PEO-hBN-NaClO$_4$ Polymer Composite Electrolyte for Sodium Ion Batteries

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Abstract

A new polymer electrolyte (conducting sodium-ion) based on Polyethylene oxide (PEO) matrix comprising NaClO$_4$ and nano sized hexagonal boron nitride was fabricated via the technique of solution casting for use in sodium ion batteries. Interaction of PEO with Na-ion was investigated with fourier transform infrared (FT-IR) which reveals the extend of Na-ion solvation by PEO (EO:Na). The crystallinity of the polymer electrolyte was investigated with X-ray diffraction (XRD) and thermal properties of the composites were studied with differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The DSC results show that the melting temperature (T_m) of PEO decreases addition of both NaClO$_4$ and hBN. TGA results showed that all the composites membranes were thermally stable till 300 ^{o}C. Surface morphology of the composite was examined using scanning electron microscopy (SEM) which also reveals the homogeneous dispersion of nano hBN in the polymer matrix. Ionic conductivity of the polymer composite was studied with impedance spectroscopy and PEO5hBN10Na sample showed maximum ion conductivity of approximately 1.4×10^{-3} S/cm at 100 ^{o}C.

Keywords: Sodium ion battery; Polymer composite electrolyte; PEO; hBN; Ioinic conductivity.

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1. Introduction

Sodium ion batteries (SIBs) were initially explored aboard Lithium ion (LIBs) batteries since 1980s. Due to some benefits possessed by lithium batteries, to wit higher energy density attributed lower mass and higher potential, shifted the battery research in favor of lithium batteries and away from sodium [1]. As such LIBs comprising of lithium-ion conducting electrolyte and two lithium insertion electrodes, have become prospering and sophisticated energy storage devices since the first commercialization of LIB, carbon/LiCoO2 cell, in 1991 [2]. Salts such as $LiCF_3S0_3$, $LiC10_4$ and $NaClO_4$, may be dissolved in high-molecular-weight poly(ethy1ene oxide, to yield solid electrolytes [3]. Attention has been focused on the study of PEO based polymer electrolytes complexed with lithium and sodium salts because of their direct application in high energy density rechargeable batteries [4]. Utilization of solid polymer electrolytes in electrochemical devices depends on various factors like mechanical, thermal properties, and ionic conductivity [5]. Several modifications in the structure of these polymer electrolytes have been realized in order to enhance their electrical conductivity and to improve their thermal, mechanical and electrochemical properties.

Unluckily, the scarceness of lithium is a cause for concern. As lithium is constantly mined from natural deposits, its availability exhausts to unsustainably depleted levels. This signifies that future LIBs may need backing up technologies to meet growing consumer need. Thus, it is crucial to seriously reckon the future political, economic and social consequences of this global lithium fixation [6]. Sodium is available in groovy abundance with a low cost: natural sodium is more than 1000 times more abundant than lithium [7] and has electrochemical similarities with lithium (which have been intensively explored) [8]. On these bases, SIBs is suggested as ideal alternative to LIBs.

Battery electrolytes are classically given less attention as compared to the active materials (the electrodes) [8, 9]. The reason at the back this is that the electrodes properties define the system energy density and hence most eye-catching. But the role of electrolyte should, nevertheless, not be disregarded because it is in boastfully part responsible for life-length and realistic possible performance in terms of practical reachable rate capability, safety, capacity [8]. Most of research on battery uses liquid electrolytes. Liquid electrolyte comprise flammable liquid solvent that exhibit high risk of fire hazard and induce difficulties of waste disposal and management. These troubles can be resolved by the use solid polymer electrolyte [10]. After P.V. Wright discovery of ionic conductivity of PEO alkali metal salt complexes 1973 [11], polymer electrolytes (PEs) got substantial attention due to their prospective applications in several electrochemical field [12]. Even though numerous PEs kinds are been explored, PEO is to date one of the most promising contestant as a host for PEs [12]. It possesses superior mechanical stability till its melting point, high compliance and significant good ionic conductivity due to rich electron heteroatom on its backbone with metal (Li, Na etc) salt.

Nanostructured for polymers nano-composites have received interest for the past two decades because of their exciting bulk and surface properties. Controlling polymers nanostructure addition of nano particles has chaired the structural and functional improvements of property in various systems of polymer as a material answer to incessant demands for advanced industrial sectors [13]. For the purpose of this, inorganic materials like TiO_2, SiO_2, graphene, and carbon nanotube have been used to develop novel polymer composite electrolyte in order to

attain good ionic conductivity, mechanical, thermal, and chemical stability [14]. In recent times, development of polymer composites comprising nanosized filler has become a admired topic in materials science [14]. Hexagonal boron nitride (hBN) is the isoelectric analog of graphite and most coveted polymorph among the other boron nitrides [14]. Hexagonal boron nitride is basically an important material with a combination of unique properties. It has been used in matrix for ceramic composites to decrease thermal expansion coefficient, improving thermal shock resistance of the composite and enhancing machinability [15].

In this work, composite polymer electrolytes with several EO:Na ratios and different weight % hBN was prepared via solution casting. The polymer electrolytes were characterized using FT-IR, XRD, TGA, DSC and SEM analysis. Na-ion conducting properties of the materials were studied by dielectric-impedance and the results were discussed and compared with previous reported studies.

2. Experimental

2.1. Materials

Poly (ethylene oxide) (PEO) ($M_w \approx$ 400,000 g/mol, Aldrıch), sodium perchlorate (NaClO$_4$) ($\geq$98.0%, Sigma-Aldrich), acetonitrile ($\geq$99.9%, Sigma-Aldrich), and (hBN, 70 nm, BORTEK, Turkey) were purchased and used without any modification.

2.2. Preparation of the samples

Required amount of PEO and NaClO$_4$ to give EO:Na ratio 10 were dissolved in 40 ml of acetonitrile and stirred for 3 hours. hBN (5% w/w) was dispersed in 10 ml of acetonitrile and stirred for 30 min followed by sonication for 30 min. Then this hBN was added into the mixture of PEO and NaClO$_4$ and stirred until a homogenous mixture was obtained. The membrane was prepared by casting of the solution on Teflon plate. The solvent was slowly evaporated at room temperature for 24 hours and then placed under vacuum at 55 ^{0} C for 24 hours to ensure complete removal of the solvent and homogeneous and white films were obtained. The procedure was repeated for 5%hBN EO: Na 10, 5% hBN EO:Na 20, 5% hbN EO:Na 40, 10% hBN EO:Na 10, 10% hBN EO:Na 20 and 10% hBN EO:Na 40. The samples were name PEO*X*hBN*Y*Na where *X* is the percentage of hBN and *Y* is the ratio ethylene oxide to Na-ion (EO:Na). Figure 1 shows the preparation of the polymer electrolyte.
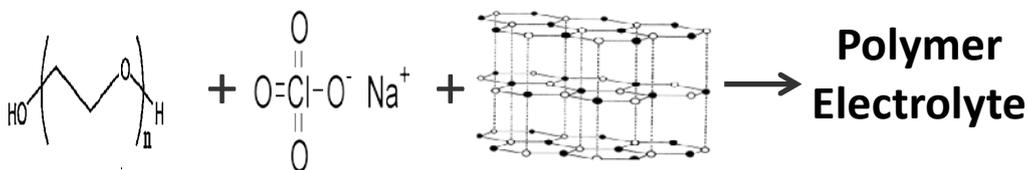
Figure 1: Preparation of the polymer electrolyte.

2.3 Characterization

A Bruker Alpha-P in ATR was used to record FTIR spectra were in the range of 4000–400 cm^{-1} in order to observe the functional group and interaction of chemicals in the system.

The polymer electrolytes thermal stabilities were analyzed with Perkin Elmer STA 6000 Thermal Analyzer. The samples were heated from 30 to 750 °C under N_2 atmosphere at a scanning rate of 10 °C min^{-1}.

In order to investigate thermal transitions of the polymer electrolytes, Perkin Elmer JADE differential scanning calorimetry (DSC) was used. The samples (~10 mg) were placed into aluminum pans. The sample and reference are heated in heat flux instruments and the temperature difference is measured. During the measurements, at first, the samples were heated from 0 to 150 °C, and then cooled from 150 to 0 °C. Finally, the second heating was performed from 0 to 250 °C at a rate of 10 °C min^{-1} under nitrogen atmosphere.

Surface morphology of the samples was examined by scanning electron microscopy (SEM), JEOL-7001 FESEM (Tokyo, Japan). Prior to the SEM measurements all of the samples were coated with gold for 150 s in a sputtering device.

XRD patterns of the polymer electrolytes and pure hBN were obtained by X-ray diffraction instrument, Rigaku Smart Lab Diffractometer operated at 40 kV and 35 mA using Cu Ka radiation. The XRD peaks were recorded in the 2θ range of 10°–70°.

The Na+ ion conductivity measurements were carried out using a Novocontrol dielectric-impedance analyzer. The membranes were sandwiched between platinum blocking electrodes, and the conductivities were measured in frequency range 1Hz and 3MHz at 10 °C intervals. The temperature was controlled with a Novocontrol cryosystem.

3. Result and discussion

Several polymer electrolytes (5%hBN EO:Na 10, 5%hBN EO:Na 20, 5%hBN EO:Na 40, 10%hBN EO:Na 10, 10%hBN EO:Na 20 and 10%hBN EO:Na 40) were prepared by varying the %weight of hexagonal boron nitride and EO:NA ratio. For all the composites, homogeneous and flexible films were obtained.

3.1. FT-IR study

FTIR was used to examine the ionic interaction between PEO host and the salt, and incorporation of hBN nanoparticle into the polymer host. The common observation to affirm the interaction of polymer hosts and the salts includes changes in the intensity of the peaks, shifting of the peaks with respect to the salt concentration, the appearance of new peaks, caused by the presence of salt in the polymer host [16], and broadening of the bands especially for the incorporation the nano particles into the polymer host. The FTIR spectra of the PE samples variegate according to their compositions and this can be able to show the complexation, occurrence, and interactions between the various constitutions [2]. Figure 2 shows the FTIR spectra of pure PEO, hBN, and NaClO4. The pristine PEO has peak at 2876 cm^{-1} (CH stretching), 1465 cm^{-1} (CH_2 scissoring), 1087 cm^{-1} (C-O stretching) 971 cm^{-1} (CH_2 twisting) and 836 cm^{-1} (CH_2 wagging) [2].

Figure 3 shows the PEOXhBNYNa composites (x = 5%, 10% and y = 10, 20, 40). As it can be seen, the C-O peaks of the composites spectra around 1080 cm^{-1} shift as the concentration of NaClO$_4$ increased. This is may be due to the different co-ordination state between PEO and the salt. There is appearance of peak at 618 cm^{-1} which is attributed to ClO$_4^-$ [17], the intensity of this peak increases due to the increase of the NaClO$_4$ as expected. There is also broad peak around 1417 cm^{-1} and is attributed to B–N stretching of the nano-hBN [18], which verified the dispersion of the nano-hBN in PEO host.
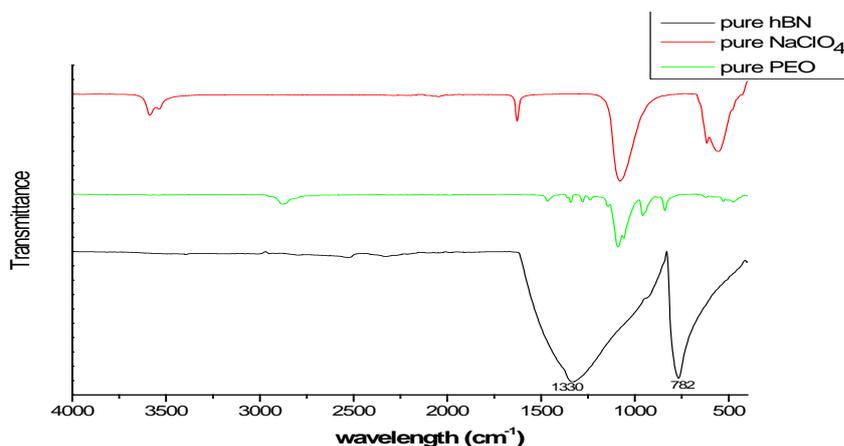
Figure 2: FT-IR spectra of pure hBN, NaClO$_4$ and PEO.
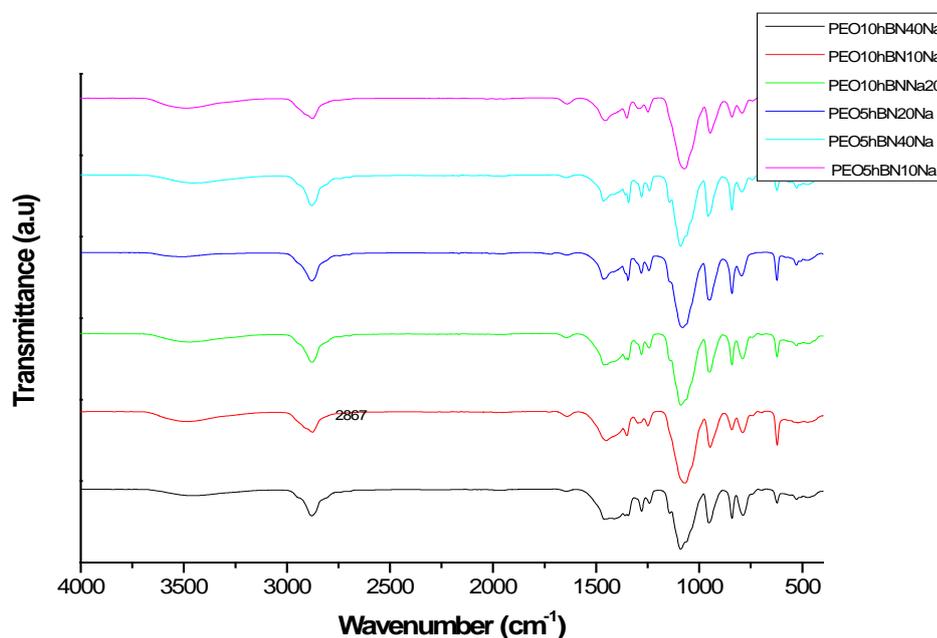
Figure 3: FT-IR spectra of PEO-hBN-NaClO$_4$ composite electrolytes.

3.2. DSC analysis

The DSC analysis was performed at scan rate of 10 °C min^{-1} under inert atmosphere by a heating cooling-

heating cycle. The sample and reference were heated from the same source, and measured the temperature difference. The samples were first heated from -50 to 100 °C, and then cooled from 100 to –50 °C. The second heating was done between -50 and 200 °C at a scan rate of 10 °C min^{-1}, and the second heating curves were evaluated and were given in Figure 4. From the literature, neat PEO exhibit T_g at -60.03 °C [19], and this temperature is not included within our measuring temperature range.

As seen in Figure 4, the endothermic peak of the melting temperature (T_m) for the neat PEO is observed at 66 °C. By addition of $NaClO_4$ salt, the peak is observed to shift to a lower temperature. This can be explained as a decrease in the degree of crystallinity compared to that of pristine PEO, Sasithorn and his colleagues [10] and Yatim and his colleagues [17] observed the same phenomenon using $NaClO_4$ and $LiCF3SO_3$ salts respectively. The behavior discloses that the mechanism may involve the formation of coordinate bonds between the ether-oxygen of PEO with metal ions of the salt, resulting in the increase of PEO chain mobility. This result is in agreement with the associated ionic conductivity enhancement in which an increased amorphization is observed with increasing $NaClO_4$ concentration.

Apart from the concentration of $NaClO_4$, incorporation of nano-hBN also affects the thermal behavior of the PEO-base composite. Although, as stated above, the T_g of pure PEO is around -60 °C and it is not within our measuring temperature range. There is report for reduction of PEO T_g by incorporation nano particles; this reduction in T_g suggests enhanced segmental flexibility of polymer chain [19]. It can be seen in figure 4, the T_m of PEO also decreases due to the incorporation of nano-hBN. This can be explained as incorporation nano-hBN within the polymer matrix can enhance thermal conductivity within the polymer which caused decrease of the melting temperature.
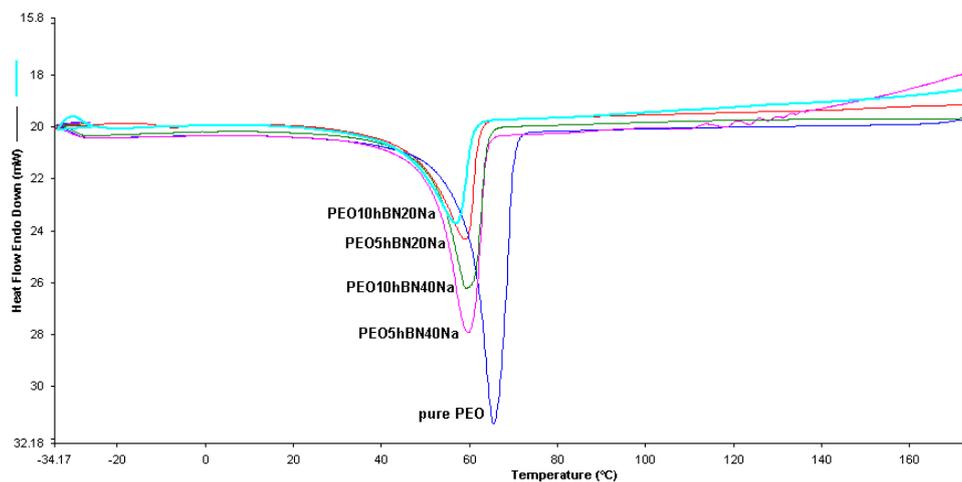
Figure 4: DSC result of pure PEO and PEO-hBN-NaClO$_4$ composite electrolytes

3.3. TGA

Thermal stability is one of the most important properties for PEs during application of SIB. TGA gives information about the possible physical changes that may happen during a thermal excitation in a polymer

electrolyte when it is applied to working systems[20]. The electrolyte should possess good thermal stability at high temperature to meet the criteria for application. Thermal stability of neat PEO and the composites were evaluated by TGA.

Prior to the measurement, the pure PEO and the composites were dried under vacuum at 100 °C for 24 h. The TGA results for pure PEO and the polymer composites were depicted in Figure 5. As shown by the TGA curve, the pure PEO decomposition occurs mainly at temperatures between 350 and 400 ^{o}C which reached a peak rate at 375 ^{o}C [21]. When the temperature reaches 800 ^{o}C, the corresponding mass loss is almost 100% i.e. all the materials is lost. Whereas for PEO-hBN-NaClO$_4$ composite electrolytes, the degradation of the material starts just before the neat PEO and the material does not degrade completely at 800 ^{o}C as opposed to pristine PEO which was completely lost, this is due to the present of inorganic NaClO$_4$ salt and the nano-hBN. For PEO-10hbN-10Na, there is still about 21% of the material left because it has the highest contents of NaClO$_4$ and nano-hBN. All the PEO-hBN-NaClO$_4$ composite electrolytes are stable up to 300 ^{o}C indicating that the composites can endure relatively high temperature for battery application.
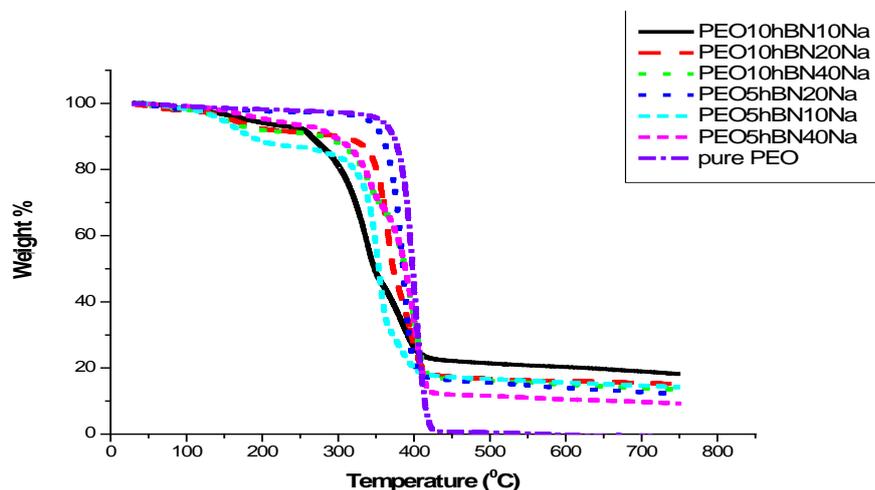
Figure 5: TGA results of pure PEO and the PEO-hBN-NaClO$_4$ composite electrolytes

3.4. SEM analysis

Study of the morphology is important in order to confirm the homogeneity of polymer blends. The SEM analysis provides detailed photographs that give important information about the surface structure which affirms the polymer blends homogeneity [14]. Several studies have reported the use of functionalized hBN, functionalization helps prevent agglomeration in various polymer matrices [14, 18]. In this study we used pure hBN directly and just sonication is enough in providing adequate blending. On preparation by solvent-casting method, homogenization of electrolyte is obtained by the use of a large amount of solvent. After the solvent removal, the presence of polymer chains precludes aggregation of salt [22]. Surface morphology of the PEO-hBN-NaClO$_4$ composite electrolytes was investigated by scanning electron microscopy (SEM) and given in Fig. 5. As expected the composites appear to be homogeneous which display that hBN uniformly dispersed into the PEO matrix. As seen in Figure 6, the surface morphology of the composites is very smooth, indicating the

domination of amorphousness in the PEO host polymer. Crystalline phase decreasing in PEO is associated with the smooth surface morphology of the polymer through interaction between ether oxygen of PEO and the salt [23].
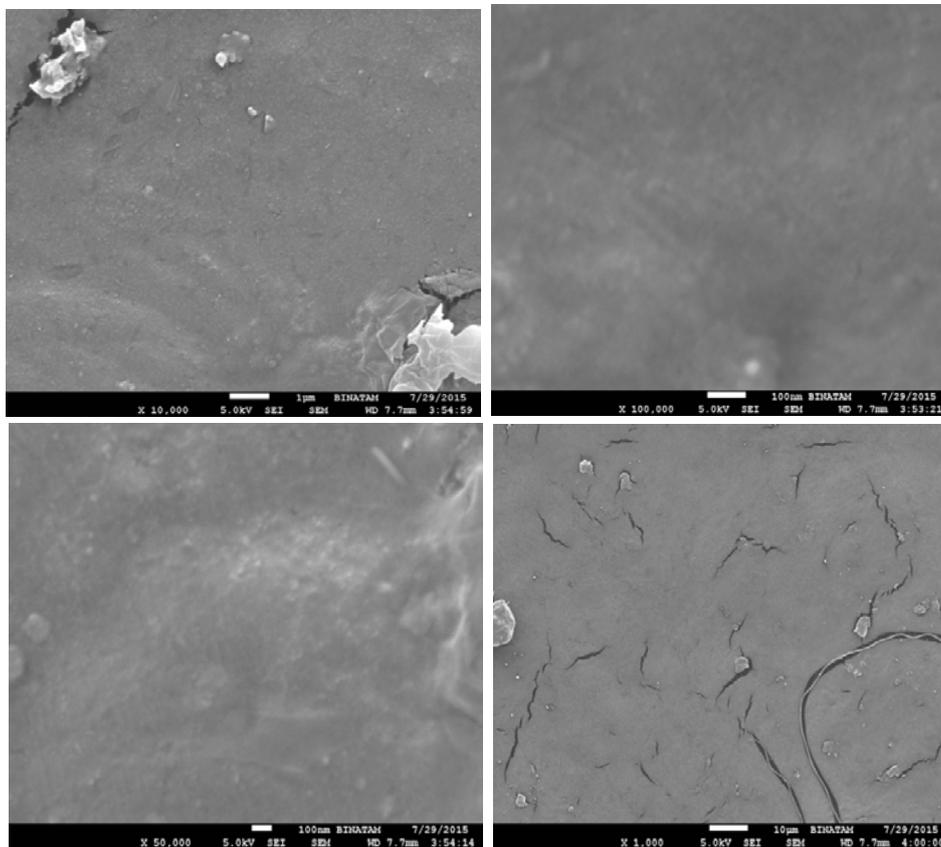
Figure 6: SEM images of PEO5hBN10Na composite electrolytes

3.5. XRD analysis

XRD measurement is a non-ravaging technique which is performed in the composite studies in order to investigate the presence of any phase alteration or crystallinity difference when two materials with different crystallinity were mixed [18, 24]. Figure 7 (a, b, c and d) show the XRD pattern of PEO5HBN10Na, PEO5hBN40Na, PEO0hBN10Na and PEO0hBN40Na respectively. Strong peaks were observed at $2\theta = 19.33$ and $2\theta = 23.6$ in PEO5HBN10Na and PEO5hBN40Na composites, are correspond to (1 2 0) and (1 1 2) crystalline peaks of PEO [17, 25]. This observation affirms that the PEO-hosted polymer blend system exhibits both crystalline and amorphous regions. The intensity of the PEO peak decreased with increasing $NaCO_3$ concentration i.e., the addition of $NaClO_4$ to the host polymer blend (PEO) reduces the peak intensity effectively, suggesting a reduction in the degree of PEO backbone crystallinity. This is may be due to the interruption of the semi-crystalline structure of the polymer by $NaClO_4$ salt [17]. The PEO peak was not observed in the similar samples but without hBN that is sample PEO10Na and PEO40Na. This could be due to the more interaction between the polymer host (PEO) and $NaClO_4$ salt which lead the replacement of some crystalline regions oriented in certain direction in the polymer backbone by non-crystalline phase due to the

coordination bonds between ether O atoms of PEO and Na^+ ions. From the literature, pristine $NaClO_4$ salt exhibit peak around $2\theta = 55$ [26], this peak was not observed in all the samples except PEO0hBN10Na which indicates the dissolution of the salt in the polymer matrix. For pristine hBN Figure [3.6 e], four peaks were observed: at 26.68° for (0 0 2) plane, 41.50° for (1 0 0) plane, 43.13° for (1 0 1) plane, and 55.12° for (0 0 4) planes [24].
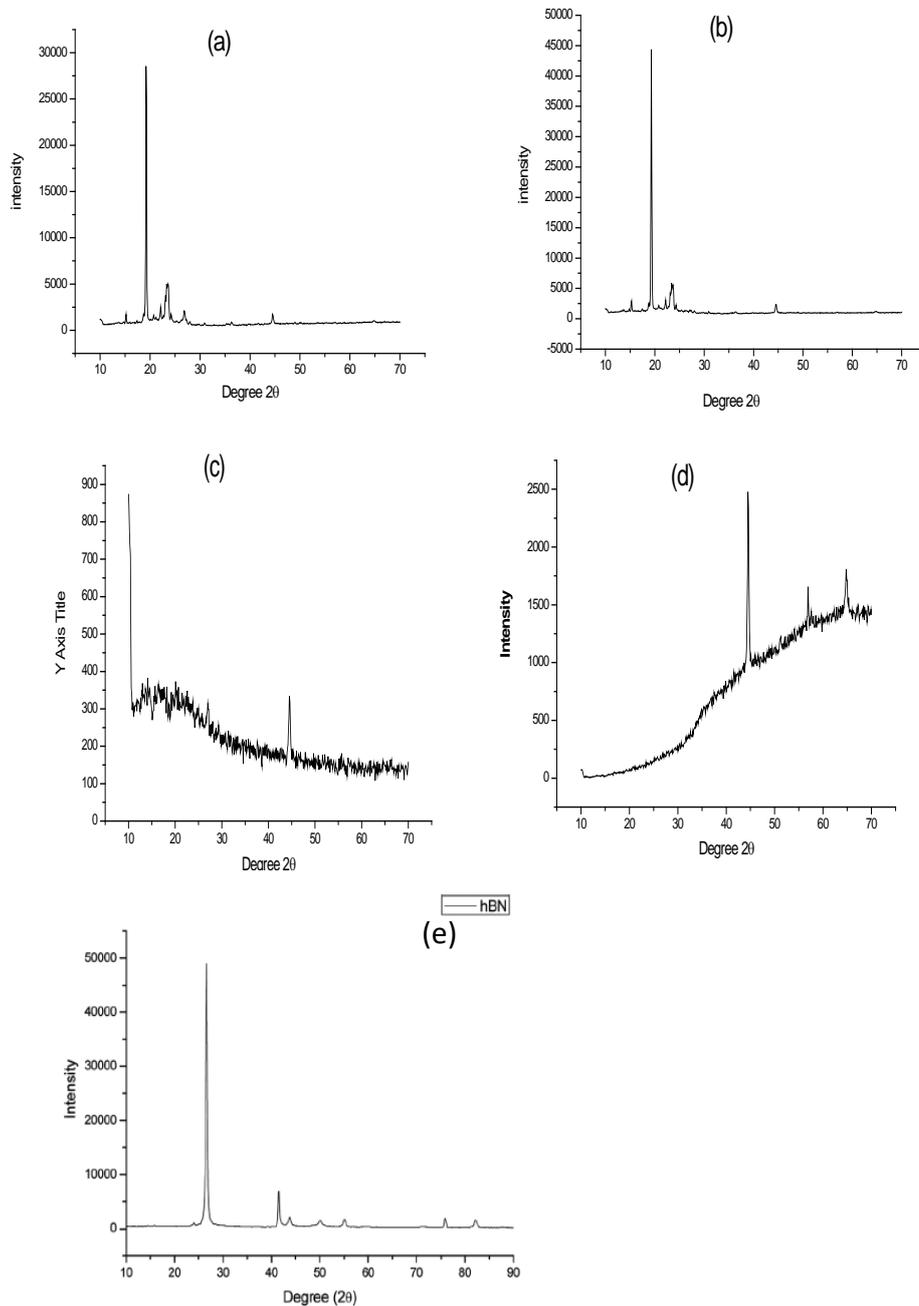
Figure 7: XRD pattern of (a)PEO5hBN40Na (b) PEO5hBN10Na (c) PEO0hBN40Na (d) PEO0hBN10Na (e) pure hBN

3.5. Conductivity measurement

Ionic conductivity is one of the most important parameter measures for SPEs. However, a proper analysis of ionic conductivity data can disclose details about the conduction mechanism. The conductivity measurement was performed in a completely water-free environment in order to avoid the contribution of humidity to the ion conductivity, and was measure in the temperature of 20 to 100 ^{o}C. Figure 8-10 show the frequency and temperature dependent AC conductivities (σ_{ac}) of PEO-hBN-NaClO$_4$ composite electrolytes. There is an increased in conductivity with increasing of log frequency, which then leveled off as a result of polarization of electrodes. The variation at the low frequency regions can be attributed to polarization, which barricades the electrode–electrolyte interface. For all composites, ionic conductivity rises with rising in temperature. As temperature rises the motion of the ion becomes faster, which in turn caused an increase in ionic conduction[20].

The DC conductivity (σ_{dc}) values were obtained from the plateaus of log σ_{ac} vs. log F by linear fitting of the data and compared in Figure 11. From the literature, pure PEO was reported to have Na$^+$ ion conductivity of 6.3 $\times$ 10^{-6} at 100 ^{o}C [17]. Here, it can be seen the associated ionic conductivity increase with the conditioning temperature, which is reasonable that the Na$^+$ carrier exhibits higher mobility at elevated temperature. Besides, a clear conductivity jump is observed between 40 and 50 ^{o}C, this could be described as the transition of PEO from semi-crystalline to amorphous phase [17], Yatim Lailun Ni'mah and his colleagues [17] obtained the same trend. Furthermore, it can be understood the ionic conductivity of PEO-based composites increases as the concentration NaClO4 salt increase from EO:Na 40 to EO:Na 10 ratio. The increase of ionic conductivity at sodium salt content was because of an increase in charge carriers due to the increased of the number of free cations, and also due to a decrease in the degree of T$_g$. The amorphousness of the SPEs contributed to fast Na-ion movement in the polymer network and lower T$_g$ steered to easier chain relaxation, which in turn led to the fast ion conduction and thus the observed improvement of ionic conductivity [10]. The percentage of nano-hBN slightly affects the ionic conductivity, with PEO-5hBN-10Na being the optimum having the highest ionic conductivity of 1.5 $\times$ 10^{-3}. Wieczorek and his colleagues [12] proposed that the enhancement in ionic conductivity of SPE/ organic or inorganic fillers composite are caused by alterations in the microstructure and morphology. The alterations of morphology and microstructure are due to the reactions of various Lewis acids and bases taking place among Lewis base centers of the polyether, Lewis acid centers of the fillers.
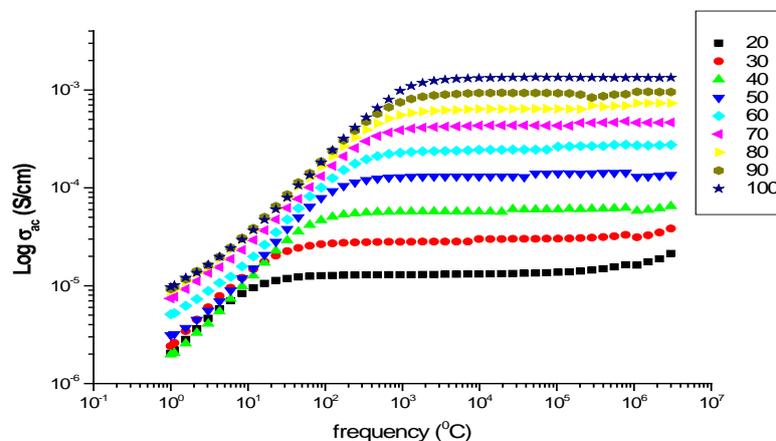
Figure 8: AC conductivity of PEO-5hBN-10Na
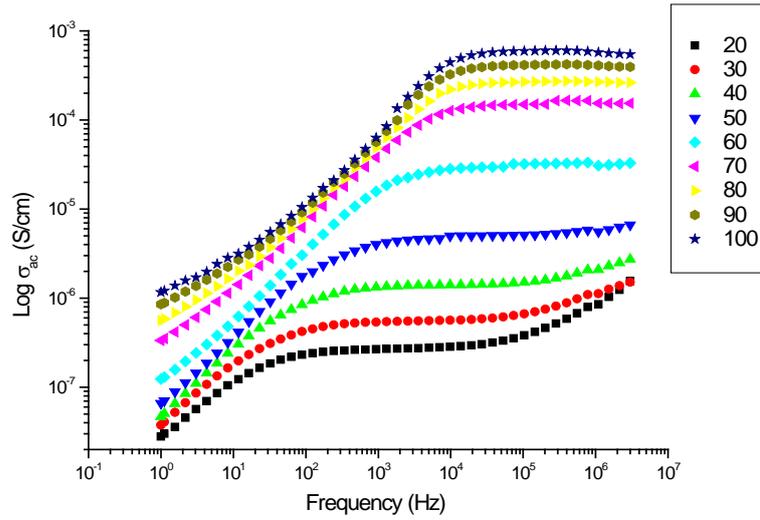
Figure 9: AC conductivity of PEO-5hBN-20Na
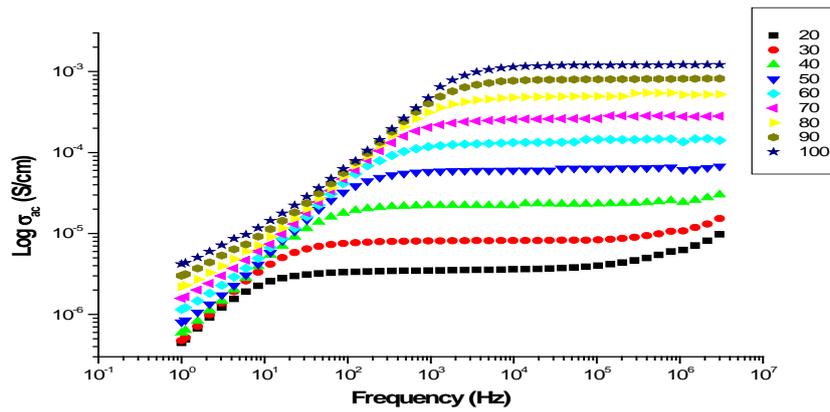
Figure 10: AC conductivity of PEO-10hBN-10Na
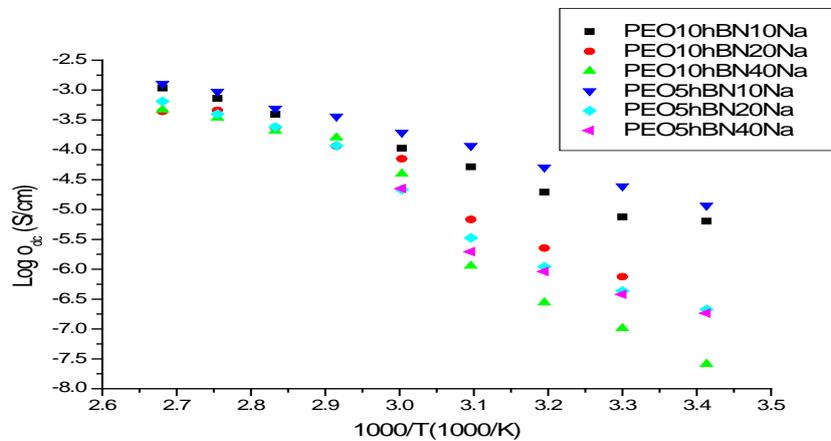
Figure11: DC conductivity of the composite membranes with reciprocal of temperature.

4. Conclusion

Novel polymer composite electrolytes, PEO-hBN-NaClO$_4$ with different EO:Na ratio and weight % hBN was successfully produced. The interaction between PEO host polymer and NaClO$_4$ salt was investigated with FT-IR. TGA evidenced that the PCEs were at least thermally stable up to 300 ^{o}C. DSC results showed that T$_m$ of the CPE decreases with increasing NaClO4 salt. The homogeneous dispersion of hBN the polymer host was verified with SEM images. XRD analysis also confirmed the incorporation of the hBN. The sodium ion conductivity was studied using dielectric-impedance spectroscopy. The conductivity increased with NaClO4 mole ratio and also with temperature. The PEO5hBN10Na sample showed maximum ion conductivity of approximately 1.4 $\times$ 10^{-3} S/cm at 100 ^{o}C.

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