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Electrical And Dielectrical Studies On Na^+ Ion Based Nano Alumina(Al_2o_3) Dispersed Solid Polymer Electrolyte System

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Abstract—Sodium-ion based PEO-80:$NaPF_6$-10:Al_2O_3-10 dispersed solid electrolyte system was synthesized through solution casting method is presented in this paper. Structural, morphological and thermal properties have been carried out by using techniques like XRD, SEM, FTIR, DSC and Impedance Spectroscopy is employed to study the electrical and dielectrical behavior of the system. FTIR studies have confirmed the presence of various vibrational modes and the interactions among molecules of polymer, salt, and nano-dispersoid. The DSC investigations indicate the melting points of pure and dispersed systems and revealed the absence of any phase transition in all the three systems. X- Ray diffactograms provide the crystalline nature of pure PEO, $NaPF_6$, Al_2O_3, and PEO-$NaPF_6$-Al_2O_3 system. SEM micrographs visualize the surface morphology of the mixed system and the distribution of Al_2O_3 within the polymer matrix. Impedance analyses is carried out to evaluate the dc ionic conductivity and activation energy. The variation of real and imaginary components of ac conductivity, dielectric constant, dielectric loss and electric modulus with temperature and frequency show the existence of various types of polarizations at low frequencies disappear at high frequency region and enhanced dc conductivity is attributed to the increased concentration of charge carriers in the dispersed system and increased hopping frequency of mobile charge carriers could be responsible for higher ac conductivity at higher frequencies.

Index Terms— Polymer Electrolyte, Al2O3, XRD, FTIR, SEM, DSC, Impedance spectroscopy.

1. INTRODUCTION

Sodium ion conducting solid electrolytes have gained immense research interest in the recent past as they are potential substitutes for Lithium ion conductors because of their electrochemical properties comparable to that of lithium ion conductors. In addition to the low cost, sodium compounds are abundantly available. The expectations in the field of battery applications are increasingly high from the point of view of their high energy storage capacity, high safety and low lost. The major challenge in high performance battery technology is to develop highly conducting electrolyte suitable for efficient transport of ions between electrodes at ambient temperatures [1,2]. Inorganic solid electrolytes are available with high ionic conductivity at room temperature but they have poor surface properties result in high resistive interfacial contacts to the electrodes [3]. In the recent years, solid polymer electrolytes have emerged as promising materials with respect to their counterpart conventional electrolyteswhich are highly corrosive, toxic liquid electrolytes [4-9]. The safety and stability of sodium ion based batteries can be enhanced by using solid polymer electrolytes as they are inert, leak proof, flexible and mechanically stable. The solid polymer electrolyte when complexes with sodium ionic salt results in high ionic conductivity in the material. Further improving the ionic conductivity in these materials can be achieved by dispersing nano powders of insulating inorganic oxides such as Al_2O_3, SiO_2, CeO_2 etc.[10]. Generally, solid polymer electrolytes composed of a soft polar polymer matrix as a carrier for dissolved metal salts. Solid polymer electrolyte is most widely used in sodium ion conducting battery research as matrix material is filled with Na ion conducting salts. PEO is widely studied polymer host because of its higher solubility for Na salts and has good structural stability and chemical stability. Introduction of nano materials into solid polymer electrolytes has become very attractive because of improved electrolyte performance, in addition to simple to mix with the polymer. Extensive research has been carried out on adding nanoparticles of Al_2O_3, SiO_2, TiO_2, ZrO_2 and CeO_2 to enhance the ionic conductivity of solid polymer electrolytes and many lithium ion batteries. PEO is the most widely studied polymer host because of its higher solubility for Na salts, its good structural and chemical stability, and the presence of flexible ethylene oxide segments and ether-bonded oxygen atoms[4,5]. Al_2O_3 plays a pivotal role in ionic conductivity, facilitating ion migration by creating additional conduction pathways and interacting with sodium ions to assist dissociation from salts like sodium perchlorate. This effect is particularly useful in maintaining ionic conductivity even at lower temperatures, where normally PEO's segmental mobility is reduced. Optimizing parameters like Al_2O_3 concentration, polymer molecular weight, and salt content enables room temperature conductivities in the range of 10^{-6} to 10^{-4} S/cm. PEO's ability to dissolve large salt concentrations and form stable complexes underpins its versatility across applications like batteries, fuel cells, and smart windows. Conductivity in PEO-based systems primarily arises from ion hopping between polymer chains, with significant increases above the crystalline-amorphous transition temperature. Ongoing research is focused on enhancing ion mobility at lower temperatures, ensuring long-term stability, and addressing the scalability and cost-effectiveness of these advanced polymer electrolyte systems[2-6].

2. SYNTHESIS OF THE MATERIAL

The solution casting method is used to prepare solid polymer electrolyte films and these are ideal for devices like batteries. Polyethylene Oxide (PEO) of 2.4 grams procured from Aldrich Inc. is dissolved in 40 ml of dimethylformamide (DMF) by stirring it thoroughly until it forms a uniform solution. The density of the solution is controlled by means of evaporation by using microwave oven. Aluminium oxide powder of 0.3 gms with particle size 60 nm is added to the solution to prevent the aggregation. To this dispersed solution 0.3 gms of sodium hexafluorophosphate salt is mixed. This mixture is stirred continuously for 48 hours using a magnetic stirrer, ensuring even dispersion for improved mechanical and electrochemical properties. After achieving a homogenous solution, the mixture is cast on a flat glass substrate. A casting blade is used to spread it evenly, controlling the film's thickness. Once cast, the film undergoes slow solvent evaporation in a vacuum oven to prevent defects like bubbles. The dried film is carefully removed and annealed to enhance crystallinity and allowing it for better interaction between the polymer and nano-alumina for optimal performance in electrochemical applications.

2. CHARACTERIZATION

2.1. Analysis of X-Ray Diffraction (XRD):

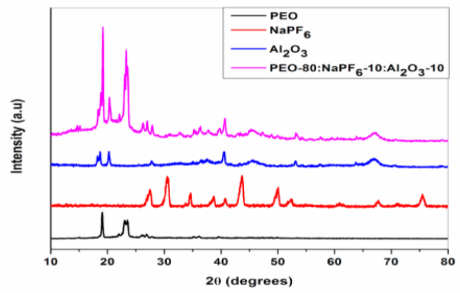

Fig. 1. X-Ray Diffraction pattern of pure PEO, $NaPF_6$, Al_2O_3 and PEO-80:$NaPF_6$-10:Al_2O_3-10 systems

Figure-1 shows the XRD patterns of the pure PEO, $NaPF_6$, Al_2O_3 and PEO-80:$NaPF_6$-10:Al_2O_3-10 dispersed system. The peaks at 19.08°, 23.1° and 23.52° are related to pure PEO, which is the characteristic of crystalline host polymer. Sharp peaks at 27.52°, 30.72°, 34.7°, 38.72°, 40.76°, 43.8°, 50.06°, 52.44°, 67.66°, 75.54° are related to pure $NaPF_6$. and are correlated with earlier reported results . The characteristic peak of $NaPF_6$ at 27.90° and 45.20° have disappeared in PEO-80:$NaPF_6$-10:Al_2O_3-10 dispersed system, which confirms the a miscibility of salt in the dispersed system. The peaks that appeared around 19° and 23° in PEO-80:$NaPF_6$-10:Al_2O_3-10 dispersed systems correspond to the un-complexed PEO.

2.2. ANALYSIS OF FOURIER TRANSFORM INFRARED:

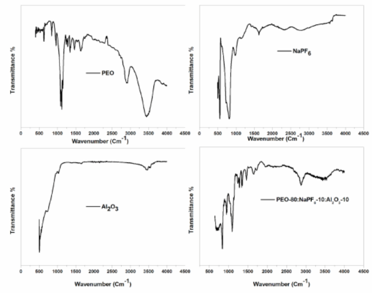

Fig.2. FT-IR of pure PEO, $NaPF_6$, Al_2O_3 and PEO-80:$NaPF_6$-10:Al_2O_3-10 systems.

Figure 2. presents the FTIR spectra for pure PEO, $NaPF_6$, Al_2O_3, and the PEO-80:$NaPF_6$-10:Al_2O_3-10 composite system across 400–4000 cm^{-1}. A peak at 3441 cm^{-1}, observed in in PEO, Al_2O_3, and the composite, corresponds to O-H stretching vibrations. In the PEO-80:$NaPF_6$-10:Al_2O_3-10 system, distinct peaks appear at 1469 cm^{-1} for CH_2 wagging and at 1660 cm^{-1} for C=C stretching. A peak around 1629 cm^{-1}, observed in all samples, shows a slight shift. Additionally, the peak at 2918 cm^{-1} shifts to a lower frequency in the composite, indicating interaction between sodium cations and the carbonyl group.

2.3. ANALYSIS OF DIFFERENTIAL SCANNING COLORIMETRY (DSC):

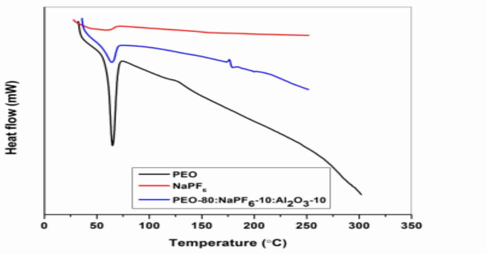

Fig. 3. DSC pattern of pure PEO, $NaPF_6$, Al_2O_3 and PEO-80:$NaPF_6$-10:Al_2O_3-10 dispersed solid polymer-electrolyte

DSC thermograms of pure form of PEO, $NaPF_6$ and PEO-80:$NaPF_6$-10:Al_2O_3-10 dispersed solid polymer-electrolyte systems are shown in figure 20. The endo-thermic peaks observed at 65.2 °C and 63.8 °C correspond to PEO and $NaPF_6$ melting temperatures (T_m), respectively. The melting temperature of the PEO-80:$NaPF_6$-10:Al_2O_3-10 system has been noticed to decrease nearly 8 °C when compared with PEO. The decrease in T_m could be due to the orientation of polymer chains caused by the interaction between Al_2O_3 nano-filler and polymer segments [7]. The glass transition temperature is usually less than T_m and is a measure of polymer chains flexibility, which increases as the T_m decreases. A decrease in the value of T_m helps in increasing the movement of polymer chains, which enhances the conductivity of polymer electrolytes [8].

2.4. ANALYSIS OF SCANNING ELECTRON MICROSCOPE:

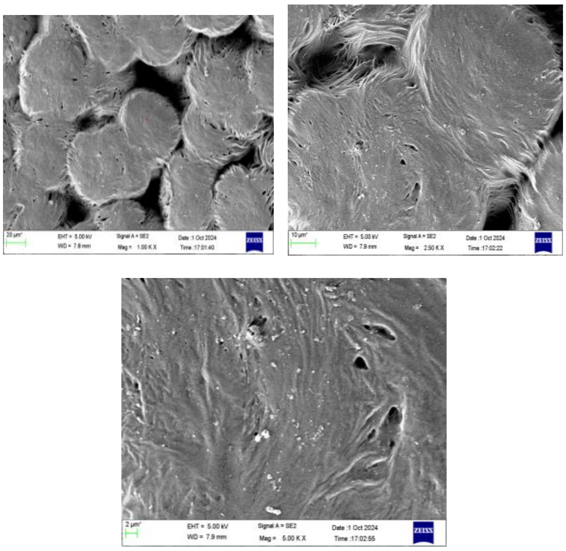

Fig. 4. SEM picture of PEO-80:$NaPF_6$-10:Al_2O_3-10 dispersed solid polymer-electrolyte with 1000 and 2500 and 5000 magnifications

Fig 4(a). shows the SEM micrograph of PEO-80:$NaPF_6$-10:Al_2O_3-10 dispersed solid polymer-electrolyte with 1000 magnification. As can seen from the figure that the surface is smooth and the crystallites are arranged randomly. Voids between the crystallites are seen significantly. Fig. 4(b) and 4(c) are also the SEM pictures of the same dispersed solid electrolyte system with 2500 and 5000 magnification respectively. The distribution of nano alumina particles can be observed in clearly in fig.4(c) apart from an uneven surface morphology of the dispersed system.

2.5. IMPEDENCE ANALYSIS:

1. Complex Impedance Spectroscopy

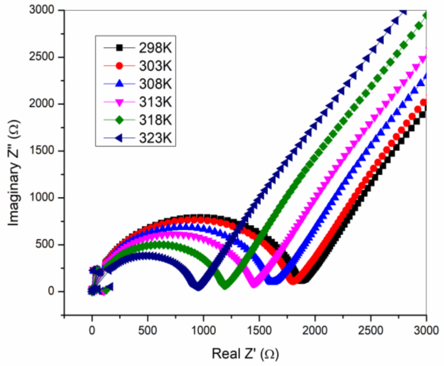

Fig.7. Nyquist plots of PEO-80:$NaPF_6$-10:Al_2O_3-10 dispersed soliid polymer-electrolyteat distinct temperatures

Complex impedance spectroscopy is useful for studying conduction and ion transport in materials.

Nyquist plots shown in fig.7 for the PEO-80:NaPF$_6$-10:Al$_2$O$_3$-10 system across various temperatures. The high-frequency semicircle and low-frequency spike indicate electrolyte properties, modeled as a combination of bulk resistance (R$_b$) and capacitance. As temperature rises, the intercept on the X-axis (R$_b$) decreases, suggesting enhanced conductivity due to ion dissociation and increased ion mobility temperature.

2. AC Conductivity:

Joncher's power-law is a widely observed phenomenon in AC conductivity behavior of polymer electrolytes, especially in the intermediate to high-frequency range. This behavior can be described using the following general equation:

$$\sigma(\omega) = \sigma_{dc} + A\,\omega^n$$

Where $\omega = 2\pi f$ is the angular frequency, $\sigma(\omega)$ is the total conductivity, σ_{dc} is the frequency-independent conductivity, $A\,\omega^n$ is the component of AC conductivity in terms of angular frequency (ω) with A as constant, which determines the strength of polarization and n is the frequency exponent [9]. The frequency-dependent conductivity exhibit three different dispersion regions namely, (i) low-frequency region, which demonstrates the space charge polarization, (ii) dc saturation zone in mid-frequency region and (iii) dc-to-ac switching at high frequency-zone, which is due to the coulombic interaction among charge carriers and disruption of polymer chains within the framework.

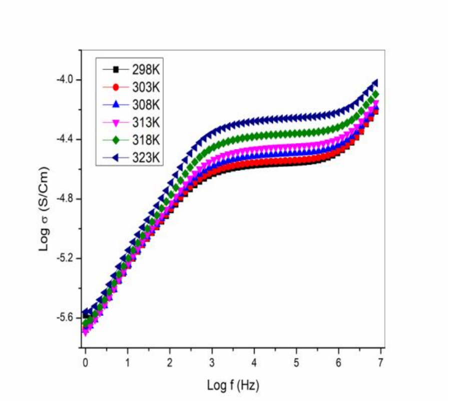

Fig.8. Frequency dependent conductivity ofPEO-80:NaPF$_6$-10:Al$_2$O$_3$-10 dispersed solid polymer-electrolyteat different temperatures

Figure 8. illustrates the AC conductivity behavior of nanofiller-dispersed electrolytes, highlighting a largely frequency-independent region up to 10 KHz, which marks the DC component. For Al$_2$O$_3$ nanofiller-dispersed electrolytes across temperatures, this frequency-independent plateau is observed, further the conductivity increases with temperature. This rise in conductivity with frequency at higher temperatures results from enhanced ion mobility due to thermally activated mechanisms.

3. DC IONIC CONDUCTIVITY

The DC ionic conductivity of an electrolyte systems is calculated by using the formula $\sigma_{dc} = \frac{t}{A\,R_b}$, where A is the cross-section area, 't' is the thickness and R$_b$ is the bulk resistance of the electrolyte.

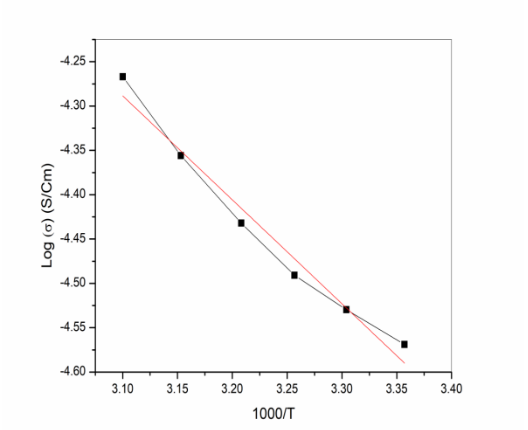

Fig.9. Variation of dc ionic conductivity of PEO-80:NaPF$_6$-10:Al$_2$O$_3$-10 dispersed solid polymer-electrolyte system with temperatures

Figure 9 presents the Log(σ) versus 1000/T plot for the PEO-80:NaPF$_6$-10:Al$_2$O$_3$-10 solid polymer electrolyte, showing a temperature-dependent increase in conductivity that aligns with the Arrhenius relation. This rise in ionic conductivity is attributed to ion dissociation and enhanced charge carrier mobility. The calculated activation energy (E$_a$) from the plot's slope supports this trend, with a maximum conductivity of 1.18×10−61.18 \times 10^{-6}1.18×10−6 S/cm, likely due to ion hopping between coordination sites and polymer segments.{[10,11].

4. DIELECTRIC PROPERTIES

The complex dielectric permittivity (ε^*) of material with frequency is given as,

$$\varepsilon^* = \varepsilon'(\omega) - j\varepsilon''(\omega)$$

Where ε' is the standard dielectric constant of the electrolyte that determines the quantity of electrical energy retained in the substance over every period of the applied alternating field.

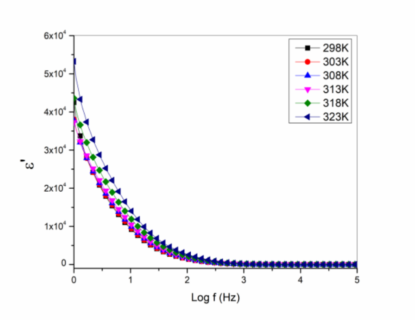

Fig.10. Frequency dependent dielectric constant of PEO-80:$NaPF_6$- 10:Al_2O_3-10 dispersed solid polymer-electrolyte at distinct temperatures

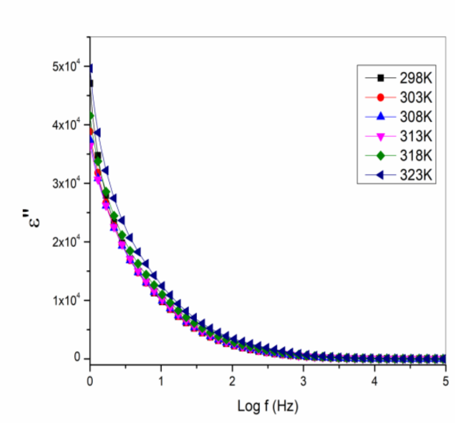

Fig.11. Frequency dependent dielectric loss of PEO-80:$NaPF_6$- 10:Al_2O_3-10 dispersed solid polymer-electrolyte at distinct Temperatures

Figure 10. illustrates the frequency-dependent dielectric constant of the Al_2O_3-dispersed solid polymer electrolyte system across temperatures. A high dielectric constant at low frequency is attributed to space charge polarization and dipole alignment, with permittivity declining in the intermediate frequency range as space charge polarization reduces. At higher frequencies, permittivity stabilizes due to a lack of polarization effects. The dielectric constant reaches a peak (5×10^4), likely from increased charge carriers due to uniform nanoparticle distribution within the PEO/$NaPF_6$/Al_2O_3 matrix.

Figure 11. shows the dielectric loss of the PEO-80:$NaPF_6$-10:Al_2O_3-10 system at various temperatures, following a similar trend. High dielectric loss at low frequency indicates a more amorphous phase, enhanced by nanofillers. A sharp increase at low frequency is due to electrode polarization, with dielectric loss rising with temperature as ion dissociation improves free carrier density and reduces relaxation time. This trend is consistent across all systems.

5. ELECTRIC MODULUS

Electric modulus study can be employed to investigate the conductivity relaxation by suppressing the electrode polarization effect. The complex electric modulus can be expressed as,

$$M^* = M'(\omega) + jM''(\omega)$$

where M' and $M''$are the real and imaginary components of electric modulus. The following equations can be used to obtain M' and M''

$$M'(\omega) = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2}$$

$$and \quad M''(\omega) = \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2}$$

The real part of modulus spectra of polymer electrolyte system at different temperatures is displayed in fig.. It is observed that the value of M' is very low (approaching zero) in the low frequency region and a continuous increase in M'value with frequency. The short-range mobility of charge carriers arising out of hopping mechanism leads to saturation value of electric modulus. As the temperature increases, the M'dispersion shifts to high-frequency zone and is attributed to the interaction between the polymer chains, which leads to a decrease in relaxation time and the movement of the charge carriers in polymer segments with temperature [12-13]

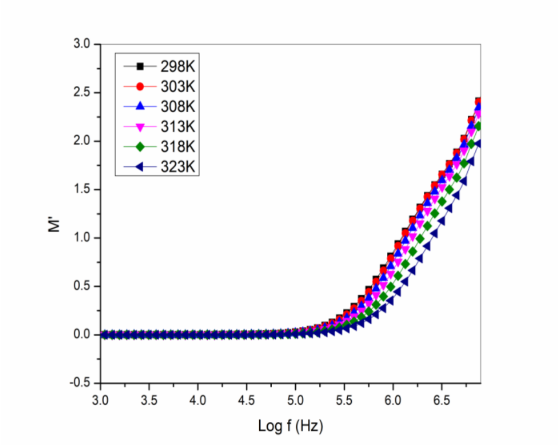

Fig.12. Frequency dependent real electric modulus of Al_2O_3 dispersed NCPEs at distinct temperatures

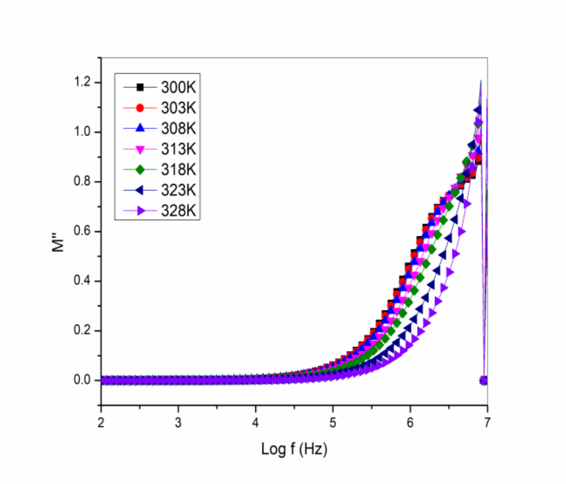

Fig.13. Frequency dependent imaginary electric modulus of PEO- 80:$NaPF_6$-10:Al_2O_3-10 dispersed solid polymer-electrolyte at distinct temperatures

Fig.13 demonstrates the variation of M'' with the frequency of Al_2O_3 dispersed nanocomposite polymer electrolyte at distinct temperatures. The existence of relaxation peaks in M'' suggests that the polymer is a good ionic conductor. Due the presence of nanofiller content, the broadening and shifting of the peaks have been observed. It can be seen that there is a shift in the peak towards the high-frequency region with temperature indicates the increased movement of the charge carriers leading to decrease in relaxation time .[14-15].

6. CONCLUSION

In conclusion, the sodium-ion-based nano Al_2O_3 dispersed solid polymer electrolyte synthesized through solution casting holds significant promise for energy storage applications. X-ray diffraction (XRD) analysis confirms the effective dispersion of nano Al_2O_3 within the polymer matrix, which plays a crucial role in enhancing the amorphous phase, a key contributor to improved ion conductivity. The FTIR spectroscopy results demonstrate a successful interaction between the polymer matrix and the nano Al_2O_3, indicating the formation of a stable composite structure.

Differential Scanning Calorimetry (DSC) further supports this, showing that the addition of nano Al_2O_3 reduces the polymer's crystallinity, which in turn increases the segmental mobility of the polymer chains, facilitating more efficient ion transport. Overall, this study highlights that incorporating nano aluminium oxide significantly boosts the thermal stability and ionic conductivity of the solid polymer electrolyte, making it a strong contender for use in sodium-ion battery applications.

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