DIELECTRIC PROPERTIES OF POLYMER ELECTROLYTE

Thesis Submitted for the Award of the Degree of

Master of Science

by

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DECLARATION

I hereby declare that the work carried out in this thesis is entirely original. It was carried out by me along with Miss Saritarani Maharaj at Department of Physics, National Institute of Technology, Rourkela. I further declare that it has not formed the basis for the award of any degree, diploma, or similar title of any university or institution.

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CERTIFICATE

This is to certify that the thesis entitled, **"Dielectric Properties of Polymer Electrolyte"** submitted by Pallavi Suhasinee Behera in partial fulfillment of the requirements for the award of Master of Science in Physics at the National Institute of Technology, Rourkela is an authentic experimental work carried out by her under our supervision. To the best of our knowledge, the experimental matter embodied in the thesis has not been submitted to any other University/Institute for the award of any degree or diploma.

Prof. Sidhartha Jena

Prof. Dillip Kumar Pradhan

ACKNOWLEDGEMENT

I am obliged to my supervisors Dr. Dillip Kumar Pradhan and Dr. Sidhartha Jena for their continuous guidance and motivation during the entire course of my project. I truly appreciate and value their esteemed guidance and encouragement. I am indebted to them for helping me in defining the problem, providing insights to the solution and ultimately guiding me to bring the thesis into present shape.

I would also take the opportunity to express my deepest gratitude to Miss Santripti Khandai, Mr. Tapabrata Dam & Mr. Satyanarayan Tripathy, for their necessary help & cooperation. I also extend my thanks to all the faculty members, PhD and M Tech(R) scholars and members of the Department of Physics, N.I.T., Rourkela for their suggestions and valued support.

I also extend my sincere thanks to all my friends and in particular to my project partner Miss Saritarani Maharaj for the immense support and encouragement I received from them.

Pallavi Suhasinee Behera

DEDICATED TO MY PARENTS

ABSTRACT

The preliminary structural, microstructural and dielectric properties of the polymer electrolytes based on Polyethylene oxide (PEO) as polymer and Sodium Iodide (NaI) as salt were investigated. The samples were prepared by solution cast method by taking different concentration of O/Na ratio (i.e., O/Na =0, 20, 40, 60, 80, 100). The structural characterization was carried out by using X ray diffraction (XRD) technique which shows that the polymer electrolyte is semi-crystalline in nature. From the XRD data the crystallite size and inter planar spacing of the polymer electrolyte were also calculated. The surface morphology was analysed by Scanning electron microscope (SEM) which shows the presence of spherulites which is the crystalline phase and it is separated by amorphous boundary. The electrical properties of the polymer electrolyte were studied using complex impedance analysis. In order to optimize the conductivity and dielectric properties, dielectric parameter, ac conductivity, and impedance of the polymer electrolyte samples were analysed.

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CHAPTER-I

INTRODUCTION

1.1 ELECTROLYTE

An electrolyte is a substance that dissociates into free ions when dissolved in solvent to produce an electrically conductive medium. Electrolyte solution is ionic in nature. If most of solute dissociates into ions then electrolyte is strong and if most of the solute does not dissociate into ions it is a weak electrolyte [1].

Electrolytes are mainly of two types depending upon the state i.e., (i) Liquid electrolyte and (ii) Solid electrolyte.

When NaCl dissolves in water it dissociates into Na^+ and Cl^- which form the liquid electrolyte. **$NaCl\ (s) \rightarrow Na^+\ (aq) + Cl^-$.**

Liquid electrolyte is used in electrochemical cells and devices as Li metal and Li-ion batteries, double layer capacitor, sensors etc.

Although liquid electrolyte is used in many conventional ionic devices, but these liquid electrolyte containing devices showed many limitations like

(i) It has short life time period.

(ii) The corrosion reactions occur between the electrolyte solutions and electrodes.

(iii) There is a possibility of leakage of chemicals.

(iv) Limited temperature range of operation

(v) It has low energy and power density.

The drawbacks of liquid electrolyte is that it is not portable i.e. it is bulky and heavy to carry to different places. Due to these limitations, the scientific community is trying to replace liquid electrolyte by solid electrolyte with high ionic conductivity [2].

1.2 SOLID ELECTROLYTE

The ionic solids having high conductivity of the order of 10^{-6} Scm^{-1} with negligible electronic conductivity of the order of 10^{-12} Scm^{-1} at room temperature called 'super ion' conductors (SICs) or solid electrolyte [3,4].

Superionic solids have the following characteristics: (i) Electrical conductivity due to ions should be high but due to electrons it should be low.

(ii) Principal charge carriers should be ions. It means that the ionic transference number (t_i) is almost equal to 1 where t, refers to the fractional contribution of the ionic conductivity to the total conductivity. In solid electrolyte, the total conductivity is the sum of the ionic and electronic contribution. The fraction of the conductivity due to ions or electrons is given by: $t_{ion} = \sigma_{ion} / \sigma_{tot,}$ $t_e = \sigma_e / \sigma_{tot,}$ where t_{ion} is the ionic transference number and t_e is the electronic transference numbers . σ_{ion} ,σ_e and σ_{tot} are conductivity due to ions, electrons and total conductivity respectively. For a purely ionic conductor $t_{ion} = 1$, for a purely electronic conductor $t_e = 1$ and for mixed conductor t_{ion} and t_e have values between 0 and 1

(iii)It should have low activation energy [5].

Usually one type of ion is predominantly mobile and conducts electricity in solid electrolyte. The main attractive properties of super-ionic conducting materials are high ionic conductivity, better stability, possibility of miniaturization of solid state devices and wide range of operating temperature, etc.

The conductivity of the conducting material with different charge carriers is given by the equation $\sigma = \Sigma_i \, q_i \, n_i \, \mu_{i,}$ where σ is the specific ionic conductivity i.e. the charge transport across a unit cross sectional area per second per unit electric field. Its unit is ohm^{-1} cm^{-1} or S cm^{-1}, n_i and q_i are the number of carrier and its charges. The ionic conductivity is the total sum of the contribution from different charge carrier.

1.3 CLASSIFICATION OF SUPER IONIC SOLIDS

Super ionic solids/conductors are also classified based on phases & microstructures [6].

(i) Framework Crystalline material

(ii) Amorphous-glassy electrolytes

(iii) Composite electrolytes

(iv) Polymer electrolytes

All the phases classified above are ordered or disordered materials. In which Framework Crystalline materials is ordered and the other three phases are disordered. The microscopically disordered materials are amorphous –glassy and polymer electrolyte and the composite material are macroscopically disordered.

In the next section, we will discuss about the polymer electrolyte as the thesis is based on polymer electrolyte.

1.4 POLYMER ELECTROLYTE

Polymer solid electrolytes (PSE) are high ion conducting polymers. PSEs are solid material which are synthesized by dissolving the salt of alkali metals of type MX (M= Na, Li, Ag, NHI, Cu, etc) and (X= I, CI, F, etc) in polymers like polyethylene oxide, polypropylene oxide, polyurethane [7]. These can be prepared in the form of bulk as well as thin films. Polymer electrolytes are mainly prepared by solution cast method, sol gel method, electro deposition method.

Polymer electrolyte has following properties due to which there is a possibility of solid electrolyte to be used in various electrochemical devices.

(I) Free from leakage

(II) It has high chemical, thermal, mechanical and electrochemical stability properties.

(III) It can be operated in a wide temperature range.

(IV) Design flexibility

For the preparation of polymer electrolyte, the polymer host and salt should have the following properties:

(i) A polar group should be present in the polymer chain so that it can form a complex with the salt. (ii) The molecular weight of the polymer should be high and the glass transition temperature should be low. (iii) The salt should have low lattice energy and bulky anions

In the present study, we are using Polyethylene oxide as host polymer and NaI as salt.

1.5 STRUCTURE AND MORPHOLOGY OF POLYETHYLENE OXIDE

Polyethylene Oxide (PEO) is represented by the formula $(OCH_2CH_2)_n$ in which n is the average number of oxy-ethylene groups. PEO is a linear polymer and the regularity of the unit is - (CH_2-CH_2-O) -, which has a crystallinity of ~70-80% of the polymer. It shows spherulite and dendrite structure [8]. In addition the ionic conductivity mainly takes place in the amorphous phase. The melting point, T_m of the crystalline phase is 65^oC and the glass transition temperature T_g of the amorphous phase is -60^oC.

1.6 LITERATURE SURVEY

Wright and co-workers worked on polymer electrolyte and were the first to report the ionic conduction in PEO-alkali metal salt complexes [9].

Karthikeyan *et. al.* studied the a.c. impedance measurements of the cells at elevated temperature as a function of time [6].

Eikerling *et. al.* prepared and studied some proton conducting polymer electrolyte membrane. Ther reported that the motion of the proton takes place due to the heterogenous membrane structure of non conducting polymer which is hydrophobic in nature and the water is filled in channel [10].

Ragavendram *et. al*. prepared and studied the plasticised PEO based solid polymer electrolyte using Lithium hexafluoarsenate ($LiAsF_6$) as salt and PEO as polymer with different composition of plasticizer [11].

Bloise *et. al.* investigated the effect of TiO_2 nanoparticles in solid composite polymer electrolyte based on PEO and $LiClO_4$ [12].

Ibrahim *et. al*. prepared solid polymer electrolyte based on Polythene oxide as polymer, $LiPF_6$ as salt and carbon nano tube as filler and studied the electrical and thermal stability properties [13].

Bruce *et. al.* gives the basic thermodynamic of formation of polymer electrolyte, which is a ionically conducting solid phases formed by dissolution of salts in polymer host [14].

Pandey *et. al.* studied the electrochemical properties of ionic liquids based gel electrolyte for super capacitors application [15].

Rajendran *et. al.* reported about synthesis and characterization of PVC/PEMA based polymer electrolyte and they found that it has good ionic conductivity at room temperature [16].

1.7 OBJECTIVES OF THE PROJECT WORK

The following are the main objective of the present work

I. Synthesis of polymer electrolyte by solution cast technique.

II. Characterization of polymer electrolytes by X-ray diffraction technique.

III. Micro structural studies using Scanning Electron Microscope (SEM)

IV. Studies of frequency dependence of dielectric and ac electrical conductivity for better understanding of ion transport mechanism in polymer electrolyte.

Materials under present investigation:

$(PEO)_x$-NaI (x=O/Na= 0, 20, 40, 60, 80, 100)

1.8 ORGANIZATION OF THE THESIS

This thesis has been discussed in four chapters.

Chapter 1: The main discussion done in first chapter is about electrolyte which consists of liquid electrolyte and solid electrolyte.Then main focus is given to solid electrolyte and structure and morphology of PEO. A brief discussion is done about polymer electrolyte i.e. about its concept and theory. Main objective of the work has been discussed in this chapter.

Chapter 2: The different methods of preparation of polymer electrolyte and principle of characterization techniques have been discussed.

Chapter 3: This chapter deals with the structural and micro structural properties is carried out by XRD and SEM. Dielectric and electrical properties of the polymer film is also discussed along with the conductivity of electrolytes.

Chapter 4: Conclusion of the present work is given.

CHAPTER-II

SYNTHESIS OF SAMPLE

2.1 METHODS OF PREPARATION

These are some different common methods discussed below which are used for the preparation of thin film.

(I) Solution casting technique:-

This is a common procedure for casting polymer electrolyte films. During preparation of polymer thin film an appropriate amount of polymer is taken and dissolved in a solvent. The solvent should be common for both salt and polymer. A magnetic stirrer is used for mixing. Some specific amount of salt is added to polymer solution and stirred for overnight. The obtained solution is now poured into a petridish. At last the dish is left for slow evaporation of the solvent followed by vacuum drying.

(II)Spin Coating:-

Spin Coating is a process used to apply uniform thin films on flat substrate. The machine used for spin coating is called a spin coater. A coating fluid is deposited onto the wafer or substrate. The substrate is accelerated up to its final, desired, rotation speed so that the fluid is spread over the substrate by means of centrifugal force. The film thickness and other properties will finally depend on the nature of the fluid (i.e. viscosity, drying rate, percentage of solid, surface tension, etc.) and the parameters chosen for the spin process. Polymer gel electrolyte thin film cannot be prepared by this process.

(III)Hot Press Technique:-

It has many advantages over solution cast technique. It is a rapid process and it is least expensive. In this process dry powder of polymer and salt is taken in a proper ratio and is mixed. Then the mixture is heated around the melting point temperature of the host polymer for sufficient time. As a result a soft lump is obtained which is then pressed between the cold metal blocks which give rise to a uniform polymer electrolyte films. After heating and pressing, the sample is then slowly cooled to room temperature.

In the present study for the preparation of Polyethylene oxide based polymer electrolytes we will use solution cast technique as it is a easier method for preparing the thin films and also less expensive.

2.2 PROCEDURE

The Polyethylene oxide based polymer electrolytes is prepared in the following ways.

- 1 gm of polyethylene oxide was taken in a conical flask.
- 20ml of Acetonitrile was added to the polymer and left overnight for swelling.
- Then the solution was stirred for 10 hour and appropriate amount of salt i.e. NaI was added to it
- Again the solution was mixed by using the magnetic stirrer.
- The solution is now poured into a petri dish.
- At last the dish is left for slow evaporation of the solvent.
- Thin film was obtained.

FLOW CHART

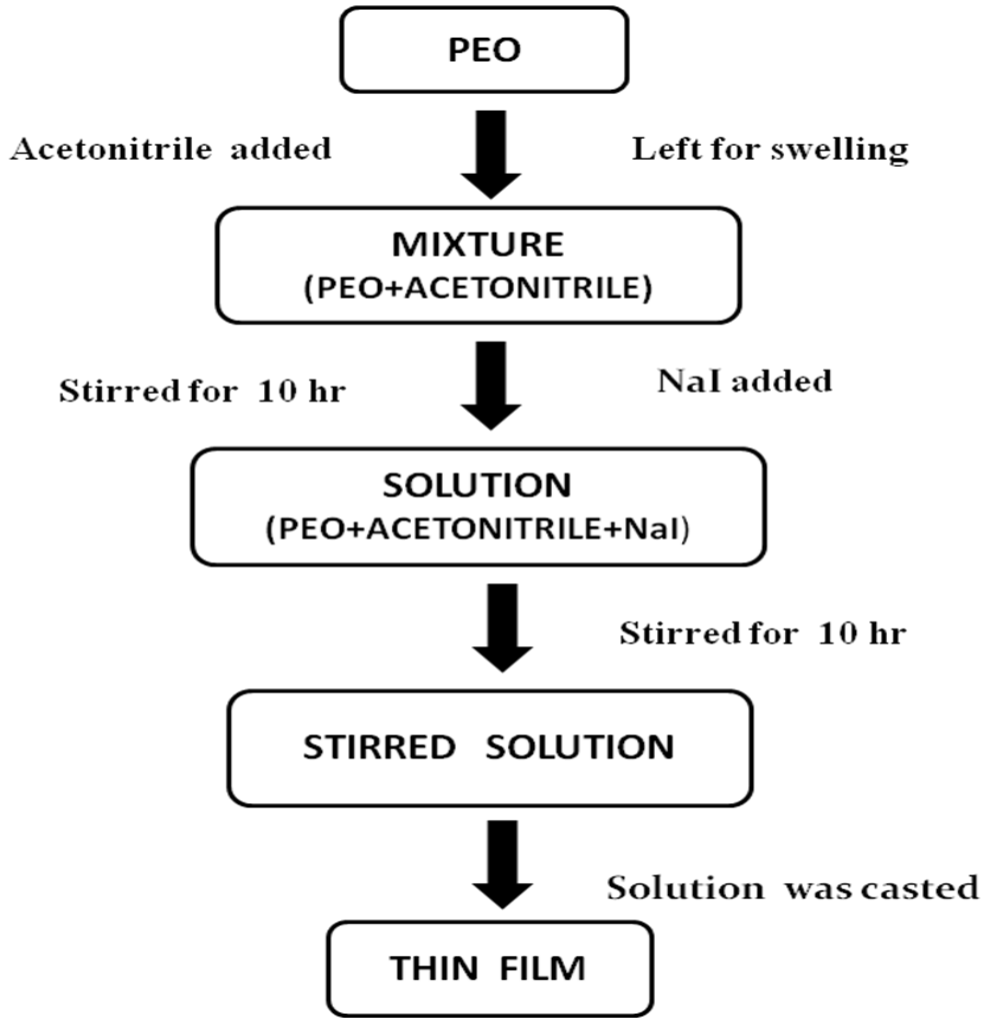


Fig 2.1 Flow chart of preparation of polymer electrolyte

2.3 CHARACTERIZATION TECHNIQUES

I. X-Ray Diffraction

XRD technique is an analytical method to identify and determine the various form of crystal structure of powder structure or solid or thin film. It also gives the lattice parameters of another microstructural parameters.

When x-ray beam hits the material it gets diffracted. We can measure the distance between the planes of crystal by applying the Bragg's law. Bragg's law gives

$$n\lambda=2d\sin\theta$$

λ- wavelength of X-ray

d-inter-planar spacing,

θ-diffraction angle

n-0,1,2,3…

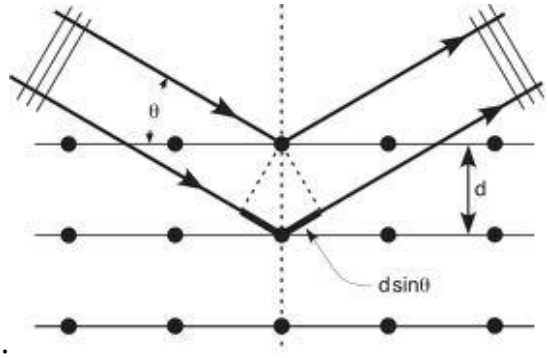


Fig 2.2 Schematic diagram of Bragg's diffraction

From XRD, the crystallite size can be found out by using the Scherer's formula

$$D=\frac{0.9\lambda}{\beta\cos\theta}$$

Where D – crystallite size, λ – wavelength($1.54A^0$), β - Full maxima half width, θ-Diffraction angle

The PEO polymer thin film is characterized by XRD technique in order to study their structural properties. The XRD data was recorded using Philips X-ray diffractometer with Cu k_α radiation ($\lambda=1.5405A^o$) in the Bragg angle range $10^o\leq2\theta\leq40^o$ at scanning rate of 2^o/min.

II. **Scanning Electron Microscope (SEM)**

The sample is scanned by the electron beam and the surface morphology is found in SEM micrographs. In SEM the electrons is collected from sample surface by emission process. Two types of electrons are used i.e., (i) secondary electrons and (ii) back scattered electron are used to get the surface morphology. In SEM the data are observed over a selected area of the sample surface. So that a two dimensional image is seen that shows different morphological properties. The Scanning electron microscope used to get SEM microgrpahs is JEOL JSM-6480LV. The sample is coated by platinum before taking the images.

III. **Dielectric Spectroscopy**

Dielectric spectroscopy is called as impedance spectroscopy which measures the dielectric properties of the medium as a function of frequency. It is based on the interaction of electric dipole with external field. It is used to measure the impedance of a system using wide range of frequency. The data obtained can be used to calculate the ac conductivity of the material at different frequency. The complex impedance measurement was carried out using PSM 1735 Impedance Analysis Package, Newton 4th Ltd. at room temperature in a wide frequency range from 100 mHz to 1 MHz with input a.c signal of 100 mV. The sample was taken in between two stainless steel electrodes.

CHAPTER-3

RESULTS AND DISCUSSIONS

3.1. XRAY DIFFRACTION

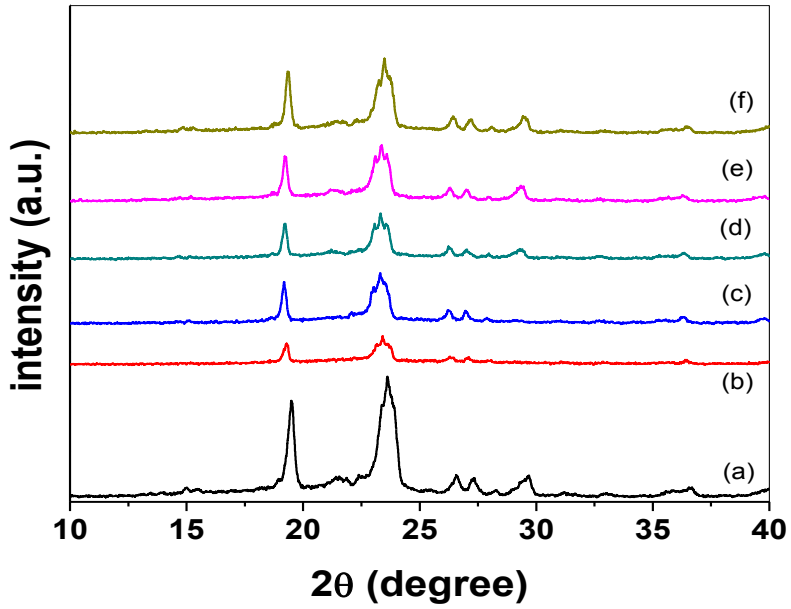


Fig 3.1 XRD Pattern of PEOx-NaI (x=0(a),20(b),40(c),60(d),80(e),100(f))

Fig. 3.1 shows the XRD pattern of pure PEO and polymer electrolyte with different O/Na ratio. The complexation of polymer with salt have been confirmed as the XRD pattern of host polymer PEO is similar to that of the XRD pattern of the polymer salt complex. The typical XRD pattern of solid polymeric films indicates the semi crystalline nature i.e. it contains both crystalline phase and amorphous phase. Here two main peaks are obtained at 19° and 23°. Peaks obtained at the 19° shifts towards the low angle side with the increase in O/Na ratio and for higher concentration reverse trend are observed.

DETERMINATION OF CRYSTALLITE SIZE:-

The crystalline size was calculated by Scherer formula and inter planar spacing was calculated by Bragg's law for different O/Na ratio(i.e. for 0,20,40,60,80,100) for peak around 19° are given in the table 3.1 below

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

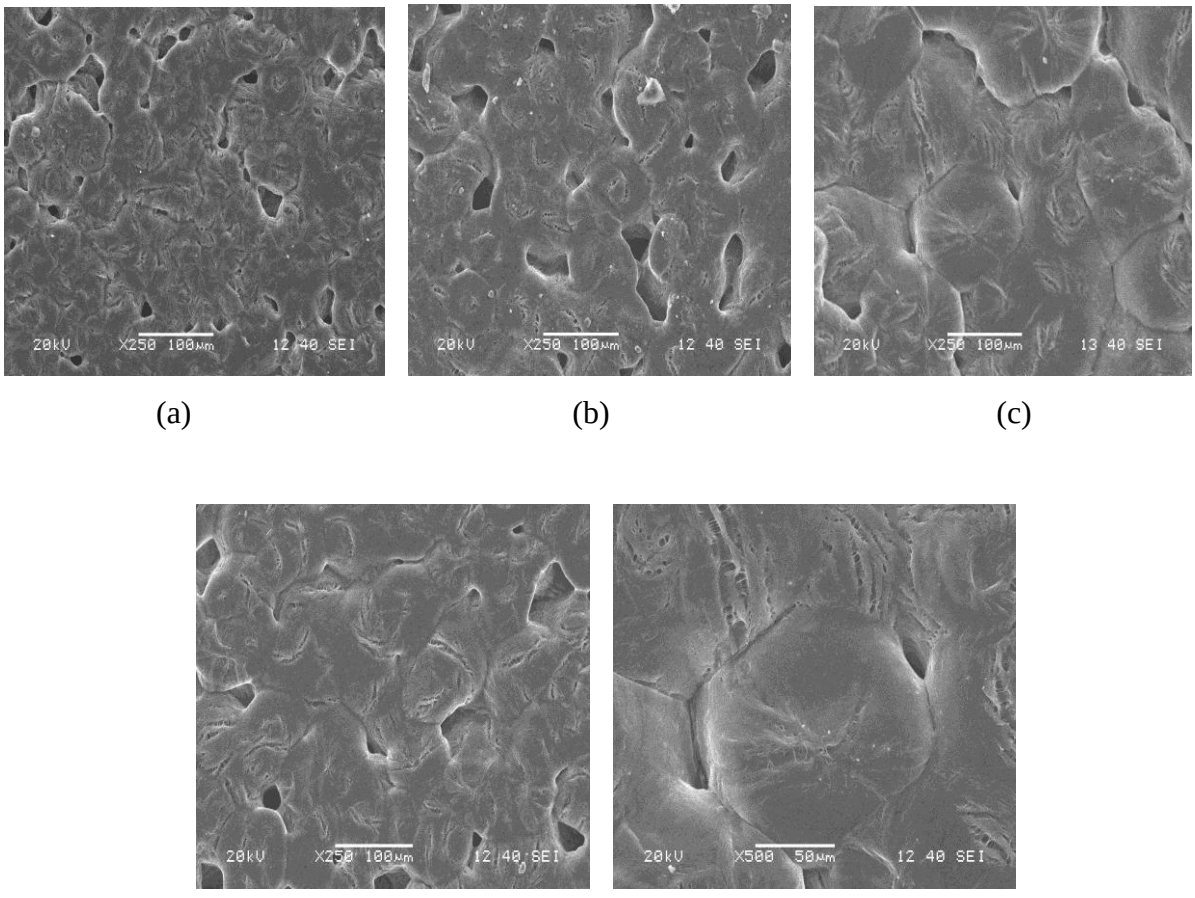
$$n\lambda = 2d \sin\theta$$

Where, D is the crystallite size, λ is the wave length of Cu k_{α} (λ = 1.5405 Å), β is the FWHM, θ is the diffraction angle of the strongest characteristic peak, d is the inter planar spacing

Table 3.1 calculation of crystallite sizes and inter-planar spacing

PEO concentration	$2\theta(^0)$	Inter-planar spacing (A)	Crystallite size (nm)
PEO	19.49	4.5515	27
PEO_{20}-NaI	19.28	4.6028	35
PEO_{40}-NaI	19.18	4.6234	37
PEO_{60}-NaI	19.21	4.6160	37
PEO_{80}-NaI	19.23	4.6122	37
PEO_{100}-NaI	19.35	4.5834	34

3.2 SCANNING ELECTRON MICROSCOPE



(a) (b) (c)

(d) (e)

Fig 3.2 SEM images for various O/Na ratio (a)O/Na=0,(b) O/Na=20, (c)O/Na=60, (d)O/Na=100,(e)O/Na=60

Fig. 3.2 shows the SEM micrographs of the polymer electrolyte with different polymer to salt ratio. The micrographs showed the presence of spherulite having lamellar microstructures. The spherulite is related to crystalline region and the region between spherulite boundary deals with amorphous phase. It gives the idea of crystalline nature with amorphous boundary. There is no systematic change in the surface morphology observed from micrographs with different polymer to salt ratio.

3.3 STUDY OF ELECTRICAL PROPERTY

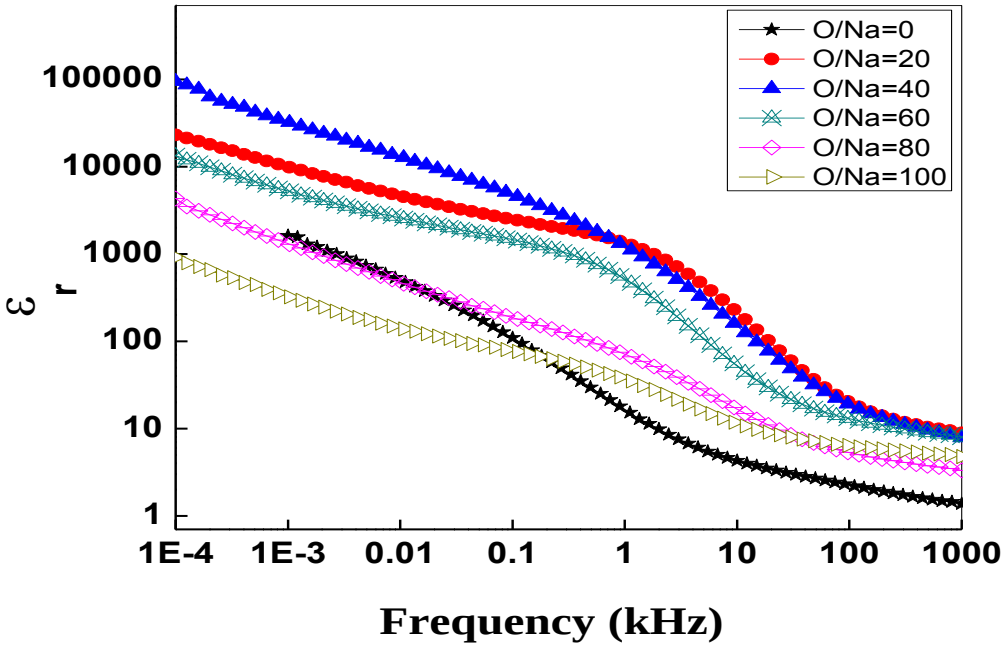


Fig 3.3 Dielectric constant vs Frequency

Fig 3.3 shows the variation of dielectric constant with frequency for different O/Na value of PEO based polymer electrolytes. Here we have seen that at lower region the frequency is dispersed and at higher frequency region it is independent. Due to relaxation process the dielectric constant decreases with increase in frequency for all concentration. In the high frequency region, the dielectric constant of polymer electrolyte is more as compared to pure polymer.

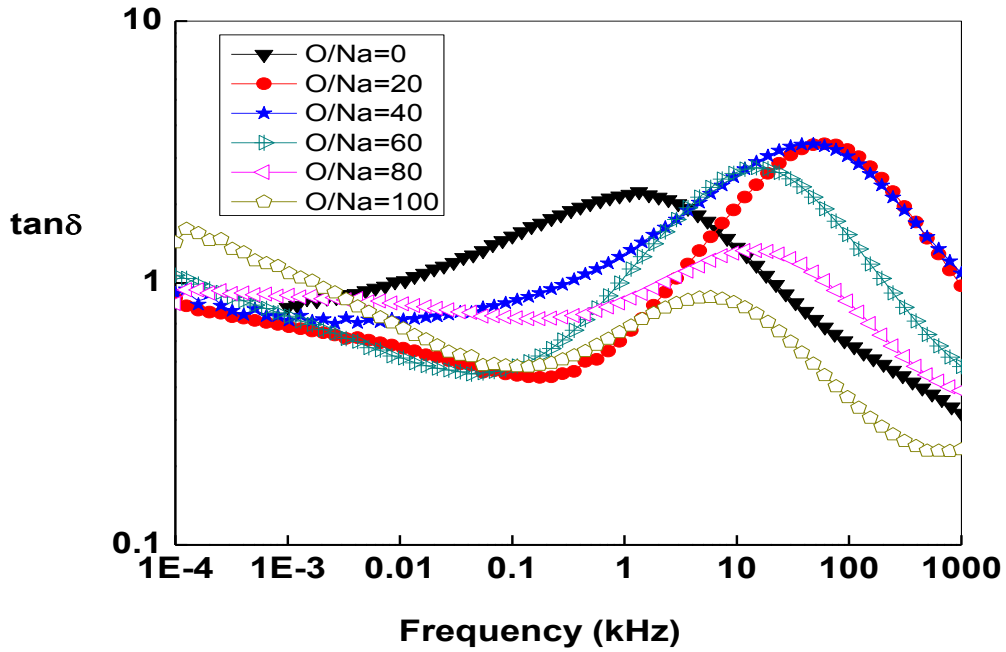


Fig 3.4 Tangent loss vs frequency

Fig 3.4 shows the variation of tangent loss with frequency. Peak appearing in the tangent loss spectra at characteristic frequencies, is different for different compositions. The presence of peak indicates the presence of relaxing dipoles in all the samples. The highest peak is observed for O/Na=20 composition. The frequency of relaxation depends on the characteristic property of dipolar relaxation.

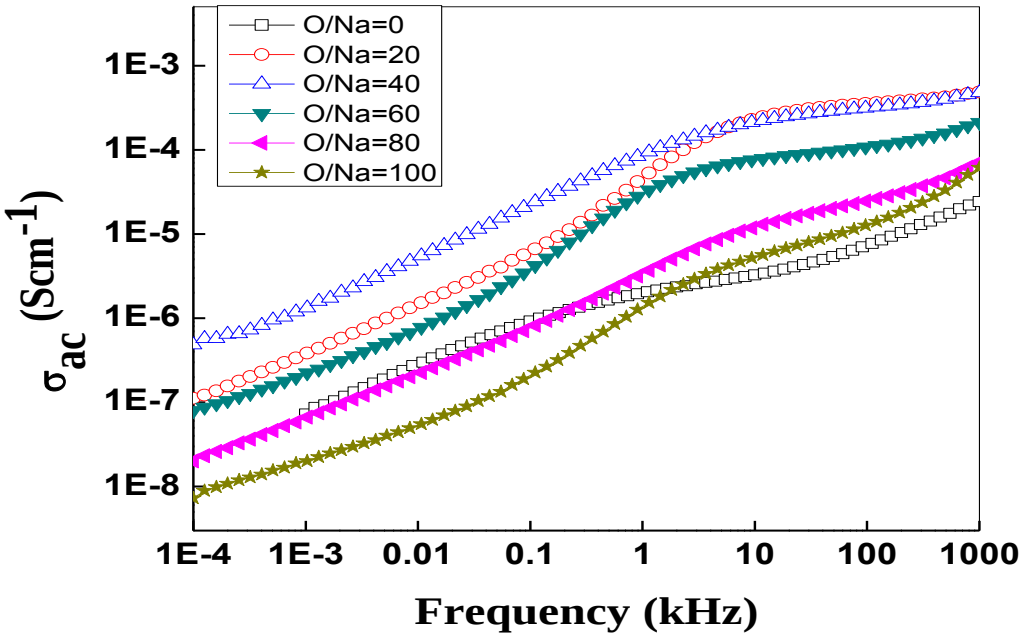


Fig3.5 σ_{ac} vs Frequency

Fig 3.5 shows the variation of ac conductivity with frequency for different value of O/Na concentration. The ac conductivity of the material was calculated from the dielectric data by using the formula $\boldsymbol{\sigma}_{ac} = \omega\, \varepsilon_r \varepsilon_0 \tan\delta$, where, $\omega = 2\Pi f$

where, f is the frequency, ε_0 is the permittivity of the free space. The ac conductivity pattern increase with increase in frequency and further increasing in frequency it remains constant. The graph shows at lower region the frequency dispersion is due to space charge polarization and the high frequency plateau indicating the dc conductivity of the material.

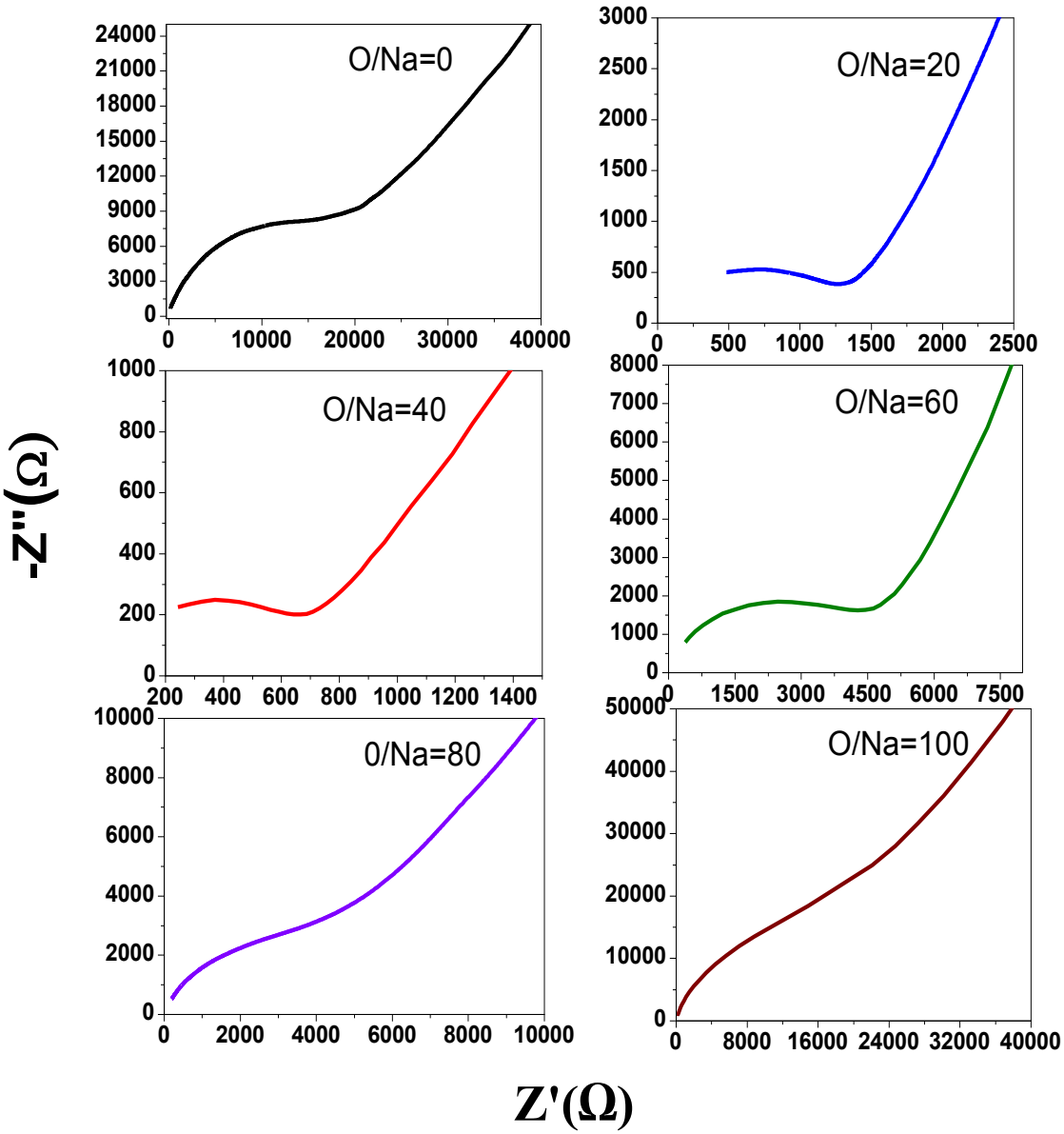


Fig3.6 Complex Impedance Plot

Fig3.6 shows the variation of real part of impedance with imaginary impedance for different O/Na ratio.(i.e O/Na=0,20,40,60,80,100). The complex impedance spectra of polymer electrolyte sample showed the broadened semi circle in the higher frequency region and a spike in the low frequency region. The low frequency spike is due to the double layer capacitance. The semicircle seen in the high frequency region is due to the bulk properties of

the material. The intercept of the semicircle on the real axis gives the bulk resistance (R_b) of the material which will help to calculate the value of d.c conductivity from the formula.

$$\sigma_{dc} = \frac{1}{R_b}\left(\frac{l}{a}\right)$$

Where R_b is the bulk resistance, l is thickness of sample and a is the area of the sample

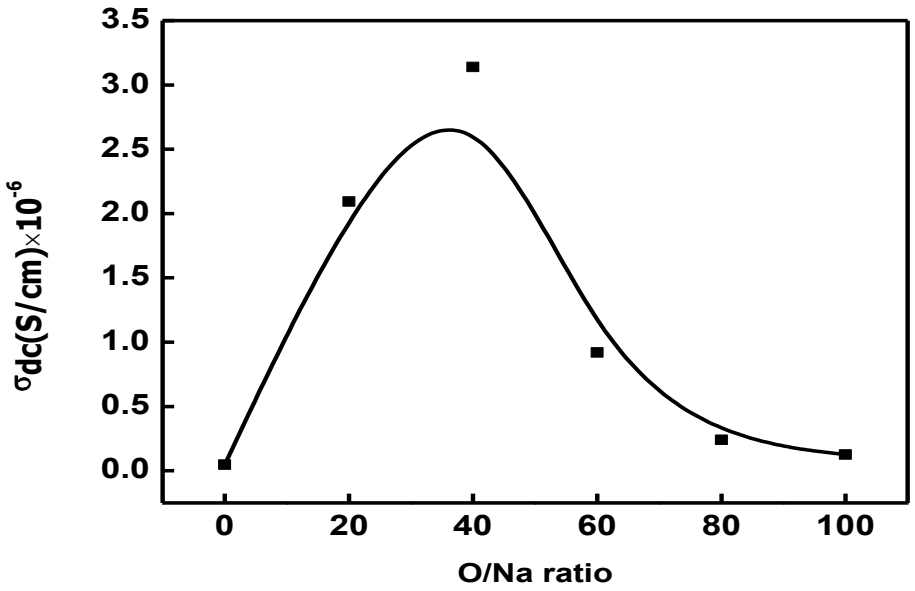


Fig 3.7 σ_{dc} vs composition

Fig 3.7 shows that the variation of dc conductivity with different value PEOx-NaI (x=0, 20, 40, 60, 80, 100). This shows that the conductivity increases with increase in concentration upto O/Na =40 and suddenly it decrease. Thus for O/Na=40 we get the highest conductivity among all.

CHAPTER-4

SUMMARY & CONCLUSIONS

Polymer electrolytes consisting of Polyethylene oxide (PEO) as polymer and sodium iodide (NaI) as salt have been prepared by solution cast technique. The sample was prepared by taking different concentration of O/Na ratio i.e (O/Na =0, 20, 40, 60, 80, 100). The structural, microstructural and electrical properties were studied.

(i)The structural characterization was carried out by using X ray diffraction (XRD) technique. The polymer electrolyte is semi-crystalline in nature (i. e., the presence of both crystalline and amorphous phase) was confirmed from XRD graph. From the XRD data, the crystallite size and inter planar spacing of the polymer electrolyte was also calculated.

(ii)The surface morphology was analysed by scanning electron microscope (SEM) which shows the presence of spherulites which is the crystalline phase and crystalline phases are separated by amorphous boundary.

(iii) The electrical properties of the polymer electrolyte were studied by using complex impedance analysis. The ac conductivity, dielectric properties and impedance of the polymer electrolyte samples were studied. The maximum conductivity was found for O/Na=40.

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