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Ionic Conductivity Study on Hydroxyethyl Cellulose (HEC) doped with NH_4Br Based Biopolymer Electrolytes

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Abstract

A biopolymer electrolytes (BEs) based on hydroxyethyl cellulose (HEC) doped with NH_4Br has been prepared via solution casting technique. XRD shows that all complexes are amorphous. Impedance of the electrolytes has been measured using electrical impedance spectroscopy (EIS) over the frequency range from 50 Hz to 1 MHz. The highest ionic conductivity obtained at room temperature is 3.61×10^{-4} Scm^{-1} for 25 wt. % of NH_4Br. The temperature-dependent of HEC based BEs system conductivity data obeys Arrhenius relationship. Conductivity enhancement in the HEC based BEs is caused not only by the increase in the concentration of NH_4Br but also by the increase in mobility and diffusion coefficient of ions. Dielectric data were analyzed using complex permittivity ε^* and complex electrical modulus M^* for the sample with the highest ionic conductivity at various temperatures.

Keywords: biopolymer electrolytes; ionic conductivity, electrical properties.

Introduction

In the world of a new era, there are so many product of battery with high cost fabrication and not environmentally friendly. The widespread use of batteries has created many environmental concerns, such as toxic metal pollution. Battery manufacture consumes resources and often involves hazardous chemicals. Electrolytes used in the commercial batteries and electronic devices today are high in conductivity, but it is hazardous and non-biodegradable, thus, it is danger to the environment and also human. The development of polymeric systems with high ionic conductivity is one of the main objectives in polymer research. This is due to their potential application as an electrolyte in solid state batteries[1-3]. Polymer battery has advantages of high ionic conductivity, high energy density, solvent-free condition, leak proof, wide electrochemical stability windows, easy processability and light weight. Generally, ionic conduction in polymer electrolytes is dominated by the amorphous elastomeric phase[4].

Since then, many polymer electrolyte systems have been investigated and many of them are based on poly(ethylene oxide) (PEO), but other polymer electrolyte systems based on natural polymers, such as cellulose derivatives, starch, chitosan and other natural macromolecules[5-8] are also worth to be investigated due to their natural abundance, low price and environmentally friendly nature[9]. One advantage of polysaccharides (cellulose, CMC, starch, pectin, etc.) and their derivatives is their ability to be processed as films/membranes with good adhesion to glass and metal surfaces as well as an excellent transparency. Several researches done on this very famous cellulose were largely investigated by various scientists around the world due to its mysterious and unexplored properties[10]. Therefore, it is a very urging to come up with a very abundant known polymer as the main composition for an ionic conductor.

In this present work, we report the ionic conductivity and electrical properties of the hydroxyethyl cellulose (HEC) - NH_4Br based BEs system.

Material and Methods

Sample Preparation: Hydroxyethyl cellulose (HEC) obtained from a Sigma Aldrich co. and ammonium bromide (NH_4Br) (Merck Co.) were used for the preparation of the biopolymer electrolyte. Distilled water was chosen as a solvent. The biopolymer electrolytes were prepared by the solution cast technique.

1g of HEC was dissolved in distilled water. Then, varied amount of NH_4Br in weight percent (5-25 wt. %) was added in HEC solution. The mixtures were stirred continuously with magnetic stirrer and bar until complete dissolution became homogenous. The mixtures were then poured into several Petri dishes and allowed to evaporate slowly at ambient temperature for films to form. The films were kept in desiccators for further drying before being characterized to ensure no water present in the BEs system. Table 1 shows the compositions and sample description for HEC based BEs system.

Characterization: To study the nature of the BEs system, the X-ray diffraction (XRD) measurements were performed using Rigaku MiniFlex 2. Prior, samples were cut into a suitable size (2 cm × 2 cm) and then adhered onto a glass slide. The glass slide was then placed in the sample holder of the diffractometer and the samples were directly scanned at 2θangles between 5°and 80°with X-rays of 1.5406 Å wavelength generated by a Cu K_{α} source.

Table-1
The composition for HEC-AB proton exchange membrane

Composition	Description
1g HEC + 0 wt. % NH_4Br	H0
1g HEC + 5 wt. % NH_4Br	H1
1g HEC + 10 wt. % NH_4Br	H2
1g HEC + 15 wt. % NH_4Br	H3
1g HEC +20 wt. % NH_4Br	H4
1g HEC + 25 wt. % NH_4Br	H5

For the electrical study, the samples were characterized using electrical impedance spectroscopy (EIS) via HIOKI 3532-50 LCR Hi-Tester to determine the conductivity of the samples. The films were cut into a suitable size and placed between the blocking steel electrodes 1 π cm2 surface area of a conductivity cell. The frequency was set to test from 50 Hz to 1 MHz. Negative imaginary impedance (-Z_i) versus real impedance (Z_r) will be obtained from the plot. The conductivity of the sample was calculated from the equation below.

$$\sigma = \frac{t}{R_b A} \tag{1}$$

Where *t* is the thickness of the sample, *A* is the area of the sample in contact with the electrode and R_b is the bulk resistance determined from Cole-Cole plot. The equations for the dielectric constant, ε_r, the dielectric loss, ε_i, the real modulus M_r and the imaginary modulus M_i can be shown as

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

$$\varepsilon_r = \frac{Z_i}{\omega C_0 ({Z_r}^2 + {Z_i}^2)} \tag{3}$$

$$M_r = \frac{\varepsilon_i}{({\varepsilon_r}^2 + {\varepsilon_i}^2)} \tag{4}$$

$$M_i = \frac{\varepsilon_r}{({\varepsilon_r}^2 + {\varepsilon_i}^2)} \tag{5}$$

Here $C_0=\varepsilon_0 A/t$ and ε_0 is the permittivity of the free space, *A* is the electrolyte–electrode contact area and *t* is thickness of the sample and $\omega=2\pi f$, *f* being the frequency in Hz.

Results and Discussion

Figure 1 shows the XRD patterns of BEs based on HEC respectively. The relative intensity of broad peak between 15° and 29° decrease with the increases in ionic dopant (NH_4Br) and this may due to the interaction of the salt with the polymer, resulting in the increasing of amorphousness in the BEs system. The broad peak is known as the 'amorphous hump' and is a typical characteristic of amorphous materials. This result can be interpreted by Hodge et al., [11] criterion, which establishes a correlation between the intensity of the peak and the degree of crystallinity. Hence the change in intensity and the broad nature of the peak suggest that the polymer and dopant complexation takes place in the amorphous region of the polymer matrix[12]. Thus, it contributes a lot to the increment of proton and transport in the amorphous phase and thus results in the improvement of conductivity[13]. The diffraction peak rises for sample H5 indicates that there is a decrease in the amorphousness of HEC based BEs system by addition more than 20 wt. % of NH_4Br. This eventually leads to the decrease in number of mobile ions in the sample and to the decrease in conductivity[14]. According to Shuhaimi et al.[15], the changing in amorphousness of polymer electrolytes system will affect the ionic conductivity.

The ionic conductivity depends on several factors, such as ionics conducting species concentration, cationic or anionic types charge carriers, the charge carriers mobility and the temperature[13,16]. Figure 2 shows the ionic conductivity of HEC–NH_4Br based BEs as a function of NH_4Br composition. It can be observed that conductivity of the sample increases about seven orders of magnitude to 3.61×10^{-4} Scm^{-1} for the sample containing 20 wt. % NH_4Br. The increase in conductivity is certainly related to the increase in the number of mobile charge carriers[17]. From XRD results, the increase in ionic conductivity with increasing salt concentration can be attributed to the increase in the amorphousness of the sample. It is inferred that the sample containing 20 wt. % NH_4Br is the most amorphous sample. For composition of NH_4Br larger than 20 wt. %, a slight decrease in the ionic conductivity of the electrolyte films is observed. This is attributed to the formation of ionic aggregates[18,19] suggests that the number of energetically available sites for mobile ions is optimum at 20 wt. % of NH_4Br composition.

The temperature dependence of the conductivity of the samples was done to study the behavior of the ionic conductivity of the HEC based BEs system. Figure 3 shows the plot of log conductivity, σ against 1000/T for all samples in the temperature range of between 303K and 353K which confirms that the ionic conductivity of the biopolymer electrolyte increase with increasing temperature for all compositions. It can be found the regression values are close to unity, suggesting that the temperature-dependent ionic conductivity for all complexes obeys Arrhenius behavior[20]. Similar results also have been reported for different types of polymer electrolytes[14, 21]. The plot from figure 3 can be considered Arrhenian by the relation,

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{kT}\right) \tag{6}$$

where σ_0 is the pre-exponential factor, E_a is the activation energy and k is the Boltzman constant.

The activation energy, E_a (combination of the energy of defect formation and the energy for migration of ions) is listed in table 2, it was calculated by linear fit from figure 3. It shows that the E_a for the conduction decreased gradually with increase in NH_4Br composition. It can be seen that Ea for conduction decreased gradually with increase in conductivity of the HEC based BEs system, implying that the ions in highly conducting samples require lower energy for migration. Since the ion transfer is greatly affected by the polymer segmental motion,[22] the electrolytes with lower value of E_a imply rapid ionic conduction and thus an increase in the ionic conductivity. The low activation energy for HEC based BEs system is due to the completely amorphous nature of polymer electrolyte that facilitates the fast H^+ ion motions in the polymer network. It has been found that the highest conductivity for HEC-BEs system containing 20 wt. % of NH_4Br has the lowest activation energy (~ 0.21 eV). It is noteworthy that the polymer electrolytes with low values of activation energies are desirable for practical applications[13].

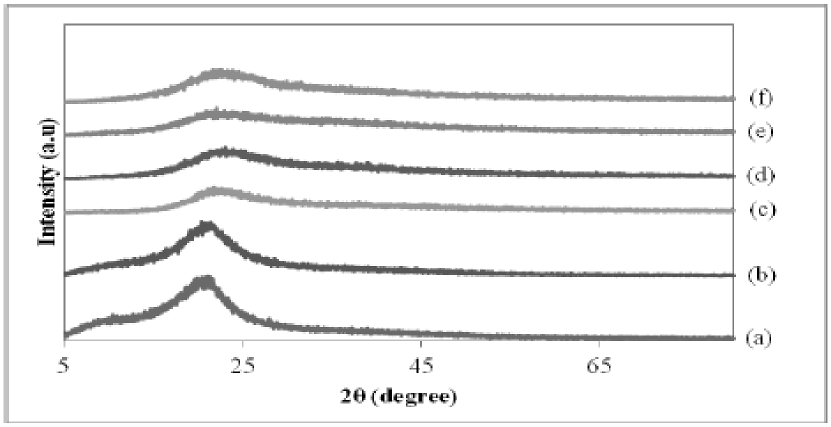


Figure-1
XRD patterns of the HEC-AB based BEs. (a) H0, (b) H1, (c) H2, (d) H3, (e) H4 and (f) H5

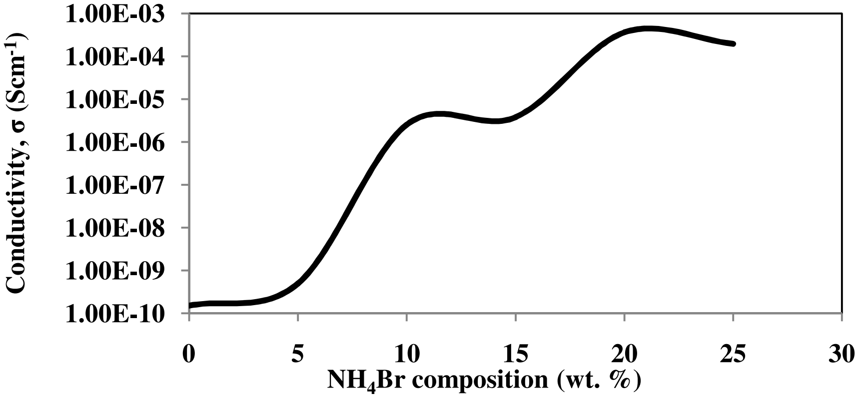


Figure-2
Ambient temperature conductivity, σ_{AT} as a function of NH_4Br composition.

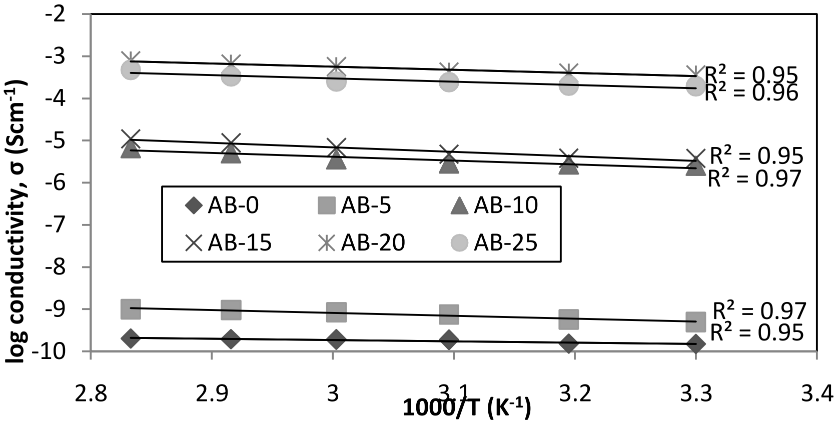


Figure-3
Temperature dependence for HEC based BEs system

The ionic conductivity of an electrolyte depends on the number of mobile and mobility of ions as expressed by the equation

$$\mu = \frac{\sigma}{nq} \qquad (7)$$

where σ is the ionic conductivity, η is the number and μ is mobility of mobile ions, and q is electron charge. It is a very important parameter in understanding the transport properties of BEs. The number of mobile ions was estimated from Rice and Roth by the equation[23]

$$\sigma = \frac{2}{3}\left[\frac{(Ze)^2}{kTm}\right] nE_A \ell \exp\left[\frac{E_A}{kT}\right] \qquad (8)$$

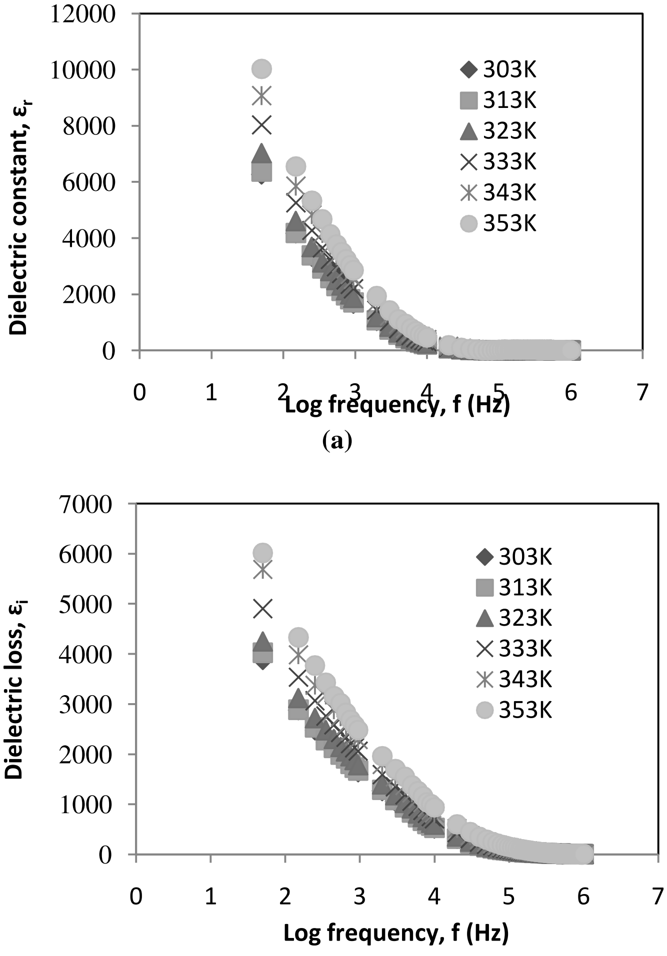
Here *Z, E_a*, and *m* are the valency, activation energy, and mass of the conducting ion, respectively, ‘ is the mean free path or distance between coordinating sites (electron-donating atoms) by using the Rice and Roth equation, *l* for hydroxyethyl cellulose (HEC) must be known. Yokota et al.,[24] found that the length of 40 rigid chain segments of bendable molecular cellulose is 60 ±15 nm. From this result, the length of one chain segment is 1.5 nm, which is used in the Rice and Roth equation for *l* [13].

Table 2 depicts the transport parameters which are related to the ionic conducitivy of HEC based BEs system.

Table-2
Transport parameters of HEC-NH_4Br based BEs system at ambient temperature

Samples	E_a eV	τ (s)	η (cm^{-3})	μ ($cm^2V^{-1}s^{-1}$)	D (cm^2s^{-1})
H0	0.56	1.45E-13	9.58 x 10^{21}	9.78E-14	2.56E-15
H1	0.55	1.46E-13	2.21E22	1.40E-13	2.66E-15
H2	0.39	1.88E-13	3.69E22	4.27E-10	1.12E-11
H3	0.33	1.89E-13	4.47E22	5.28E-10	1.28E-11
H4	0.21	2.43E-13	3.93E22	5.74E-08	1.50E-09
H5	0.23	2.33E-13	4.00E22	3.02E-08	7.88E-10

Majid and Arof,[25] reported that the ionic conductivity of a polymer is generally linked to the number of ions and the mobility of conducting species in the polymer complexes. However, in this present work, the number of ions does not significantly contribute to the conductivity compared to diffusion coefficient and ionic mobility. Imbalance of the value of η in the HEC based BEs system with the conductivity can be attributed to the increment of NH_4Br composition, which does not favor the association of ion count, but it shows the increment of mobility and diffusion parallel with the conductivity. When the conductivity increased, the irregular value of η is increasingly hard to move and this is reflected in the E_a values, which become smaller and require the ions to move with higher μ. It also can be inferred, the mobility of the ions can be reduced with decrease in amorphousness as proven by XRD result[13]**.** The decrease in conductivity value at higher dopant composition can be explained by the aggregation of ions, leading to the formation of ion clusters where the dipole interaction between the protons in the medium increases, which reduces the ion mobility and thus the conductivity[26]. These results clearly reveal that the conductivities of the HEC based BEs system are strongly influenced by the diffusion coefficient and ionic mobility.



(a)

(b)

Figure-4
Dielectric formulism (a) dielectric constant and (b) dielectric loss

The investigation of dielectric study in BEs system is a powerful approach for obtaining information about the characteristics of ionic and molecular interactions. Several of the physical and chemical properties of the polymer can evaluate and help in understanding the conductive behavior of polymer electrolytes[22]. Figure 4 represents the frequency dependence of dielectric constant, ε_r and dielectric loss, ε_i respectively, for HEC based BEs system containing 20 wt. % of NH_4Br. The sharp rise of the dielectric point (value) towards low frequencies indicates that electrode polarization has occurred which confirms non-Debye dependence[27]. On the other hand, at high frequencies, periodic reversal of the electric field occurs so fast that there is no excess ion diffusion in the direction of the field. As the frequency increases, the rate of reversal of the electric field also increases, as such; there is no charge build up at the interface which brings about a decrease in the values of the dielectric loss due to the decrease of the polarization effect by the charge accumulated[6].

Figure 5 shows the frequency dependence of the real, M_r and imaginary, M_i parts of the modulus formalism. According to Ramesh and Arof[28], the presence of peaks in the modulus formalism at higher frequencies for all polymer systems and temperatures is an indicator that the polymer electrolyte films are ionic conductors. However, in this study, the peaks are visibly absent and both M_r and M_i approach zero at low frequencies which indicates that electrode polarization is negligible. The appearance of a long tail at low frequencies indicates that there might be a large capacitance associated with the electrodes used in EIS which further confirms non-Debye behavior in the samples[29].

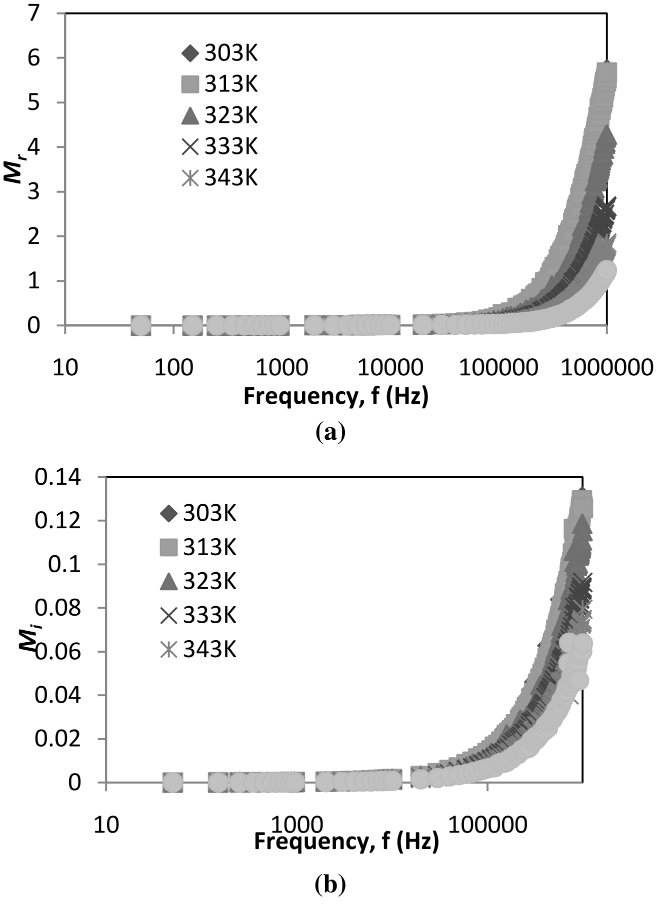


Figure-5
Modulus formulism (a) real modulus and (b) imaginary modulus

Conclusion

A biopolymer electrolytes (BEs) based on hydroxyethyl cellulose (HEC) doped with NH_4Br has been successfully prepared via solution casting technique. XRD measurements confirmed that the BEs system predominantly amorphous in nature. The highest ionic conductivity obtained at room temperature is 3.61 x 10^{-4} Scm^{-1} for 25 wt. % of NH_4Br. The temperature-dependent of HEC based BEs system conductivity data obeys Arrhenius relationship where the samples conductivity exclusively affected by the temperature and composition of NH_4Br. Conductivity enhancement in the HEC based BEs is caused not only by the increase in the composition of NH_4Br but also by the increase in mobility and diffusion coefficient of ions. The dielectric behaviors of the highest in ionic conductivity show strong dependence on frequency and temperature and also follow to the non-Debye type. All these preliminary results suggest that such HEC based biopolymer film have a good potential for applications as conducting biopolymer electrolytes.

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References

1. Hooper A. and North J.M., The fabrication and performance of all solid state polymer-based rechargeable lithium cells, *Solid State Ionics*, **9**, 1161–1166 **(1983)**
2. Acosta J.L. and Morales E., Structural, morphological and electrical characterization of polymer electrolytes based on PEO/PPO blends, *Solid State Ionics*, **85 (1-4)**, 85–90 **(1996)**
3. Kim J.Y. and Kim S.H., Ionic conduction behavior of network polymer electrolytes based on phosphate and polyether copolymers, *Solid State Ionics*, **124 (1–2)**, 91–99 **(1999)**
4. Whang W.T. and Lu C.L., Effects of polymer matrix and salt concentration on the ionic conductivity of plasticized polymer electrolytes, *J. Appl. Polym. Sci.*, **56 (12)**, 1635-1643 **(1995)**
5. Machado G.O., Prud'homme R.E. and Pawlicka A., Conductivity and Thermal Analysis Studies of Solid Polymeric Electrolytes Based On Plasticized Hydroxyethyl Cellulose, *e-Polymers*, **115**, 1-9 **(2007)**
6. Mudigoudra B.S., Masti S.P. and Chougale R.B., Thermal Behavior of Poly (vinyl alcohol)/ Poly (vinyl pyrrolidone)/ Chitosan Ternary Polymer Blend Films, *Res. J. Recent Sci.,* **1(9),** 83-86 **(2012)**
7. Kadir M.F.Z., Majid S.R. and Arof A.K., Plasticized chitosan–PVA blend polymer electrolyte based proton battery, *Electrochim. Acta*, **55 (4)**, 1475-1482 **(2010)**
8. Pawlicka A. and Donoso J.P., Polymer Electrolytes based on Natural Polymers", Woodhead Publishing Limited, Cambridge **(2010)**

9. Lorcks J., Properties and applications of compostable starch-based plastic material, *Polym. Degrad. Stab.*, **59 (1-3)**, 245-249 **(1998)**

10. Miller K.S. and Krochta J.M., Oxygen and aroma barrier properties of edible films: A review. *Trends Food Sci. Tech.*, **8 (7)**, 228-237 **(1997)**

11. Hodge R.M., Edward G.H. and Simon G.P., Water absorption and states of water in semicrystalline poly(vinyl alcohol) films, *Polym. J.*, **37(8)**, 1371-1376 **(1996)**

12. Ramya C.S., Selvasekarapandian S., Savitha T., Hirankumar G., Baskaran R. and Angelo P.C., Conductivity and thermal behavior of proton conducting polymer electrolyte based on poly (*N*-vinyl pyrrolidone), *Eur. Polym. J.*, **42 (10)**, 2672-2677 **(2006)**

13. Samsudin A.S., Khairul Wan. M. and Isa M.I.N., Characterization on the potential of carboxy methylcellulose for application as proton conducting biopolymer electrolytes, *J. Non-Cryst. Solids*, **358 (8)**, 1104-1112 **(2012)**

14. Samsudin A.S. and Isa M.I.N., Structural and ionic transport study on CMC doped NH4Br: A new types of Biopolymer Electrolytes, *J. Appl. Sci.*, **12 (2)**, 174-179 **(2012)**

15. Shuhaimi N.E.A., Teo L.P., Majid S.R. and Arof A.K., Transport studies of NH_4NO_3 doped methyl cellulose electrolyte, *Synth. Met.*, **160 (9-10)**, 1040-1044 **(2010)**

16. Schantz S. and Torell L.M., Evidence of dissolved ions and ion pairs in dilute poly (propylene oxide)-salt solutions, *Solid State Ionics*, **60 (1-3)**: 47-53 (1993)

17. Samsudin A.S. and Isa M.I.N., Structural and electrical properties of carboxy methylcellulose- dodecyltrimethyl ammonium bromide-based biopolymer electrolytes system, *Int. J. Polymer. Mater.*, **61 (1)**, 30-40 **(2012)**

18. Raphael E., Avellaneda C.O., Manzolli B. and Pawlicka A., Agar-based films for application as polymer electrolytes, *Electrochim. Acta*, **55 (4)**, 1455-1459 **(2010)**

19. Neyertz S. and Brown D. Local structure and mobility of ions in polymer electrolytes: A molecular dynamics simulation study of the amorphous PEO_xNaI system, *J. Chem. Phys.*, **104 (10)**, 3797-3809 **(1996)**

20. Rajendran S. and Uma T., Experimental investigations on PVC–$LiAsF_6$–DBP polymer electrolyte systems, *J. Power Sources*, **87 (1-2)**, 218-222 (2000)

21. Hashmi S.A., Kumar A., Maurya K.K. and Chandra S., Proton-conducting polymer electrolyte I. The polyethylene oxide NH $_4ClO_4$ system, *J. Phys. D: Appl. Phys.*, **23 (10)**, 1307-1314 **(1990)**

22. Ramesh S. and Arof A.K., Electrical conductivity studies of polyvinyl chloride-based electrolytes with double salt system, *Solid State Ionics*, **136**, 1197-1200 **(2000)**

23. Rice M.J. and Roth W.L., Ionic transport in super ionic conductors: a theoretical model, *J. Solid State Chem.*, **4 (2)**, 294-310 (1972)

24. Yokota S., Ueno T., Kitaoka T. and Wariishi H., Molecular imaging of single cellulose chains aligned on a highly oriented pyrolytic graphite surface, *Carbohydr. Res.*, **342 (17)**, 2593-2598 **(2007)**

25. Majid S.R. and Arof A.K., Proton-conducting polymer electrolyte films based on chitosan acetate complexed with NH_4NO_3 salt, *Physica B*, **355 (1)**, 78-82 **(2005)**

26. Buraidah M.H. and Arof A.K. Characterization of chitosan/PVA blended electrolyte doped with NH_4I. *J. Non-Cryst. Solids*, **357 (16-17)**, 3261-3266 **(2011)**

27. Govindaraj G., Baskaran N., Shahi K. and Monoravi P., Preparation, conductivity, complex permittivity and electric modulus in AgI-Ag_2O-SeO_3-MoO_3 glasses, *Solid State Ionics,* **76 (1-2)**, 47-55 **(1995)**

28. Ramesh S. and Arof A.K. Ionic conductivity studies of plasticized poly (vinyl chloride) polymer, *Mater Sci. Eng. B.*, **85 (1)**, 11-15 **(2001)**

29. Ramesh S., Koay H.L., Kumutha K. and Arof A.K., FTIR studies of pvc/pmma blend based polymer electrolytes, *Spectrochim. Acta A.*, **66 (4-5)**, 1237-1242 **(2007)**