Copyright © 2015, American-Eurasian Network for Scientific Information publisher

American-Eurasian Journal of Sustainable Agriculture

ISSN: 1995-0748

JOURNAL home page: http://www.aensiweb.com/AEJSA 2015 Special; 9(2): pages 1-7.

Published Online 11 February 2015. **Research Article**

Conduction Mechanism of Solid Biopolymer Electrolytes System Based on Carboxymethyl cellulose – Ammonium chloride

[1]Nur Hidayah Ahmad, [2]Mohd. Ikmar Nizam Mohamad Isa

[1]School of Fundamental Science, Universiti MalaysiaTerengganu, 21030 Terengganu, Malaysia.

Received: 31 December 2014; **Revised:** 26 January 2015; **Accepted:** 28 January 2015

ABSTRACT

Solid biopolymer electrolytes (SBEs) system based on carboxymethyl cellulose (CMC) doped with ammonium chloride (AC) has been prepared via solution casting technique. Impedance study shows the highest ionic conductivity, σ, was found to be (1.43 ± 0.02) x 10^{-3} S/cm at room temperature (303 K) for sample containing 16wt. % of ammonium chloride. The conductivity of the CMC–AC was found to increase relatively to the AC content and temperature. The temperature-dependent of solid biopolymer electrolyte obeys Arrhenius behaviour which $R^2 \approx 1$. The activation energy was found to be capsized with the conductivity. The Quantum mechanical tunnelling (QMT) is the best possible mechanism to present the hopping method in the CMC–AC system studied.

Keywords: SBE, CMC, AC, ionic conductivity

INTRODUCTION

Recently, the problem of solid waste has become more than an issue, especially electronic waste such as batteries because the chemicals used in commercial batteries are hazardous and nonbiodegradable. In addition, the chemicals used in commercial products are toxic and expensive, such as titanium and cadmium sulphate. Thus, it would put the environment and also humans nation in jeopardize [1, 2]. To overcome this problem, many researchers are looking for a better material for solid polymer electrolytes refer to their desirable characteristics that show good compatibility with electrodes, no leakage, low self-discharge, elasticity, and easy processability [3, 4].

Natural polymers are particularly interesting due to their abundance in nature, very low cost and principally, biodegradation properties [1]. Therefore, among the polymers which become the focus of the present study were polyethylene oxide (PEO) [5, 6], polyvinyl alcohol (PVA) [7], methyl cellulose [3], polyvinyl chloride (PVC) [8-10] and chitosan [11-13].

Since Wright discovered ionic conductivity in a PEO/Na+ complex in 1975, researchers started to be more concerned with solid polymer electrolytes (SPEs), in particular for improvement of the ionic conductivity [14]. SPEs are suitable for high-temperature operation and possess good thermal stability, electrolyte proof, less flammability and low toxicity [12, 15].

In this research, carboxyl methylcellulose (CMC) was chosen due to its superior properties as a polymer host and doped with ammonium chloride (AC). Ammonium chloride (AC) was chosen since ammonium salts are claimed to be good proton donors to the polymer matrix ion [16]. Besides that,

Corresponding Author: Mohd Ikmar Nizam Mohamad Isa, School of Fundamental Science, Universiti Malaysia Terengganu, 21030 Terengganu, Malaysia. Tel: +609 6684930/4931, E-mail: ikmar_isa@umt.edu.my

NH_4^+ is believed to be responsible for the ionic conduction [3].

Experimental method:

Sample preparation

Carboxymethyl cellulose (CMC) was obtained from Acros Organic Co. without further petrification. In the preparation, 2.0g CMC was then diluted into distilled water. The solution was stirred for a few hours at room temperature. Different weight percentages of AC (R & M Marketing) were added and further stirred until it become homogenous. To prepare the CMC-AC solid bio-polymer electrolyte, the amount of CMC was fixed while the amount of AC was varied from 2 – 20 wt. %. All the mixtures were then cast into petri dishes and allowed to evaporate to form films. The films were kept in the desiccator (with silica gel desiccant) to ensure that the films are dry.

Impedance spectroscopy:

The electrical conductivity of the electrolytes was determined by using EIS via HIOKI 3532-02 LCR Hi-Tester that was interfaced to a computer with frequency in the range of 50Hz to 1MHz. The electrolyte samples were sandwiched between two stainless steel blocking electrodes of a conductivity cell which are connected to a computer. The value of the bulk resistance (R_b) was determined from the Cole-Cole plots. Conductivity (σ) was calculated using equation:

$$\sigma = \frac{t}{R_b A} \qquad (1)$$

Here t is the thickness of the electrolyte samples and A is the electrode-electrolyte contact area. The impedance measurement on each electrolyte sample at room temperature was done for six times and the average value was considered for the calculation of the conductivity value. At various temperatures for temperature dependence analysis, the impedance measurement was carried out for one time. A digital thickness gauge (Mapra Technik Co.) was employed to measure the thickness of the electrolytes. The thickness of the electrolytes was found to be 0.008 – 0.080 mm.

Result and discussion

Impedance analysis:

Figure 1a, b, c, d, e, f shows the Cole-Cole plots of sample CMC-AC system tested at room temperature doped with different concentration of AC at ambient temperature. The Cole-Cole plot of the electrolyte containing 0, 2, 8, 12, 16, 20 wt. % AC shows incomplete semicircle curve. These figures show two well defined regions; a high frequency incomplete semicircle related to the parallel combination of a resistor and a capacitor and a low frequency spike representing formation of double layer capacitance at the blocking electrode-electrolyte interface which causes the inclination and is better known as the polarization effect due to migration of ions [17-19].

The semicircle part of the impedance spectrum in the high frequency region is related to ionic conduction in the bulk of the electrolyte and can be modelled as a parallel resistor due to the mobile ions inside the polymer matrix and capacitor due to the immobile polymer chain circuit network where the capacitance is usually of the order of nano-Farads [20, 21]. With increasing salt composition, a local effective pathway is constructed in the liquid phase for ionic conduction, as a result, ions can transport quickly in the liquid phase as the electric potential alternates between the positive and negative electrodes in an alternating field.

Ionic conductivity:

The conductivity, σ, plot was show in figure 2. According to Figure 2, the addition of AC beyond 16wt% lessens the conductivity. The highest conductivity obtained for AC-16wt.% is 1.43 x 10^{-3} S/cm. The effect of increases of conductivity CMC-AC could be due to the enhancement of ionic mobility and the number of charge carrier or free ions [18, 22, 23]. Meanwhile, the decreases in conductivity could be due to the formation of ion pairs and aggregates. The formation of ion pairs produces neutral species and thus reduces the number of free ions [22, 23].

Temperature-dependent:

In order to analyze the mechanism of ionic conduction in the SBEs system, the temperature-dependent study was carried out. Log σ against 1000/T plot for various compositions of SBEs system based on CMC–AC in the temperature range of 303 – 353 K is displayed in Figure 3. The plot shows that the ionic conductivity of the SBEs system increases with increasing temperature for all salt composition which obeys the Arrhenius behaviour which $R^2 \approx 1$. This is because the ionic mobility and the degree of salt dissociation are also temperature dependent [12]. The plot can be considered as Arrhenius behaviour by the relation,

$$\sigma = \sigma_o \exp\left(\frac{E_a}{kT}\right) \qquad (2)$$

Where σ_o is the pre-exponential factor, E_a is activation energy, k is the Boltzmann constant, and T is absolute temperature. The calculated E_a value for each AC electrolyte is tabulated in Table 1. The value of E_a found to ranging from 0.14 – 0.37 eV for AC electrolytes. The higher conducting electrolyte has the lower E_a value. This is in agreement with the fact that the density of ions in the electrolyte increases with the increase in AC content causes the activation energy drop and vice versa.

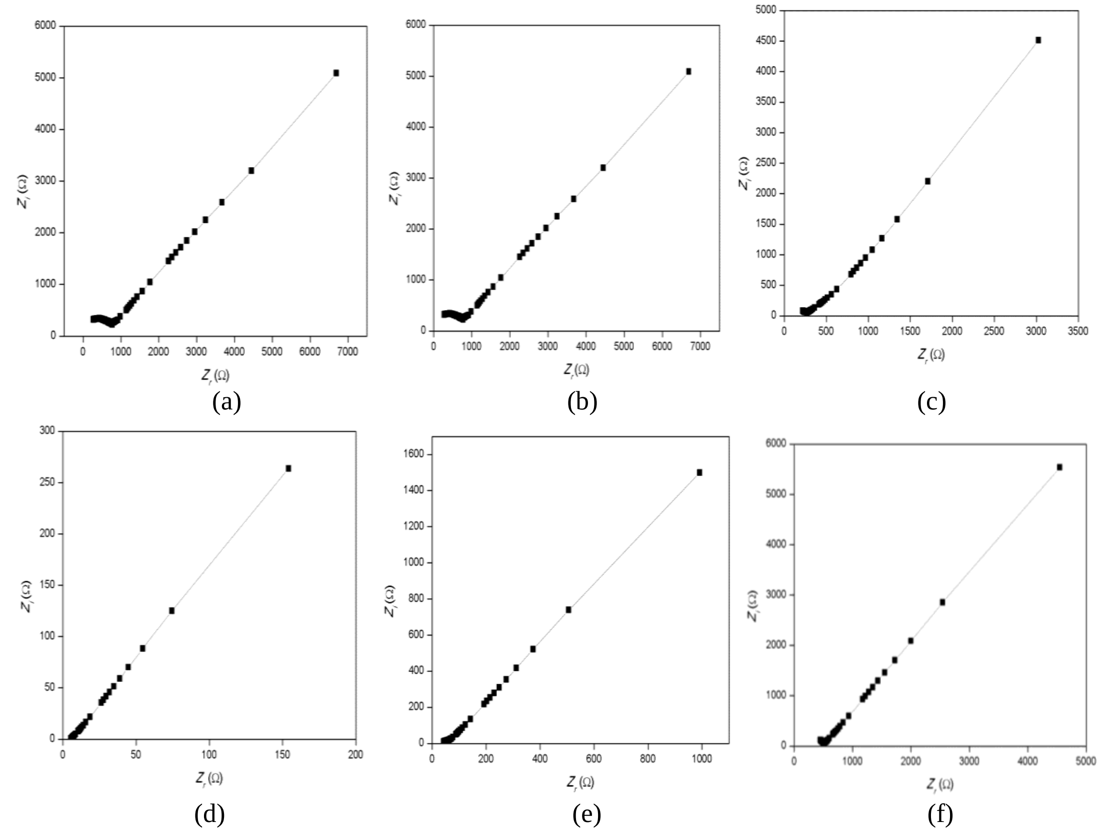

Fig. 1: Cole-cole plot of SBEs containing (a) CMC-0wt%AC (b) CMC-2wt% AC (c) CMC-8wt% AC (d) CMC-12wt% AC (e) CMC-16wt% AC (f) CMC-20wt% AC at room temperature.

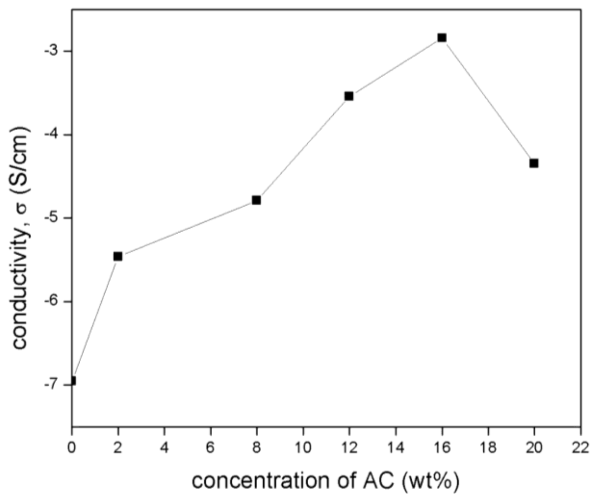

Fig. 2: Room temperature conductivity as a function of AC concentration.

Table 1: Ionic Conductivity and Activation Energy of SBEs Based on CMC-AC System Measured at Room Temperature.

Sample AC, (wt. %)	Conductivity, σ (S/cm)	Activation energy, E_a (eV)
0	1.11E-07	0.37
2	3.45E-06	0.34
8	1.62E-05	0.32
12	2.85E-04	0.20
16	1.43E-03	0.14
20	4.50E-05	0.28

Abbreviation: wt. %. Weight percentage

Conduction Mechanism:

Ionic conduction mechanism of an electrolyte can be determined by equation 3 and 4 by employing Jonscher's universal power law [11, 12, 24, 25]:

$$\sigma(\omega) = \sigma_{ac} + \sigma_{dc} \quad (3)$$

$$\sigma(\omega) = A\omega^s + \sigma_{dc} \quad (4)$$

Where σ (ω) is the total conductivity, σ_{ac} is the ac conductivity, and σ_{dc} is the dc conductivity. The ac conductivity is represented by $A\omega^s$, where A is constant at a particular temperature, ω is the angular frequency ($\omega = 2\pi f$) and s is the power law exponent. The ac conductivity can also be obtained using equation [12]:

$$\sigma_{ac} = \varepsilon_o \varepsilon_i \omega \quad (5)$$

By substituting $\sigma_{ac} = A\omega^s$ into equation (3), the value of exponent s was determined by plotting the following relation:

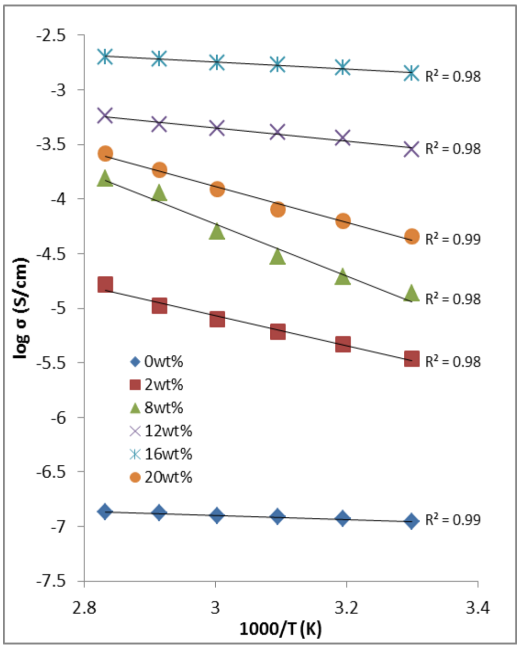

Fig. 3: Log σ against 1000/T plot for various compositions of SBEs system based on CMC–AC in the temperature range of 303–353 K.

$$\ln \varepsilon_i = \ln \frac{A}{\varepsilon_o} + (s-1)\ln \omega \quad (6)$$

and;

$$\varepsilon_i = \frac{Z_r}{\omega C_o (Z_r^2 + Z_i^2)} \quad (7)$$

Figure 4 depicts the frequency, lnω dependence of dielectric loss, ε_i at selected temperatures. The dielectric loss increases with increasing temperature for a particular frequency but it decreases with the increase in frequency at a specified temperature. From figure, it can be seen clearly that there are two different slopes. In the low frequency region, stronger frequency dependence of dielectric loss is observed. This dielectric loss-frequency behaviour in the low frequency region is contributed to space charge polarization, which occurs when there is more than one phase having different conductivities existing within the same material and electrode polarization [26]. Electrode polarization arises due to the accumulation of ions at the electrode–electrolyte interface. In the high frequency region, the direction of the electric field changes at a faster rate. Hence, most of the ions will be in the bulk of the sample and slighter ions can pile up at the interface [27]. Therefore, the values of ε_i decrease with the increase in frequency. The exponent s was determined from the slope of plots in Figure 5. In this work, the slope is only taken in the frequency region of 12 < Inω < 16 since at high frequency region, no or minimal impact of electrode polarization occurs [12, 28].

CMC-AC SBEs can be fitted to the equation s = 0.0023T+1.0281. From this fitting equation, s→1 when T→0. To determine the electrical conduction mechanisms of 4 types theoretical models have been proposed based on the analysis of ac conductivity [11, 29] such as:

i. Overlapping large polaron tunnelling (OLPT) model: In the OLPT model, the exponent s is temperature dependent. The exponent *s* is predicted to decrease with increasing temperature, reaching a minimum value at a given temperature before continuing to increase with increasing [11, 12, 28, 30].

ii. Correlated barrier hopping (CBH) model: In the CBH model, exponent *s* decreases with increasing working temperatures, but no minimum in exponent *s* is observed [11, 18, 31]. The exponent *s* is predicted to be temperature dependent with exponent *s* → 1 as T → 0K [32].

iii. Small polaron hopping (SPH) model: In the SPH model, the exponent *s* increases with increasing temperature [24, 33]. In this model, small polaron is formed by the addition of the charge carrier to a site, which results in a large degree of local lattice distortion. These small polarons are assumed to be localized so that their distortion clouds do not overlap, so the hopping energy is not dependent on intersite separation [16].

iv. Quantum mechanical tunnelling (QMT) model: In the QMT model, the exponent *s* is almost equal to 0.8 and increases slightly with temperature or independent of temperature [24, 30]. According to Psarras [34], ionic hopping from one site to neighboring site occurs not just by jumping over a potential barrier but can also be accompanied by quantum mechanical tunneling. Hence, from the observations on the behavior of the exponent *s* with the temperature in the CMC-AC system (Figure 5), it can be fitted to the equation *s*= 0.0005x + 0.2767. Thus, it can be implied that QMT model is more applicable in explaining the conduction mechanism of carboxymethyl cellulose-ammonium chloride biopolymer electrolyte. Buraidah and Arof [13] reported that the conduction mechanism for chitosan-PVA-NH_4I occurred by way of QMT model in which the plot of exponent s against T can be fitted to the equation *s*=0.00004T + 0.1256 [13]. Their result is comparable with the present work which the polarons is made up by the protons and their stress fields are able to tunnel through the potential barrier that exists between two possible complexation sites [11].

Conclusion:

SBEs system based on CMC-AC has been prepared via solution casting technique. In CMC-AC system, the SBE containing 16wt% AC obtains the highest conductivity value of (1.43 ± 0.02) x 10^{-3} S/cm at room temperature and it has E_a value of 0.14 eV. The effect of increase with increasing temperature for the highest conducting SBE in CMC-AC system is due to the enhancement of ionic mobility and the number of charge carrier or free ions. The ionic conduction mechanism for the highest conducting in CMC-AC SBEs system is best explained by QMT model.

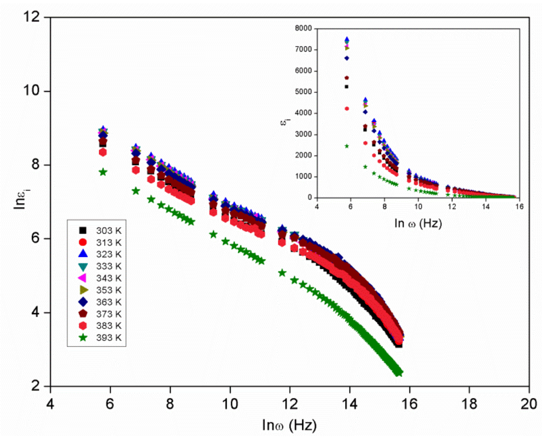

Fig. 4: Variation of Inε_i with frequency at different temperatures for the highest conducting SBE in CMC-AC system.

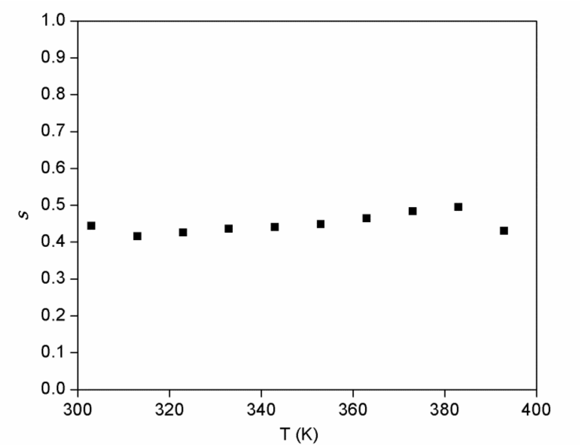

Fig. 5: Variation of exponent s with temperature for the highest conducting SBE in CMC-AC system.

Acknowledgement

The authors would like to thank Ministry of Education Malaysia (MOE) for financial support through Fundamental Research Grant Scheme (FRGS) Vot. 59271 and Exploratory Research Grant Scheme (ERGS) Vot. 55101, and University Malaysia Terengganu (UMT) for technical support and facilities.

References

1. Chai, M.N., M.A. Ramlli and M.I..N. Isa, 2013. Proton Conductor of Propylene Carbonate–Plasticized Carboxyl Methylcellulose–Based Solid Polymer Electrolyte. *International Journal of Polymer Analysis and Characterization*, 18(4): 297-302.
2. Fonseca, C.P., D.S. Rosa, F. Gaboardi and S. Neves, 2006. Development of a biodegradable polymer electrolyte for rechargeable batteries. *J. Power Sources*, 155: 381-384.
3. Nik Aziz, N.A., N.K. Idris and M.I.N. Isa, 2010. Solid Polymer Electrolytes Based on Methylcellulose: FT-IR and Ionic Conductivity Studies. *International Journal of Polymer Analysis and Characterization*, 15(5): 319-327.
4. Chai, M.N. and M.I.N. Isa, 2013. Electrical Characterization and Ionic Transport Properties of Carboxyl Methylcellulose-Oleic Acid Solid Polymer Electrolytes. *International Journal of Polymer Analysis and Characterization*, 18(4): 280-286.
5. Madhu Mohan, V., V. Raja, A.K. Sharma, 2005. Narasimha Rao VVR. Ionic conductivity and discharge characteristics of solid-state batterybased on novel polymer electrolyte (PEO + NaBiF4). *Materials Chemistry and Physics*, 94: 177-181.
6. Michael, M.S., M.M.E. Jacob, S.R.S. Prabaharan, S. Radhakrishna, 1997. Enhanced lithium ion transport in PEO-based solid polymer electrolytes employing a novel class of plasticizers. *Solid State Ionics*, 98: 167-174.
7. Selvasekarapandian, S., G. Hirankumar, J. Kawamura, N. Kuwata, T. Hattori, 2005. 1H solid state NMR studies on the proton conducting polymer electrolytes. *Materials Letters*, 59(22): 2741-2745.
8. Chandra Sekhar, P., P. Naveen Kumar, U. Sasikala, V.V.R.N. Rao and A.K. Sharma, 2012. Investigations on lithium ion complexed polyvinyl chloride (PVC) solid polymer electrolyte films. *Engineering Science and Technology: An International Journal*, 2(5): 908-912.
9. Ramesh, S. and A.K. Arof, 2001. Ionic conductivity studies of plasticized poly(vinyl chloride) polymer electrolytes. *Materials Science and Engineering: B*, 85(1): 11-15.
10. Sreenivasachari, A., 2013. Preparation, Investigation and discharge characteristics of (PVC+PC+NaClO4) Polymer Electrolyte Systems. *International Journal of Applied Research and Studies*, 2(8): 1-12.
11. Majid, S.R. and A.K. Arof, 2007. Electrical behavior of proton-conducting chitosan-phosporic acid-based electrolytes. Physica B, 390: 209-215.
12. Shukur, M.F., R. Ithnin and M.F.Z. Kadir, 2014. Electrical properties of proton conducting solid biopolymer electrolytes based on starch-chitosan blend. *Ionics*, 20(7): 977-999.
13. Buraidah, M.H. and A.K. Arof, 20011. Characterization of chitosan/PVA blended electrolyte doped with NH4I. *Journal of Non-Crystalline Solids*, 357(16-17): 3261-3266.
14. Murata, K., S. Izuchi and Y. Yoshihisa, 2000. An overview of the research and development of solid polymer electrolyte batteries. *Electrochimica Acta*, 45: 1501-1508.
15. Wu, F., T. Feng, C. Wu, Y. Bai, L. Ye and J. Chen, 2010. Thermally stable hyperbranched polyether-based polymer electrolyte for lithium-ion batteries. *Journal of Physics D: Applied Physics*, 43(3): 035501.
16. Samsudin, A.S. and M.I.N. Isa, 2012. Structural and Electrical Properties of Carboxy Methylcellulose-Dodecyltrimethyl Ammonium Bromide-Based Biopolymer Electrolytes System. *International Journal of Polymeric Materials*, 61(1): 30-40.
17. Ravi, M., Y. Pavani, K. Kiran Kumar, S. Bhavani, A.K. Sharma, V.V.R. Narasimha Rao, 2011. Studies on electrical and dielectric properties of PVP:KBrO4 complexed polymer electrolyte film. *Materials Chemistry and Physics*, 130(1-2): 442-448.
18. Samsudin, A.S., J.J.P. Tham and M.I.N. Isa, 2013. Investigation of a Biodegradable Polymer Electrolytes Based on Carboxy Methylcellulose and its Potential Application in Solid-State Batteries. *Advanced Materials Research*, 802: 99-103.
19. Samsudin, A.S., M.I.N. Isa and N. Mohamad, 2011. New types of biopolymer electrolytes : Ionic conductivity study on CMC doped with NH_4Br. *Journal of current engineering research*, 1(1): 7-11.
20. Samsudin, A.S., W.M. Khairul and M.I.N. Isa, 2012. Characterization on the potential of carboxy methylcellulose for application as proton conducting biopolymer electrolytes. *Journal of Non-Crystalline Solids*, 358(8): 1104-1112.
21. Woo, H.J., S.R. Majid and A.K. Arof, 2011. Conduction and thermal properties of a proton conducting polymer electrolyte based on poly (ε-caprolactone). *Solid State Ionics*, 199-200: 14-20.

22. Ramly, K., M.I.N. Isa and A.S.A. Khiar, 2011. Conductivity and dielectric behaviour studies of starch/PEO+x wt-%NH4NO3 polymer electrolyte. *Materials Research Innovations*, 15(1): 82-85.
23. Basri, N.H. and N.S. Mohamed, 2009. Conductivity studies and dielectric behaviour of pvdf-hfp- pvc-liclo 4 solid polymer electrolyte. *Solid State Science and Technology*, 17(1): 63-72.
24. Chai, M.N. and M.I.N. Isa, 2012. Investigation on The Conduction Mechanism of Carboxyl Methylcellulose - Oleic Acid Natural Solid Polymer Electrolyte *International Journal of Advanced Technology & Engineering Research*, 2(6): 36-39.
25. Psarras, G.C., E. Manolakaki and G.M. Tsangaris, 2003. Dielectric dispersion and ac conductivity in-Iron particles loaded-polymer composites. *Composites Part A: Applied Science and Manufacturing*, 34(12): 1187-1198.
26. Basak, P., S.V. Manorama, Investigations on the mechanisms of ionic conductivity in PEO-PU/PAN semi-interpenetrating polymer network-salt complex polymer electrolytes: An impedance spectroscopy study. *The Journal of Physical Chemistry B*, 109(3): 1174-1182.
27. Kamarudin, K.H. and M.I.N. Isa, 2013. Structural and DC Ionic conductivity studies of carboxy methylcellulose doped with ammonium nitrate as solid polymer electrolytes. *International Journal of Physical Sciences*, 8(31): 1581-1587.
28. Buraidah, M.H., L.P. Teo, S.R. Majid, A.K. Arof, 2009. Ionic conductivity by correlated barrier hopping in NH4I doped chitosan solid electrolyte. *Physica B: Condensed Matter*, 404(8-11): 1373-1379.
29. Akgul, U., Z. Ergin, M. Sekerci, Y. Atici, 2008. AC conductivity and dielectric behavior of [Cd(phen)2(SCN)2]. *Vacuum*, 82: 340-345.
30. Mansour, S.A., I.S. Yahia and F. Yakuphanoglu, 2010. The electrical conductivity and dielectric properties of C.I. Basic Violet 10. *Dyes and Pigments*, 87(2): 144-148.
31. Hegab, N.A. and H.M. El-mallah, 2009. AC Conductivity and Dielectric Properties of Amorphous Te 42 As 36 Ge 10 Si 12 Glass. *Acta Physica Polonica A*, 116(6): 1048-1052.
32. El-deen and L.M. Sharaf, 2000. The ac conductivity studies for Cu2O-Bi2O3 glassy system. *Materials Chemistry and Physics*, 65: 275-281.
33. Mott, N., 1968. Conduction in glasses containing transition metal ions. *Journal of non-crystalline solids*, 1: 1-17.
34. Psarras, G.C., 2006. Hopping conductivity in polymer matrix – metal particles composites. *Composites: Part A*, 37: 1545-1553.