

STUDIES OF IONIC CONDUCTIVITY AND A.C. CONDUCTION MECHANISM OF 2-HYDROXYETHYL CELLULOSE BASED SOLID POLYMER ELECTROLYTES

NUR HAFIZA MR MUHAMARUESA AND MOHD IKMAR NIZAM MOHD ISA*

Advanced Materials Team, Ionic State Analysis (ISA) Laboratory, School of Fundamental Science, Universiti Malaysia Terengganu, 21030 Kuala Nerus, Terengganu, Malaysia.

*Corresponding author: ikmar_isa@umt.edu.my

Abstract: Solid polymer electrolyte (SPE), which contained of 2-hydroxyethyl cellulose (2-HEC) and ammonium nitrate (NH_4NO_3), was prepared using solution casting method. The ionic conductivity and a.c. conduction mechanism of the SPE was analysed using electrical impedance spectroscopy (EIS). The highest ionic conductivity of $(4.51 \pm 0.10) \times 10^{-4} \text{ Scm}^{-1}$ was achieved for film containing 12 wt.% of NH_4NO_3 . The temperature dependence of exponent s was observed to be almost independent of temperature. This conduction mechanism study of 2-HEC- NH_4NO_3 SPE was proven to follow quantum mechanical tunneling (QMT) model.

Keywords: Solid polymer electrolytes, 2-hydroxyethyl cellulose, ammonium nitrate, ionic conductivity, quantum mechanical tunneling.

Introduction

In recent year, solid polymer electrolytes (SPE) have received numerous studies as they show good potential for application in energy storage system (Yusof *et al.*, 2014). In contrast to liquid electrolyte, SPE promises excellent mechanical stability, leakage free, lightweight, flexibility in design and ease of production, which is in great demand for battery technology (Hafiza *et al.*, 2014; Tiruye *et al.*, 2016).

2-Hydroxyethyl cellulose (2-HEC) has been chosen as the polymer host in this SPE system. 2-HEC is derived from cellulose and known as water-soluble polymer. This polymer is widely used in cosmetic, industrial application, pharmaceuticals products, as well as thickening and stabilizing agents (Abdel-Halim, 2014). In fact, organic polymer is usually known as insulator based electronic component which gives the lowest ionic conductivity value (10^{-12} - $10^{-18} \text{ Scm}^{-1}$) (Hafiza & Isa, 2014). With the addition of ammonium nitrate in different composition (in wt.%), it is expected can enhance the ionic conductivity value.

In this study, the influence of NH_4NO_3 compositions on the ionic conductivity of 2-HEC

SPE is reported and the conduction mechanism involved in the system is also investigated.

Method

2.00 g of 2-HEC powder (Sigma-Aldrich) was dissolved in 100 ml of distilled water. Different amount of NH_4NO_3 (4-24 wt.%) were added into the solution and stirred until homogenous. The solution of 2-HEC- NH_4NO_3 SPEs were casted into different petri dishes and dried in the oven at 50 °C.

For film characterization, the nature of SPE can be determined from X-ray diffraction (XRD) analysis using Rigaku MiniFlex II diffractometer equipped with an X'celerator using Cu K α radiation in the range of 5° to 75°. The ionic conductivity, σ of SPE was characterized using HIOKI 3532-50 LCR Hi-Tester that interfaced to a computer in the frequency range of 50 Hz to 1 MHz. The σ was calculated using Eq. 1 (Khairul *et al.*, 2014; Shukur *et al.*, 2013),

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

where A is area of electrode-electrolyte contact, t is thickness of SPE and R_b is bulk resistance

which obtained from interception of negative imaginary impedance, $-Z_i$ vs. real impedance, Z_r .

Result and Discussion

Figure 1 presents the variation of ionic conductivity and activation energy as a function of NH_4NO_3 composition. The activation energy was calculated using the Arrhenius equation as

follow:

$$\sigma = \sigma_o \exp^{-E_a/kT} \quad (2)$$

where σ is the conductivity of the sample at room temperature (Scm^{-1}), σ_o is the pre-exponential factor, E_a is the activation energy, k is the Boltzman constant and T is the value of temperature that measured in kelvin (K) (Bakar *et al.*, 2015).

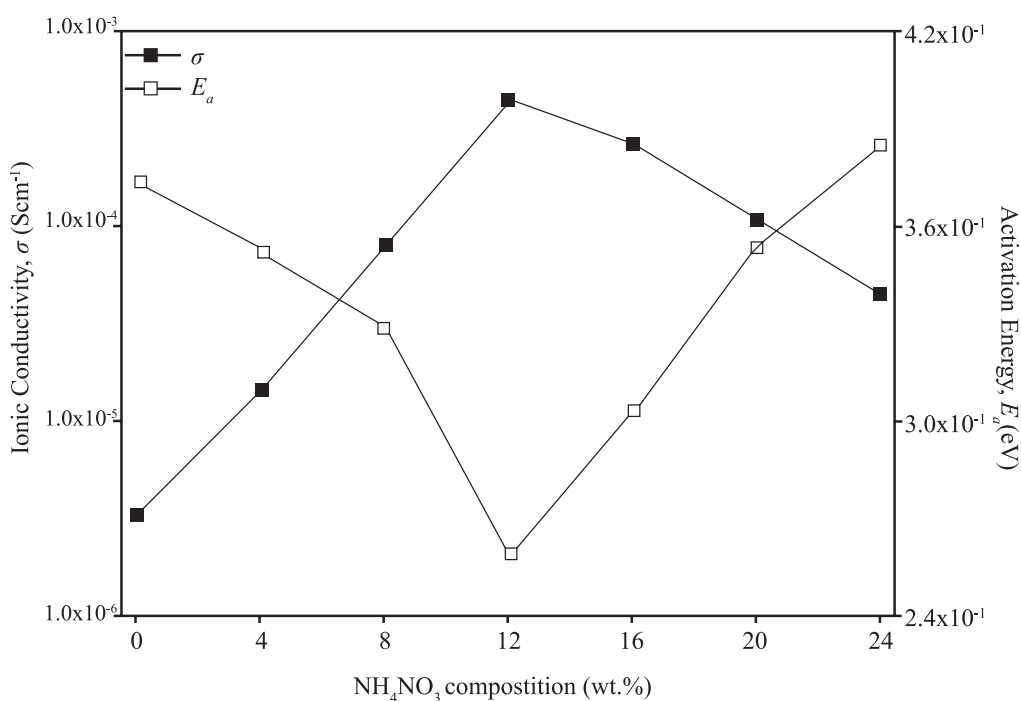


Figure 1: Ionic conductivity and activation energy of 2-HEC- NH_4NO_3 SPEs at room temperature

In Figure 1, the ionic conductivity of free salt SPE is $(3.33 \pm 0.05) \times 10^{-6} \text{ Scm}^{-1}$, and increased to $(4.51 \pm 0.10) \times 10^{-4} \text{ Scm}^{-1}$ for 12 wt.% NH_4NO_3 SPE. The increase of ionic conductivity with the addition of NH_4NO_3 may be attributed to the increase in number of charge carrier and amorphous nature (Hema *et al.*, 2009; Kamarudin & Isa, 2013). As expected, the addition of NH_4NO_3 has increased the amorphous nature of SPE as proven from XRD analysis (Figure 2) where the highest conducting SPE has the highest amorphous nature (corresponding to the lowest crystallite size value, L). The increase of amorphousity and ionic conductivity is due to the reduction

of energy barrier which lead to decrease in activation energy. This causes high ion mobility through the system and so does the ionic conductivity (Fonseca *et al.*, 2006; Khairul *et al.*, 2014). In contrary, the subsequent decrease of ionic conductivity at above 12 wt.% NH_4NO_3 may be due to the decrease in amorphous nature (corresponding to the increase of crystallite size value, L) and overcrowded of ions which tend to form ion cluster thus limits the ion migration through the SPE system (Fonseca *et al.*, 2006; Hema *et al.*, 2009). This study is in agreement with the fact that lower activation energy is desirable to promote ionic conductivity to higher value (Samsudin *et al.*, 2012).

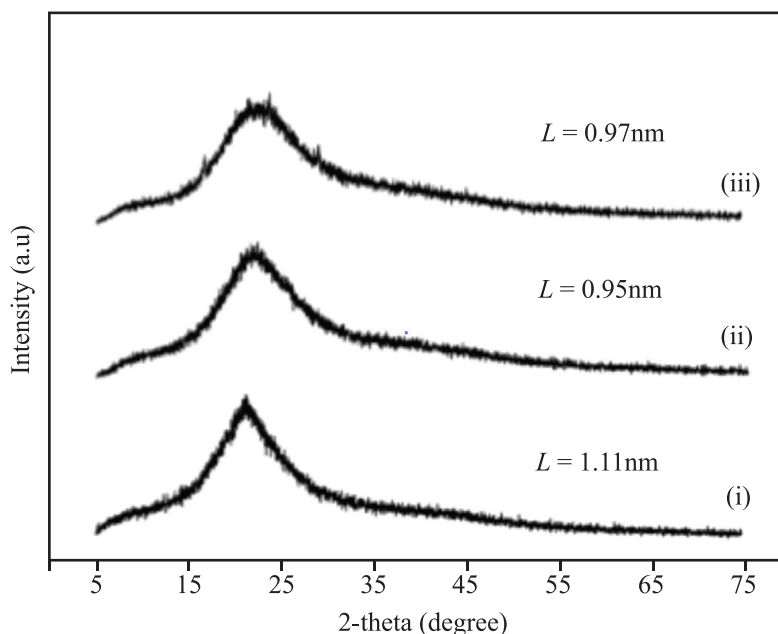


Figure 2: XRD spectrum and crystallite size, L for i) 0 wt.% NH_4NO_3 SPE, ii) 12 wt.% NH_4NO_3 SPE and iii) 24 wt.% NH_4NO_3 SPE at room temperature

Figure 3 represents the frequency dependence of dielectric loss for the highest conducting SPE. As observed in Figure 3, it shows the value of dielectric loss is very high at low frequency and decrease as the frequency increased thereafter, it becomes constant at higher frequency applied. In low frequency region ($5 < \ln \omega < 12$), the decrement of dielectric loss is attributed to space charge polarization and electrode polarization. Space charge occurs when there is more than one phase having different conductivities present in the same material, while electrode polarization arises due to accumulation of ions at electrode-electrolyte interface (Buraidah *et al.*, 2009; Bakar *et al.*, 2015). In high frequency region ($12 < \ln \omega < 16$), the direction of electric field changes at a faster rate, which causes the reduction of electrode polarization as well as the decrease in dielectric loss to a constant value (Bhide & Hariharan, 2007; Khair & Arof, 2010).

The study of a.c. conduction mechanism is performed to explain the hopping process occurred in between two sites of 2-HEC and NH_4NO_3 at minimum effect of polarization (El Mkami *et al.*, 2000; Buraidah *et al.*, 2009). The value of exponent s is obtained from the slope of $\ln \epsilon_i$ against $\ln \omega$. From the plot of s against T (Figure 4), a small gradient value of s obtained from the fitting equation of $s = 0.00006x + 0.02099$ is independent with temperature. This indicates that the ionic conduction of 2-HEC- NH_4NO_3 SPE is accompanied by quantum mechanical tunneling (QMT) model. This result is comparable to other polymer-salt system (Majid & Arof, 2007; Buraidah & Arof, 2011; Shukur *et al.*, 2013; Hafiza & Isa, 2014). In quantum mechanical phenomenon, the polaron which is made up of conducting proton together with their stress fields, are attempting to travel and tunnels through the potential barrier that exist between two possible complexion sites with the addition of NH_4NO_3 in the present SPE system (Shukur *et al.*, 2013).

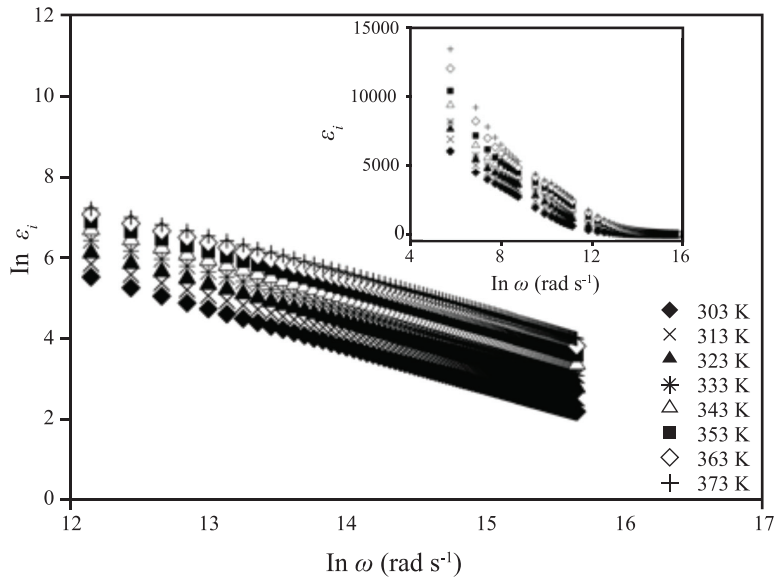


Figure 3: Frequency dependence of $\ln \epsilon_i$ at elevated temperatures for the highest conducting SPE

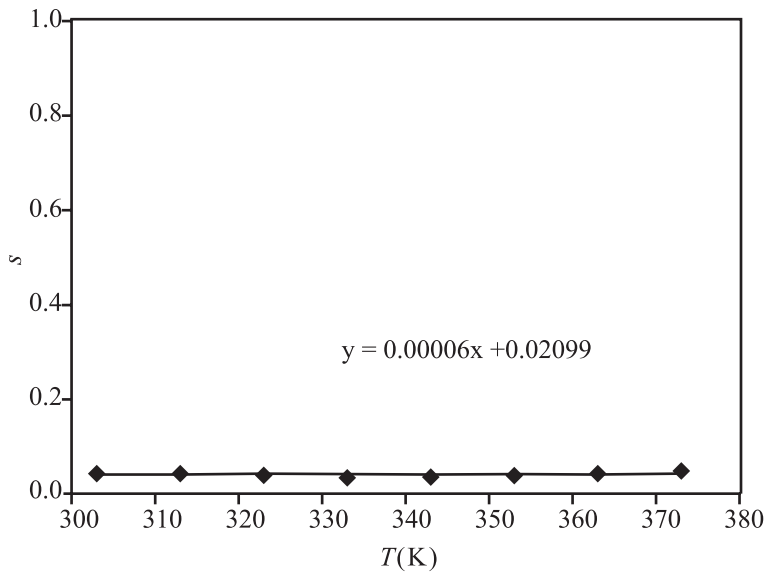


Figure 4: Temperature dependence of exponent s for the highest conducting SPE

Conclusion

Solid polymer electrolytes (SPEs) based on 2-hydroxyethyl cellulose (2-HEC) incorporated with different compositions of ammonium nitrate (NH_4NO_3) were successfully prepared using solution casting technique. The ionic conductivity was significantly increased to $(4.51 \pm 0.10) \times 10^{-4} \text{ Scm}^{-1}$ with the addition of 12- NH_4NO_3 SPE. The ionic conductivity enhancement was found to be influenced by the amorphous nature of the SPE and due to the decrease in activation energy. The a.c. conduction mechanism study showed the plot of exponent s is independent to temperature and best explained by QMT model.

Acknowledgements

The authors would like to acknowledge Ministry of Higher Education Malaysia (MOHE) for ERGS (vot. 55101) and FRGS (vot. 59319 & vot. 59452) grant, MyBrain15 for MyPhD scholarship awarded and Advanced Materials Team for the endless supports given.

References

- Abdel-Halim, E. S. (2014). Chemical modification of cellulose extracted from sugarcane bagasse: Preparation of hydroxyethyl cellulose. *Arabian Journal of Chemistry*, 7(3): 362-371.
- Bakar, N. Y., Hafiza, M. N., Bashirah, A. N. A., & Isa, M. I. N. (2015). Electrical studies of carboxy methylcellulose-chitosan blend biopolymer doped dodecyltrimethyl ammonium bromide solid electrolytes. *American Journal of Applied Sciences*, 12(1): 40-46.
- Bhide, A., & Hariharan, K. (2007). Ionic transport studies on $(\text{PEO})_6 \cdot \text{NaPO}_3$ polymer electrolyte plasticized with PEG_{400} . *European Polymer Journal*, 43(10): 4253-4270.
- Buraidah, M. H., & Arof, A. K. (2011). Characterization of chitosan/PVA blended electrolyte doped with NH_4I . *Journal of Non-Crystalline Solids*, 357(16-17): 3261-3266.
- Buraidah, M. H., Teo, L. P., Majid, S. R., & Arof, A. K. (2009). Ionic conductivity by correlated barrier hopping in NH_4I doped chitosan solid electrolyte. *Physica B: Condensed Matter*, 404(8-11): 1373-1379.
- El Mkami, H., Deroide, B., Backov, R., & Zanchetta, J. V. (2000). Dc and ac conductivities of $(\text{V}_2\text{O}_5)_x(\text{B}_2\text{O}_3)_{1-x}$ oxide glasses. *Journal of Physics and Chemistry of Solids*, 61: 819-826.
- Fonseca, C. P., Rosa, D. S., Gaboardi, F., & Neves, S. (2006). Development of a biodegradable polymer electrolyte for rechargeable batteries. *Journal of Power Sources*, 155(2): 381-384.
- Hafiza, M. N., Bashirah, A. N. A., Bakar, N. Y., & Isa, M. I. N. (2014). Electrical properties of carboxyl methylcellulose/chitosan dual-blend green polymer doped with ammonium bromide. *International Journal of Polymer Analysis and Characterization*, 19(2): 151-158.
- Hafiza, M. N., & Isa, M. I. N. (2014). Ionic conductivity and conduction mechanism studies of cmc/chitosan biopolymer blend electrolytes. *Research Journal of Recent Sciences*, 3(11): 50-56.
- Hema, M., Selvasekarapandian, S., Arunkumar, D., Sakunthala, A., & Nithya, H. (2009). FTIR, XRD and ac impedance spectroscopic study on PVA based polymer electrolyte doped with NH_4X (X= Cl, Br, I). *Journal of Non-Crystalline Solids*, 355(2): 84-90.

- Kamarudin, K. H., & Isa, M. I. N. (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.
- Khairul, W. M., Isa, M. I. N., Samsudin, A. S., Adli, H., & Ghazali, S. (2014). Conductive biodegradable film of *N*-octyloxyphenyl-*N'*-(4-methylbenzoyl) thiourea. *Bulletin of Materials Science*, 37(2): 357-369.
- Khiar, A. S. A., & Arof, A. K. (2010). Conductivity studies of starch-based polymer electrolytes. *Ionics*, 16(2): 123-129.
- Majid, S. R., & Arof, A. K. (2007). Electrical behavior of proton-conducting chitosan-phosphoric acid-based electrolytes. *Physica B: Condensed Matter*, 390(1-2): 209-215.
- Samsudin, A. S., Khairul, W. M., & Isa, M. I. N. (2012). Characterization on the potential of carboxy methylcellulose for application as proton conducting biopolymer electrolytes. *Journal of Non-Crystalline Solids*, 358(8): 1104-1112.
- Shukur, M. F., Ithnin, R., Illias, H. A., & Kadir, M. F. Z. (2013). Proton conducting polymer electrolyte based on plasticized chitosan-PEO blend and application in electrochemical devices. *Optical Materials*, 35(10): 1834-1841.
- Tiruye, G. A., Muñoz-Torrero, D., Palma, J., Anderson, M., & Marcilla, R. (2016). Performance of solid state supercapacitors based on polymer electrolytes containing different ionic liquids. *Journal of Power Sources*.
- Yusof, Y. M., Illias, H. A., & Kadir, M. F. Z. (2014). Incorporation of NH_4Br in PVA-chitosan blend-based polymer electrolyte and its effect on the conductivity and other electrical properties. *Ionics*, 20(9): 1235-1245.