✚IJESRT

INTERNATIONAL JOURNAL OF ENGINEERING SCIENCES & RESEARCH TECHNOLOGY

CHARACTERIZATION OF PEO CONDUCTING POLYMER ELECTROLYTE COMPLEXED WITH KNO₃ ALKALI SALT AND NB₂O₅ NANO-FILLER

Y.Aparna*, S.Ram Kumar and P.Srinivasa Subbarao
* Department of Physics, Jawaharlal Nehru Technological University, Kukatpally, Hyderabad, India

ABSTRACT
Conducting solid phase polymer electrolyte (SPE) films were synthesized using solution casting technique. In the present study the polyethylene oxide [PEO] complexed with potassium nitrate [KNO_3] as alkali salt group and Nb_2O_5 as nano fillers with weight percentile [5-15%] ratios. The complexation of KNO_3 salt with the polymer matrix PEO has been characterized by X-Ray Diffraction, surface morphology, EDAX and AC conductivity studies. The AC conductivity measurements were done in the temperature range of 303K–333 K using AC conductivity set up. From electrical conductivity studies it is observed that the conductivity order increased from fifth order to third order. The conductivity in polymer electrolyte system is due to ions of alkaline salts and Nb_2O_5 nano-fillers which are present in polymer matrix. Several electrical and dielectric characterizations were done for these films and the results will be discussed in detail.

Keywords: Polymer electrolyte, polymer nano-composite, solution cast technique, AC conductivity, activation Energy, dielectric constant, dielectric loss, electric modules.

INTRODUCTION
Poly-ethylene oxide grounded solid polymer electrolytes have interesting properties such as salt-compositional variability, chemical compatibility, electrode couples, good electrode electrolyte contacts and mechanical properties. These thin films can be fabricated in desirable shapes and sizes and the studies have received much technological interest. These properties make PEO as an interesting material for a variety of applications, including lightweight, high energy density for fabrication of rechargeable batteries[1], fuel cell[2], super capacitors[3], electrochemical display devices[4] etc. In order to improve the conductivity of PEO based electrolytes, at lower operational temperatures, researchers made many strategies to incorporate a variety of nanoscale inorganic fillers such as SiO_2[5], Al_2O_3[6], TiO_2[7], ZnO[8], ZrO_2[9] and CeO_2[10] without affecting the other physical properties like mechanical stability, electrolyte reactivity towards electrode etc.[11-14].

It is observed that the nano sized fillers play a vital role in inhibiting the PEO chain crystallization kinetics, expansion of amorphous phase region in polymer matrix and providing specific surface interactions with electrolyte components. The basic supposition in various investigations have considered the Lewis acid–base type surface chemical group of inorganic fillers interact on cations and anions, promotes the disassociation of the ion pairs so that the electrolytes can free more free carriers and remains in amorphous state for charge carriers to transfer K+ ions[15–20].

It is also found that physical properties of polymer electrolyte composites depend on the filler concentration as well as the nature of filler. However, the mechanism of ionic conductivity enhancement and the role played by the nano-sized fillers is still not well realized. Almost the composite polymer electrolytes in the past three decades were mainly based on alkali metal salt schemes, with especially attention given to lithium. There have been elite literatures on solid polymer nano-composite electrolytes established on sodium and potassium complex

arrangements though it has lower lattice energy. Compared to lithium, potassium is soft, cost ineffective, more abundant and easier to maintain contact to other components in the electrochemical devices. In the present study a systematic effort has been made for the polymer electrolyte system composed of potassium nitrate (KNO_3) as salt and Nb_2O_5 at (5-15Wt. %) as nano filler. The electrical conductivity is measured as a function of Nb_2O_5 concentration has been carried out to identify the optimum conducting composition (OCC) of the composite polymer electrolyte.

MATERIALS AND METHODS
Experimental:
Poly-ethylene oxide based polymer-salt electrolyte with nano filler thin films, were prepared by solution casting technique. PEO and KNO_3 molar ratio 70:30 was taken from the optimized phase diagram of PEO-KNO_3 system [21] as a secondary host and PEO as primary host polymer matrix. The standard and simple technique solvent casting method was used to prepare PEO-KNO_3 and composite polymer electrolyte films using methanol as the common solvent. PEO (Aldrich) with molecular weight, MW =106 g/mol and KNO_3 (sigma) with MW=101 g/mol were dried in oven at 313K, for 1 hour prior to use.

First, the weighted quantity of PEO and KNO_3 were dissolved in methanol solvent and stirred thoroughly for 4 hours at 308K temperature. The viscous solution was then put onto a Teflon petri dish and allowed to dry at room temperature for overnight. Lastly, the film was dried in oven at 318K for 18–24 hours to evaporate any residual solvent. Nb_2O_5 dispersed in composite polymer electrolytes in different weight percentages (5, 10, 15 Wt. %) were also prepared following the same subroutine mentioned above. Thin films were then preserved in a vacuum desiccator for the long term stability. Stable films from 5 Wt. %, 10 Wt. % and 15 Wt. % of Nb_2O_5 were prepared. Films are found very brittle beyond this concentration.

X-ray diffraction patterns of the pure Nb_2O_5 and the composite films were recorded by means of a high-resolution Rigaku X-ray diffractometer with Cu-Kα radiation over the Bragg angle (2θ) ranges from10°–80°. The average size of the pure Nb_2O_5 was estimated using XRD studies.

Surface morphology of the samples and electrical properties of electrolytes were conventionally characterized by the standard techniques. In this procedure, mobile ions are blocked at the electrodes to generate space charge region. Electrical conductivity is determined by the movement of ionic space charge between the blocking electrodes under the application of AC field. AC conductivity of the composite polymer electrolyte films was evaluated by means of Agilent LCR Precision Meter; model no 4980E as its frequency responses upon 2 MHz with an external temperature setup, temperature range of 318 K–343 K. For this, the nanocomposite electrolyte films were introduced between two polished copper blocking electrodes and temperature was monitored by Yudian PID temperature controller Model No. A1 used thermocouple sensor.

RESULTS AND DISCUSSION
XRD:
XRD spectra of pure PEO, PEO-KNO_3 and varying concentration of dispersed Nb_2O_5 filler composite polymers specimens were shown in the figure.1 below. In figure.1 peaks at 2θ= 18.9° and 23°, corresponds to PEO and they confirms the crystallinity of PEO. When KNO_3 was added to polymer matrix, decrease in crystallinity was observed and confirmed by observing the intensity variation. It gives an idea that the crystalline state of PEO is disturbed by the K^+ ions and oxygen's in polymer composite matrix. After the addition of Nb_2O_5, we can observe the characteristic peaks of Nb_2O_5 which in PEO-KNO_3 polymer salt composite.
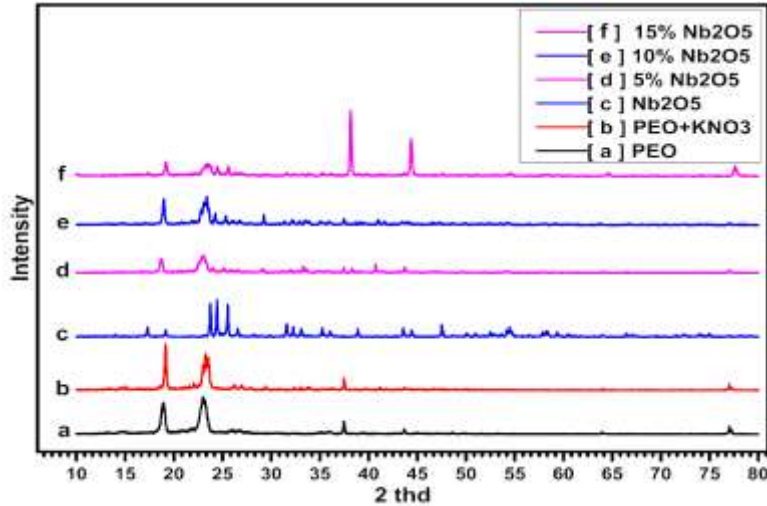
Figure 1: [a] PEO, [b] PEO-KNO₃, [c] Nb₂O₅ ,[d] 5Wt.% Nb₂O₅, [e] 10Wt.% Nb₂O₅, [f] 15 Wt.% Nb₂O₅.

According Scherrer formula the crystalline size of material was estimated using equation (1) shown below. From this crystalline size of pure PEO, PEO-KNO₃ is estimated and is around 483.85 nm, 48.22 nm respectively. But when 5, 10, 15 Wt. % of Nb_2O_5 is added the crystalline sizes were reported as 49.76 nm, 57.26 nm, 46.53 nm respectively. From this it is noticed that the adding of 15 Wt. % is reduced its crystalline size. Due to the aggregation in nanocomposite the size increases with the increase in the percentage of Nb_2O_5. The average size of the nanocomposite is around 51.33 nm.

$$t = \frac{0.9}{\beta \cos(\theta)} \text{------------ (1)}$$

From the XRD of the sample shown in figure.1[c], it is also clear that the Nb_2O_5 particles are with a crystalline size of 44.63 nm. In figure.1 (a) the peaks at 2θ = 19.1° and 23.5° are corresponding to (1 2 0) and (1 1 2) crystalline peaks of PEO [22]. The featured peaks of pure PEO in $(PEO)_{70}$:$(KNO_3)_{30}$ complex (figure.1,[b]) show variation in intensity suggesting that the ordering of the pure PEO is disturbed due to coordination interactions between the K^+ ions and oxygen's of poly-ethylene oxides polymeric chain. After the addition of Nb_2O_5 nano-filler in polymer electrolyte specimens, some fresh peaks appear which corresponds to the resembling peaks of Nb_2O_5 presence in spectrums of figure 1.[d], [e], [f]. The size of Nb_2O_5 nanoparticles grows with the increase in concentration due to the aggregation in the composite with PEO matrix. This is confirmed from size determination using Scherrer formula equation (1) based on XRD data.

SEM - EDAX :
Furthermore, PEO molecules are deposited on the surface of larger particles due to the interaction between PEO and Nb_2O_5. As a result of these, the surface morphology of the electrolyte with 15 Wt.% is different from 5 Wt.% & 10Wt.% of Nb_2O_5 filler in matrix composite which were shown in figure.2 and corresponding EDAX results shown in figure.3.
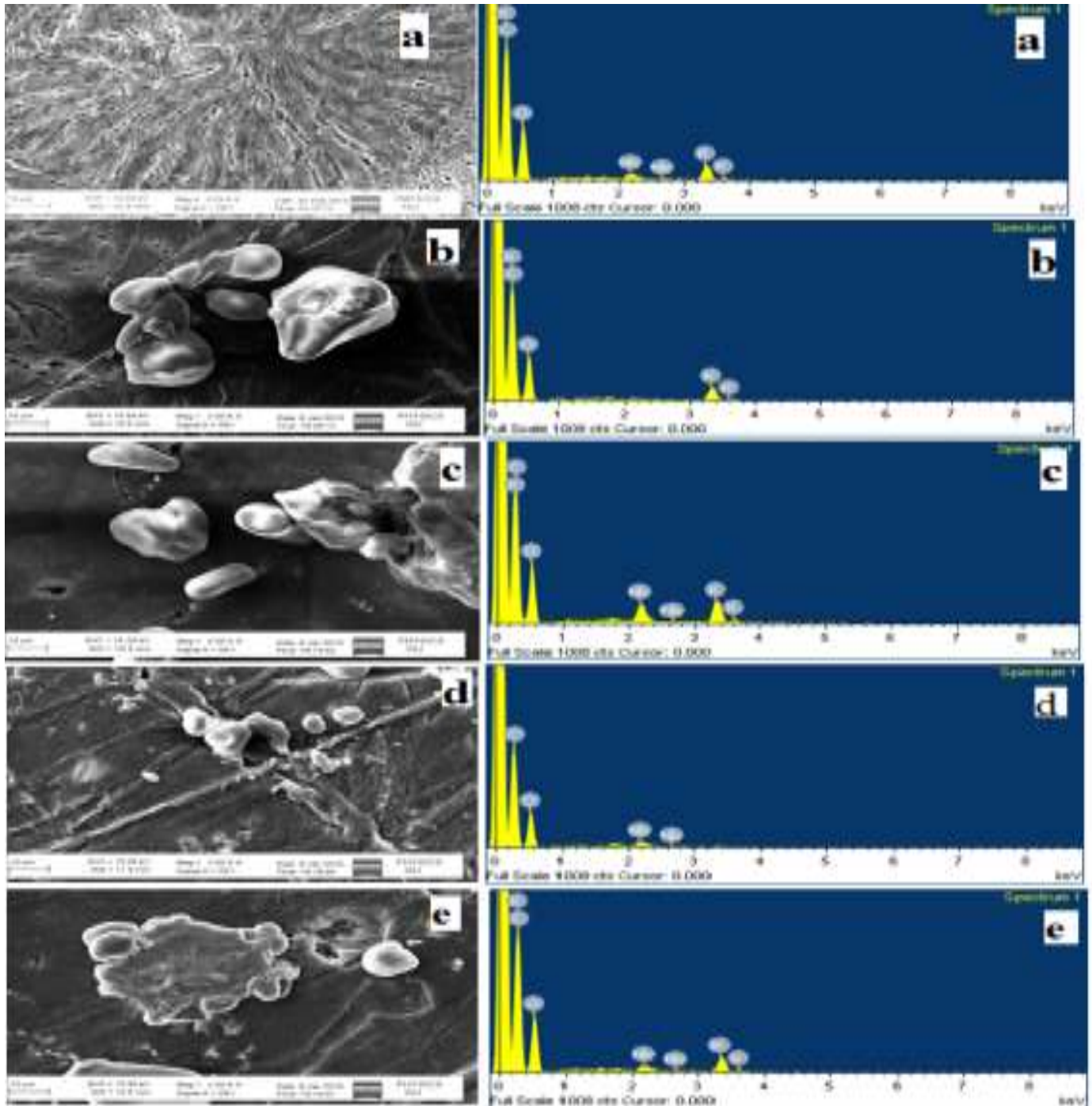
Figure.2: SEM images [a] PEO, [b] PEO-KNO₃,
[c]Nb₂O₅,[d]5Wt.%Nb₂O₅
[e]10Wt.%Nb₂O₅[f]15 Wt.% Nb₂O₅

Figure 3: EDAX results [a]PEO, [b]PEO-KNO₃,
[c]Nb₂O₅,[d]5Wt.%Nb₂O₅
[e]10Wt.%Nb₂O₅. [f]15 Wt.% Nb₂O₅

The SEM image in figure.2 shows the morphology of pure PEO is compared with PEO-KNO$_3$ and Varying Wt. % of Nb$_2$O$_5$ substituted in PEO-KNO$_3$ matrix. Figure.3 represents the EDAX results confirmation of the elements in each of respective SEM images correspondingly. The SEM image in figure.2.[a] clearly shows that the morphology of pure PEO is very rough without any crystallites are particles on it and confirmed the elements present in PEO with EDAX result figure.3.[a]. In figure.2. [b] PEO-KNO$_3$ show very smooth matrixes and clear surface morphology with rarely substituted grains on the surface and the respective EDAX results as figure.3 [b]. From the figure.2. [c], [d], [e] which look like in flakes with rare presence and mostly sphere shaped granules on the polymer matrix. Thus from this three figures we understand that there was a significant change in the morphology after the casting of KNO$_3$ and Nb$_2$O$_5$ on PEO compared with pure PEO. From the EDAX results figure.3 [c], [d], [e] represents the elements of PEO, KNO$_3$ and Nb$_2$O$_5$ and the variation of the concentration of Nb$_2$O$_5$ fillers. Among the SEM images figure.2[c],[b] the figure.2[e] has good results in electrical properties due to the imbursement of the Nb$_2$O$_5$ granules distribution such that it shows well mechanical strength in polymer matrix than others. Among them as shown in figure.2 [e] Nb$_2$O$_5$ well dispersed and mechanically well stretched in PEO matrix.

Electrical studies:
The temperature dependence of AC conductivity of PEO-KNO$_3$ (70:30) and composite polymer electrolytes for dissimilar concentrations of Nb$_2$O$_5$ are represented in figure 4. It is observed that the conductivity plots have mostly positive temperature coefficients within the evaluated temperature range of 303K to 333K. In experimental observation as samples were start melts from 323K temperature also we can notice in figure.4. A typical drop or raise at this temperature. These behaviors are ordered with Arrhenius type charge conduction in polymer electrolyte nanocomposites which can be expressed by below equation (2).

$$\sigma = \sigma_0 \exp(-E_a / kT) \text{ ----------- (2)}$$

Whereas the pre-exponential factor, E$_a$ is the activation energy and 'k' is the Boltzmann's constant. The variation of activation energy (E$_a$) was above and below the melting temperatures reputed as Region I, Region II in figure.4.
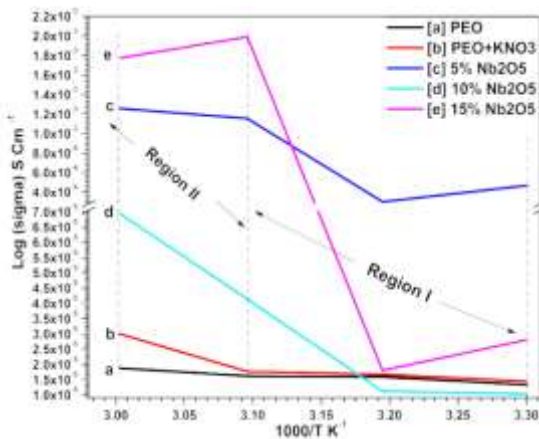

Figure. 4: Arrhenius type Temperature dependent conductivity plots of [a] PEO, [b] PEO: KNO3: 70:30, [c] 5 wt. % Nb2O5; [d] 10 wt. % Nb₂O₅; [e] 15 wt. % Nb₂O₅.
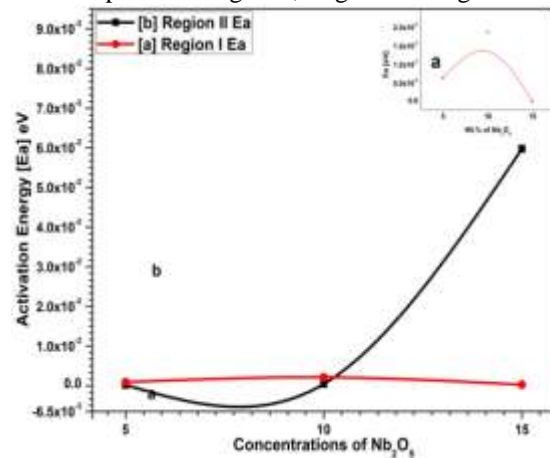

Figure. 5: Variation of activation energy (Ea.) with differ concentrations of (a) above the melting temperature and (b) below the melting temperature with Nb2O5 concentration.
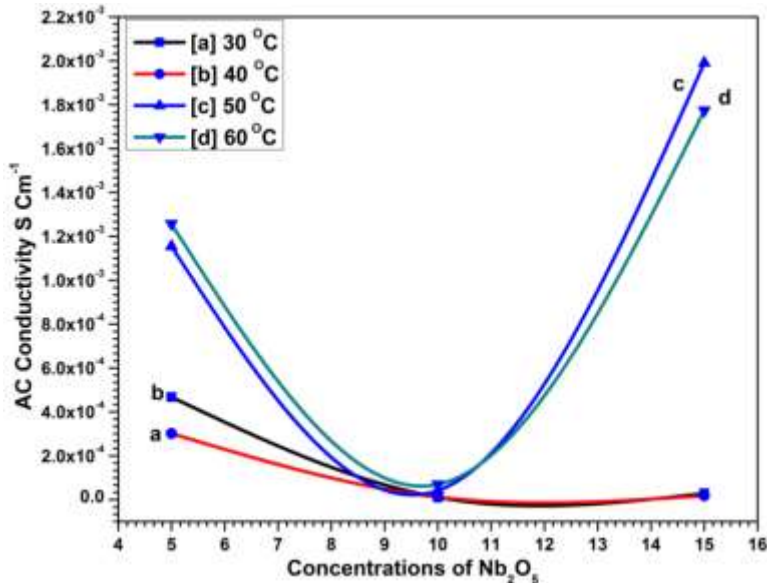
Figure.6: Conductivity variation with Nb$_2$O$_5$ concentration at different temperatures.

The variation of AC conductivity with respective varying Nb$_2$O$_5$ Wt. % observed in figure.6. As the filler deposited polymer composites has low conductivity range at low temperatures shown in figure 6[a], [b] and in figure.6[c], [d] the temperature reaching and crossing the melting temperature. The variation of conductivity varies rapidly for 10 and 15 Wt. % concentrations of Nb$_2$O$_5$.

Dielectric studies:

The real part of the dielectric permittivity or dielectric constant, ε' and imaginary part of dielectric permittivity or dielectric loss, ε'', for the samples measured in the frequency range 20 Hz to 2MHz various temperatures is shown in figure 7(a), (b) and (c) it is observed that the dielectric constant,ε' (ω) is decreased rapidly at lower frequencies and indicated nearly frequency independent behavior at higher frequency ranges [24]. The bulk polarization of sample results from presence of electrodes, which don't transfer the charge species into the external circuit. At higher temperatures,ε' (ω) is observed to be increased and it might be due to migration of the potassium ion and Nb^{2+} in NCPE. At lower frequency range, the charge carriers will no longer be capable to revolve sufficiently rapidly, so their oscillation will begin to lay behind this field resulting in a decrease of dielectric permittivity, ε'(ω). At low frequency region, the permanent dipoles align themselves along the field and add fully to the entire polarization of dielectric. At higher frequency range, the variation in the field is really rapid for the dipoles to coordinate themselves, so their contribution to the polarization and hence, to dielectric permittivity can turn negligible. Consequently, the dielectric permittivity,ε' (ω) decreases with increasing frequency. The decrease of the dielectric constant ε' can also explain from interfacial polarization. The interfacial polarization develops as a result of conflict in conducting stage, but is interrupted at grain boundary due to lower conductivity. In general poly-crystalline materials, the grains shows semi conducting behavior while the grain boundary are insulators.
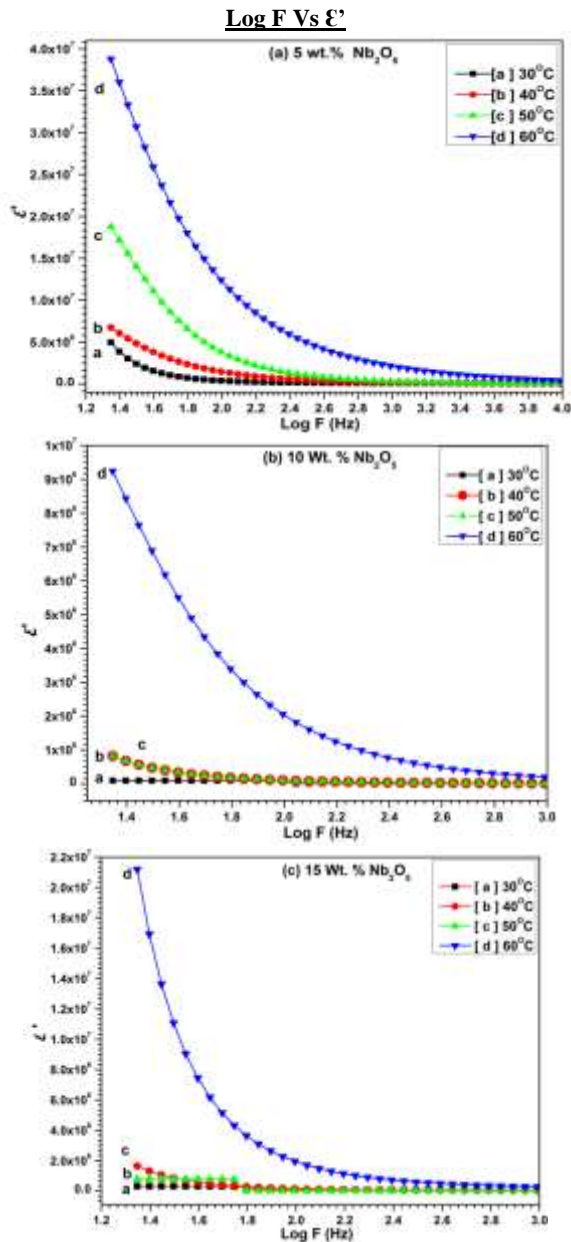
Log F Vs Ɛ'

Log F Vs Ɛ"

Figure.7. (a),(b) and (c) Variation of the real part of dielectric constant (Ɛ') with respect to frequency at various temperatures of 5,10,15 Wt.% Nb₂O₅ respectively
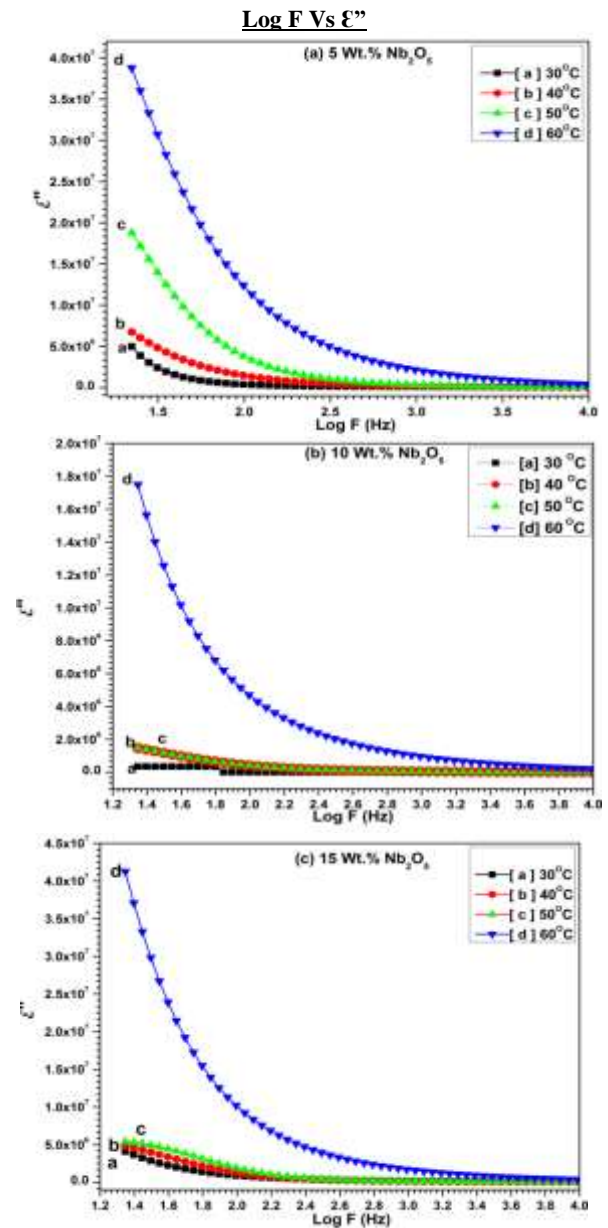
Figure.8. (a),(b) and (c) Variation of the imaginary part of dielectric loss (Ɛ") with respect to frequency at various temperatures of 5,10,15 Wt.% Nb₂O₅ respectively.

The frequency dependence of the dielectric loss, $\mathcal{E}''$ (ω) at different temperatures is shown in figure 8 (a), (b) & (c). The maximum in dielectric loss $\mathcal{E}''$ (ω) peaks shifts toward lower frequency range as the temperature increase indicating a thermal activated behavior. Mostly, the dielectric losses ($\mathcal{E}''(\omega)$) at low frequencies are much higher than those occurring at higher frequencies at specific temperature. This kind of dependence of $\mathcal{E}''(\omega)$ on frequency is typically associated with losses by conduction.

CONCLUSION

The X-ray diffraction pattern of polymer electrolyte complexes with salt and nano filler confirmed the formation of $PEO-KNO_3-Nb_2O_5$ and the corresponding peak positions were observed. The estimated particle size of the samples from SEM studies is about 184nm ~ 354 nm. And the elemental confirmation was done to the respective SEM images of the samples correspondingly. The plot of log conductivity against reciprocal temperature obeys Arrhenius rule. The ionic conductivity range of the sample collections was found to be varied from 1.874×10^{-5} S/cm to 1.99×10^{-3} S/cm by increase in temperature from room temperature to 333 K. Conductivity at room temperature is improved from third order to fifth order of magnitude by incorporating Nb_2O_5 nanoparticles(mention %). Lowering of crystallinity, an increase of free ion concentration and prominent acid–base interaction with Nb_2O_5 nanoparticle enhance the ionic conductivity of $PEO-KNO_3$ electrolyte nanocomposite at 15wt. % Nb_2O_5. Transport parameters such as activation energy E_a have been calculated. The activation energy calculated from the Arrhenius plots was found to be 0.059 eV. The dielectric constant $\mathcal{E}'$ and dielectric loss $\mathcal{E}''$ was observed to decrease with increase in frequency.

ACKNOWLEDGEMENTS

REFERENCES

[1] B. Scrosati, Application of Electroactive Polymers, Chapman and Hall, London, 1993.
[2] F.M. Gray, Polymer Electrolytes, The Royal Society of Chemistry, Letchworth, HN, 1997.
[3] T.J.P. Vaia, G.W. Beall, Polymer–Clay Nanocomposites, John Wiley & sons Ltd., NY, 2002.
[4] F. Croce, G.B. Appetecchi, L. Persi, B. Scrosati, Nature 394 (1998) 456–458.
[5] F. Croce, R. Curini, A. Martinaelli, L. Persi, F. Ronci, B. Scrosati, R. Caminiti, J.Phys. Chem. B 103 (1998) 10632–10638.
[6] K.S. Ji, H.S. Moon, J.W. Kim, J.W. Park, J. Power Sources 117 (2003) 124–130.
[7] C.W. Nan, L. Fan, Y. Lin, Q. Cai, Phys. Rev. Lett. 91 (2003) 266104 (1–4).
[8] A. Yuan, J. Zhao, Electrochim. Acta 51 (2006) 2454–2462.
[9] M. Morita, H. Noborio, N. Yoshimoto, M. Ishikawa, Solid State Ionics 177 (2006). 715–720.
[10] X.M. Qian, N.Y. Gu, Z.L. Cheng, X.R. Yang, E.K. Wang, S.J. Dong, Electrochim. Acta. 46 (2001) 1829–1836.
[11] X.L. Wang, A. Mei, M. Li, Y.H. Lin, C.W. Nan, J. Appl. Phys. 102 (2007) 054907.(1–6).
[12] Z.M. Dang, L.Z. Fan, S.J. Zhao, C.W. Nan, Mater. Res. Bull. 38 (2003) 499–507.
[13] H.M. Xiong, X. Zhao, J.S. Chen, J. Phys. Chem. B 105 (2001) 10169–10174.
[14] A. Dey, S. Karan, S.K. De, Solid State Ionics 178 (2008) 1963–1968.
[15] W. Wieczorek, J.R. Stevens, Z. Florjanczyk, Solid State Ionics 85 (1996) 67–72.
[16] F. Croce, L. Persi, B. Scrosati, F. Serraino-Fiory, E. Plichta, M.A. Hendrickson, Electrochim. Acta 46 (2001) 2457–2461.
[17] S.H. Chung, Y. Wang, L. Persi, F. Croce, S.G. Greenbaum, B. Scrosati, E. Plichta, J.Power Sources 97–98 (2001) 644–648.
[18] P.K. Singh, R. Pratap, A. Chandra, Prog. Cryst.Growth Charact.Mater. 44 (2002).175–182.
[19] M. Marcinek, A. Bac, P. Lipka, A. Zaleska, G. Zukowska, R. Borkowska, W. Wieczorek, J. Phys. Chem. B 104 (2000) 11088–11093.
[20] W. Wieczorek, Z. Florjanczyk, J.R. Stevens, Electrochim. Acta 40 (1995). 2251–2258.
[21] C. Vachon, M. Vasco, M. Perrier, J. Prudhomme, Macromolecules 26 (1993).4023–4031.
[22] Arup Dey, Kajari Das, Karan. S, De.S.K. Spectrochimica Acta Part A 83 (2011) 384–391
[23] L.F. Hu, Z.L. Tang, Z.T. Zhang, J. Power Sources 166 (2007) 226–232.
[24] Chandra babu, B.; Naresh, V.; Jaya Prakash, B.; Buddhudu, S. Ferroelectrics Lett.2011,38, 124.