A Novel Approach to Design High Resistive Polymer Electrolytes Based on PVC: Electrochemical Impedance and Dielectric Properties

Hwda Ghafur Rauf[1], Jihad M. Hadi[2], Shujahadeen B. Aziz[3,], Rebar T. Abdulwahid[3,4], Muhammed S. Mustafa[5]*

[1] Department of Medical Laboratory Science, College of Science, Komar University of Science and Technology, Sulaimani 46001, Kurdistan Regional Government, Iraq.
[2] Department of Medical Laboratory of Science, College of Health Sciences, University of Human Development, Kurdistan Regional Government, Iraq.
[3] Hameed Majid Advanced Polymeric Materials Research Lab., Physics Department, College of Science, University of Sulaimani, Qlyasan Street, Sulaimani 46001, Kurdistan Regional Government, Iraq.
[4] Department of Physics, College of Education, University of Sulaimani, Old Campus, Sulaimani 46001, Iraq.
[5] Department of Chemistry, College of Science, University of Sulaimani, Qlyasan Street, Sulaimani, Kurdistan Regional Government, Iraq.
[*]E-mail: shujahadeenaziz@gmail.com

In this work, a novel hypothesis is presented which reveals the possibility of using the concept of polymer electrolyte to design high resistive solid electrolytes. Solution casting methodology was used to fabricate solid polymer electrolytes (SPEs) based on PVC and doped with ammonium thiocyanate salt (NH$_4$SCN). The impact of ammonium thiocyanate salts on the PVC has been investigated using different quantities of salt. Various approaches have been used to characterize the electrochemical behavior of the films, like electrical impedance spectroscopy EIS, Bode plot, and dielectric properties. The EIS reveals an increase in ionic conductivity with increasing salt concentration and then dropped at the highest amount of salt due to ion aggregation. The uppermost conductivity of (2.86×10^{-8}) S/cm has attained for the electrolyte incorporated 20 wt.% of salt. Our hypothesis has been clarified regarding the shortcoming ionic conductivity of PVC-based polymer electrolytes at room temperature. Bode plots differentiate the reduction in resistance or impedance with increasing salt concentration. The complex dielectric permittivity for the samples verified a non-Debye type behavior. Moreover, rising both dielectric constant and dielectric loss at low-frequency regions were a clear indication of the increase in dielectric polarization of the films. The PVC-NH$_4$SCN system has a capacitive behavior, as demonstrated by the real part of the electric modulus. Ion conduction occurs through the viscoelastic relaxation dynamic, as evidenced by peaks appearance in the imaginary portion of the electric modulus.

1. INTRODUCTION

Over decades, polymer electrolytes (PEs) have been widely investigated by researchers across the world due to their significance in theoretical studies and possible application in many areas such as electrochemistry, polymer chemistry, inorganic and organic chemistry [1]. Electrochemical devices such as electrochromic display devices, energy conversion units like batteries and fuel cells, supercapacitors, photochemical solar cells, and sensors have all employed polymer electrolytes [2, 3]. The development of polymer electrolytes with excellent ionic conductivity is a vital objective in polymer research field [4]. Researchers have been fascinated by the preparation of solid polymer electrolytes (SPEs) due to their superior properties like weighing less, leak-proofed, and dryness [5]. In addition, SPE has been employed like a crucial material in a variety of solid-state electrochemical systems. To fabricate the SPEs, an inorganic salt is dissolved in the chain of polar polymers, which provides a path for free ions to make the polymers ionically conductive [6]. Poly (vinyl chloride) (PVC) as a host polymeric material is one of the most popular options due to its ease processing, cost-effectiveness, high affinity for solvents, and also its excellent mechanical and thermal properties. In addition, PVC has been found to be compatible with a wide range of additives [7]. The existence of the electron donor atoms in polymeric chain structure allows the formation of the polymer-salt complexes, which is crucial for a polymer to act as an ionic conductor. In the PVC polymer, chlorine atoms are present, and their lone pair of electrons enables solvation of inorganic salts, resulting in the development of a conductive ion solution [8, 9]. However, the main drawback of PVC-based polymer electrolytes is their low ionic conductivity using ammonium based-salts. This is caused by reproducing of ammonium salts via interaction between chlorine atom of the PVC with cations from the salt.

Several methods have been conducted to improve ionic conductivity, as well as electrochemical stability of the polymers-based electrolytes, so as to enhance their use in electrochemical device applications at room temperature [10]. Inorganic salts, particularly ammonium salts, can be used to solve the conductivity issue of SPE for energy device applications [11]. The tiny size ion, such as Li^+, has been widely used; nevertheless, it is highly polluting due to its non-biodegradability and high cost [12]. Furthermore, ammonium-based salts are frequently employed in the generation of polymer electrolyte systems due to their capacity to obtain high ionic conductivity, while maintaining good compatibility and thermal stability [13]. Numerous studies have shown their excellent polymer electrolyte characteristics, for instance ammonium thiocyanate (NH_4SCN) [14], ammonium iodide (NH_4I) [15], ammonium chloride (NH_4Cl) [16], ammonium nitrate (NH_4NO_3) [17], and ammonium fluoride (NH_4F) [18]. Furthermore, an electrolyte including NH_4SCN salt requires less amount of energy to breakdown the ionic bonds, attributing to its low lattice energy of 572 kJ/mol compared to the above-mentioned salts. Correspondingly, the cation (NH_4^+) and anion (SCN^-) radius for the NH_4SCN has found to be 151 picometers and 213 picometers, respectively. The provided anions and cations of the dissolved salt are recombined throughout solvent evaporation. This could be attributed to their higher electrostatic force than cations and functional group of the host polymer. On the other hand, the smaller ionic radius is significant for improved intercalation into the layered cathode structure [19]. In this work a solid polymer

electrolyte (SPE) is prepared by dissolving NH₄SCN salt in the PVC host polymer, and this combination is scientifically called polymer electrolyte regardless of its conductivity performance. The results illustrates that the prepared polymer electrolyte systems have some free ions with little movement, which means that the medium can be called an electrolyte. Due to the limited free ions and restricted movement of these ions within the system the electrolyte has shown high resistive values. To our knowledge this is due to the major role of (Cl-) functional group on the sites of the PVC backbone, which is very actively attract the free cations of any salts (including NH₄SCN) dissolved in the PVC host polymer. Based on the results shown in later sections, the concept of polymer :salt system can be used to fabricate high resistive solid electrolytes.

2. EXPERIMENTAL DETAILS

2.1. Materials

Polyvinyl chloride (PVC) with relatively high molecular weight of (~233,000 g/mol) was used as the polymeric host material. Ammonium thiocyanate (NH₄SCN) salt was employed as the ionic sources. Tetra hydro furan (THF) with 99.9% of purity was used like a solvent. Sigma-Aldrich (Kuala Lumpur, Malaysia) provided all of the aforementioned chemicals, which were utilized directly with no further purification.

2.2. Preparation of films

To prepare the PVC-based solid polymer electrolyte, five individual systems were fabricated. For each system, 1 gram of PVC was dissolved in 50 mL of tetra hydro furan (THF) for ~1 hour at room temperature. Then, various quantities of ammonium thiocyanate (NH₄SCN) salt were added to the individual samples. The solutions were stirred continually by means of magnetic stirrer so as to obtain homogenous mixtures. The salt quantities were varied from 5 to 25 wt.% in steps of 5%. The electrolyte samples were codded as PVCNH1, PVCNH2, PVCNH3, PVCNH4, and PVCNH5 for PVC containing 5 wt.%, 10 wt.%, 15 wt.%, 20 wt.%, and 25 wt.% of the (NH₄SCN) salt, respectively. Eventually, the solutions were then poured into several dry and clean glass petri dishes, enclosed by filter paper to avoid contaminants. Then, allowed to gradually evaporate at ambient temperature until free-solvent PVC based SPE films were produced.

2.3 Characterization techniques

An LCR meter (HIOKI 3531 Z Hi-tester, Japan) linked to a computer was used to measure the impedance of the manufactured films. To ensure an excellent contact, the manufactured samples were sliced into tiny circular films with its diameter of (2 cm) and then placed between two electrodes of stainless steel (SS) under spring pressure. At room temperature, the measurements were taken at frequencies ranging from 50 Hz to 1 MHz. The complex impedance (Z*), real, and imaginary

components (Z', and Z") were calculated and shown as a Nyquist plot of (Z' against Z"). As a result, the bulk resistance (R_b) was calculated by intersecting the Nyquist plot with the real axis.
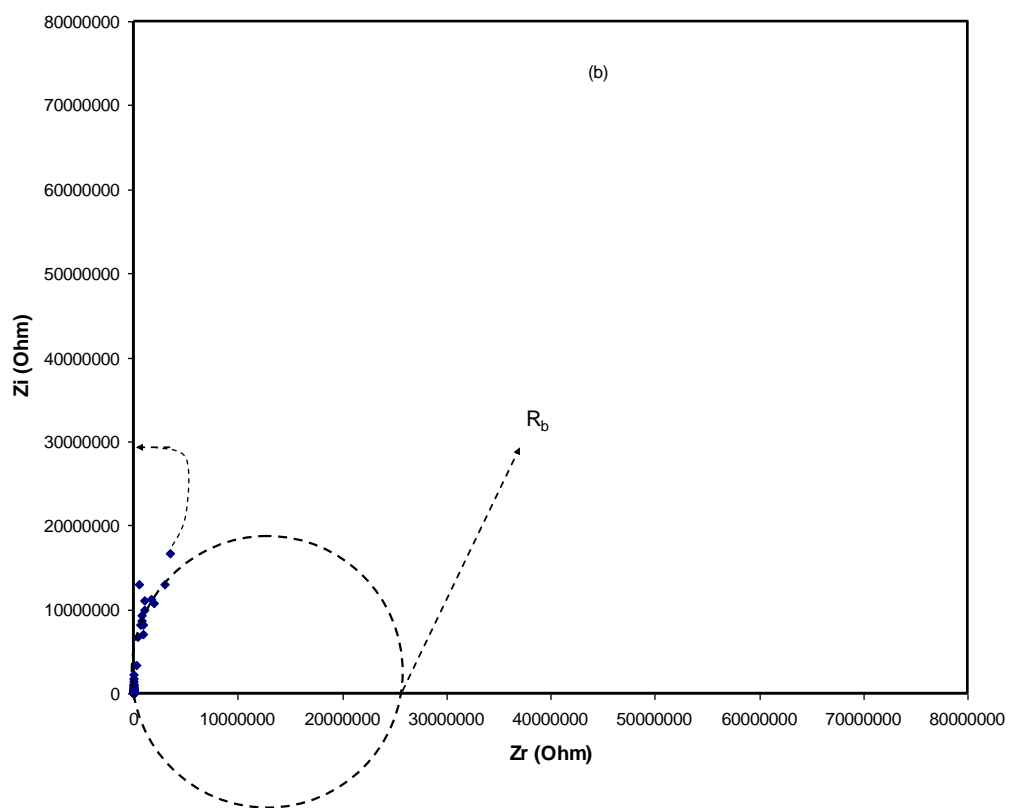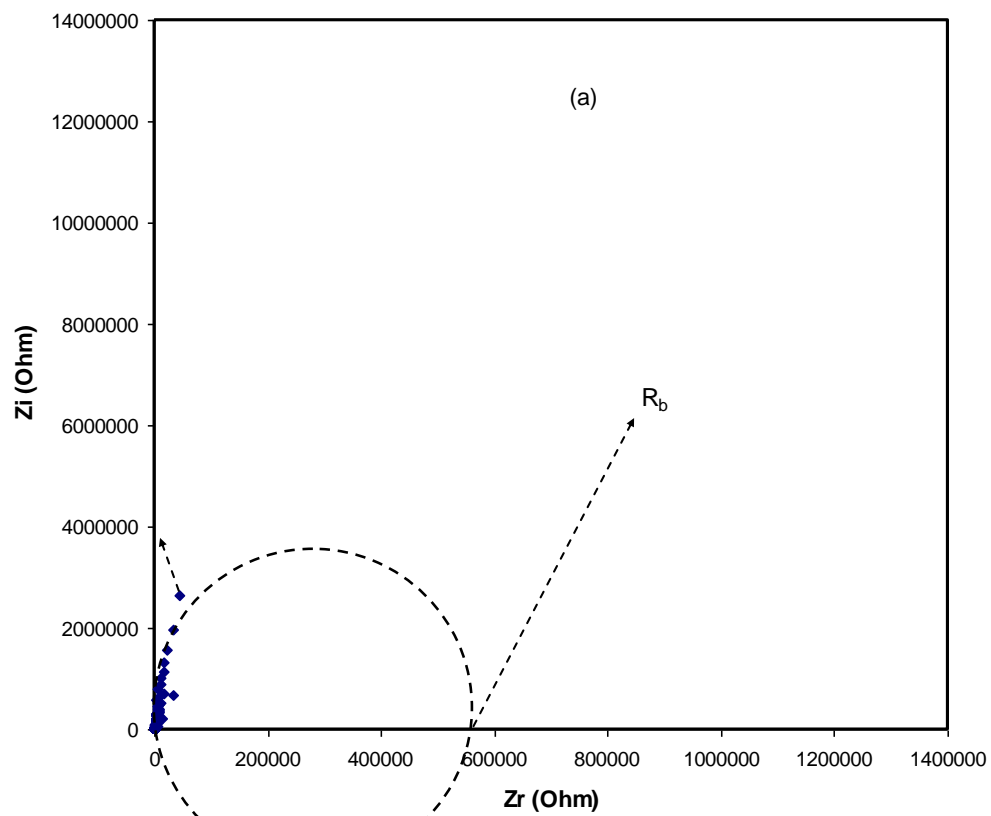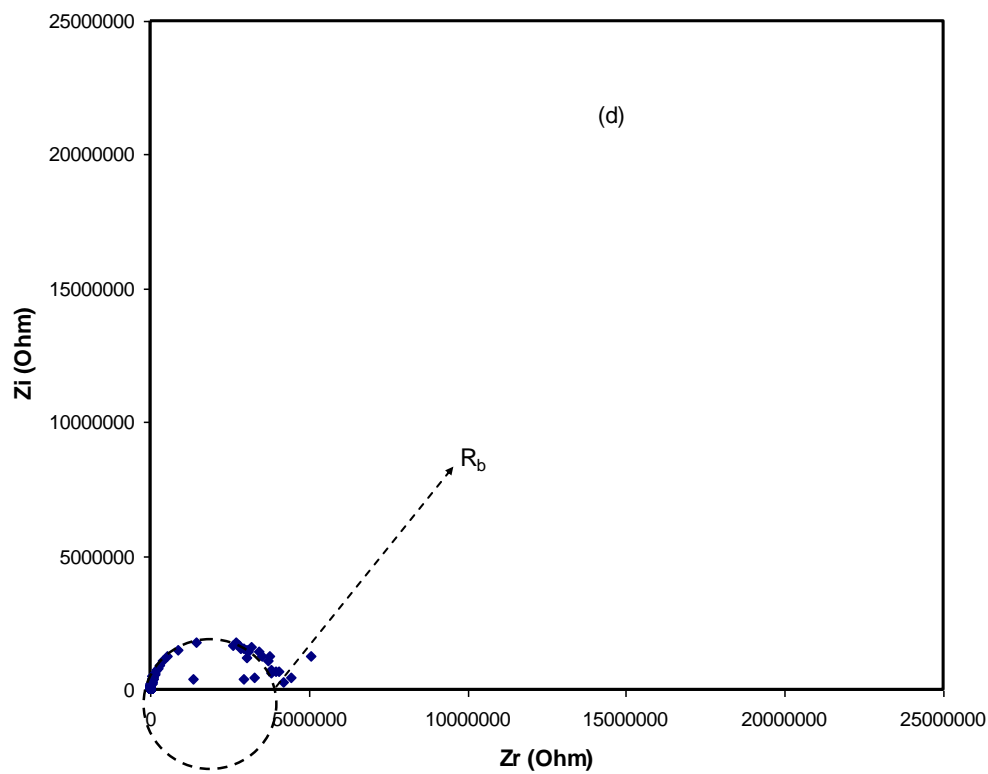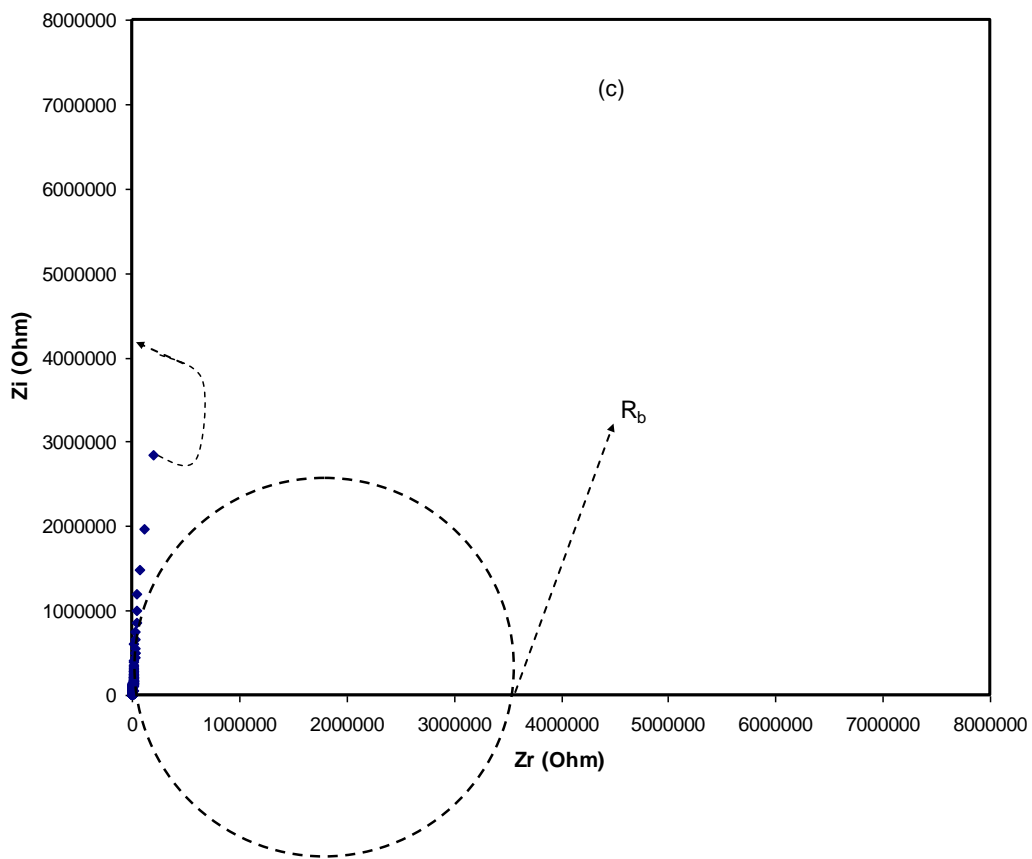
3. RESULT AND DISCUSSION

3.1 Impedance spectroscopy

As a member of an advanced material class, polymer electrolytes were frequently used in devices. Electrical impedance spectroscopy (EIS) is essential for investigating the electrical characteristics of a wide variety of polymeric electrolyte materials. It is also an effective method for evaluating the ionic conductivity of novel materials utilized in energy storage systems. **Figure 1 (a-e)** depicts the plots of impedance spectroscopy for the PVCNH based electrolyte systems. In general, impedance responses are describing a half-circle in the low-frequency areas while high-frequency regions exhibit a straight line [20-22]. These reaction ranges are related to ion conduction in the electrolyte's bulk and the effect of electrode polarization, respectively. In general, in an impedance plot, the semicircle is a parallel combination of bulk resistance (R_b). Therefore, the straight line is equivalent to a capacitive element with the intersection on the real axis as an (R_b) in series [23, 24]. In this work, there is only a semicircle without spike at a 20 wt.% of salt content, while other samples displayed no semicircle, and the data have been shifted towards the Y-axis. This means that the system almost has capacitor behavior with high resistivity. As a result, lower room temperature ionic conductivity is obtained. Previous works have stated that the PVC host-based polymer electrolyte without blending possess low ionic conductivity. The main reason is due to its functional group (i.e., chlorine atom) attached to the chain. Our hypothesis regarding the low ionic conductivity has been clarified in **Figure 2**. The chlorine atom reacts with the cations of the salt (i.e., NH_4^+), which leads to reproducing the salt of ammonium chloride (NH_4Cl) salt. In this case, it is difficult for the cation to transport from one functional group to the next, resulting in a decrease in ionic conductivity. Therefore, the conductivity cannot be improved with the addition of ammonium thiocyanate, resulting in just a semicircle, which appeared in the impedance plot. The following equation was used to compute the DC ionic conductivity of the PVC-NH_4SCN systems based on the (R_b) value and sample dimensions [25-27]:

$$\sigma_{dc} = \left(\frac{1}{R_b}\right) \times \left(\frac{t}{A}\right) \qquad (1)$$

Here, *A* denotes the area of the electrodes, and *t* represents the thickness of the sample. In polymer-based electrolytes, ionic conductivity has strongly relied on the effectiveness of the number of ion carriers and their mobility. The effective number of ion carriers depends on the rate of dissolved ion concentration. Ionic mobility is enhanced by the segmental motion of the polymer chain in a polymer electrolyte, which is generated by the dissolution of ions in the polymer [28, 29].
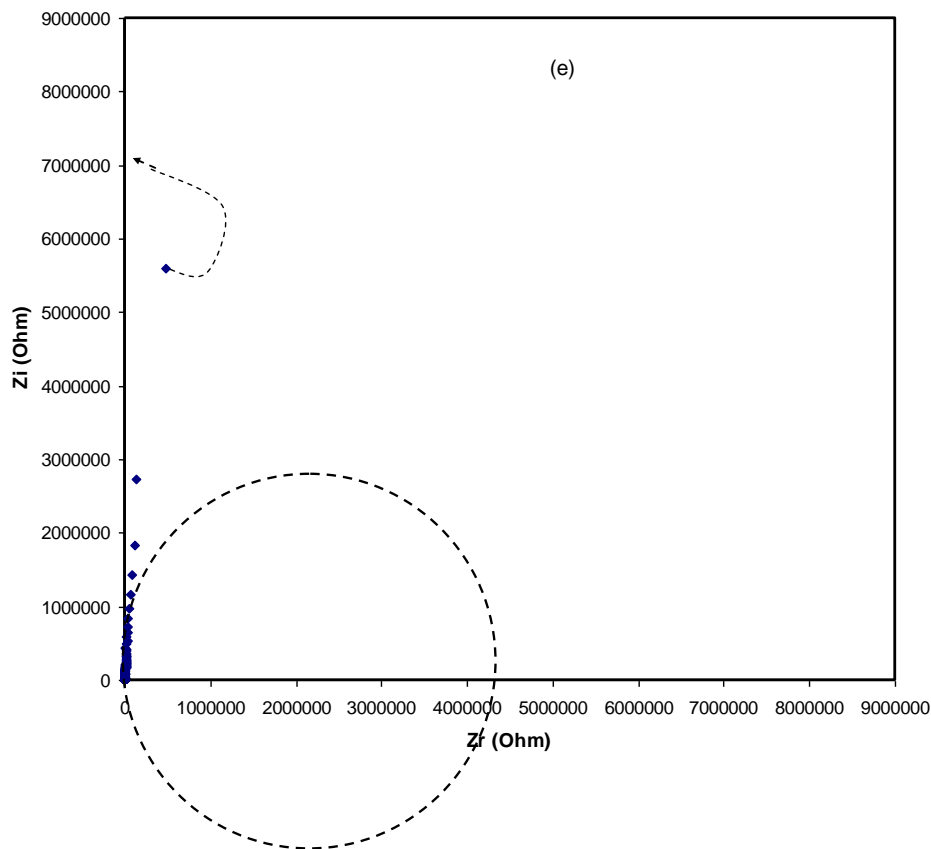
Figure 1. Impedance plots for the PVC samples (a) PVCNH1, (b) PVCNH2, (c) PVCNH3, (d) PVCNH4, and (e) PVCNH5.

From the above equation, the ionic conductivity is obviously greater for lower bulk resistance value, and the uppermost ionic conductivity was obtained for the electrolyte incorporated with 20 wt.% of NH$_4$SCN salt. **Table 1** summarizes the (σ_{dc}) ionic conductivity for the PVCNH electrolyte films. It can be noted that the ionic conductivity is increase with the increment of the salt content up to 20wt.% of NH$_4$SCN, while it drops beyond the 20 wt.%, attributing to the blocking effect or immobile polymer chains [30]. Our previous study [7] for the glycerol plasticized system of PVC-NH$_4$SCN displayed the highest ionic conductivity of ~10^{-6} S/cm, which could be due to the effect of glycerol plasticizer that provides more channels for ions to comfortably move through the polymer matrix. A comparable result of ionic conductivity has documented by Muhamad [31], for the solid polymer electrolyte system of PVC-NaI.

Table 1. Room temperature dc ionic conductivity for the PVCNH-based solid polymer electrolyte.

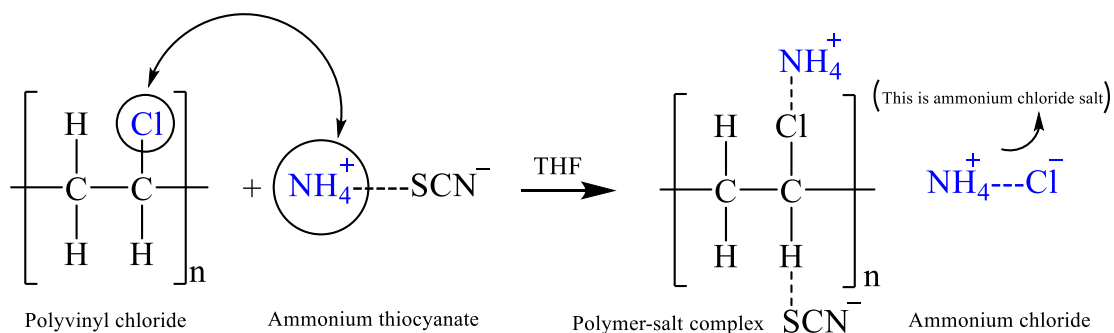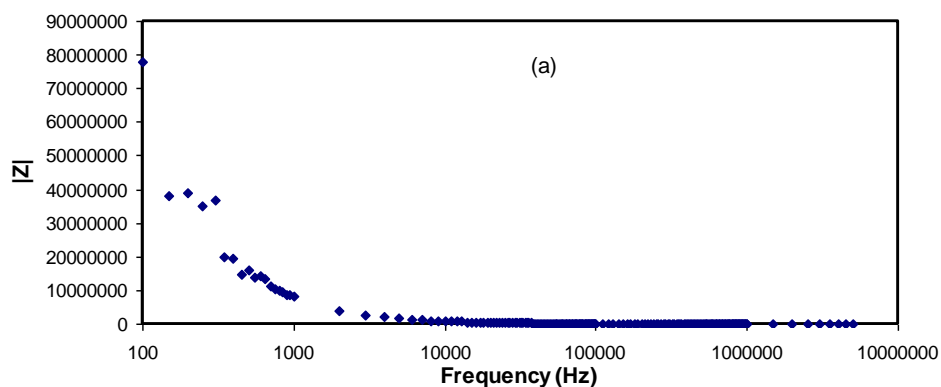| Sample designation	(σ_{dc}) Ionic conductivity S/cm
PVCNH1	2.15×10^{-8}
PVCNH2	4.57×10^{-10}
PVCNH3	3.27×10^{-9}
PVCNH4	2.86×10^{-8}
PVCNH5	2.72×10^{-9}

Figure 2. Interaction between PVC host polymer and NH$_4$SCN salt.

Furthermore, studying the Bode plot supports the previous explanation and recommended a half circle for Nyquist plots. **Figure 3** presents the Bode plot for the PVCNH based solid polymer electrolytes at room temperature. Typically, the Bode plot possess three distinct regions that are capacitive (low frequency plateau), high frequency charge transfer regions, and diffusion (i.e., inclined region), as demonstrated by earlier studies [32]. In this work, the Bode plot clearly shows three distinct areas. The capacitive behavior is assigned to the plateau area at low frequency, while the charge transfer areas and diffusion have corresponded to the plateau region at the intermediate frequency. The semicircle is connected with ion transport in the amorphous area of electrolytes, and the spike is referred to diffusion contribution, as shown in impedance plots [33, 34]. As demonstrated in **Figure 3,** the charge transfer resistance declined with increased amounts of the NH$_4$SCN salt. In the Bode plot, the low-frequency dispersion area is attributed to ion diffusion, whereas the high-frequency area is assigned to charge transport resistance. These outcomes highlight that the prepared polymer electrolytes exhibit high resistivity. Generally, electrolyte is considered as the heart of many energy storage and energy conversion devices such as battery, supercapacitor, solar-cell, fuel cell, etc. From a physics standpoint, producing polymer electrolytes with relatively high dc ionic conductivity is very important. From the chemists' one, it is vital that the films possess low charge transfer resistance [35, 36]. However, due to the high resistive behavior of the prepared electrolyte, it is not eligible for energy related application. Nevertheless, this so called highly resistive electrolyte can be employed in fabrication of electrolytic resistors, which has many applications sensors industry [35].
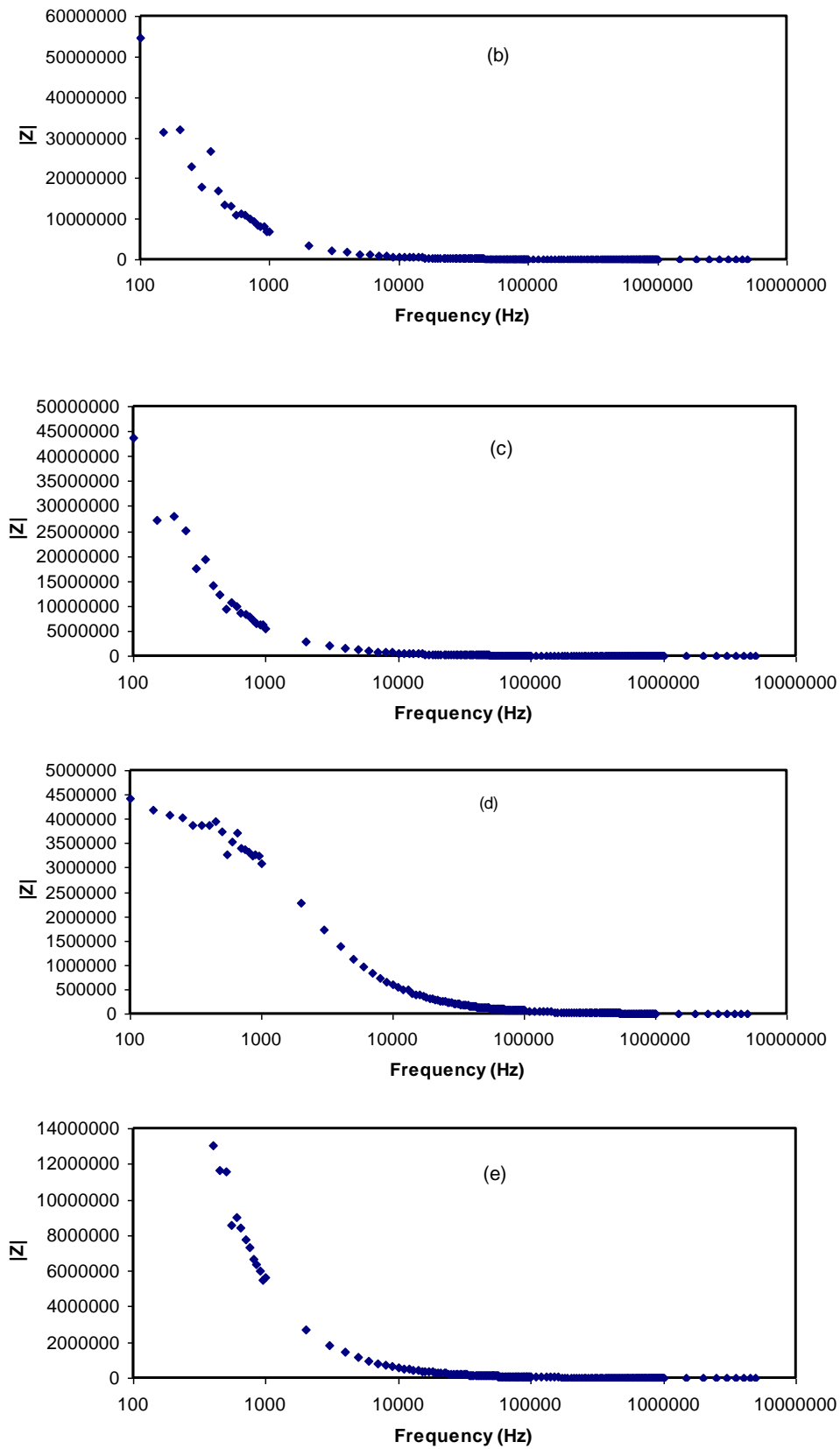
Figure 3. Bode plots for the PVC containing (a) PVCNH1, (b) PVCNH2, (c) PVCNH3, (d) PVCNH4, and (e) PVCNH5.

3.2 Dielectric properties

The electrical characterization including, dc ionic conductivity, dielectric permittivity($\varepsilon*$), and electric modulus study ($M*$) are crucial for comprehending the ionic transport mechanism. Ion-conduction in solid polymer electrolytes is considered the heart of electrochemical devices. In terms of storing and losing electrical energy, the dielectric constant and loss (ε' and ε'') have been characterized. **Figures 4 and 5** display dielectric constant (ε') and (ε'') against frequency for the PVCNH electrolyte systems, respectively [37-40]. The following relations were used to figure out the (ε') and (ε'') values:

$$\varepsilon' = \frac{Z''}{\omega C_\circ (Z'^2 + Z''^2)} \qquad (2)$$

$$\varepsilon'' = \frac{Z'}{\omega C_o (Z'^2 + Z''^2)} \qquad (3)$$

Where, C_o is denoting the capacitance, and ω stands for the angular frequency, which is provided by ($\omega = 2\pi f$) and ($\varepsilon_o A/t$), correspondingly. ε_o denotes the free space permittivity. It should be highlighted that the PVCNH4 film has the greatest dielectric constant at a low-frequency area. It may be related to a polarization of the electrodes as well as space charge influence. The increase of dielectric constant is reflecting the increased charge carrier densities and amorphous area of the system [41]. The amplification of the values, therefore, increases with the increment of the salt concentrations and verifying that the charging and ionic mobility in the films are increased. Moreover, both (ε') and (ε'') values are decreased with the increment of frequency and recorded their optimum values at low frequencies. This is showing the effect of polarization owing to ions accumulated close to the electrodes, and dipoles at high dispersion frequency regions do not respond to the field variation [42-45].
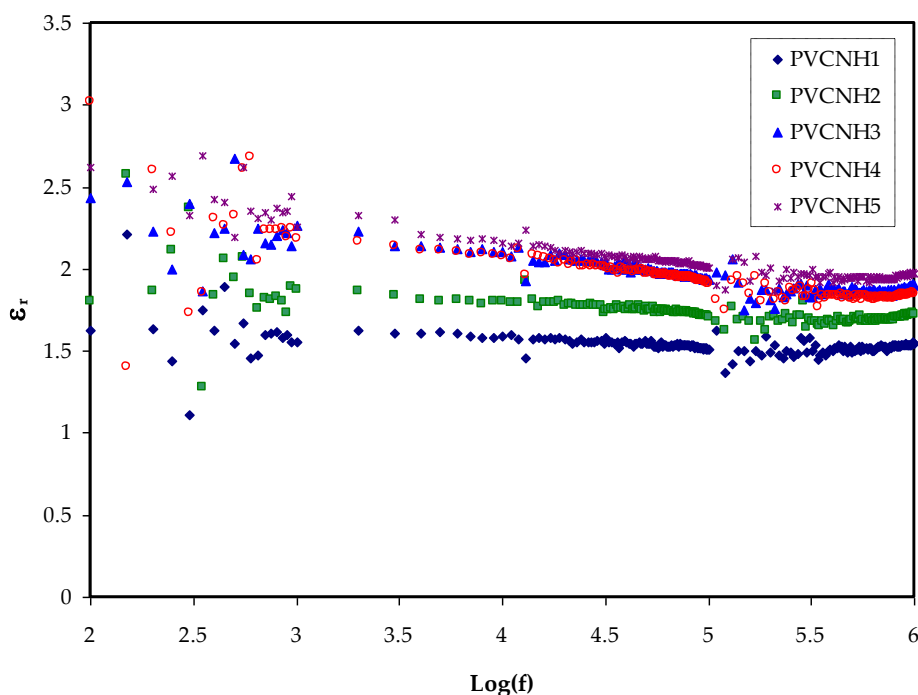

Figure 4. Dielectric constant (ε') versus frequency for the PVCNH electrolyte samples.
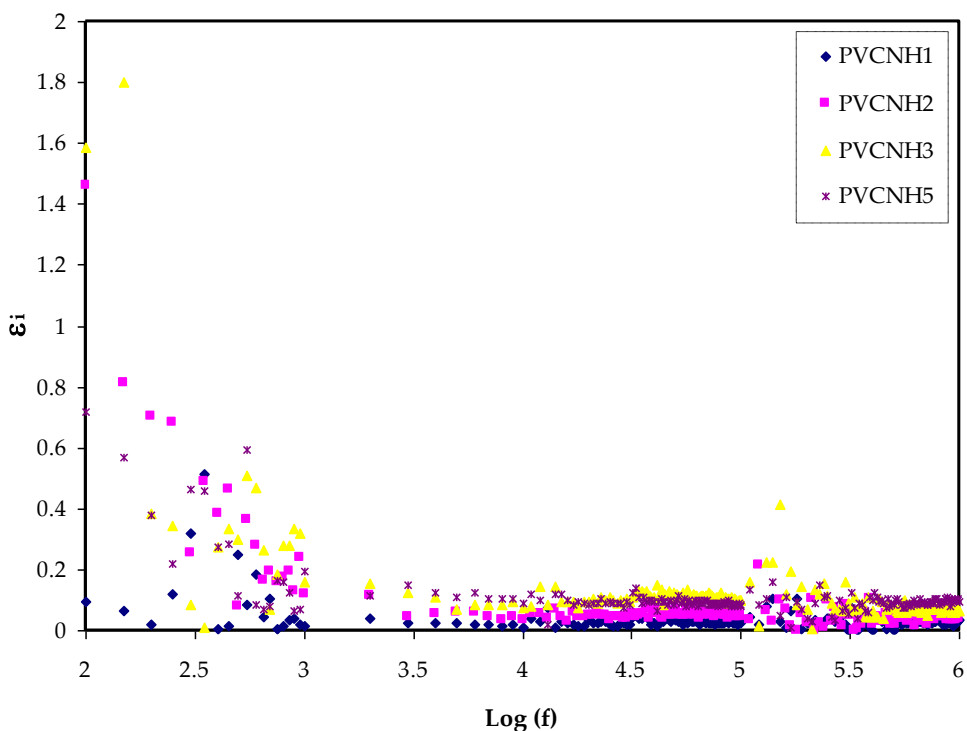
Figure 5. Dielectric loss (ε'') versus frequency for the PVCNH electrolyte samples.

Another crucial electrical parameter that has to be investigated is the electric modulus study. Aids through the electric modulus includes the understanding of bulk relaxation in low frequency regions. Thus, such a typical issue can be solved using electric modulus formalism like the charging injection phenomenon, the polarization of electrodes, and conditional impacts which they are tending to confuse relaxation in an exhibition of dielectric permittivity [46, 47]. **Figures 6 and 7** display the real (M_i) and imaginary (M_r) components of the electric modulus (M^*) for the PVCNH samples, respectively. Transformed real and imaginary components were used to attain the electric modulus formalism. The real (M_r), and imaginary (M_i) components of the electric modulus (M^*) were determined via the following relations [48-50]:

$$M' = \frac{\varepsilon'}{(\varepsilon'^2 + \varepsilon''^2)} = \omega C_o Z'' \qquad (4)$$

$$M'' = \frac{\varepsilon''}{(\varepsilon'^2 + \varepsilon''^2)} = \omega C_o Z' \qquad (5)$$

As it is clear from the figures, the (M_r) values drop with decreasing frequencies until they hit zero, indicating the eliminating of the polarization. However, the (M_r) increases with the increment of frequency. This might be due to the fact that the relaxing process takes place at different frequencies. The perceived diffusion is basically as of conductivity relaxation over a wide range of frequencies, suggesting the presence of relaxation time associated with a loss peak in the imaginary part of modulus study [51]. The higher capacitance caused by the polarization effect (PE) has indicated by lower values

of the (M_i) at lower frequencies. Therefore, the presence of peaks in the imaginary part of modulus verified that the PVCNH electrolyte systems are ionic conductors. Furthermore, the charge of ions moved across coordinated sites of the polymer electrolyte in the areas of the low-frequencies, resulting in conduction in the polymer electrolyte [52].
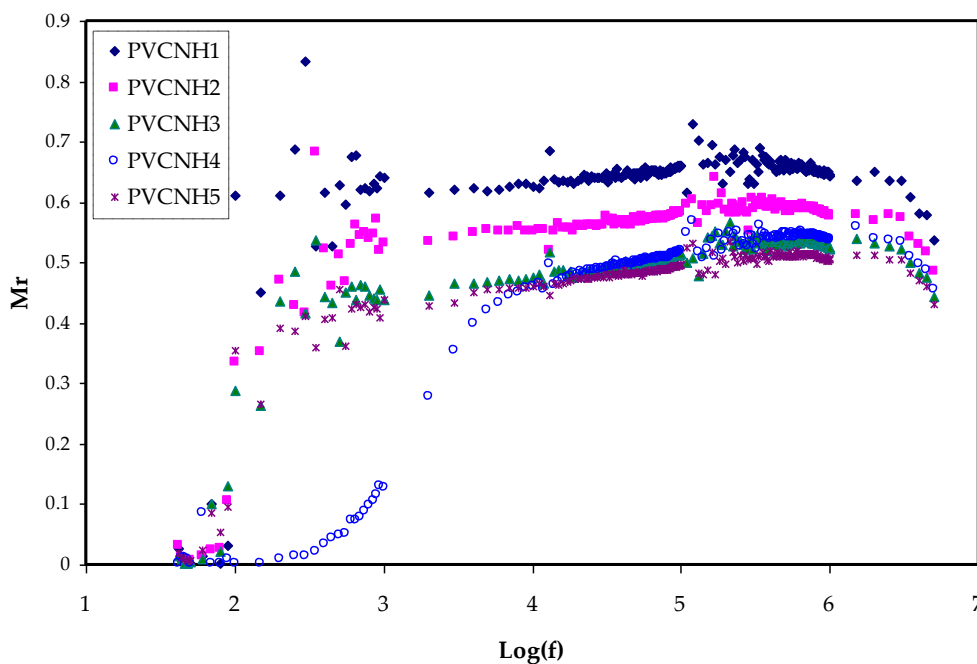

Figure 6. Real part (M_r) of electric modulus spectra versus frequency for the PVCNH samples.
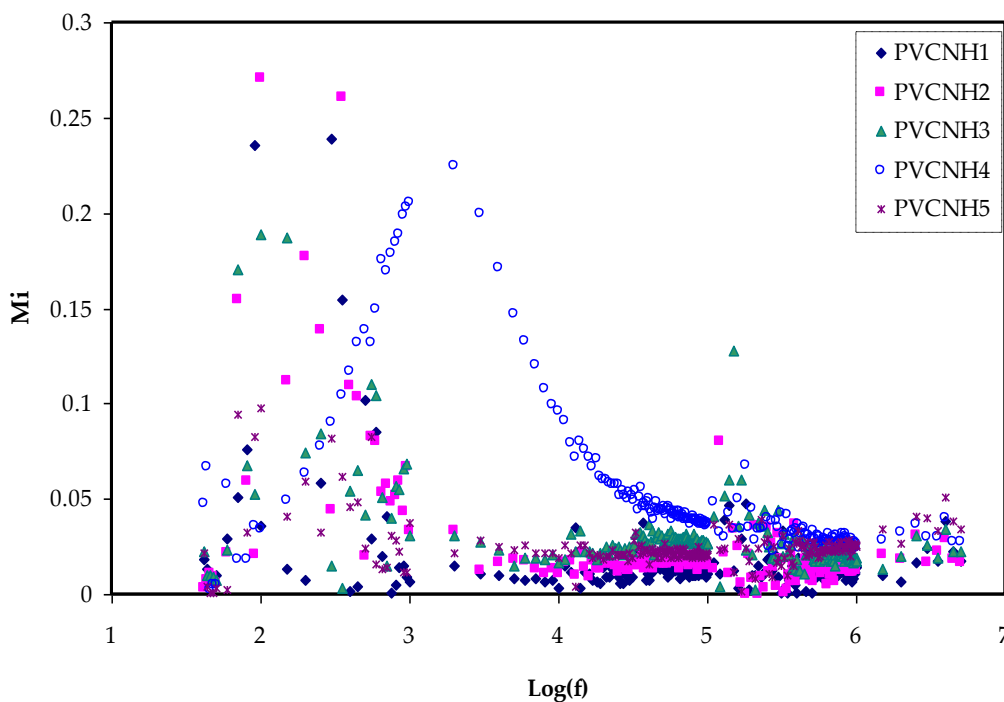

Figure 7. Imaginary part (M_i) of electric modulus spectra versus frequency for the PVCNH samples.

4. CONCLUSION

In conclusion, the influence of NH_4SCN salt as an ionic source in improving PVC-based solid polymer electrolyte via solution casting technique was investigated. The electrical characteristics of the PVC polymer electrolyte films at room temperature were investigated using impedance and dielectric measurements. It was demonstrated that increasing the quantity of salt was improved the system's ionic conductivity. According to the EIS study, raising the NH_4SCN concentration is reduces the resistance of charge transfer due to an increase in charge carrier density. The maximum ionic conductivity was obtained for the PVCNH4 based electrolyte, which was (2.86×10^{-8}) S/cm. The dielectric study confirmed the conductivity trends, and it was improved that the ions relaxations are non-Debye behavior. The dielectric modulus was investigated; the existence of peaks in the imaginary parts of the modulus indicates that the polymer electrolytes are ionic conductors.

CONFLICTS OF INTEREST
The authors declare no conflicts of interest.

References

1. J.M. Hadi, S.B. Aziz, M.S. Mustafa, M.H. Hamsan, R.T. Abdulwahid, M.F.Z. Kadir, H.O. Ghareeb, *J. Mater. Res. Technol.*, 9 (2020) 9283.
2. R.C. Agrawal, R.K. Gupta, *J. Mater. Sci.*, 34 (1999) 1131.
3. N.A.M. Noor, M.I.N. Isa, *Adv. Mater. Res.*, 1107 (2015) 230.
4. S. Ramesh, K.H. Leen, K. Kumutha, A.K. Arof, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.*, 66 (2007) 1237.
5. S. Ramesh, A.H. Yahaya, A.K. Arof, *Solid State Ionics*, 152–153 (2002) 291.
6. S.B. Aziz, J.M. Hadi, E.M. Elham, R.T. Abdulwahid, S.R. Saeed, A.S. Marf, W.O. Karim, M.F.Z. Kadir, *Polymers (Basel).*, 12 (2020) 1938.
7. J.M. Hadi, S.B. Aziz, M.S. Mustafa, M.A. Brza, M.H. Hamsan, M.F.Z. Kadir, H.O. Ghareeb, S.A. Hussein, *Int. J. Electrochem. Sci.*, 15 (2020) 4671.
8. F.H. Muhammad, R.H.Y. Subban, T. Winie, *Mater. Today Proc.*, 4 (2017) 5130.
9. P. Vickraman, S. Ramamurthy, *Mater. Lett.*, 60 (2006) 3431.
10. S.B. Aziz, F. Ali, H. Anuar, T. Ahamad, W.O. Kareem, M.A. Brza, M.F.Z. Kadir, O.A. Abu Ali, D.I. Saleh, A.S.F.M. Asnawi, J.M. Hadi, S.M. Alshehri, *Alexandria Eng. J.* (2021).
11. J.M. Hadi, S.B. Aziz, M.F.Z. Kadir, Y.A. El-Badry, T. Ahamad, E.E. Hussein, A.S.F.M. Asnawi, R.M. Abdullah, S.M. Alshehri, *Arab. J. Chem.*, 14 (2021) 103394.
12. S.D. Gong, Y. Huang, H.J. Cao, Y.H. Lin, Y. Li, S.H. Tang, M.S. Wang, X. Li, *J. Power Sources*, 307 (2016) 624.
13. S.B. Aziz, M.M. Nofal, M.F.Z. Kadir, E.M.A. Dannoun, M.A. Brza, J.M. Hadi, R.M. Abdulla, *Materials (Basel).*, 14 (2021) 1994.
14. M.S. Mustafa, H.O. Ghareeb, S.B. Aziz, M.A. Brza, S. Al-zangana, J.M. Hadi, M.F.Z. Kadir, *Membranes (Basel).*, 10 (2020) 1.

15. M.A. Brza, S.B. Aziz, H. Anuar, S.M. Alshehri, F. Ali, T. Ahamad, J.M. Hadi, *Membranes (Basel).*, 11 (2021) 296.

16. S. Sikkanthar, S. Karthikeyan, S. Selvasekarapandian, D. Arunkumar, H. Nithya, K. Junichi, *Ionics (Kiel).*, 22 (2016) 1085.

17. S.B. Aziz, E.M.A. Dannoun, M.H. Hamsan, H.O. Ghareeb, M.M. Nofal, W.O. Karim, A.S.F.M. Asnawi, J.M. Hadi, M.F.Z.A. Kadir, *Polymers (Basel).*, 13 (2021) 1.

18. N.A. Nik-Aziz, N.K. Idris, M.I.N. Isa, *Int. J. Phys. Sci.*, 5 (2010) 748.

19. N.A. Shamsuri, S.N.A. Zaine, Y.M. Yusof, W.Z.N. Yahya, M.F. Shukur, *Ionics (Kiel).*, 26 (2020) 6083.

20. M.M. Nofal, S.B. Aziz, J.M. Hadi, R.T. Abdulwahid, E.M.A. Dannoun, A.S. Marif, S. Al-Zangana, Q. Zafar, M.A. Brza, M.F.Z. Kadir, *Materials (Basel).*, 13 (2020) 1.

21. S.B. Aziz, M.M. Nofal, R.T. Abdulwahid, M. F. Z. Kadir, J.M. Hadi, M.M. Hussien, W.O. Kareem, E.M.A. Dannoun, S.R. Saeed, *Results Phys.*, 29 (2021) 104770.

22. X. Qian, N. Gu, Z. Cheng, X. Yang, E. Wang, S. Dong, *Electrochim. Acta*, 46 (2001) 1829.

23. S.B. Aziz, A.S.F.M. Asnawi, R.T. Abdulwahid, H.O. Ghareeb, S.M. Alshehri, T. Ahamad, J.M. Hadi, M.F.Z. Kadir, *J. Mater. Res. Technol.*, 13 (2021) 933.

24. A.S. Samsudin, M.I.N. Isa, *Bull. Mater. Sci.*, 35 (2012) 1123.

25. M.H. Hamsan, S.B. Aziz, M.M. Nofal, M.A. Brza, R.T. Abdulwahid, J.M. Hadi, W.O. Karim, M.F.Z. Kadir, *J. Mater. Res. Technol.*, 9 (2020) 10635.

26. A.K. Arof, S. Amirudin, S.Z. Yusof, I.M. Noor, *Phys. Chem. Chem. Phys.*, 16 (2014) 1856.

27. S.B. Aziz, M.A. Brza, E.M.A. Dannoun, M.H. Hamsan, J.M. Hadi, M.F.Z. Kadir, R.T. Abdulwahid, *Molecules*, 25 (2020) 4503.

28. S. Ramesh, G.B. Teh, R.F. Louh, Y.K. Hou, P.Y. Sin, L.J. Yi, *Sadhana - Acad. Proc. Eng. Sci.*, 35 (2010) 87.

29. J.M. Hadi, S.B. Aziz, S.R. Saeed, M.A. Brza, R.T. Abdulwahid, M.H. Hamsan, R.M. Abdullah, M.F.Z. Kadir, S.K. Muzakir, Membranes (Basel)., 10 (2020) 1.

30. S.B. Aziz, A.S.F.M. Asnawi, M.F.Z. Kadir, S.M. Alshehri, T. Ahamad, Y.M. Yusof, J.M. Hadi, *Polymers (Basel).*, 13 (2021) 1183.

31. F.H. Muhammad, R.H.Y. Subban, T. Winie, Mater. Today Proc., 4 (2017) 5130–5137.

32. S.B. Aziz, R.B. Marif, M.A. Brza, M.H. Hamsan, M.F.Z. Kadir, *Polymers (Basel).*, 11 (2019) 1.

33. F.Ç. Cebeci, H. Geyik, E. Sezer, A. SezaiSarac, *J. Electroanal. Chem.*, 610 (2007) 113.

34. A. Eftekhari, *J. Mater. Chem. A*, 6 (2018) 2866.

35. R. Vergaz, D. Barrios, J.M. Sánchez-Pena, C.G. Pozo-Gonzalo, M. Salsamendi, *Sol. Energy Mater. Sol. Cells*, 93 (2009) 2125.

36. White, H., & Van Atta, E. *Review of Scientific Instruments*, 3(5), (1932) 235.

37. Pritam, A. Arya, A.L. Sharma, *Ionics (Kiel).*, 26 (2020) 745.

38. M.H. Hamsan, M.F. Shukur, S.B. Aziz, M.F.Z. Kadir, *Bull. Mater. Sci.*, 42 (2019) 1.

39. S.K. Deraman, N.S. Mohamed, R.H.Y. Subban, *SainsMalaysiana*, 43 (2014) 877.

40. A.M. Zulkifli, N.I. Aqilah Mat Said, S.B. Aziz, E.M. Ali Dannoun, S. Hisham, S. Shah, A.A. Bakar, Z.H. Zainal, H.A. Tajuddin, J.M. Hadi, M.A. Brza, S.R. Saeed, P.O. Amin, Molecules, 25 (2020) 4115.

41. M.M. Nofal, J. M. Hadi, S.B. Aziz, M.A. Brza, A.S.F.M. Asnawi, E.M.A. Dannoun, A.M. Abdullah, M.F.Z. Kadir, *Materials*, 14 (2021) 4859.

42. A. Arya, A. L. Sharma, *J. Phys. D. Appl. Phys.*, 51 (2018) 045504.

43. M.A. Brza, S.B. Aziz, H. Anuar, F. Ali, R.T. Abdulwahid, J.M. Hadi, *Int. J. Electrochem. Sci.*, 16 (2021) 1.

44. M. Jaipal Reddy, P.P. Chu, *Electrochim. Acta*, 47 (2002) 1189.

45. A.M. Zulkifli, N.I.A.M. Said, S.B. Aziz, S. Hisham, S. Shah, A.A. Bakar, Z.H.Z. Abidin, H.A. Tajuddin, L. Sulaiman, M.A. Brza, J.M. Hadi, S. Al-Zangana, *Int. J. Electrochem. Sci.*, 15 (2020) 7434.

46. H. Smaoui, L.E.L. Mir, H. Guermazi, S. Agnel, A. Toureille, *J. Alloys Compd.*, 477 (2009) 316.
47. S.L. Agrawal, M. Singh, M. Tripathi, M.M. Dwivedi, K. Pandey, *J. Mater. Sci.*, 44 (2009) 6060.
48. J.M. Hadi, S.B. Aziz, M.M. Nofal, S.A. Hussen, M.H. Hamsan, M.A. Brza, R.T. Abdulwahid, M.F.Z. Kadir, H.J. Woo, *Membranes* (Basel)., 10 (2020) 1.
49. N.A.M. Noor, M.I.N. Isa, *Adv. Mater. Res*., 1107 (2015) 230.
50. S.B. Aziz, *Adv. Mater. Sci. Eng*., 2016 (2016) 1.
51. S.B. Aziz, *J. Inorg. Organomet. Polym. Mater*., 28 (2018) 1942.
52. C.S. Ramya, S. Selvasekarapandian, G. Hirankumar, T. Savitha, P.C. Angelo, *J. Non. Cryst. Solids*, 354 (2008) 1494.