt% of NH_3PO_4 in the temperature range of 298K- 373K

IV. CONCLUSION

Electrolyte systems based on cornstarch doped with NH_3PO_4 has been successfully prepared via solution cast technique. The electrolyte containing 25 wt% NH_3PO_4 obtains the highest conductivity value of 7.27 x 10^{-6} Scm^{-1} at room temperature and has Ea value of 0.26 eV. The increase in conductivity with increasing temperature for the highest conducting electrolyte in cornstarch- NH_3PO_4 system is due primarily to the increase in the mobility of free ions. Dielectric studies suggest that the samples in this study show non-Debye behavior. From FTIR analysis, the complexation between the electrolyte components is proven by the shifting of hydroxyl and C-O-C bond stretching bands.

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