

Study on ionic conduction of solid bio-polymer hybrid electrolytes based carboxymethyl cellulose (CMC)/polyvinyl alcohol (PVA) doped NH_4NO_3

M. A. Saadiah, and A. S. Samsudin

Citation: [AIP Conference Proceedings](#) **2030**, 020223 (2018); doi: 10.1063/1.5066864

View online: <https://doi.org/10.1063/1.5066864>

View Table of Contents: <http://aip.scitation.org/toc/apc/2030/1>

Published by the [American Institute of Physics](#)

AIP | Conference Proceedings

Get **30% off** all
print proceedings!

Enter Promotion Code **PDF30** at checkout



Study on Ionic Conduction of Solid Bio-polymer Hybrid Electrolytes Based Carboxymethyl Cellulose (CMC)/ Polyvinyl Alcohol (PVA) Doped NH_4NO_3

M A Saadiah^{1,2} and A S Samsudin^{2,a)}

¹*Department of Chemistry, Centre for Foundation Studies, International Islamic University Malaysia, 26300 Gambang, Pahang*

²*Advanced Materials Group, Faculty of Industrial Sciences & Technology, Universiti Malaysia Pahang, 26300 Kuantan, Pahang Malaysia*

^{a)}Corresponding author: ahmadsalihin@ump.edu.my

Abstract. Carboxymethyl cellulose (CMC)/ polyvinyl alcohol (PVA) blend (80/20 wt %) as host solid bio-polymer electrolytes complexed with different weight percentage ratios of NH_4NO_3 were prepared via solution casting approach. Impedance spectroscopy was carried out to disclose the electrical response of the CMC/PVA hybrid electrolytes as a function of various weight percentage of NH_4NO_3 salt. It is found that the CMC/PVA blend complexed with 30 wt % of NH_4NO_3 was demonstrated relatively higher room temperature conductivity by the order of 10^{-4} S/cm. The dielectric behaviour has been analyzed via complex permittivity (ϵ^*) and complex modulus (M^*) which varies anomalously with percentage of NH_4NO_3 confirms the non-Debye behaviour. Besides that, the temperature dependent dc conductivity of polymer electrolyte seems to obey Arrhenius relation, and the activation energies decrease with an increase in NH_4NO_3 . Thus, confirming their potential as promising candidates of all-solid-state proton conducting electrolyte in the electrochemical devices.

INTRODUCTION

Progress in the area of green energy storage devices is intimately linked with the enhancement in the ionic conductivity. Therefore, prior importance is given to the application of bio-material in the development of polymer hybrid system which aims at environmental benignancy and sustainable sources. The increasing demand in the application of low cost and eco-friendly material has gained immense significance such as carboxymethyl cellulose (CMC) [1, 2]. Another abundant of biodegradable polymer including carrageenan [3, 4], alginate [5, 6], polyhydroxyalkanoate (PHA) [7] and polyvinyl alcohol (PVA) [8, 9] are commonly used in the preparation of bio-polymer electrolyte system. However, carboxymethyl cellulose (CMC), the earth abundance material can be regarded as the most outstanding bio-polymer due to its superior chemical stability, thermostability biodegradability, and biocompatibility [10]. Besides, PVA is also widely used as a bio-polymer electrolyte due to hydrophilic properties, non-hazardous, biocompatibility and biodegradability [11]. Therefore, CMC and PVA have potential towards the development of solid bio-polymer hybrid electrolytes (BHEs).

However, the conductance ability of the solid bio-polymer hybrid electrolyte was relatively lower, thus enormous effort has been devoted to boost the ionic conductivity [12, 13]. Among these, the doping of acid, base and salt into a polymer electrolyte system is found to be the simplest approach for the modification of chain flexibility and polymer-polymer chain interactions [14, 15]. This will improve the segmental motion within the polymer by creating free volume. Consequently, the ions can migrate more easily which will in turn increase the ionic conductivity [16]. Ammonium salt (NH_4^+) is considered as a good proton donor in order to develop proton conduction process [17]. A study on the incorporation of 50 wt % of ammonium thiocyanate (NH_4SCN) into cellulose acetate gives conductivity value of 3.31×10^{-3} S/cm [18]. Another research on blending polyvinyl alcohol, poly (N-vinyl pyrrolidone and L-Asparagine doped with ammonium bromide (NH_4NO_3)) which suggest that the proton conducting polymer blend system has conductivity of 2.34×10^{-4} S/cm [19]. Another study on

the proton conducting polymer electrolyte based on potato starch complexed with ammonium iodide (NH₄I) reported a conductivity value of 2.40 x 10⁻⁴ S/cm [20].

Herein, the present work is to report the enhancement in electrical properties of proton conducting polymer blend system comprising bio-material of CMC blend with PVA and doped by various amount of ionic dopants namely ammonium nitrate (NH₄NO₃). In this regard, the proton conducting bio-polymer hybrid electrolytes are characterized via Electrochemical Impedance Spectroscopy (EIS) for electrical properties. Notably, to date, there is no report on the application of NH₄NO₃ into the hybrid electrolyte system of CMC/PVA which is expected to overcome the limitation in conductivity. Indeed, this proton conducting BHEs system holds great promise in the long perspective of electrochemical device where low cost alternatives and green energy storage materials are desirable.

METHODS

Carboxymethyl cellulose (CMC)/ polyvinyl alcohol (PVA) hybrid (80/20 wt %) as host solid bio-polymer electrolytes complexed with different weight percentage ratios of NH₄NO₃ were prepared via solution casting approach [21]. Various percentage of NH₄NO₃ as ionic dopants was added into 98 mL of CMC/PVA solution with the interval of 5 wt %. The solution has been casted into Petri dishes and left to dry in desiccator containing silica gel to avoid moisture. The composition of the CMC and PVA used is shown in Table 1.

TABLE 1. List of designation of the BHEs with their composition respectively.

Sample Notation	NH ₄ NO ₃ (%)
D0	0
D1	5
D2	10
D3	15
D4	20
D5	25
D6	30
D7	35
D8	40

Electrochemical Impedance Analysis (EIS)

A computer-controlled HIOKI 3532-50 LCR Hi-Tester with applied frequency ranges from 50 Hz to 1 MHz was used to investigate the dielectric characterization of the proton conducting BHEs system from temperature 303 K to 353 K. The sample was cut in circular shape of 2 cm diameter, sandwiched between two stainless steel electrodes and the measurements were taken in every 10 K interval. The bulk resistance (R_b) value was obtained from the plot of imaginary impedance (Z_i) versus real impedance (Z_r) enable the calculation of ionic conductivity, σ determined using equation (1) below:

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

Where y is a thickness of the sample and A (cm²) the cross-sectional area of the BHE film.

Complex permittivity (ϵ^*)

Complex permittivity is important to explain the mechanism and interactions of ions in the BHEs system [22]. The complex permittivity can be defined as:

$$\epsilon^* = \epsilon_r + j\epsilon_i \quad (2)$$

where ϵ_r is the dielectric constant (real part of complex permittivity) that define the ability as stored charges in a material while ϵ_i is the dielectric loss (imaginary of complex permittivity) that measure the energy loss to move ions under applied electric field. Both terms can be calculated using equation as follows:

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

$$\varepsilon_i = \frac{Z_r}{\omega C_o(Z_r^2 + Z_i^2)} \quad (4)$$

Complex modulus (M^)*

The complex modulus is highlighted as a key tool to provide a prospect in the investigation of relation process in solid polymer electrolyte [23]. The real modulus, M_r , and imaginary modulus, M_i was calculated using the equation (5) and (6) respectively:

$$M_r = \frac{\varepsilon_r}{(\varepsilon_r^2 + \varepsilon_i^2)} \quad (5)$$

$$M_i = \frac{\varepsilon_i}{(\varepsilon_r^2 + \varepsilon_i^2)} \quad (6)$$

RESULTS AND DISCUSSION

Numerous approaches on ionic conductivity enhancement of solid bio-polymer hybrid electrolyte including doping technique are applied. Un-doped polymer electrolyte usually offers relatively lower conductivity, making doped polymer electrolyte become more favourable in terms of conductance ability. The conductivity measurement of CMC/PVA BHE system doped NH_4NO_3 has been carried out via impedance spectroscopy where impedance spectrum is beneficial to analyze the microstructural behaviour of the polymer electrolyte system [24]. Figure 1 corresponds to the conductance plot for all composition of the BHEs system in this work. The plot elucidates the real part of *ac* conductivity obtained through the impedance measurement as a function of frequency [25, 26]. The conductance plot confirms the occurrence of three distinct regions which are the low frequency spike, medium frequency plateau and spike at higher frequency [27]. The spike observed at low frequency region for sample D2 until D8 is due to the space charge polarization happen at the electrode-electrolyte inter-phase. On the other hand, the spike appeared at high frequency is attributed to the bulk relaxation phenomenon and shown by sample D0 and D1 whereas the plateau region is the frequency independent connected with the *dc* conductivity of the BHEs [28].

The plot ionic conductivity dependency on the NH_4NO_3 salt concentration for different composition is presented in Figure 2. Salt NH_4NO_3 was incorporated to the blend electrolyte in order to supply the charge (H^+) carriers for the conduction enhancement [29]. The result of this work show good correlation where conductivity increases from 9.12×10^{-6} S/cm to 1.70×10^{-3} when 30 wt. % of NH_4NO_3 was added. The increment is predominantly governed by the presence of free NH_4^+ that is interacted with the polar group of the host hybrid polymer, CMC/PVA. Afterwards, addition of NH_4NO_3 above 30 wt. % causes the conductivity to drop which can ascribed to the overcrowded or saturated of ions which leads to salt aggregation and decreasing the ion mobility [30, 31].

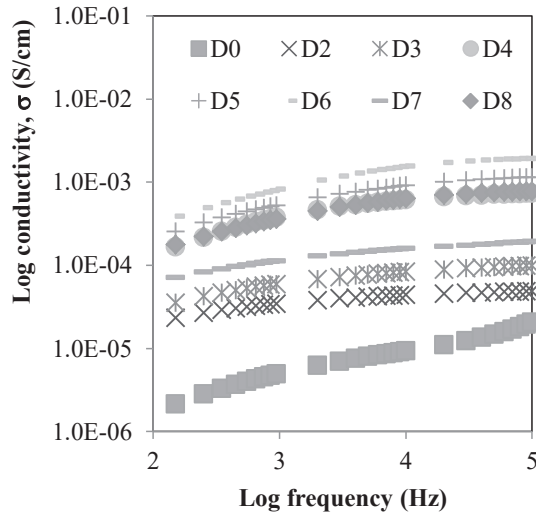


FIGURE 1. Cole-Cole plot for all compositions of CMC/PVA-NH₄NO₃ BHEs system.

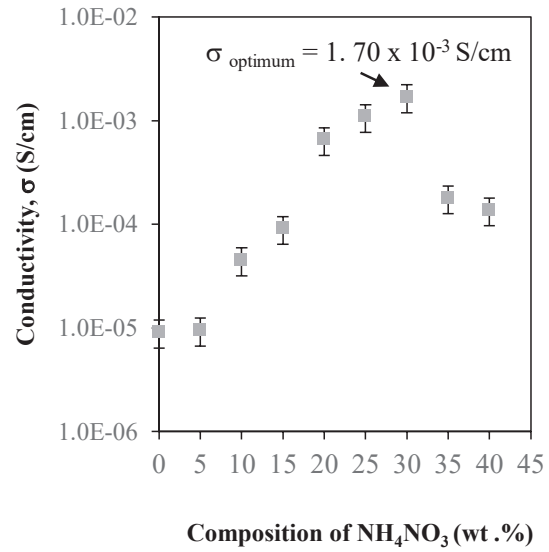


FIGURE 2. Conductivity value of CMC/PVA doped NH₄NO₃ at ambient temperature.

Figure 3 shows the temperature dependence ionic conductivity for all composition of the BHEs system. Noted from the figure, the linear variation of the reciprocal temperature ($1000/T$) against log conductivity reveals the BHEs system in this work has R^2 closed to unity ($R^2 \sim 1$). Therefore, the system is said to be thermally activated based on Arrhenius behavior and in accordance to the following equation;

$$\sigma = \sigma_0 \exp \left(\frac{-E_a}{kT} \right) \quad (7)$$

where σ is the conductivity, σ_0 is pre-exponential factor, E_a is activation energy and k is Boltzmann constant. Further analysis on activation energy can be calculated from the Arrhenius plot and presented in Figure 4. The activation energy can be determined from the slope of the Arrhenius plot and is found to be 0.086 eV for the highest conducting BHEs system [32]. It is well known that, as the activation energy decreases, the energy barrier for the ion to transport also decreases and hence increases the conductivity [33]. Besides, a decrease in activation energy in blend electrolyte system is due to shorter transit sites contributed by PVA [34].

Ironically, polar compounds able to exhibit the dielectric dispersion properties when applied under certain range of electric field [35]. The dielectric behavior of the BHEs system brings important insights into the amount of charge stored in a material. Figure 5 (a) and (b) depicts the dielectric constant (ϵ_r) and dielectric loss (ϵ_i) for various composition of NH₄NO₃. Effect of electrode polarization and space charge and causes both ϵ_r and ϵ_i to increase sharply at lower frequency. It is observed that the highest ϵ_r and ϵ_i are given by the highest conducting BHEs system containing 30 wt. % of NH₄NO₃ which implies on increment of charge accumulation that leads to the increment of the equivalent capacitance [36, 37]. The dielectric plots indicates that there is no appreciable relaxation peaks can observed in the frequency regime employed in the present work, and confirming the non-Debye nature.

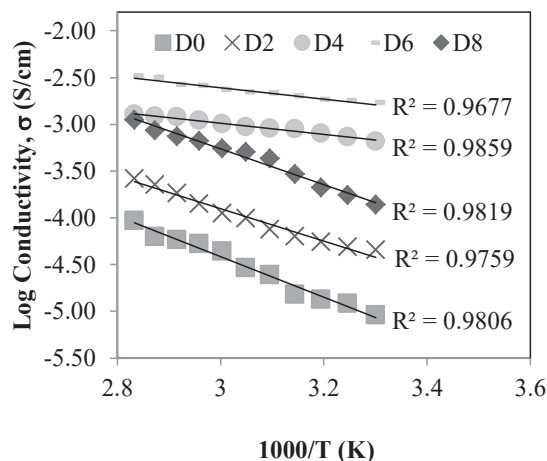


FIGURE 3. Variation of conductivity with temperature dependence for various compositions of CMC/PVA-NH₄NO₃ BHEs system.

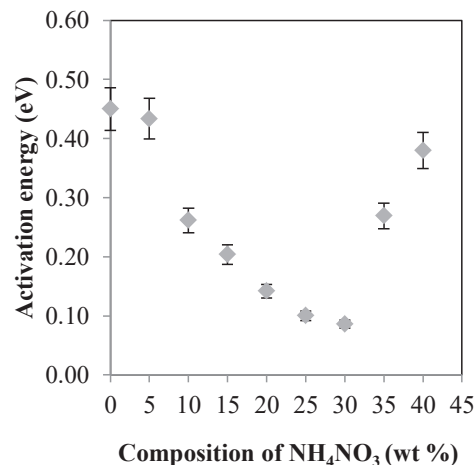


FIGURE 4. Activation energy of CMC/PVA-NH₄NO₃ BHEs system.

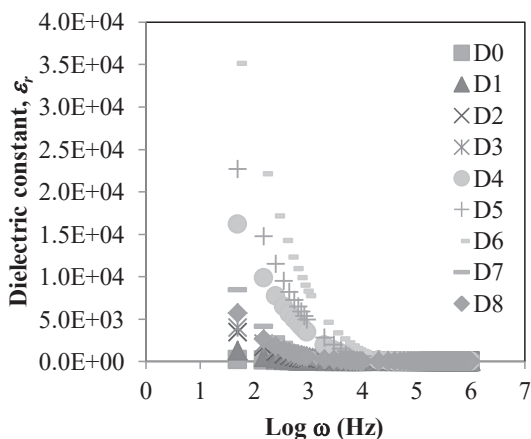


FIGURE 5(a). Dielectric constant for all composition of CMC/PVA-NH₄NO₃ BHEs system.

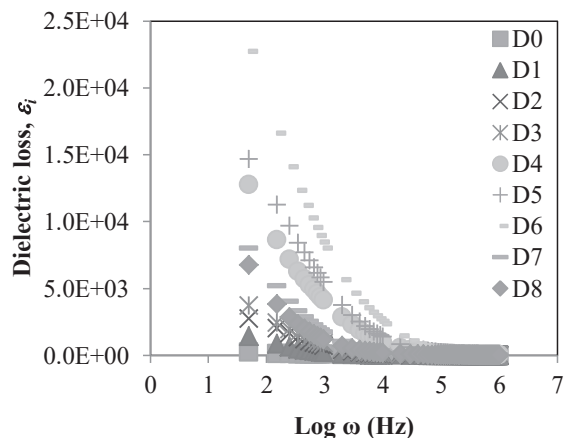


FIGURE 5(b). Dielectric loss for all composition of CMC/PVA-NH₄NO₃ BHEs system.

The dielectric moduli of real modulus (M_r) and imaginary modulus (M_i) are shown in figure 6(a) and (b) respectively. Both M_r and M_i plots show a plateau or approaches to zero at lower frequency and start to increase at higher frequency. At low frequency, both M_r and M_i almost approaching zero for all composition ascribed by the high capacitance triggered by the electrode polarization, and this result is similar with previous researcher [38].

There is no appearance of peak in the M_r and M_i plot which could be due phenomenon where the real part of complex modulus (M^*) resembles of the real part of complex permittivity (ϵ^*) [23]. Upon the addition of NH₄NO₃ conductivity increases attributed to the short range movement of charge carriers and causes lower peak or plateau at higher frequency indicated shorter relaxation time.

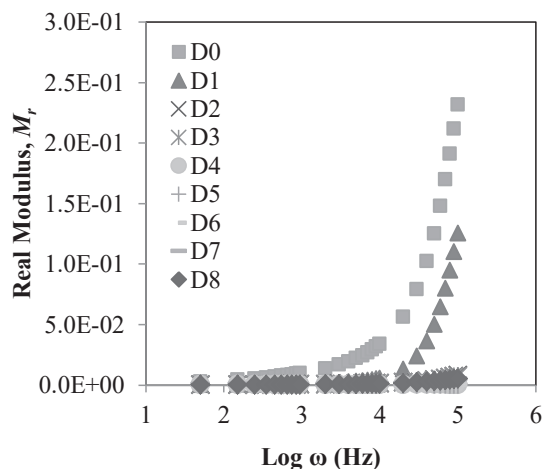


FIGURE 6(a). Real modulus for all composition of CMC/PVA-NH₄NO₃ BHEs system.

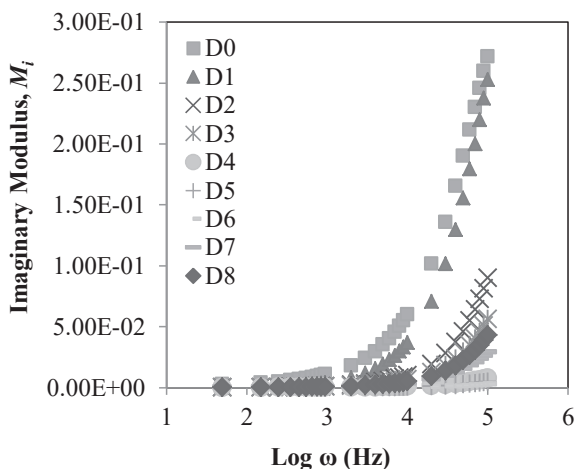


FIGURE 6(b). Imaginary modulus for all composition of CMC/PVA-NH₄NO₃ BHEs system.

CONCLUSION

Solid bio-polymer electrolyte CMC/PVA doped NH₄NO₃ was exposed to 50 Hz until 1 MHz of electric field at elevated temperature 303 K to 353 K. This study shows that:

- The modification of the BHEs using NH₄NO₃ able to increase the conductivity from $\sim 10^{-6}$ to $\sim 10^{-3}$ S/cm. The enhancement of ionic conductivity ascribed to the movement of charges (H⁺) carrier provided by the NH₄⁺ salt.
- Variation in ionic conductivity as a function of temperature exhibits Arrhenius law.
- The result of activation energy is found to be inversely related to the conductivity.
- The conductivity and dielectric constant pursue parallel trend with increasing NH₄NO₃ composition.
- The dielectric and modulus formalism confirmed the non-Debye nature of the BHEs system in this work.
- The BHEs system study in this work can be improvised by the addition of plasticizer to assist the solvation of the salt.

ACKNOWLEDGEMENT

The authors would like to express gratitude to Ministry of Higher Education for FRGS (RDU170115), Faculty of Industrial Sciences and Technology, University Malaysia Pahang, for the help and support given for the completion of this research.

REFERENCES

1. N. H. Ahmad and M. I. N. Isa, *Carbohydr. Polym.* **137**, (2016), pp. 426-432.
2. Francesca Colò, Federico Bella, R. Jijeesh Nair, Matteo Destro and Claudio Gerbaldi, *Electrochim. Acta* **174**, (2015), pp. 185-190.
3. V. Moniha, M. Alagar, S. Selvasekarapandian, B. Sundaresan and G. Boopathi, *J. of Non-Cryst. Solids* **481**, (2018), pp. 424-434.
4. N.K. Zainuddin and A.S. Samsudin, *Mater. Today Communications* **19**, (2018), pp. 199-209.
5. S. D. Pasini Cabello, S. Mollá and N. A. Ochoa, J. Marchese, E. Giménez, V. Compañ, *J. of Power Sources* **265**, (2014), pp. 345-355.
6. Kazunari Soeda, Masaki Yamagata and Masashi Ishikawa, *J. of Power Sources* **280**, (2015), pp. 565-572.
7. V. Dall'Asta, V. Berbenni, P. Mustarelli and E. Quartarone, *Electrochim. Acta* **247**, (2017), pp. 63-70.
8. A.L. Saroj, S. Krishnamoorthi and R.K. Singh, *J. Non-Cryst. Solids* **473**, (2017), pp. 87-95.
9. A. Alakanandana, A .R. Subrahmanyam and J. Siva Kumar, *Materials Today: Proceedings*, (2016), pp. 3680-3688.
10. Y. S. Zhu, S. Y. Xiao, M. X. Li, Z. Chang, F. X. Wang, J. Gao and Y. P. Wu, *J. Power Sources* **288**, (2015), pp. 368-375.

11. M. F. Z. Kadir, S. R. Majid and A. K. Arof, *Electrochim. Acta* **55**, (2010), pp. 1475-1482.
12. A. S. A. Khair and A. K. Arof, *Int. J. Math. Comput. Phys. Electr. Comput. Eng.* **5**, (2011), pp. 1662-1666.
13. M. N. Hafiza, A. N. A. Bashirah, N. Y. Bakar and M. I. N. Isa, *Int. J. Polym. Anal. Charact.* **19**, (2014), pp. 151-158.
14. S. Monisha, T. Mathavan, S. Selvasekarapandian, A. Milton Franklin Benial, G. Aristatil, N. Mani and D. Vinoth Pandi, *Carbohydr. Polym.* **157**, (2017), pp. 38-47.
15. M. I. H. Sohaimy and M. I. N. Isa, *Polym. Bull.* **16**, (2016), pp. 1031-1034.
16. R. A. Senthil, J. Theerthagiri and J. Madhavan, *J. Phys. Chem. Solids* **89**, (2016), pp. 78-83.
17. M. Kumar and S.S. Sekhon, *Eur. Polym. J.* **38**, (2002), pp. 1297-1304.
18. S. Monisha, S. Selvasekarapandian, T. Mathavan, A. Milton Franklin Benial, Sinddhuja Manoharan and S. Karthikeyan, *J. Mater. Sci. Mater Electron.* **27**, 9314 (2016).
19. V. Parameswaran, N. Nallamuthu, P. Devendran, E.R. Nagarajan and A. Manikandan, *Physica B: Condensed Matter* **515**, (2017), pp. 89-98.
20. M. Kumar, T. Tiwari and N. Srivastava, *Carbohydr. Polym.* **88**, (2012), pp. 54-60.
21. M. A. Saadiah and A. S. Samsudin, "Electrical study on carboxymethyl cellulose-polyvinyl alcohol based bio-polymer blend electrolyte" (IOP Conference Series: Materials and Science Engineering, Forthcoming 2018), In-press
22. L. A. Utracki, "Polymer blends handbook" (Kluwer Academic Publishers, Dordrecht, 2002).
23. B. Gnansagar, N.L. Patel and F. S. Singh, *Mater. Sci. and Eng., B* **225**, (2017), pp. 150-159.
24. S. R. Majid and A. K. Arof, *Physica B: Condensed Matter* **355**, (2005), pp. 78-82.
25. T. M. W. J. Bandara, M. A. K. L. Dissanayake, I. Albinsson and B. E. Mellander, *Solid State Ionics* **189**, (2011), pp. 63-68.
26. M. Hema, S. Selvasekarapandian, A. Sakunthala, D. Arunkumar and H. Nithya, *Physica B* **403**, (2009), pp. 2740-2747.
27. P. Tamilselvi and M. Hema, *Physica B* **437**, (2013), pp. 53-57.
28. M. Siekierski and W. Wieczorek, J. Przyłuski, *Electrochim. Acta* **43**, (1998), pp. 1339-1342.
29. M. H. Hamsan, M. F. Shukur and M. F. Z. Kadir, *Ionic* **23**, 3429 (2017).
30. A. S. Samsudin and M. I. N. Isa, *J. App. Science* **12**, (2012), pp. 174-179.
31. N. H. Ahmad and M. I. N. Isa, *Adv. Mater. Res.* **1107**, (2015), pp. 247-252.
32. El-Sayed, S. Mahmoud, K.H., Fatah, A.A. and A. Hassen, *Physica B* **406**, (2011), pp. 4068-4076.
33. N. Y. Bakar, M.N. Hafiza, A. Bashirah and M. I. N. Isa, *American J. of Appl. Sci.* **12**, (2015), pp. 40-46.
34. M. H. Buraidah and A. K. Arof, *J. Non-Crys. Solids* **357**, (2011), pp. 3261-3266.
35. N. E. Hill, W. E. Vaughan, A. H. Price and M. Diaries, "Dielectric properties and molecular behaviour" (Van Nostrand Reinhold Co., London, 1969).
36. K. Ramly, M. I. N. Isa and A. S. A. Khair, *Mater. Res. Innovations* **15**, (2011), pp. 82-85.
37. S. Ramesh, A. H. Yahya and A. K. Arof, *Solid State Ionic* **152**, (2002), pp. 291-294.
38. M. I. N. Isa and A. S. Samsudin, *Int. J. Polym. Anal. Charact.* **22**, (2017), pp. 447-454.