SYNTHESIS AND CHARACTERIZATION OF PMMA-BASED POLYMER GEL ELECTROLYTE

Thesis Submitted for the Award of Degree of

M.Sc. in Physics

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 Ranjeeta Giri at Department of Physics, National Institute of Technology, Rourkela. I further declare that to the best of my knowledge the carried out experimental work has not formed the basis for the award of any degree, diploma, or similar title of any university or institution.

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<u>CERTIFICATE</u>

This is to certify that the thesis entitled "SYNTHESIS AND CHARACTERIZATION OF PMMA-BASED POLYMER GEL ELECTROLYTE" being submitted by **Priyadarshini Padhi** 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.

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ABSTRACT

PMMA based Polymer Gel Electrolytes have been prepared with different concentrations of salt (NaI) by gelation method. This study has been carried out to understand the effect of salt concentration on conductivity of polymer gel electrolyte. The prepared samples are characterized by XRD, optical microscopy, FTIR and Dielectric spectroscopy. The XRD studies revealed that the prepared polymer gel electrolyte samples are semi-crystalline in nature. Optical Microscopy study confirmed the results obtained from the XRD analysis. FTIR Spectroscopy study indicated the bands present in the samples were not affected for different salt concentration, which indicates that the polymer does not participate in the complexation process. The dielectric and electrical properties of the material were studied by the dielectric spectroscopic technique in a wide frequency range at room temperature. The d. c. conductivity of samples was calculated using complex impedance plots.
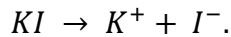
CONTENTS

CHAPTER- I

INTRODUCTION

1.1 ELECTROLYTE:

An electrolyte is any substance that has free ions. For example dissociated salt into its constituent ions in a solution is an electrolyte. These ions act as an electrically conductive medium, which helps in conduction of electricity [1]. When KI, is added to water, the salt dissociates into its component ions.

$$KI \rightarrow K^+ + I^-.$$

Generally electrolyte is used in fuel cells or electrochemical cells such as battery for conduction of electricity and energy storage.

1.2 CLASSIFICATION OF ELECTROLYTE

Based on the physical state of electrolytes can be classified into two categories such as:

(i) Liquid electrolyte and (ii) Solid electrolyte

1.3 LIQUID ELECTROLYTE

When salt is dissolved in liquid solvent it forms liquid electrolyte. For example when KI is dissolves in water forms liquid electrolyte. Liquid electrolytes have very good ion conductivity of the order of $10^{-2} \, S/cm$ [2]. Although in the present era, liquid electrolyte is used in many conventional devices, there are many inherent disadvantages of using liquid electrolyte. These are:

1. Narrow range of operating temperature.
2. Leakage of harmful liquids or grassing.
3. Corrosion reaction between electrode and electrolyte.
4. Low energy and power density.
5. Relatively short life time.

To overcome all the above disadvantage, the ideas of using solid electrolytes has been conceived [3].

1.4 SOLID ELECTROLYTE

The ionic solids which have high conductivity at room temperature are known as solid electrolyte. The conduction is due to the movement of ions through voids, or empty

crystallographic positions, in their crystal lattice structure. The cation or anion of the structure must be free to move in the structure as charge carrier. They have ion conductivity of the order of 10^{-6} S/cm [**4**].

There are some essential features of a solid electrolyte like [**5**]:

1. High ion conductivity of order 10^{-1} to 10^{-4} S cm^{-1} and low electron conductivity less than 10^{-12} S cm^{-1}
2. Low activation energy (E_a < 0.3 e V)

1.5 ADVANTAGES OF SOLID ELECTROLYTE

1. Longer life cycle than typical liquid electrolyte batteries
2. Broad range of temperature tolerance
3. Prevention from leakage of electrolyte
4. Reaction products are not inflammable.

Though solid electrolytes have many advantages over liquid electrolyte but conductivity in solid electrolyte is less than the required value for device applications usually of the order of 10^{-3} S cm^{-1}.

1.6 CLASSIFICATION OF SOLID ELECTROLYTE

On the basis of microstructure and physical properties, solid electrolyte can be classified as the following four types:

1. Framework crystalline materials

2. Amorphous – glassy electrolytes

3. Composite electrolytes

4. Polymer electrolytes

From the above four types Framework Crystalline materials is ordered and the other three phases are disordered. While the glassy and polymer electrolytes are microscopically disordered the composite electrolytes are macroscopically disordered [**6**].

1.6.1 FRAMEWORK CRYSTALLINE MATERIALS

Crystalline solid electrolytes are those which conduct H^+, Li^+, Na^+, K^+, O^{2-} as well as numerous divalent and trivalent cations. The bonding is generally due to ionic and covalent. The ion conductivity occurs due to hopping mechanism from site to site along channel in crystal structure. The number of sites available for the mobile ions is usually greater than the number of

mobile ions present. The mobile ions have high diffusion coefficient and are therefore ion conductors. Examples of crystalline solid electrolytes are AgI, CuI etc [7].

1.6.2 AMORPHOUS GLASSY ELECTROLYTE

The amorphous glassy electrolytes are more advantageous than framework crystalline materials because (i) their compositions can be changed, (ii) they have high ionic conductivity, (iii) there are no grain boundaries and (iv) thin films can be formed from it. The glassy electrolyte usually having the chemical composition, MX: M_2O: A_xO_y. A_xOy is the oxide, which can be B_2O_3, P_2O_5, SiO_2, MoO_3 etc. M_2O is the network modifier, which can be Ag_2O, Li_2O, Cu_2O, Na_2O etc. MX is the dopant salt which can be silver halides, alkali halides, copper halides, etc. Most of the glassy electrolytes are obtained by quenching from the liquid state, which results in a little variation of atomic structure from the original liquid [8].

1.6.3 COMPOSITE ELECTROLYTE

Composite electrolyte is a class of solid electrolyte which has high ionic conductivity which occurs through interfaces. It is a multi-phase solid system (generally two phase) where an inert phase particle (second phase) is added to an ion conducting (first phase) host material to increase the conductivity. The increased conductivity depends upon concentration and particle size of the inert phase [9].

1.6.4 POLYMER ELECTROLYTE

In mid-1970, it was recognized by P. V. Wright and his co-worker that, potassium salt form complexes with Poly(ethylene oxide) (PEO) and Poly(propylene oxide) (PPO) giving rise to the solid polymer electrolyte [10]. But in late 1970, the technological applications of these materials in various solid state electrochemical devices were realized. Solid polymer electrolytes are formed by complexation of polar polymers like poly(ethylene oxide), poly(propylene oxide), poly(ethylene glycol) etc. with ionic salts of mono-valent alkali metal or divalent transition metal ammonium salts, having low lattice energy and bulky anionic salts. Polymer electrolytes have the advantages over the solid crystalline and glassy electrolytes; because the solid crystalline and glassy electrolytes are hard and brittle materials. However polymer electrolytes are true solids, but at atomic level it is capable in providing liquid like degrees of freedom. It forms a bridge

between liquid electrolytes and solvent free ceramic or molten electrolyte. It has many advantages over other solid electrolyte such as (i) ease of processing, (ii) good interfacial contact with electrodes (iii) good flexibility, (iv) light weight and (v) free from leakage. They have good mechanical properties, low electronic conductivity, high chemical, electrochemical and thermal stabilities etc. Solid polymer electrolyte can be classified into following types:

1. Conventional Polymer Salt Complex

2. Plasticized Polymer Electrolyte

3. Composite Polymer Electrolyte

4. Polymer Gel Electrolyte

1.6.4.1 Conventional Polymer Salt Complex

Dry solid polymer electrolyte can be prepared by complexation of a salt in a polar polymer host like PPO, PEO etc. and also known as polymer – salt complex. The observed ionic conductivity of this polymer – salt complex is very low as compared to the desired value [**11**].

1.6.4.2 Plasticized Polymer Electrolyte

It can be prepared by adding a plasticizer, which is a low molecular weight and high dielectric constant material to the conventional polymer salt complex. The introduction of a plasticizer significantly improves the ionic conductivity as well as flexibility to the system, but the mechanical strength decreases. Still the observed ionic conductivity is below the desired level [**12**].

1.6.4.3 Polymer Gel Electrolyte

Polymer gel electrolyte can be prepared by adding non-conducting polymer to a liquid electrolyte in a balanced ratio so that polymerization will produce a gel. The polymer is added to give the mechanical support to the system. So at macroscopic level it behaves like a solid and liquid like properties is observed at microscopic level [**13**].

1.6.4.4 Composite Polymer Electrolyte

Composite polymer electrolyte is prepared by adding small fraction of micro or nano-size inorganic or organic filler particles with the conventional solid polymer electrolyte. It is generally analogous to composite electrolyte. But due to the addition of fillers the electrical conductivity and mechanical stability increases. However the observed ionic conductivity is still below the desired level [14].

As my project work is on polymer gel electrolyte so a detailed description is given below.

1.7 POLYMER GEL ELECTROLYTE

Gel is a substance which has solid like cohesive property and liquid like diffusive property. Polymer gel electrolytes are generally prepared by adding a high molecular weight non-conducting polymer to a liquid electrolyte i.e., salt dissolved in polar solvent. Ethylene carbonate (EC), propylene carbonate (PC), dimethyl formamide (DMF), diethyl carbonate (DEC), dimethyl carbonate (DMC) etc. are generally used as solvent. The salt provides ion for conduction and it should have low activation energy. The salt can be is usually of alkali metals. The macro-molecular polymer provides the mechanical strength to the system. Polymers like poly(acrylonitrile) (PAN), poly(methyl methacrylate) (PMMA), poly(vinylidene fluoride) (PVDF) etc are generally used for preparation of gel electrolyte [15]. Solvents are usually of low molecular weight; which increases the conductivity by providing a locally mobile co-ordination environment for ion motion. Polymer gel electrolytes have high ionic conductivity as required for device application such as lithium batteries, super-capacitors and electrochemical devices. Although the ionic conductivity is observed to be up to the desired level, the electrochemical stability and mechanical stability is barrier for device applications.

1.8 LITERATURE SURVEY

M. Deepa *et. al*. studied the ionic conductivity and viscosity of liquid and PMMA based gel electrolyte. Liquid electrolytes comprising lithium salts ($LiClO_4$, $LiN(CF_3SO_2)$) dissolved in solvent PC and a binary mixture of PC and EC show conductivity of the order of $10^{-2} \, S \, cm^{-1}$. Gel electrolytes were synthesized by incorporation of PMMA up to 25 wt% in these liquid electrolytes, which shows the conductivity value 10^{-3} S/cm with a very high macroscopic

viscosity. So they concluded that gel electrolytes can be visualized as highly viscous liquid electrolytes encaged in a polymeric matrix and the polymer PMMA provides mechanical stability to the gel [16].

Z. Osman *et. al.* prepared (PMMA based) polymer gel electrolyte using solvent casting techniques from EC-PC mixed solvent and various concentration of $LiBF_4$ salt. They observed that the ionic conductivity of the samples increased with increase in salt concentrations and after reaching the optimum value it decreases due to the saturation of the salt. The ionic conductivity value found to be 2.24×10^{-3} S/cm at room temperature for 20 wt% of $LiBF_4$ [17].

Hee-Tak Kim *et. al*. prepared a (PVC-PMMA) polymer blend electrolyte with different plasticizers for Li ion battery. It was reported that the polymer blend electrolytes exhibited phase – separated structure which consists of PVC – rich phase and an electrolyte – rich phase. At the constant blend ratio of PVC/PMMA = 4/6, mechanical property and ion conductivity increases [18].

X. Helan Flora *et. al*. prepared polymer blend electrolytes using solution casting technique. They studied for various concentration of $LiClO_4$ salt with the constant ratio of PAN and PMMA. The maximum ionic conductivity was found for the polymer electrolyte containing PAN (75 wt %) – PMMA (25 wt %) – $LiClO_4$ (8 wt %) to be 0.56 x 10^{-5} S cm^{-1} at 303 K [19].

A. Manuel Stephan in his review paper reported the ion conductivity and morphology of polymer gel electrolyte of five different polymer hosts. The ion conductivity of the polymer host increases when plasticizer is added, whereas the ionic conductivity decrease with increase amount of polymer in polymer gel electrolyte [20].

Jiri Vondrak *et. al*. prepared PMMA based polymer gels containing Li, Na, Mg, and Zn perchlorates and PC as plasticizers. From the resistivity studies they conclude that the resistivity of a gel with a smaller cation is higher than that of a gel containing a larger cation [21].

Y. H. Liao *et. al.* prepared a self-supported P(MMA-AN-VAc) based gel polymer electrolyte containing $LiPF_6$ as salt. It is found that, the above gel electrolytes have high thermal stability of 310 °C, good mechanical strength, electrochemically stability up to 5.6 V and conductivity of $3.48 \times 10^{-3} S/cm$ at ambient temperature [22].

Hong-Ryun Jung *et. al.* synthesized PMMA/PVC blend membrane by electro – spinning method using DMF as solvent. Among the PMMA/PVC – based gel polymer electrolyte, the electrolyte comprising of 10wt% PMMA and 90wt% PVC has the highest ionic conductivity of value $7.8 \times 10^{-3} S\ cm^{-1}$ [23].

S. N. Asmara *et. al.* prepared PMMA based magnesium ion gel polymer electrolyte using EC:DEC (2:1) as solvent. The highest conductivity of $5.58 \times 10^{-5} S\ cm^{-1}$ and electrochemical stability up to 2.42 V was obtained for polymer/solvent in mass ratio 40/60. The highest conducting gel polymer electrolyte has been used to fabricate an electric double layer capacitor (EDLC) [24].

Hee-jin Rhoo *et. al.* prepared polymer gel electrolyte in solution casting technique by taking the blend of PVC-PMMA as the host polymer, mixture of EC-PC as plasticizer and $LiCF_3SO_3$ as salt. They studied the effect of the PMMA – PVC blend ratio and the plasticizer content on the ionic conductions of the system. The mechanical property was improved by the incorporation of PVC into the electrolyte system. But the ionic conductivity decreased with increasing the PVC/PMMA ratio and increased with increasing the plasticizer content [25].

D. Saikia *et. al.* investigated the ion transportation in P(VDF-HFP)–PMMA–$LiCF_3SO_3$–(PC+DEC) – SiO_2 fumed composite gel polymer electrolyte system. SiO_2 dried fumes were used as fillers to get composite gel polymer electrolyte. Samples were prepared by solvent casting technique with varying the solvent – filler ratio. Increase in ion conductivity was observed due to addition of fillers. Highest ion conductivity of $1 \times 10^{-3} S\ cm^{-1}$ at 303 K is observed for 20wt% P(VDF-HFP), 10wt% PMMA, 10wt% $LiCF_3SO_3$, 56wt% (PC + DEC) and 4wt% SiO_2 fumed [26].

S. Rajendran *et. al.* prepared polymer electrolyte system containing PMMA as host polymer, LiBF$_4$ and LiAsF$_6$ as salt, plasticizer DBP and inorganic filler ZrO$_2$ powder. The prepared samples were studied using FTIR and impedance spectroscopy. From the FTIR study they observed that the complex formation in PMMA – LiBF4/LiAsF$_6$ – DBP – ZrO$_2$ and the complex remains mainly in the amorphous phase. Impedance spectroscopy study showed the increase in conductivity is due to the addition of ZrO$_2$. The maximum values of conductivities obtained are $4.6\times10^{-5}\ S\ cm^{-1}$ and $1.9\times10^{-4}\ S\ cm^{-1}$ for samples with 10 weight ratio of ZrO$_2$ to PMMA– LiBF$_4$/ LiAsF$_6$ –DBP polymer electrolyte systems respectively at 304 K [27].

Xinping Hou *et. al.* prepared gel polymer electrolyte using solution casting technique by taking PMMA and ABS polymer blend, EC/PC (1:1 by weight) andLiClO$_4$. Dual – phase structure was observed from the SEM and DSC analysis. They reported that the plasticizer – rich phase provided a path for the ion transport and the ABS – rich phase acted as a mechanically supportive matrix. The ionic conductivity of the electrolytes decreased with the increasing ABS/PMMA ratio and increased with the increasing plasticizer content at 15% LiClO$_4$ content. Due to incorporation of ABS the desirable mechanical property had developed which was confirmed from the stress – strain curves [28].

1.9 Objectives:

Based on the literature survey, the main objective of our work is as follows:

- To prepare PMMA- based polymer gel electrolyte by taking different concentrations of the salt with respect to the solvent.
- To get information about the amount of crystalline and amorphous content in the prepared polymer gel electrolyte samples, X- ray diffraction technique will be adopted.
- To characterize the samples by optical microscopy, so as to analyze the surface morphology of the samples.
- To get the information about the bonds present in the sample, FTIR spectroscopy characterization will be adopted.
- To find out the detailed electrical properties of the polymer gel electrolytes, Complex impedance/Dielectric Spectroscopy characterization techniques will be used.

CHAPTER-II

SAMPLE PREPARATION AND CHARACTERIZATION TECHNIQUE

2.1   METHODS OF SAMPLE PREPARATION:

There are different common methods to prepare different polymer electrolyte are available in literature. Some of them are discussed below.

2.1.1 Solution Cast Technique:

It is a very common method for preparation of polymer gel electrolyte. In this method, suitable amount of polymer is dissolved in a polar solvent, and then a required amount of salt is added to it. The solutions obtained should be stirred for 10 to 12 hours using the magnetic stirrer, for complexation of polymer host and salt. The polymer solution is then poured into a petridish and then the free standing polymer electrolyte films will be formed through slow evaporation of the solvent and followed by vacuum drying.

2.1.2 Hot Press Technique:

In this process dry powder of polymer and salt is taken in a suitable ratio and is mixed thoroughly by agate mortar. Then the mixture is heated above the melting point temperature of the host polymer for sufficient time for polymer – salt complexation. The prepared soft lump 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. It has many advantages over solution cast technique such as it is a rapid process and it is least expensive. Using this method dry and solvent free electrolyte can be prepared.

2.1.3 Gelation Method:

This is the common technique used generally for preparation of gel. In this method first the salt will be added in the solvent and stirred up to complete dissolution of salt. Then the polymer is added slowly and stirred for some time. Then the prepared solution is casted in petridish and left for few hours for gelation.

In our sample preparation method we have used the gelation method to prepare the sample as it is very easy and less expensive method.

To calculate the required amount of salt for preparation of the polymer gel electrolyte, we have used the following formula [29]

$$\frac{O}{Na} = \frac{Mass\ of\ solvent}{Mass\ of\ salt} \times \frac{mol.wt.of\ salt}{mol.wt.of\ solvent} \times n$$

Where $n = number\ of\ active\ oxygen.$ And in my case active oxygen, $n = 1$

2.2 MATERIALS USED

For preparation of polymer gel electrolyte, poly(methyl methacrylate) (PMMA), Propylene Carbonate (PC), Ethylene Carbonate (EC) and NaI are used.

2.2.1 POLYMER: poly(methyl methacrylate) (PMMA)

PMMA is a high molecular weight polymer, which provides mechanical strength and flexibility to the gel electrolyte. Melting point of PMMA is 160°C.
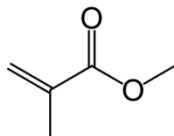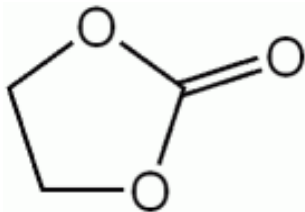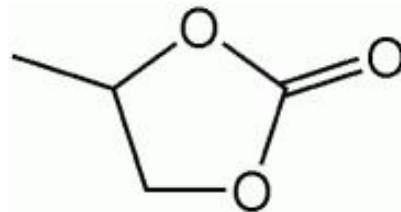

Fig.1 Structure of PMMA

2.2.2 SOLVENT:

Ethylene Carbonate (EC): EC is taken as the solvent. It donates active oxygen for complex formation. EC has a molar mass of 88.06 g/mol and melting point of $34 - 37$ °C. Molecular formula of EC is $C_3H_4O_3$.

Propylene Carbonate (PC): PC has molar mass 102.09 g/mol and melting point $- 48.8$ °C. Molecular formula of PC is $C_4H_6O_3$.

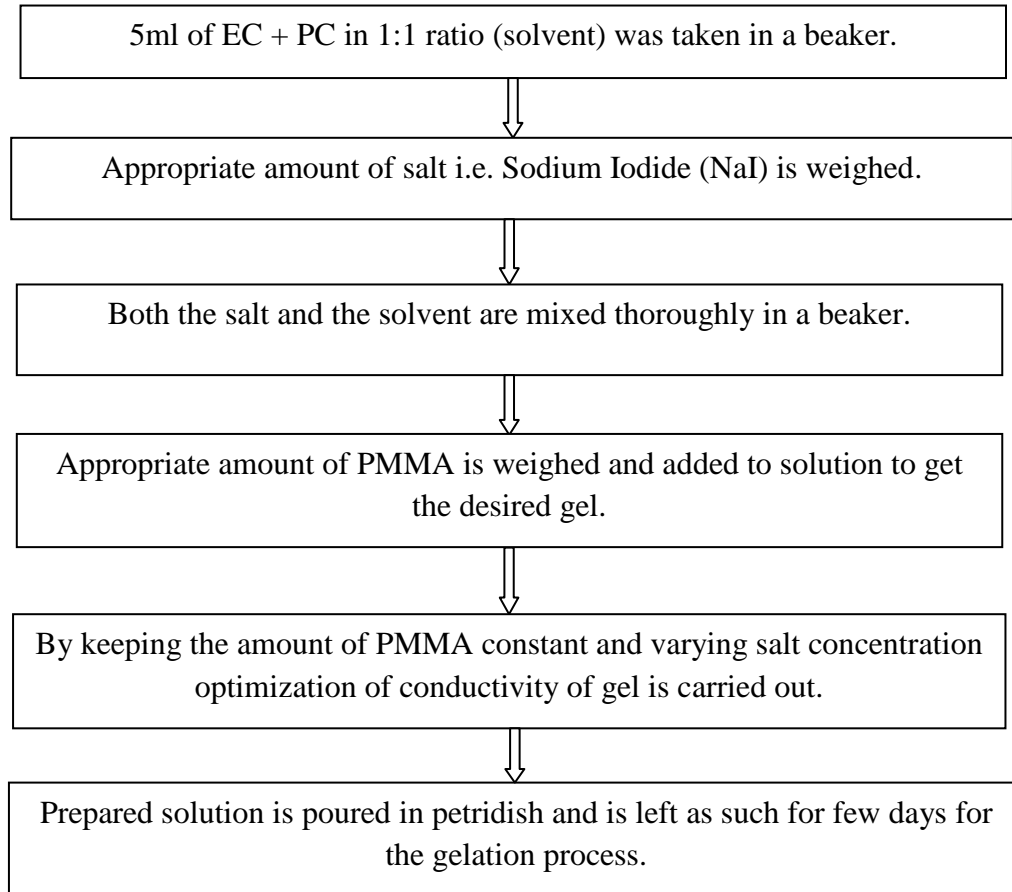**Fig. 2(a) Structure of Ethylene Carbonate**   **Fig. 2(b) Structure of Propylene Carbonate**

2.2.3 SALT: Sodium Iodide (NaI): NaI has molar mass 149.89 g/mol. It has low lattice energy and bulky anion which helps in easy dissociation and there by facilitating the complexation.

2.3 PROCEDURE OF SAMPLE PREPARATION

3 ml of Propylene Carbonate (PC) was taken in a clean beaker and required amount of Ethylene Carbonate (EC) was dissolved in it, to get a solvent of EC + PC in 1:1 molar ratio. The required amount of salt i.e. Sodium Iodide (NaI) was weighed. The weighed NaI is added slowly to the EC + PC solvent. It was then mixed thoroughly with a stirrer. Then a required amount of polymer i.e. poly(methyl methacrylate) (PMMA) was weighed 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. The same procedure was followed to prepare different samples of gel by keeping the amount of PMMA constant and by changing the concentration of salt. Then the prepared gels were spread on separate petridishes and left as such for few days for gelation process.

2.4 FLOW CHART FOR GEL POLYMER ELECTROLYTE BY GELATION METHOD

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┌─────────────────────────────────────────────────────────────┐
│   5ml of EC + PC in 1:1 ratio (solvent) was taken in a beaker.│
└─────────────────────────────────────────────────────────────┘
                              ⇓
┌─────────────────────────────────────────────────────────────┐
│  Appropriate amount of salt i.e. Sodium Iodide (NaI) is weighed.│
└─────────────────────────────────────────────────────────────┘
                              ⇓
┌─────────────────────────────────────────────────────────────┐
│   Both the salt and the solvent are mixed thoroughly in a beaker.│
└─────────────────────────────────────────────────────────────┘
                              ⇓
┌─────────────────────────────────────────────────────────────┐
│  Appropriate amount of PMMA is weighed and added to solution to get│
│                      the desired gel.                          │
└─────────────────────────────────────────────────────────────┘
                              ⇓
┌─────────────────────────────────────────────────────────────┐
│  By keeping the amount of PMMA constant and varying salt concentration│
│         optimization of conductivity of gel is carried out.    │
└─────────────────────────────────────────────────────────────┘
                              ⇓
┌─────────────────────────────────────────────────────────────┐
│  Prepared solution is poured in petridish and is left as such for few days for│
│                     the gelation process.                      │
└─────────────────────────────────────────────────────────────┘
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Fig. 3 Flow chart for preparation of polymer gel electrolytes.

2.5 CHARACTERISATION TECHNIQUES USED

The prepared gel polymer electrolytes are characterized by the following techniques

1. XRD
2. Optical Microscopy
3. FTIR Spectroscopy
4. Dielectric Spectroscopy

2.5.1 X-Ray Diffraction (XRD)

X-Ray Diffraction technique is an analytical method used to study crystal structure, phase, chemical composition and physical structure of materials or thin film.The X-ray diffraction pattern of a pure substance is like the fingerprint of the substance.

This technique is based on Bragg's law i.e. $n\lambda = 2dsin\,\theta$
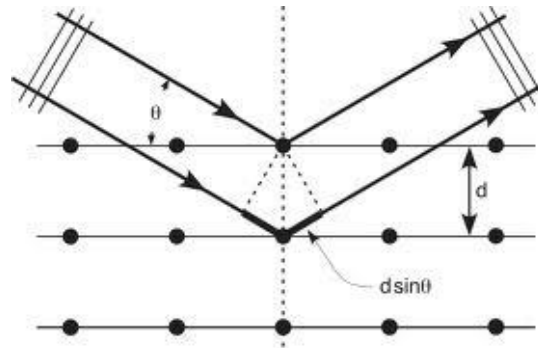
Fig 4. Schematic diagram of Bragg's law

When the X – rays of wavelength of few Å is incident on the sample, having the same interatomic distances in crystalline solids, the diffracted rays interact to produce constructive interference. By observing the diffracted rays and by using Bragg's law inter-atomic spacing (d) can be calculated. The intensity pattern of the XRD spectra also enables us to calculate fraction of amorphous content in a semi crystalline polymer.

2.5.2 Optical Microscopy

Optical Microscope is a type of microscope which uses visible light and a system of lenses to magnify images of small samples. Basic optical microscopes can be very simple, although there are many complex designs to improve resolution and sample contrast. The image of the optical microscopy can be captured by normal light sensing camera or by CCD camera.

2.5.3 Dielectric Spectroscopy

It is a non-destructive technique used to study the electrical properties of material. By applying sinusoidally varying alternating voltage to a sample the dielectric properties as a function of frequency is recorded here. Dielectric properties like small molecule rotation in liquids, large molecule reorientation in polymers, 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 solids and gel electrolyte can be measured. In our case only the impedance, phase capacitance, tangent loss parameters were measured.

2.5.4 FTIR Spectroscopy

Fourier transform infrared spectroscopy (FTIR)is an important technique for identification and characterization of a substance. It is based on the absorption spectrum of sample for each wavelength. A beam containing IR radiations of many frequencies is passed through a sample at once, and measures how much of that beam is absorbed by the sample. The resulting spectrum represents the molecular – absorption and transmission, creating a molecular finger print of the sample. No two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful and unique for several types of analysis like identification of unknown material, amount of component in a mixture etc.

CHAPTER-III

RESULTS AND DISCUSSIONS

3.1 XRD
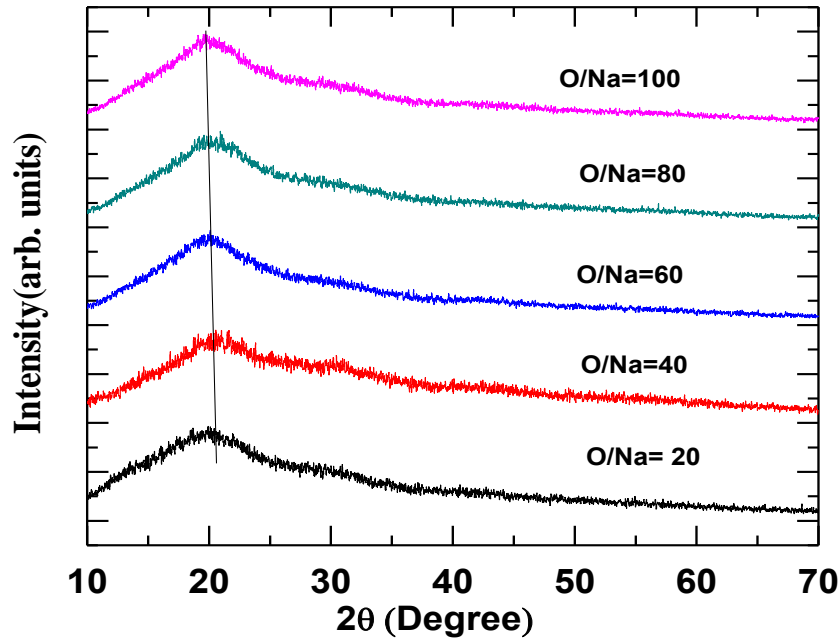
Fig.5 XRD patterns of samples for different salt concentrations

The XRD studies carried out using a Philips X'pert X-Ray Diffractometer using $Cu - K_\alpha$ radiation ($\lambda = 1.5405$ Å) in the 2θ range of 10° - 70° at the scan speed of 2° per min at room temperature. From the XRD data we observed a broad hump around 19° - 20 °. We can conclude from the observations that the prepared polymer gel electrolyte samples are semi-crystalline in nature. From Fig.5, it is observed that the hump shifts slightly towards left with increase in O/Na concentration.

Using Bragg's law i.e. $n\lambda = 2dsin\theta$, the inter-planar spacing for different samples are calculated by taking $n = 1$, λ = wavelength of $X - ray$ (1.5405 Å), θ = angle of diffraction.

The inter – chain separation is calculated by using the formula:

$$R = \left(\frac{7}{2\pi}\right) \times \left(\frac{\lambda}{2sin\Theta}\right)$$

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

**Table 3.1 Inter-chain separation and Inter-planar spacing of polymer gel electrolytes:**

O/Na	2θ (degree)	Inter chain separation $R=(7/2\pi)\times(\lambda/2\sin\theta)$ (Å)	Inter planar spacing $d=\lambda/2\sin\theta$ (Å)
20	20.48	4.8279	4.3313
40	20.34	4.8609	4.3609
60	20.1	4.9183	4.4124
80	19.9	4.9647	4.4563
100	19.68	5.0196	4.5056

With the increase of O/Na ratio (i.e., with decrease in salt concentration) the inter chain separation and inter planar spacing increases gradually.
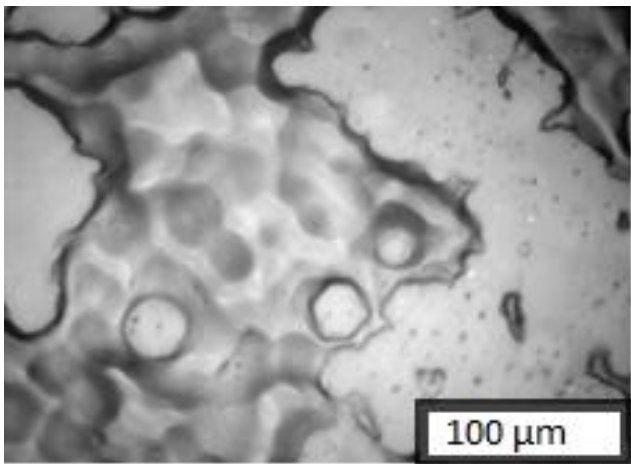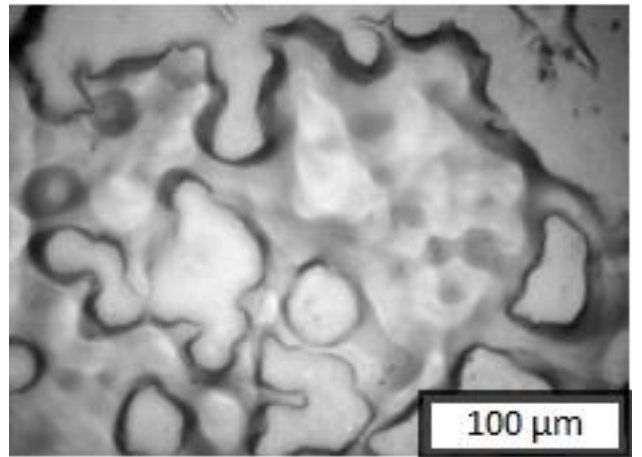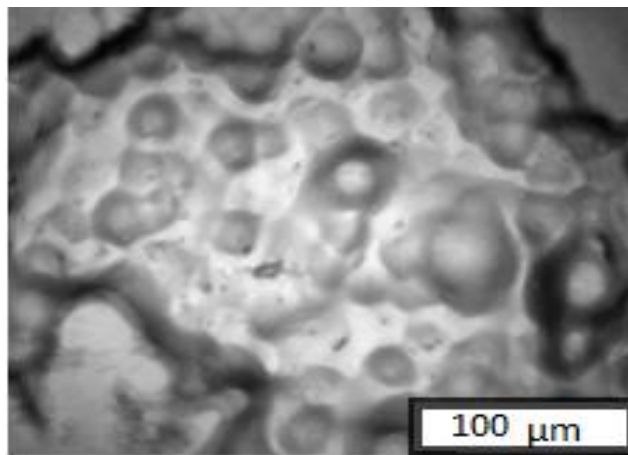
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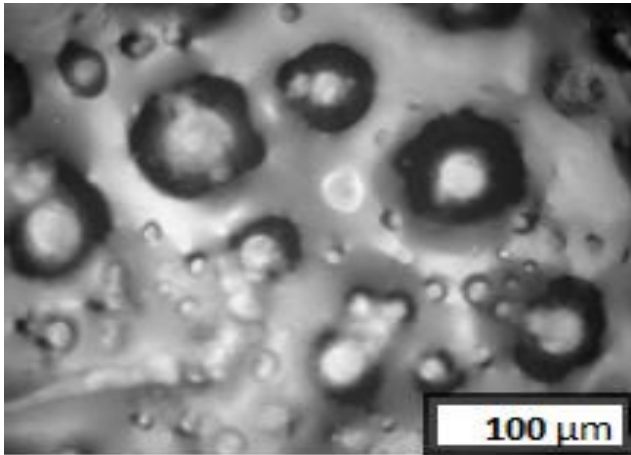
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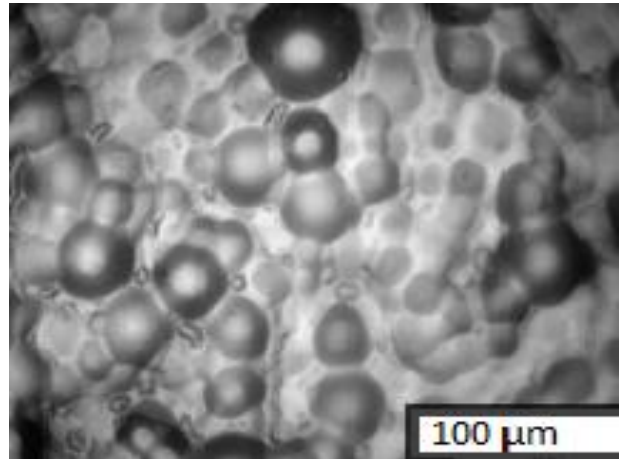
6(b)

6(c)

6(d)

6(e)

Fig. 6(a), 6(b), 6(c), 6(d), 6(e) optical microscopy image for O/Na=20, 40, 60, 80 & 100 respectively

The optical microscopy has been carried out using Olympus BX51 microscope with various magnifications at room temperature. Optical microscopy shows the presence of distinct spherulites when the selected magnification is 50X. The region between spherulite boundaries is amorphous in nature and we can conclude that polymer gel electrolytes are semicrystaline in nature having amorphous boundary between the crystalline spherulite. This is supporting the XRD result.

3.3 FTIR SPECTROSCOPY

FTIR Spectra of the prepared samples were recorded from range of wavenumber $400 - 3000$ cm^{-1} with the help of Thermo Nicolet, NEXUS – 870 Infrared spectrometer at room temperature.
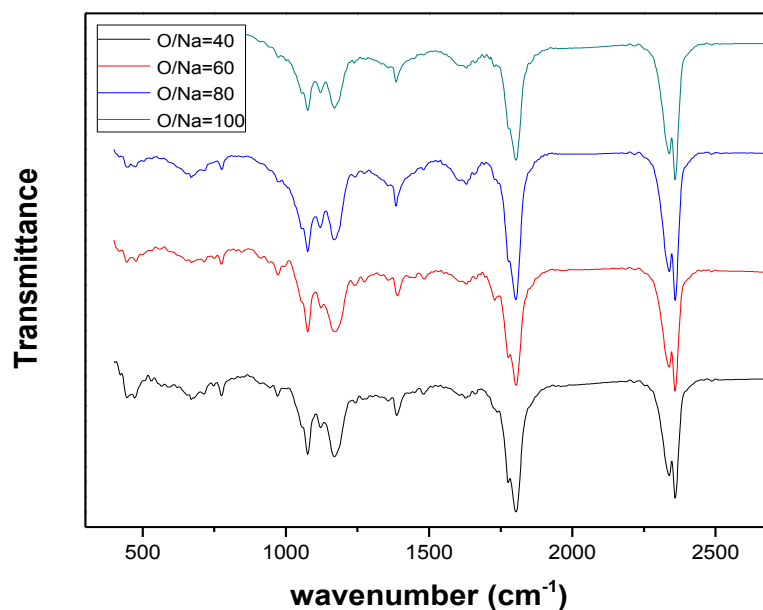
Fig. 7 FTIR spectra for O/Na= 40, 60, 80 & 100

The Fig. 7 shows the FTIR spectroscopy plot of Transmittance Vs Wavenumber for different O/Na concentrations. All the FTIR spectra for different O/Na ratio are alike. All the bands present have been assigned in Table 3.2. We can conclude that the polymer is not participating in any complexation process in the preparation of polymer gel electrolyte.

Table 3.2 bands present correspond to the absorption spectra.

Wavenumber (cm^{-1})	Assignment	Reference
1076	C – O	[30]
1170	C – C	[31]
1382	C – O	[32]
1804	C = O	[33]
1630	C = C	[34]
2360	atmospheric CO_2 Present in sample cell	[35]

Thus the polymer is only giving physical stability to the gel electrolyte.

3.4 DIELECTRIC SPECTROSCOPY

The dielectric/complex impedance spectroscopic studies were carried out using PSM 1735 Impedance analysis Package of Newton 4th Limited in the frequency range of 100 mHz to 1 MHz at room temperature. The data were recorded with an input signal of amplitude 100 mV. The obtained data was analyzed and thus the conductivity of the sample was calculated.
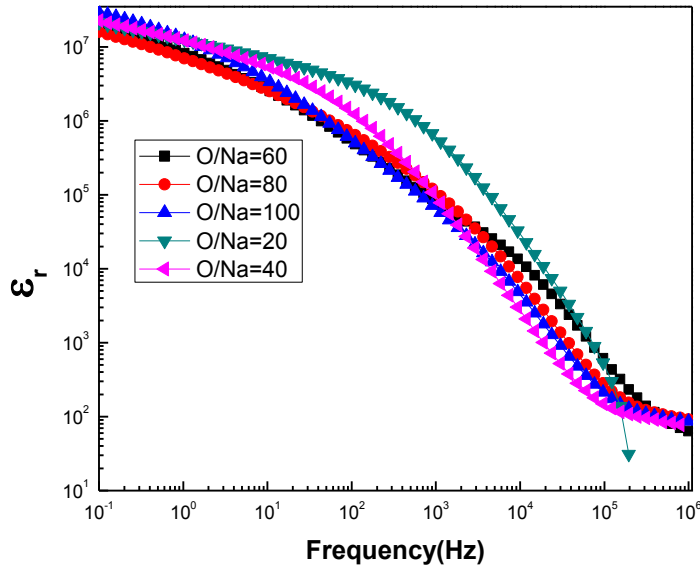

Fig. 8 ε_r vs Frequency plots for O/Na= 20, 40, 60, 80 & 100

Figure 8. shows the variation of relative permittivity (ε_r) with frequency for different O/Na ratio. From the graph we can observe that ε_r has higher values at lower frequency which decreases sharply with increase in frequency. Decrease in dielectric constant with increase in frequency is due to the dipolar relaxation. The low frequency region where there is sharp decrease in dielectric constant is observed may be due to electrode polarization phenomena.
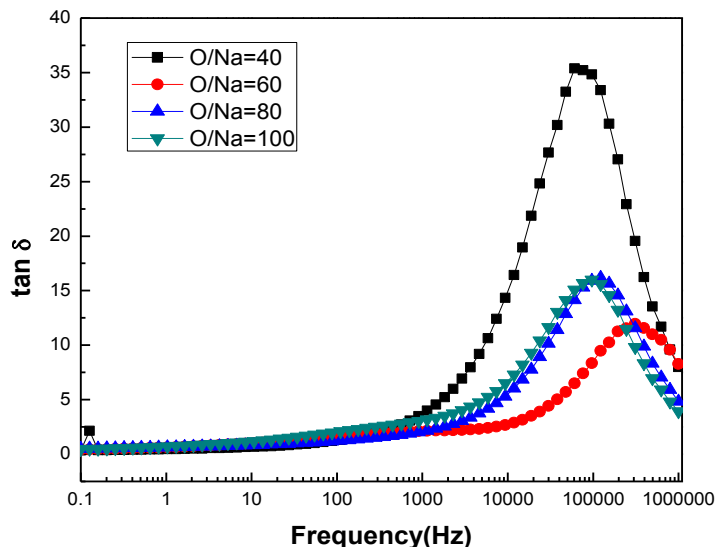
Fig. 9 tan δ vs Frequency plots for O/Na= 40, 60, 80 & 100

Fig.9 shows the variation of tangent loss with frequency for different compositions of the prepared polymer gel electrolyte samples. The peak position is different for different compositions. The appearance of peaks suggests the presence of relaxing dipoles in the samples.
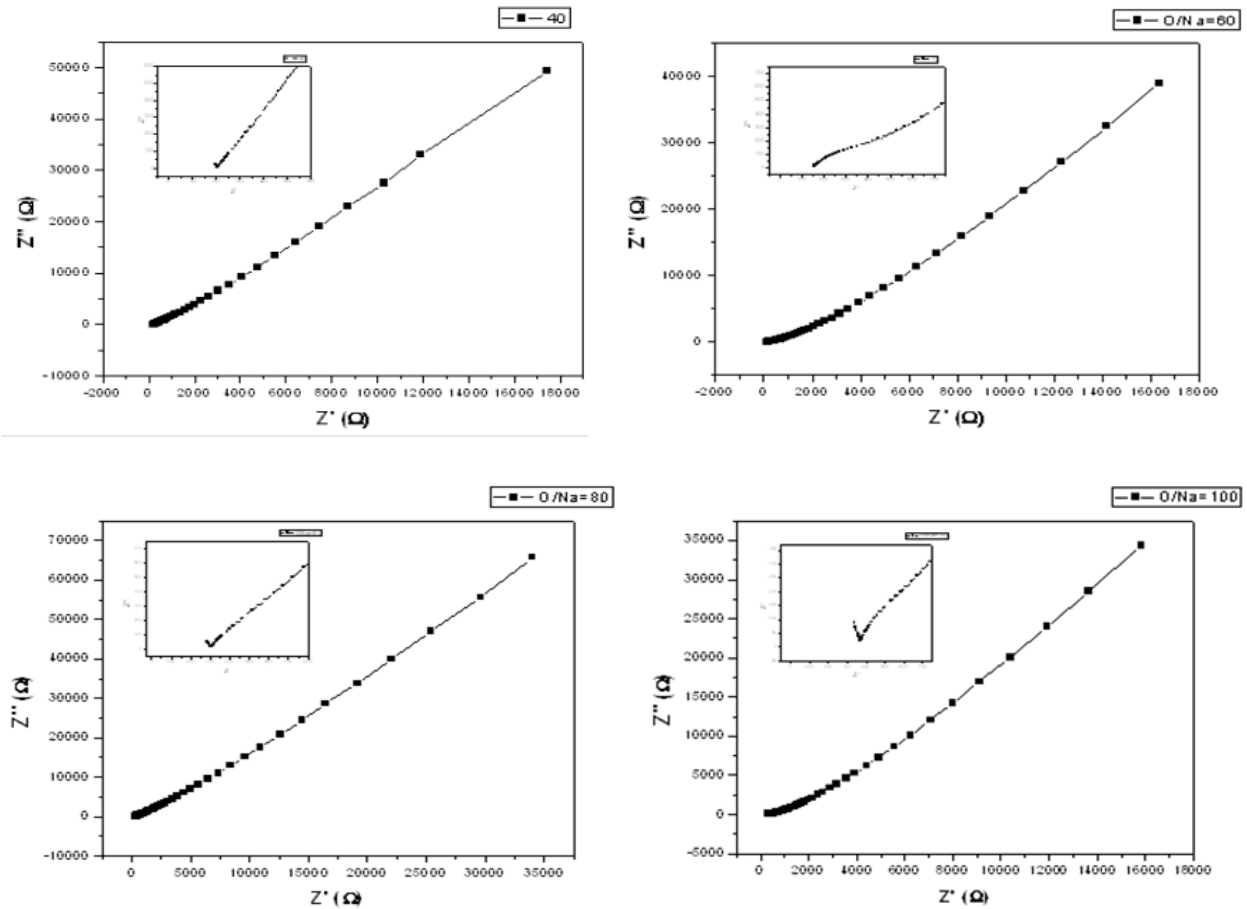
Fig. 10 Complex impedance plots for O/Na= 40, 60, 80 & 100 respectively at room temperature

Figure 10 represents the complex impedance plot of prepared gel electrolyte samples for various concentrations salt to solvent ratio. The graph shows spike in the low frequency region and semi-circular arc in the high frequency regions (in inset; not clearly visible due to lack experimental data). The spike in low frequency region appears due to the electrode polarization phenomena at the material electrode interface. The semicircular arc in the high frequency region is appearing due to the bulk properties of the material. The intercept of the semicircular arc on the real axis (Z') give rise to the bulk resistance of the materials.

The d. c. conductivity calculated by using the relation:

$$\sigma_{dc} = \left(\frac{1}{R_b}\right) \times \left(\frac{t}{A}\right)$$

Where σ_{dc} is the d.c. conductivity, R_b is the bulk resistance in ohm, l is the thickness of the polymer gel electrolyte and A is the area of the electrode.

The calculated values of d.c. conductivity is shown in table below.

Table 3.3 d.c. conductivity for different compositions:

O/Na	σ_{dc}(S/cm)
40	2.86×10^{-4}
60	3.06×10^{-4}
80	2.37×10^{-4}
100	1.83×10^{-4}
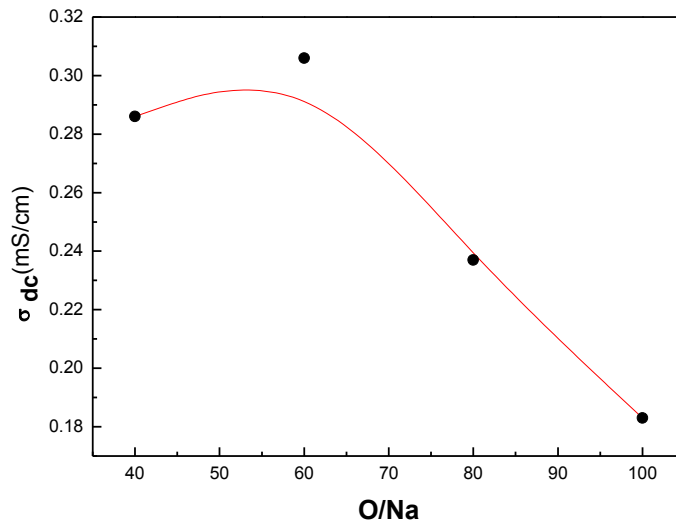
Fig. 11 Variation of $\sigma_{d.c.}$ vs O/Na ratio

Fig. 11 infers that with the increase of O/Na ratio, at first d.c. conductivity increases, but after obtaining a maxima, it decreases. Highest d.c. conductivity is found to be $3.06 \times 10^{-4}\ S/cm$ for O/Na=60.

CHAPTER-IV

CONCLUSIONS

➢ Polymer gel electrolytes were synthesized by gelation method taking Poly(methylmethacrylate) (PMMA) as polymer, (EC + PC) Ethylene Carbonate + Propylene Carbonate as solvent and sodium iodide (NaI) as salt. Different samples were prepared by taking O/Na = 20, 40, 60, 80 and 100.

➢ They are characterized by XRD, Optical Microscopy, FTIR and Dielectric spectroscopy.

➢ XRD analysis of the prepared polymer gel electrolytes revealed that the samples are semicrystalline in nature. With decrease in salt concentration, inter − planar spacing and the inter chain length are increases.

➢ From the optical microscopic images, the spherulites are clearly visible and their size ranges from $5 - 20 \ \mu m$. Optical Microscopy study confirmed the results obtained from the XRD analysis.

➢ FTIR Spectroscopy study confirms that the polymer is not participating in any complexation process in the preparation of polymer gel electrolyte.

➢ The complex impedance study of the sample indicated the bulk property of the material in the high frequency region and from bulk resistance d.c. conductivity was calculated. The d.c. conductivity of the material is found to be highest $3.06 \times 10^{-4} \ S/cm$ for O/Na=60. The d.c. conductivity initially increases with increase in O/Na ratio and attains maximum at O/Na = 60 then decreases.

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