

SYNTHESIS AND CHARACTERIZATION OF POLYMER GEL ELECTROLYTE

Thesis submitted for the award of degree of

Master of Science

By

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Under the Academic Autonomy

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DECLARATION

I hereby inform that the work carried out in this thesis is entirely original. It was carried out by me along with Miss Paradarsini Parida and Mr. Manoranjan Samal 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 “**Synthesis and Characterization of Polymer Gel Electrolyte**” being submitted by **Swagatika Bhoi** in partial fulfilment of the requirements for the award of the degree of Master of Science in Physics at 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.

Date:

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ACKNOWLEDGEMENTS

I am highly grateful 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 advice, 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 Mr. Tapabrata Dam, Mr. Satyanarayan Tripathy and Miss Santripati Khandai for their necessary help and cooperation. I would also like to thank all the faculty members, all PhD scholars and all 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 partners Miss Paradarsini Parida and Manoranjan Samal for the immense support and encouragement I received from them. Moreover, I would like to thank my friends Miss Saritarani Maharaj and Miss Pallavi Suhasinee Behera for their much needed help throughout the project schedule.

I express my love and gratitude from the bottom of my heart to my parents without the blessings of whom the present work would not have been a success.

Swगतिका Bhoi

DEDICATED TO MY PARENTS

ABSTRACT

A series of PVDF based polymer gel electrolytes (PGEs) with different compositions of O/Na were prepared and the structural, morphological and electrical properties were characterized. For the formation of gel, solvent (i.e. DMF), salt (i.e. NaI) and polymer (i.e. PVDF) were taken as starting materials. By gelation method, different compositions of polymer gel electrolyte were prepared by keeping the amount of PVDF constant and changing the O/Na ratio (i.e. 20, 40, 60, 80, and 100). During the preparation process the polymer: solvent ratio was taken to be 2:3. Three characterization techniques such as XRD, SEM and Dielectric Spectroscopy were used to get information about the structure, morphology; frequency dependent dielectric and conductivity behaviour of the prepared samples of PGE. XRD analysis showed the semi crystalline behaviour and SEM study confirmed the result observed from XRD analysis. The electrical properties were investigated and d. c. conductivity was from the complex impedance plot. The dielectric parameters (i.e., dielectric constant and tangent loss) were also studied in a wide frequency range.

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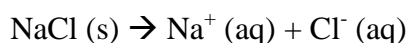
CHAPTER-1

INTRODUCTION

The discovery of electrochemical cell by Alessandro Volta (in 1800), was a major breakthrough in the field of science and technology. Basically cells are of two types i.e. Electrolytic cell and Electrochemical cell. In an electrolytic cell passage of current brings in chemical change and electrical energy is converted into chemical energy whereas in electrochemical cell a chemical change brings in passage of current. In other words chemical energy is converted into electrical energy [1].

A cell consists of two electrodes and an electrolyte. The electrode at which oxidation occurs is called anode and the electrode at which reduction occurs is called cathode.

Arrhenius was the first person who studied electrolytes and different characteristics of ions such as conductivity, concentration etc [2]. Electrolytes are substances which conduct electricity as a result of dissociation of salt into its constituent ions in solution. The most common examples of electrolytes are NaCl and CuSO₄. Electrolyte solutions are formed by addition of a salt with a solvent. For example when NaCl is mixed with water, NaCl dissociates into ions which is shown by the following reaction [3]:



Most of the electrochemical cells such as Batteries and fuel cells, electrolytes are used to conduct electricity and to store energy [4]. In fuel cell electrolyte helps the ions to move between cathode and anode so as to continue the power generating process, thereby keeping the reactive oxygen away from hydrogen [3].

1.1- CLASSIFICATION OF ELECTROLYTES:

Depending on the state (i.e. solid or liquid state), electrolyte is classified into two categories:

1 – Liquid Electrolyte

2 – Solid Electrolyte

1 - LIQUID ELECTROLYTE:

When a salt dissolves in a solvent (which can be water or polar solvent), liquid electrolyte is formed i.e. NaCl dissolves in H₂O to form liquid electrolyte. The most appreciable property of liquid electrolyte is its high ionic conductivity of the order of 10⁻² Scm⁻¹. However liquid electrolyte poses many disadvantages which include:

- (i) narrow range of temperature for operation
- (ii) corrosion of electrodes leading to damage to the devices
- (iii) low energy and power density
- (iv) larger weight of devices due to the use of liquid electrolyte.

To overcome these difficulties solid electrolyte was given priority in the recent years.

2 - SOLID ELECTROLYTE:

The solids which show high ionic conductivity are known as super ionic solids or solid electrolytes or fast ion conductors or hyper ionic solids [5]. In relation with this topic we have a branch of physics known as Solid State Ionics in which we study about the physical, chemical and technological aspects of high ionic conduction in solids.

The reasons which provided an edge to solid electrolyte are: non-occurrence of internal shorting between cathode and anode, prevention from leakage of electrolyte, no fear of reaction products catching fire, wide range of temperature tolerance, better durability, and possibility of miniaturized devices [6].

High ionic conductivity (10⁻¹ to 10⁻⁴ Scm⁻¹), low electronic conductivity (<10⁻⁶ Scm⁻¹), Low activation energy ($E_a < 0.3$ e V) and ionic charge carriers which are principal charge carrier (i.e. ionic transport number ($t_{ion} \approx 1$)) are the essential features of an ideal solid electrolyte. [5]

PROBLEMS OF SOLID ELECTROLYTE:

Although solid electrolyte has been used in various fields, it possesses some drawbacks also. One of its major drawbacks is that, if we compare with liquid electrolyte the conductivity of solid electrolyte is very less. If we are able to achieve conductivity similar to that of liquid electrolyte then it will be an achievement and further advancement in technology would be possible.

1.2 - CLASSIFICATION OF SOLID ELECTROLYTES

On the basis of different microstructure and physical properties [5]:

- 1- Framework crystalline materials
- 2- Amorphous glassy electrolytes
- 3- Polymer electrolytes
- 4- Composite electrolytes

Among them Polymer electrolyte is the scope of this project work.

POLYMER ELECTROLYTES:

Polymer electrolytes can be formed by mixing polymers having polar group and ionic salts. The Polar polymers can be PEO (Polyethylene oxide), PPO (Polypropylene oxide), PEG (Polyethylene glycol), etc. and ionic salts can be monovalent or divalent alkali metal, transition metal or ammonium salts. The distinct features of polymer electrolytes as compared to other solid electrolytes are; greater flexibility, capacity to form thin films, good processing ability, lesser weight, and higher ionic conductivity. Methodologies like copolymerization, plasticization, dispersion of organic and inorganic fillers and radiation of gamma rays are used in preparation of polymer electrolytes; tend to enhance the electrical conductivity, electrochemical and mechanical stability.

APPLICATIONS OF POLYMER ELECTROLYTE:

Because of the suitable ionic conductivity, electrical conductivity, electrochemical and mechanical stability polymer electrolytes can be used in solid state batteries, fuel cells, sensors, supercapacitors, electrochromic display devices (ECDs), photo-electrochemical solar cells (PESCs) [5].

1.3 - TYPES OF POLYMER ELECTROLYTE [7]:

Depending upon the preparation routes, polymer electrolyte can be classified into the following categories:

A - CONVENTIONAL POLYMER SALT COMPLEX OR SOLID POLYMER ELECTROLYTE (SPE):

This polymer electrolyte are polymer – salt complex, which can be prepared by dissolving lithium salts (LiX, where X can be I, Cl, Br, ClO₄) with polar polymer hosts like PEO, PPO etc.

B - PLASTICISED POLYMER SALT COMPLEX:

This can be prepared by mixing liquid plasticizers with polymer – salt complex. By this process no doubt the conductivity is increased but the mechanical and electrochemical stability are reduced.

C - POLYMER GEL ELECTROLYTE:

This can be formed by mixing organic liquid solvent with a salt and then polymer is added to give mechanical stability, which results in formation of gel. The solvent used here is called as liquid plasticizer, the salt used is usually alkali metal salt and the polymer used can be PMMA (Polymethyl methacrylate), PVDF (Polyvinylidene difluoride) etc. The polymer gel electrolytes usually possess high electrical conductivity as compared to dry polymer electrolyte.

D - COMPOSITE POLYMER ELECTROLYTE:

They can be prepared by adding small amount of fillers (inorganic / organic) in polymer – salt complex. Due to the addition of fillers, the electrical conductivity as well as stability increases [7].

1.4 - MORE ON POLYMER GEL ELECTROLYTE

As our field of study is polymer gel electrolyte a detailed description is given below.

The term ‘polymer gel electrolyte’ includes three terms i.e. polymer, gel and electrolyte. Polymers are substances of high molecular weight formed by union of small molecular substances known as monomers held together by covalent bonds. Gels are substances which have jelly like structures. In the steady state it does not flow. Gels are liquid but due to the presence of 3- D crosslink network they behave as solid.

Basically polymer gel electrolyte is in solid state phase at the macroscopic level in which the non – aqueous electrolyte is mixed with a polymer matrix and due to which liquid like conductivity is observed. They are formed from plasticizers, a polymer and a salt. Liquid

plasticizers have low molecular weight. Propylene carbonate (PC), ethylene carbonate (EC), dimethyl formamide (DMF), diethyl carbonate (DEC), dimethyl carbonate (DMC) etc are usually used as plasticizers. The salt can be alkali metal salt having low lattice energy and bulky anions. Polymers like polyacrylonitrile (PAN), polymethylmethacrylate (PMMA), polyvinylidene fluoride (PVDF) etc are used as polymer host. They act as gelling agent in the preparation of polymer gel electrolyte [7].

Through tremendous research work, till now ionic conductivity of the order 10^{-3} Scm^{-1} has been achieved in case of polymer gel electrolyte. However its mechanical strength and stability is low which makes it unsuitable for applications in various fields [8].

1.5 - MECHANISM INVOLVED:

ION TRANSPORT PHENOMENA

Temperature and conductivity are very closely related to each other. The temperature dependent conductivity can be well explained with the help of the two conduction mechanisms [7]:

ARRHENIUS TYPE EQUATION:

The change in conductivity with temperature in electrolyte is mainly governed by Arrhenius type equation. Here the lattice remains constant but the ions change their positions. A plot between $\log \sigma$ and $1/T$ comes out to be a straight line. The equation can be expressed as:

$$\sigma = \sigma_0 \exp \left[-\frac{E_a}{kT} \right]$$

Where E_a is the activation energy and σ is the conductivity, k is the Boltzmann constant and T is the temperature.

VOGEL – TAMMAN - FULCHER (VTF) TYPE RELATION:

Polymer electrolytes usually show VTF type relation because there is movement of both the ions as well as polymer segments. Along with the change in position of ions the polymer segments also relax. The equation is expressed as:

$$\sigma = \sigma_0 \exp \left[-\frac{E_a}{(T - T_0)} \right]$$

Where σ is the conductivity, E_a is the pseudo activation energy and T_0 is the equilibrium glass transition temperature which is 50°C below glass transition temperature. In contrast with the linear plot in case of Arrhenius type, the VTF conductivity versus $1/T$ plot is nonlinear. In view of Free Volume Theory, due to expansion in the material results in formation of large empty spaces. Moreover there is enough space available for ions to move and also for polymer segmental motion. Thus the transportation or mobility is decided by the empty space or volume present in the material.

1.6 - TYPES OF GEL:

PEO - BASED POLYMER GEL ELECTROLYTE:

For preparation of this electrolyte EC and/or PC are taken as plasticizers. LiClO_4 , LiCFSO_3 , $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ etc are used as the salt. This electrolyte has a conductivity of 10^{-3}Scm^{-1} . The polymer used (i.e. PEO) is not soluble to a greater extent with the solvent resulting in poor mechanical strength of the gels [7].

PAN - BASED POLYMER GEL ELECTROLYTE:

The polymer used is PAN (Polyacrylonitrile). Lithium salts are the principle salt used here. The Li^+ ion transference number were found to be very high in case of PAN- based gel electrolyte.

PMMA - BASED POLYMER GEL ELECTROLYTE:

The polymer, solvent and salt are PMMA, EC and/or PC and Lithium and sodium salts respectively. An ionic conductivity of 10^{-3}S cm^{-1} has been achieved in this gel electrolyte.

PVDF - BASED POLYMER GEL ELECTROLYTE:

PVDF is the polymer, EC/PC or DMF is the solvent and lithium salts such as LiCF_3SO_3 , LiPF_6 or $\text{LiN}(\text{SO}_3\text{CF}_3)_2$ or NaI is mainly taken as the salt. PVDF based gel has good electrochemical properties but they are reactive to lithium and lithium salts. [7]

1.7 - LITERATURE SURVEY:

Upadhyaya et. al. prepared PMMA based Na⁺ ion conducting gel electrolytes by taking the mixture of PMMA+ PC and PMMA+(EC+ PC) in different ratio and also different concentrations of NaClO₄. They successfully achieved an ionic conductivity of 10⁻³ S cm⁻¹ at a temperature of 25°C [8].

Wachtler et. al. prepared gel membranes based on PVDF/EC-PC/SiO₂ with Li-ion conducting salts. Vibrational spectroscopy and galvanostatic cycling tests showed that the structure of PVDF host is dependent on many factors like amount of polymers, electrolyte and salt; and also on the preparation method followed [9].

Yamamoto et. al. were successful in testing 4.2 V Li- ion polymer batteries (LIPB) with physical gel electrolyte based on poly(vinylidene fluoride) PVDF polymer with a liquid electrolyte. The performance of cell LIPB with a stable PVDF based gel electrolyte is better than other polymer gel electrolyte [10].

Panero and Scrosati developed different types of gel membranes to be used in advanced design and plastic like electrochemical devices. They formed membranes by taking LiPF₆, ethylene carbonate dimethyl carbonate (EC-DMC) solution and a poly (acrylonitrile) host [11].

Gentili et. al. tried to find out the effect of using ceramic fillers on solid- like, gel type lithium conducting polymer electrolytes to form composite gel polymer electrolytes. Due to the inclusion of fillers mechanical stability and lithium interfacial properties are increased making it useful in rechargeable batteries. But the transport properties are not changing [12].

Appetecchi et. al. prepared composite gel electrolyte by using ceramic powders like Al₂O₃ into lithium salt solution in a poly (acrylonitrile) (PAN) network. Since they have high ionic conductivity, electrochemical stability, no leakage possibility and stable lithium electrode interface, these composite gel membranes can be used in lithium ion polymer batteries and high energy battery [13].

Kontos et. al. prepared gel electrolyte by mixing LiI - I₂ solution in a polyethylene oxide matrix with TiO₂ filler. They observed that the properties of prepared gel electrolytes were compared with the liquid studied by nuclear magnetic resonances relaxometry and diffusion measurements. They also related the ionic conductivity with the ionic diffusion and dissociation of ions. [14]

Sekhon described polymer as a vital constituent of polymer gel electrolytes, the salt present in the polymer gel electrolyte helps in conduction and the solvent present aid to dissociate the salt along with providing a medium for ion conduction. He found that conductivity of lithium ion conducting polymer gel electrolytes decrease with the addition of polymer while in proton conducting gel electrolytes, the conductivity increase with the addition of polymer [15].

Guangchao Li et. al. stressed on the preparation, physical and electrochemical properties of Li-ion conducting poly (vinylidene fluoride-co-hexafluoropropylene) [P(VDF- HFP)] based gel polymer electrolytes. To prepare microporous membranes, they used phase separation or inversion methods [16].

Balaji described about synthesis of Polyacrylonitrile (PAN), Polyurethane (PU), PAN-Polyethylene oxide (PEO) based gels. He observed a porous morphology in PAN and PAN-PEO based gel electrolytes and platelet morphology in PU based gel electrolytes. The DC conductivity of polymer gel electrolytes of polymer matrices at room temperature was found to be of the order of $10^{-3} \text{ S cm}^{-1}$. His findings revealed that PU based gel electrolytes can be used more for application purposes than PAN and PAN- PEO based gel electrolytes [17].

Kalpana et. al. described on fabrication of carbon aerogel supercapacitor with an alkaline polymer gel electrolyte. They showed that the electrolyte used acts as a separator having a thickness of 3 mm and a conductivity of $10^{-2} \text{ S cm}^{-1}$ at room temperature. Characterization of capacitor was done by cyclic voltammetry, impedance spectroscopy and galvanostatic cycling [18].

1.8 - OBJECTIVE OF THE WORK

The main objective the work based on literature survey was to synthesize PVDF- based polymer gel electrolyte by taking different compositions of O/Na. After synthesizing different samples of PGE they were characterized by X- ray diffraction technique to know the amount of crystalline and amorphous content, inter - planar spacing and inter-chain length in the prepared polymer gel electrolyte samples. Also scanning electron microscopy was used to get information on the surface morphology of the samples. At the end the dielectric properties were studied and the conductivities of the PGE samples were calculated using Dielectric Spectroscopy.

1.9 - ORGANIZATION OF THESIS:

CHAPTER – 1 includes Introduction i.e. classification of electrolytes, classification of solid electrolytes, types of polymer electrolyte, polymer gel electrolyte, mechanism involved, types of gel, literature survey, objective of the work.

CHAPTER – 2 includes sample synthesis i.e. synthesis of Polymer gel electrolyte, materials under investigation, procedure, flow chart and the principle of three characterization techniques i.e. XRD, SEM, Impedance analysis.

CHAPTER – 3 describes the results and discussions made on the various graphs plotted from the data obtained from the characterization processes (i.e., XRD, SEM, Impedance analysis).

CHAPTER – 4 includes summary and conclusion drawn from the synthesis and characterization of polymer gel electrolyte.

CHAPTER- 2

SAMPLE SYNTHESIS

2.1 - SYNTHESIS OF POLYMER GEL ELECTROLYTE:

We can follow different methods for the synthesis of polymer gel electrolytes, of which three of the ways are described as follows [7]:

SOLUTION CAST METHOD:

For preparation of polymer electrolyte films and gels solution cast method is one of the earliest used methods. In this method the salt and the solvent are mixed thoroughly and then polymer is added. The solution/gel formed is then spread out on a petri dish for film formation.

For preparation of polymer electrolyte, polymer and salt are mixed in a polar solvent with appropriate ratio and stirred using a magnetic stirrer so that complexation would take place. The prepared polymer electrolyte is then spread uniformly on a petri dish. And after evaporation of the solvent a film is formed.

HOT PRESS (EXTRUSION) TECHNIQUE:

Gray et al for the first time used this technique [7]. Hot press technique is faster and less expensive than solution cast method. Using this technique, a dry and solution free polymer electrolyte film can be prepared.

The peculiarity of this technique is that the powdered form of polymer and salt are taken and then mixed in agate mortar. The mixture is then heated above the melting point of polymer for complexation of polymer – salt. In the same way for Composite polymer electrolytes also the polymer, salt and filler particles are mixed thoroughly and then heated in order to get solid polymer composite electrolyte. In both of the cases a soft lump is formed. As the name suggests, the formed lump is pressed between two cold metal blocks or twin roller to form a uniform film.

GELATION METHOD:

This technique is used specially for preparation of gel taking comparatively lesser time than the other methods mentioned above.

In this method the solvent is first taken into which the salt is added. After stirring for a few minutes, the polymer is added slowly. Again it is stirred for about 2-3 minutes; the prepared solution is casted in petri dish and left as such for few hours for gelation to take place.

2.2 - MATERIALS UNDER INVESTIGATION

Polymer, solvent and salt are the three constituents which are used for synthesis of polymer gel electrolyte.

POLYMER: PVDF (Polyvinylidene difluoride) [3]

PVDF is of high molecular weight which provides mechanical strength and flexibility to the polymer gel electrolyte.

MOLECULAR FORMULA: $-(C_2H_2F_2)_n-$

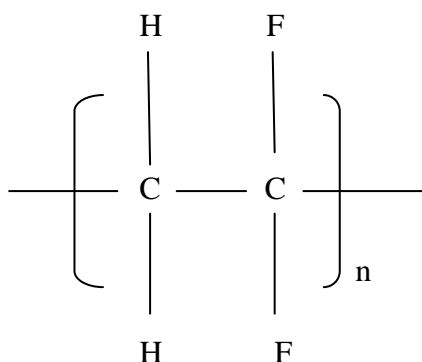


Fig 2.2.1 - Structure of PVDF

SOLVENT: DMF (Dimethylformamide)

DMF is in liquid form and it donates the oxygen having co-ordinate bond for complexation of solvent and salt during the formation of gel. It has high dielectric constant helping in dissociation of ions.

MOLECULAR FORMULA: $(CH_3)_2NC(O)H$

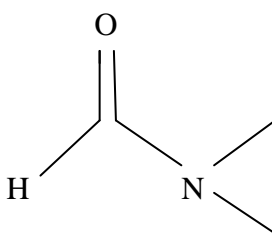


Fig 2.2.2 - Structure of DMF

SALT: NaI

NaI has low lattice energy and bulkier anion which helps in easy dissociation of the cations and there by facilitating complexation.

For making different compositions of polymer gel electrolyte of different compositions the following formula is used.

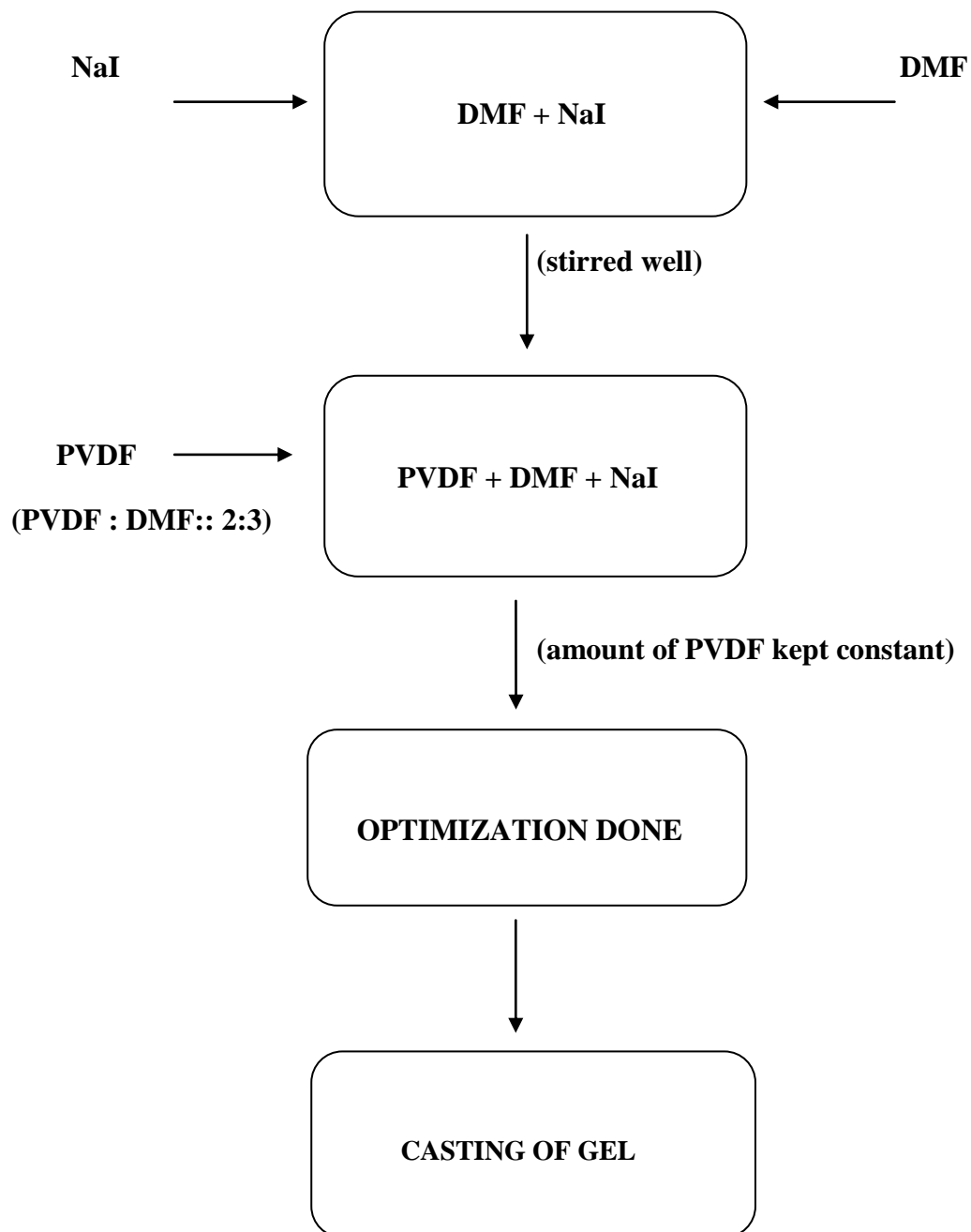
$$\frac{O}{Na} = \left(\frac{\text{mass of solvent}}{\text{mass of salt}} \right) \times \left(\frac{\text{mol.wt. of salt}}{\text{mol.wt. of solvent}} \right) \times n$$

Where n = number of active oxygen

2.3 - PROCEDURE:

5 ml of solvent i.e. N, N- Dimethylformamide (DMF) was taken in a clean beaker and the required amount of salt i.e. Sodium Iodide (NaI) was weighed. The weighed NaI is added slowly to the DMF. It was then mixed throughly with a stirrer for about 3 min for complexation to occur. The weighed polymer i.e. Polyvinylidene Fluoride (PVDF) was taken and mixed well with the already prepared solution. It was continuously stirred till all the polymer taken got mixed with the salt and solvent. The polymer and solvent were taken in 2: 3 ratios. By keeping the amount of PVDF constant and by changing the concentration of salt, different samples of gel were prepared. The prepared gels were spread on separate Petri dishes and left as such for few days for completion of gelation process.

2.4 - FLOW CHART FOR PREPARATION OF POLYMER GEL ELECTROLYTE



2.5 - CHARACTERIZATION TECHNIQUES

X - RAY DIFFRACTION TECHNIQUE:

X- Ray Diffraction Technique has been considered as an efficient technique for qualitative and quantitative analysis of crystalline compounds. XRD provides information on the nature of crystalline phases, structural make up of phases, degree of crystallinity, amount of amorphous content, microstrain and size and orientation of crystallites for wider ranges of samples from crystalline to amorphous materials [19].

X-ray diffraction pattern is considered to be the fingerprint of the substance. The basic principle of XRD is that, a collimated beam of X-ray is made to fall on the crystal and there by the angle at which the beams diffracted are measured. Sir William H. Bragg and Sir W. Lawrence Bragg were the first persons to put forth a relation showing the angle at which beam of X-ray of a specific wavelength diffracts from a crystalline surface [20]. The relation is known as Bragg's Law which is:

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

Where n = integer representing the order of diffraction peak, λ = wavelength of X – ray, d = inter – plane distance of (atoms, ions or molecules) and θ = scattering angle.

SCANNING ELECTRON MICROSCOPY:

In the modern tools and techniques available, SEM is regarded as one of the widely used instruments. SEM is such an instrument by the help of which we can observe particles up to micron and submicron ranges.

High energy electron beams are generated in the SEM and then they are focussed on to the specimen. The electrons interact with the atoms of the sample resulting in production of signals that have information about the samples surface topography, composition and other surface properties [3]. In the SEM various types of signals are produced such as secondary electrons, back scattered electrons, characteristics X-rays, and transmitted electrons. Each of the signals is due to a particular type of interaction between the incident electrons and the specimen and gives different information about the samples [21].

The main use of SEM is to provide topographical information. The secondary electrons produced by the interaction of the beam with the specimen gives the topographical information

of the sample. The secondary electrons are magnetically attracted by the secondary electron detector, which then hit the scintillator emitting photons in the process. By the help of these photons, amplification of the original signal is done and there by topography of the surface is known [22].

DIELECTRIC SPECTROSCOPY:

This technique helps in measurement of dielectric properties of a medium as a function of frequency. It is a very efficient tool for studying the dielectric and electrical properties for both electrical and non electrical applications [23]. From the past few years this technique has been used extensively in various fields like fuel cell testing, electrochemical battery and electrical microstructural characterization.

The technique measures impedance for a wide range of frequencies of the system. Due to this we are able to know the frequency response, energy storage and dissipation properties of the system. The data collected from the dielectric spectroscopy is graphically represented through Nyquist plot or Cole – Cole plot [24].

Dielectric spectroscopy examines many dielectric processes such as small molecule rotation in liquids (chemical and physical diagnostics), large molecule reorientation in polymers (physical diagnostics), bulk conduction in solids and liquids and separation of electrode effects, surface conduction and grain boundary change in porous materials and interstitial ion effects in various solids [23].

The frequency dependent properties can be expressed by different terms [24]:

Complex impedance, $Z^* = Z' - jZ''$

Complex admittance, $Y^* = Y' + jY''$

Complex permittivity, $\epsilon^* = \epsilon' - j\epsilon''$

Complex modulus, $M^* = \frac{1}{\epsilon^*} = M' + jM''$

$$\tan\delta = \frac{\epsilon''}{\epsilon'} = \frac{M''}{M'} = -\frac{Z'}{Z''} = \frac{Y'}{Y''}$$

CHAPTER-3

RESULTS AND DISCUSSIONS

3.1 - X - RAY DIFFRACTION TECHNOLOGY:

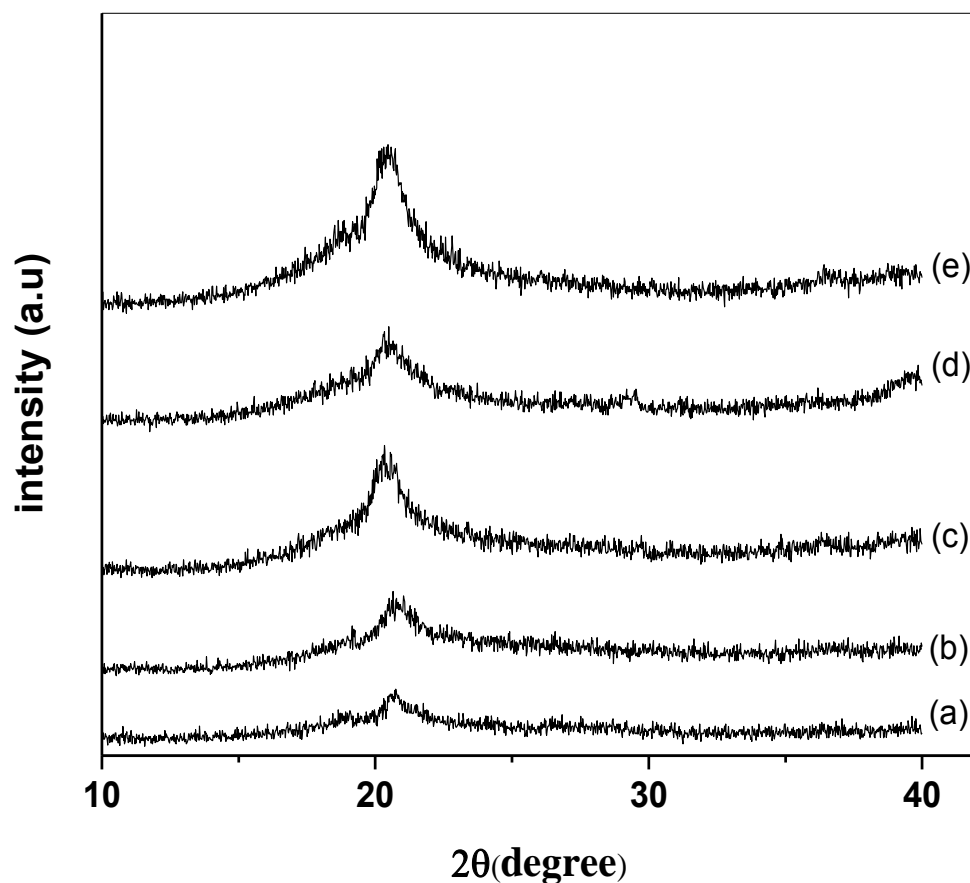


Fig. 3.1 - XRD patterns for different compositions where (a)=[O/Na=20], (b)=[O/Na=40], (c)=[O/Na=60], (d)=[O/Na=80] and (e)=[O/Na=100]

The XRD patterns were recorded at room temperature using Philips X-Ray Diffractometer with $\text{CuK}\alpha$ radiation ($\lambda=1.5405 \text{ \AA}$) in 2θ (Bragg's angle) range ($10^\circ \leq 2\theta \leq 40^\circ$) at a scan speed of $3^\circ/\text{min}$.

XRD analysis have been done to know the crystallinity, inter planar spacing and inter chain separation of the polymer gel electrolyte samples. Fig. 3.1 shows XRD pattern for various compositions of O/Na, which comprises of a crystalline peak over a broad hump due the amorphous phase. Since we find the presence of both crystalline and amorphous phase, we

conclude that the prepared polymer gel electrolyte samples are semi-crystalline in nature. In addition to this it is also seen that with increase in composition the peak became sharper and more intense. The plot showed that for O/Na=100 the peak is the sharpest one denoting the increase in crystallinity.

The inter - planar spacing is calculated from Bragg's Law i.e. $n\lambda = 2d\sin\theta$, where n=order of diffraction, λ = wavelength of X - ray (1.5405 Å), θ = angle of diffraction. Likewise, the inter - chain separation is calculated by using the formula:

$$R = \frac{7}{2\pi} \times \frac{\lambda}{2\sin\theta}$$

Where R is the inter chain length, λ is wavelength of X-ray, θ is the scattering angle.

TABLE 3.1 showing the O/Na, 2θ , θ , d and R values where 2θ = scattering angle, d = inter - planar spacing, R = inter - chain length

O/Na	2θ (in degree)	θ (in degree)	d (Å)	R (Å)
20	20.63	10.31	4.3053	4.7989
40	20.79	10.39	4.2725	4.7623
60	20.39	10.19	4.3554	4.8547
80	20.44	10.22	4.3449	4.8429
100	20.40	10.20	4.3533	4.8524

The values of 'd' and 'R' have been calculated and shown in Table 3.1. It is seen that for the first composition i.e. O/Na=20, the 2θ value is 20.63° , the inter - planar spacing 'd' is 4.3053 Å and inter chain length is 4.7989 Å. Similarly for O/Na=100 the values of 2θ , d and R are 20.40° , 4.3533 Å, 4.8524 Å respectively. Summing up the above results we can say that, by increasing the composition i.e. with decrease in the amount of salt (NaI); the 2θ value is decreasing while the inter-planar spacing and the inter chain length are increasing.

3.2 - SCANNING ELECTRON MICROSCOPY:

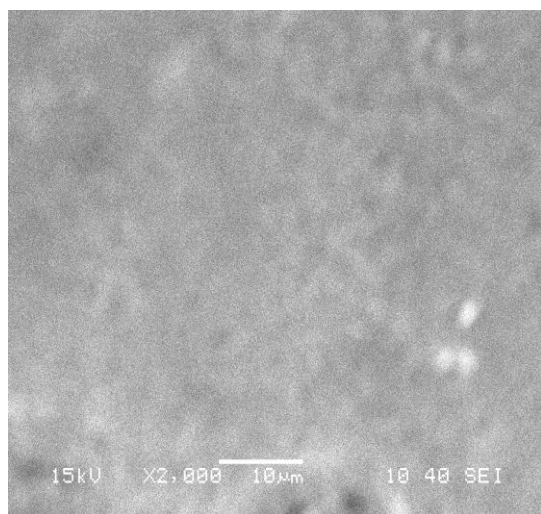


Fig. 3.2.1 for O/Na=40

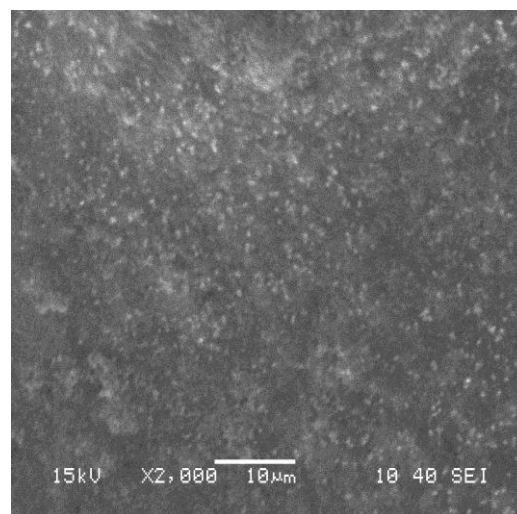


Fig. 3.2.2 for O/Na=60

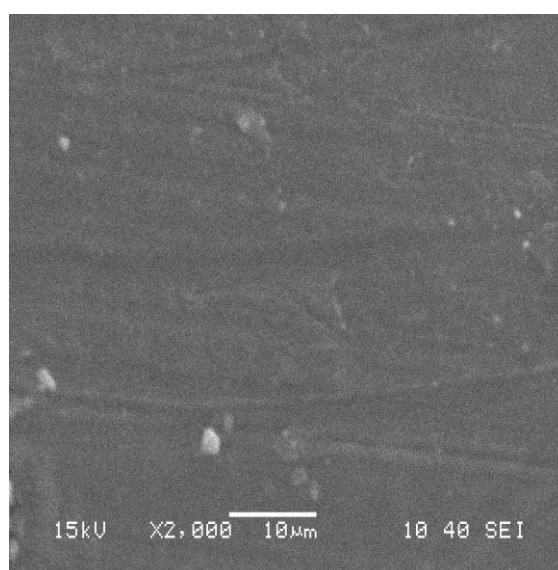


Fig.3.2.3 for O/Na=100

Scanning electron micrographs of PVdF based polymer gel electrolyte were taken by using JEOL; JSM-6480 LV, for different compositions of O/Na (20, 40, 60, 80, 100) as shown in Figure 3.2. A close look on the SEM micrograph shows that for O/Na=20, the amorphous content is more and as we increase the composition (by decreasing the salt content) the surface roughness increases denoting the increase in crystallinity. At the highest composition i.e. O/Na =100 the micrograph show more crystalline regions. Thus for higher compositions the sample

become more crystalline. SEM also show the semi-crystalline behaviour. The result found SEM is in correlation with the results of XRD analysis.

3.3 - DIELECTRIC SPECTROSCOPY

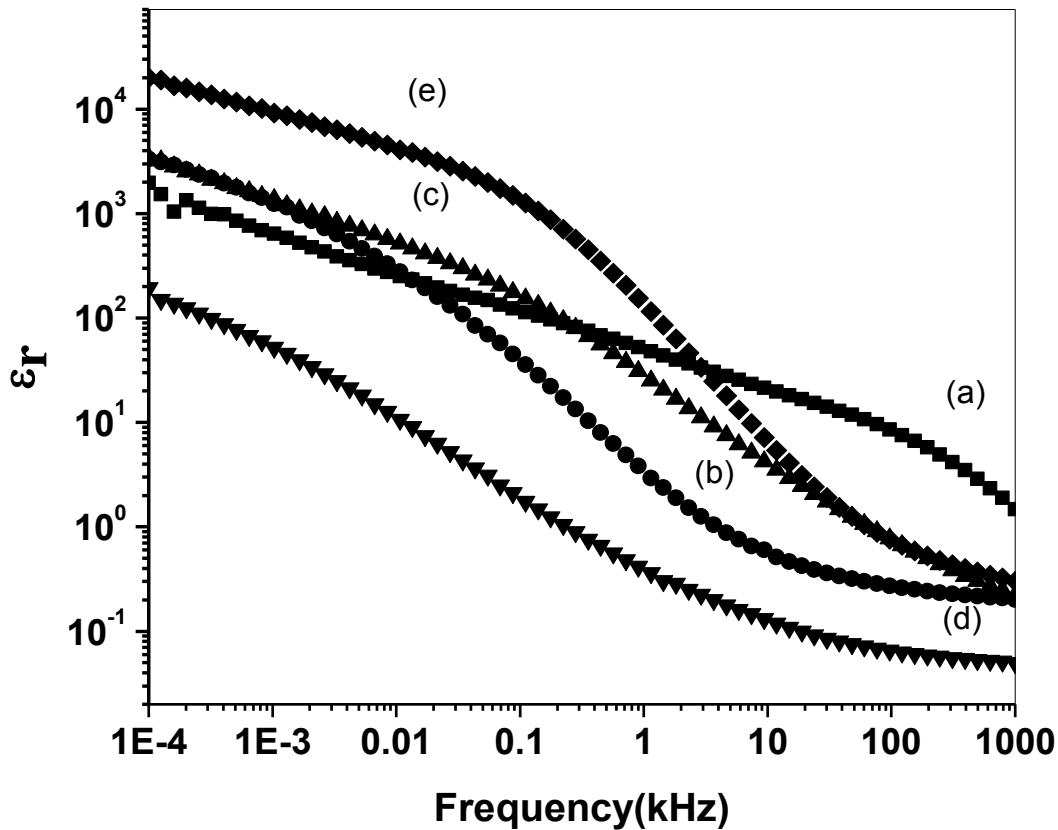


Fig 3.3.1 - Variation of dielectric constant at different frequencies for different composition where (a) is [O/Na = 20], (b) is [O/Na = 40], (c) is [O/Na = 60], (d) is [O/Na = 80] and (e) is [O/Na = 100].

Dielectric data was recorded using PSM 1735 IMPEDANCE ANALYSIS system in a wide frequency range of 100 mHz to 1MHz with supplied a. c. perturbation 100mV. The value of ϵ_r can be found from the formula $\epsilon_r = \frac{C_p}{C_0}$ where C_p is capacitance of a parallel plate capacitor and C_0 is the capacitance without any dielectric. C_0 can be found from the formula $C_0 = \frac{\epsilon_0 A}{d}$ where 'A' is the area of the sample and 'd' is the thickness of the sample. Fig 3.3.1

shows the variation of dielectric constant with change in frequency. It is found that dielectric constant is decreasing with increasing frequency. At low frequency region there is strong dispersion with frequency but at high frequency region it is independent. The low frequency region where there is decrease in dielectric constant is due to electrode polarization. There is further decrease in dielectric constant with increase in frequency due to the dielectric polarization.

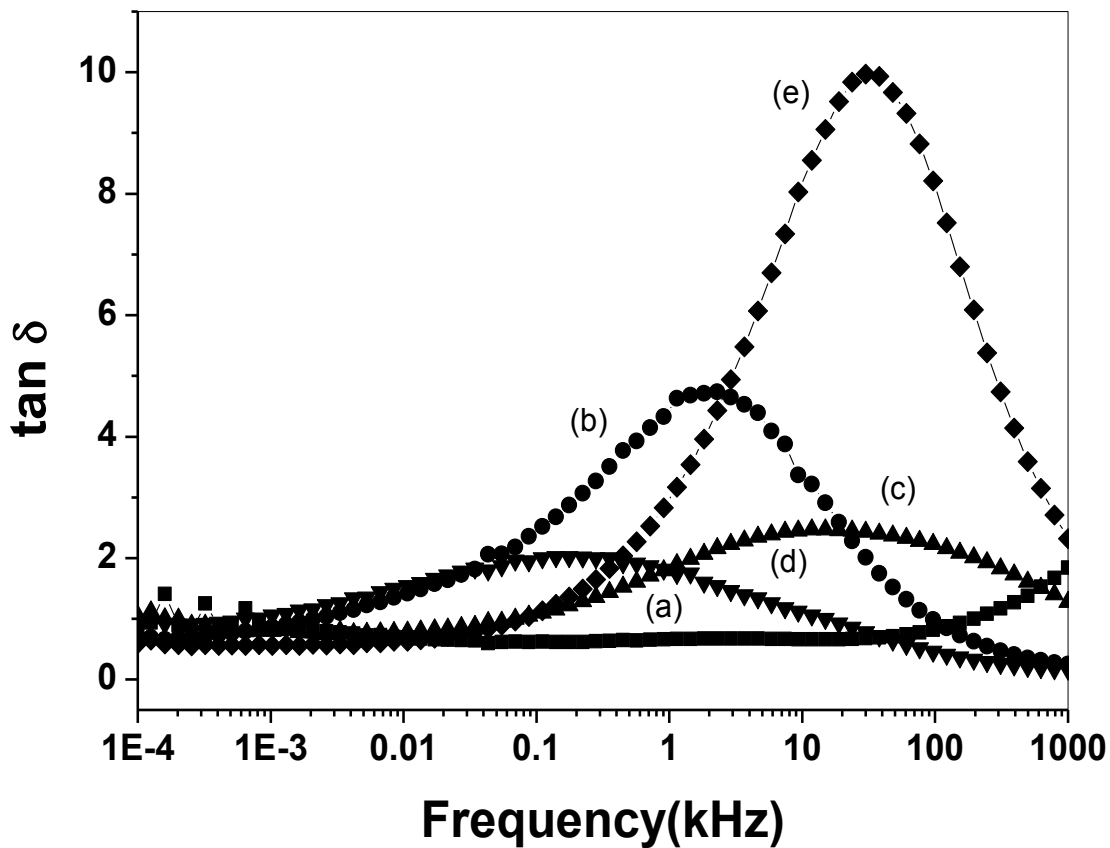


Fig.3.3.2 - Variation of Dielectric loss at different frequencies where (a) is [O/Na = 20], (b) is [O/Na = 40], (c) is [O/Na = 60], (d) is [O/Na = 80] and (e) is [O/Na = 100].

Fig.3.3.2 shows the variation of tangent loss with increase in frequency for different O/Na ratio. From the graph it has been observed that, each tangent spectrum is characterized by appearance of a peak at a particular frequency, which is different for different composition. The observed peak suggest the presence of relaxing dipoles in the polymer electrolyte. For the last composition taken i.e. for O/Na=100, we get the highest peak.

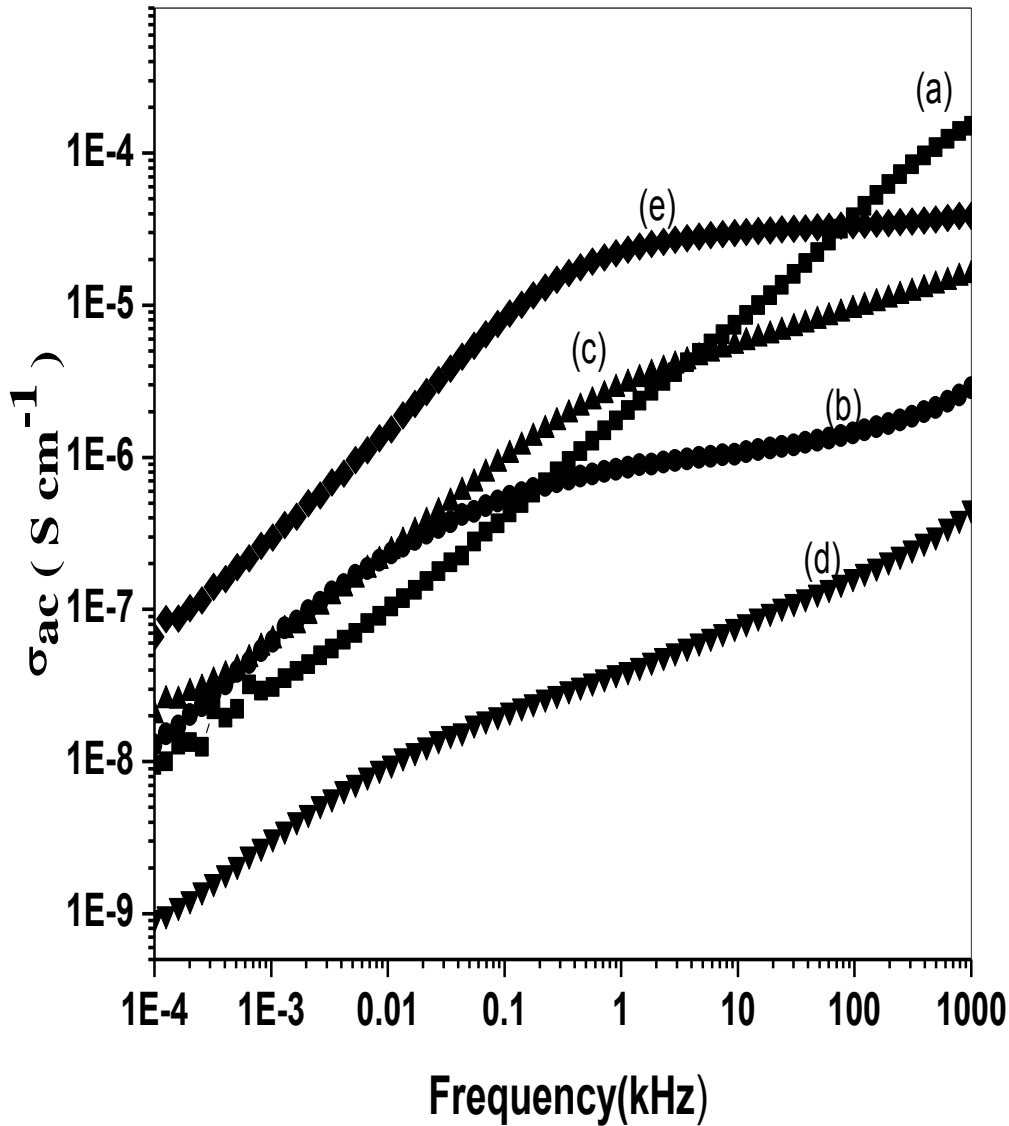


Fig.3.3.3 - Variation of a. c conductivity at different frequencies where (a) is [O/Na = 20], (b) is [O/Na = 40], (c) is [O/Na = 60], (d) is [O/Na = 80] and (e) is [O/Na = 100].

The a. c conductivity can be calculated from the formula given by $\sigma_{ac} = 2\pi f \epsilon_0 \epsilon_r \tan \delta$. The a. c conductivity pattern indicates increase in a. c conductivity with increase in frequency but at higher frequency region we observe the plateau i.e. the a. c conductivity is remaining constant with increase in frequency. The increase in a. c conductivity in the low frequency region is due to metal electrode interface and the frequency independent plateau region is due to d. c conductivity.

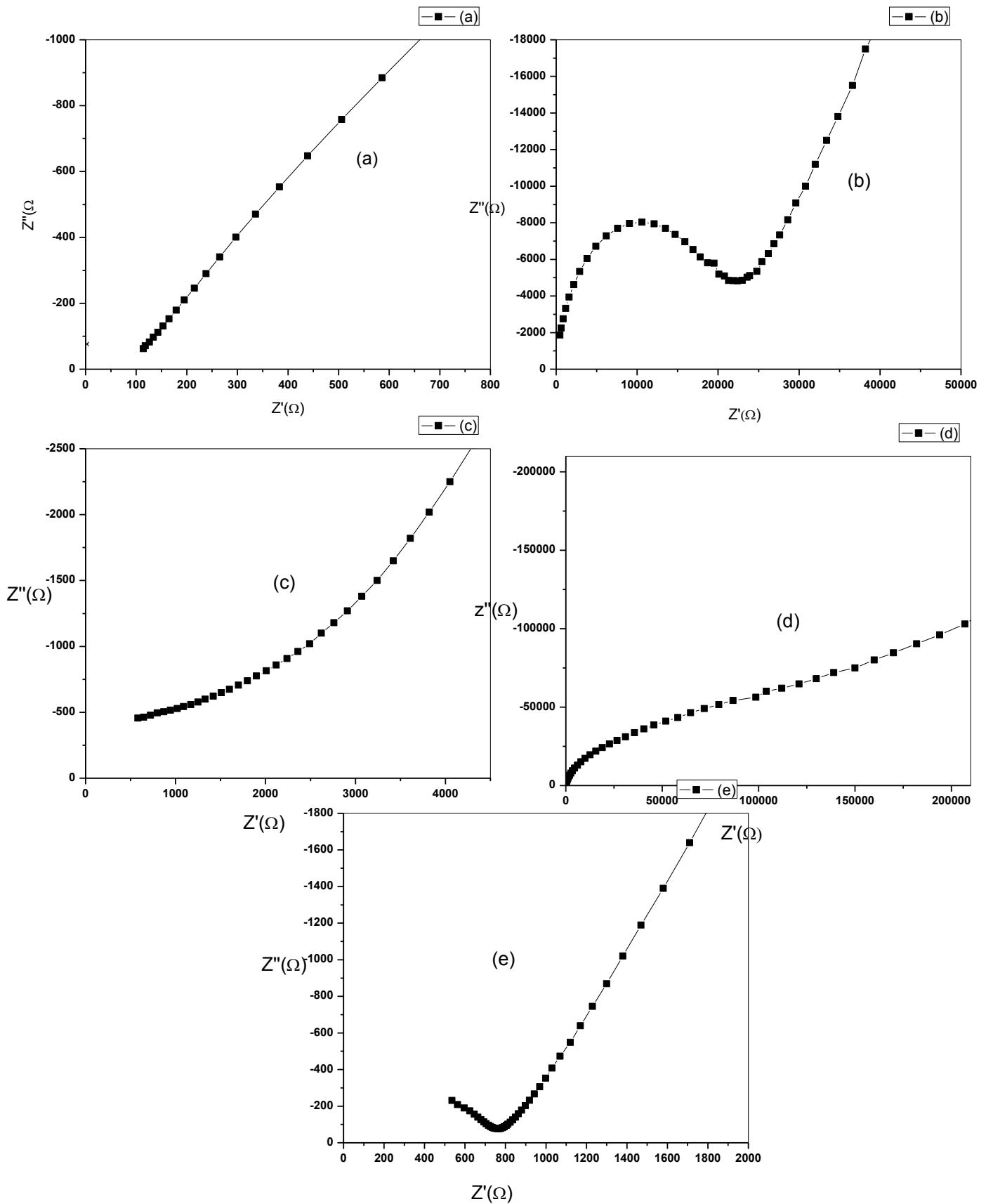


Fig. 3.3.4 Complex Impedance plots where (a) is $[O/Na = 20]$, (b) is $[O/Na = 40]$, (c) is $[O/Na = 60]$, (d) is $[O/Na = 80]$ and (e) is $[O/Na = 100]$.

Fig.3.3.4 shows the variation of Z'' with Z' for different compositions. The complex impedance spectra (Nyquist plot) comprises of a semicircular arc in the high frequency region followed by a spike in the low frequency region. The semi - circular arc is due to the bulk property of the material. The intercept of the semicircle on the real axis gives the value of bulk resistance. As mentioned earlier there is spike formation at low frequency which is because of metal electrode interface.

From the above shown plots, first we have calculated the bulk resistance and then the d. c conductivity. By using the formula written below we can find the conductivity of the prepared samples of polymer gel electrolyte.

$$\sigma_{dc} = \frac{1}{R_B} \times \frac{d}{A}$$

Where σ_{dc} is the d. c conductivity, R_B Bulk Resistance, 'd' is the thickness of the sample and 'A' is the area of the sample

TABLE 3.3 showing σ_{dc} for various compositions of O/Na where σ_{dc} is the d. c conductivity.

O/Na	σ_{dc} (Scm⁻¹)
20	5.63×10^{-4}
40	2.27×10^{-6}
60	3.35×10^{-5}
80	6.01×10^{-7}
100	8.23×10^{-5}

For different compositions the conductivity values were calculated and the maximum conductivity was found in the sample having lowest O/Na composition i.e. O/Na = 20. So the highest conductivity was found to be 5.63×10^{-4} Scm⁻¹.

CHAPTER-4

SUMMARY AND CONCLUSIONS

Various samples of polymer gel electrolyte were prepared by taking different compositions of O/Na (i.e. 20, 40, 60, 80, 100) and were characterized by three different experimental techniques such as X-ray diffraction technique, Scanning electron microscopy and Dielectric spectroscopy. The following conclusions were drawn from the present study:

- 1- X-ray diffraction technique was used to find out the phase, inter planar spacing and the inter chain length of the polymer gel electrolyte samples.
- 2- The XRD pattern showed the presence of both crystalline and amorphous phase. The presence of humps representing amorphous phase and peaks representing crystalline phase, indicates that polymer gel electrolyte is semi-crystalline in nature.
- 3- From scanning electron microscopy it was found that with increase in composition the crystallinity is increasing. The presence of amorphous phase as well as the crystalline phase confirmed the results obtained from XRD.
- 4- Dielectric Spectroscopy was carried out to analyse the dielectric and electrical behaviour of polymer gel electrolyte. Frequency dependent dielectric constant and dielectric loss suggests the presence of relaxing dipoles. The frequency dependent a. c conductivity showed presence of space charge polarization in the low frequency region and translation motion of ions giving rise to dc conductivity in the high frequency region. From the complex impedance spectra bulk resistances were obtained to calculate the d. c conductivity.
- 5- Conductivity of the prepared polymer gel electrolyte samples were calculated from Complex impedance plot. It was observed that the composition (O/Na=40) had higher conductivity.

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