Chapter 2

Experimental Methods

2.1 Preparation of Polymer Electrolyte

The polymer electrolytes prepared in the present work are complexes of inorganic salt with polymer host. Both the precursor salt and the polymer are solids. The complex-forming reaction is $mMX + (\text{-RY-})_n \rightarrow (MX)_m.(\text{-RY-})_n$. Here (MX) and (-RY-) respectively denotes the inorganic salts and the polymer repeat unit. It is a solid-solid reaction [51].

In the present investigation, the polymer being studied is Poly (vinyl chloride), PVC. The inorganic salt is $LiClO_4$ (Lithium perchlorate anhydrous,Fluka). PVC and $LiClO_4$ were taken in different weight ratios and dissolved in Tetrahydrofuran (THF). The mixtures were continuously stirred with a magnetic stirrer at room temperature for about 8 hours to ensure complete dissolution. The solutions were then cast in different petri dishes and allowed to dry at room temperature. When THF evaporated, a free-standing film was obtained. These films were kept in dessicator for further drying and complete evaporation of the solvent before being experimented.

2.2 Sample characterization

The electrical conductivity of all prepared samples was being measured by impedance spectroscopy. Other characterization techniques that were carried out were X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive analysis of X-rays (EDAX).

2.3 X-Ray Diffraction (XRD)

X-Ray diffraction studies help to identify the degree of crystallinity and the structure of crystalline form. Since the degree of crystallinity plays an important role in determining the conductivity, this study is crucial. The

structure of the materials can be made visible by X-ray diffraction. In any crystalline compound (most solids are crystalline), the atoms are arranged in a regular, three dimensional pattern unique to that compound. X-rays striking a crystal interact with the atoms creating waves of scattered x-rays that intensify each other in certain directions. Bragg showed that intensification occurs when the rays diffracted from parallel atomic planes are in phase (when the path difference is an integral number of wavelength). This is shown schematically underneath in figure[2.1] and is represented by :
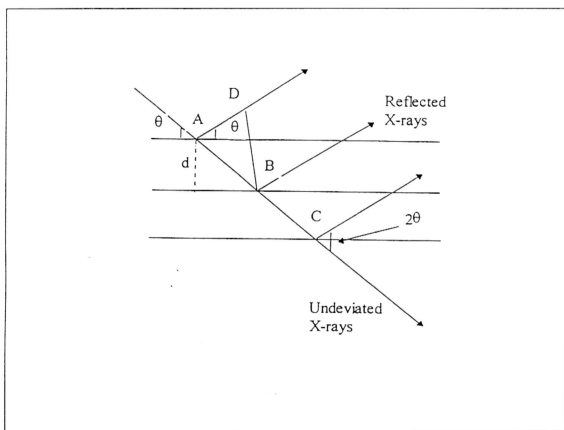
Fig[2.1]: A schematic representation of Bragg's condition.

$$n\lambda = 2d\sin\theta \qquad\qquad (1)$$

where λ is the wavelength, d the interplanar spacing, θ the **angle of incidence**

(and diffraction) and n is the integer. From this equation, crystalline materials should give peaks due to the d spacing while amorphous materials should be free of peaks implying no definite d spacing [52].

X-ray diffractometer works on the principle that, when a sample is irradiated, the x-rays are diffracted in directions characteristic of the compounds present in the sample under analysis. By measuring the angles at which diffraction peaks occur and their intensities, the type and the amount respectively of the sample's constituent compounds can be determined.
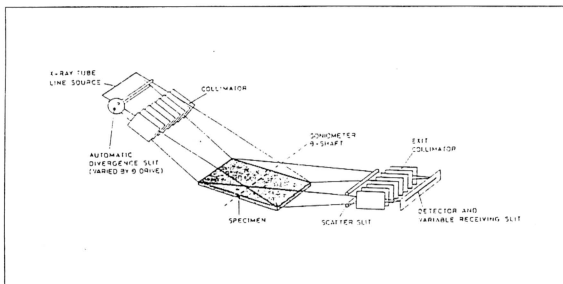

Fig:[2.2]: Layout of the X-Ray Diffractometer.

Configuration of an x-ray powder diffractometer:

The basic diffractormeter consists generally of :

- x-ray generator

- x-ray tube with filter system for monochromatisation of the x-ray beam

- collimators to optimize the resolution of the optical system

- sample holder in which the specimen is held

- goniometer, for accurate positioning of specimen (theta axis) and detector (two theta axis)

- detector for measuring the intensity of the diffracted x-rays

- control electronics

- output devices.

Variation of the angle of incidence (theta) and diffraction (two theta) is done automatically by means of a stepping motor. The specimen and the detector are rotated at 1:2 angular velocity to maintain focussing conditions. The diffracted x-rays are detected, converted into an electrical signal and fed through an amplification system to the appropriate output devices.

The most commonly used x-ray diffraction technique is the powder method. In this technique, a powdered specimen is utilized so that there will be a random orientation of many crystals to ensure that some of the particles will be oriented in the x-ray beam to satisfy the diffraction condition of Bragg's law [53].

2.4 Scanning Electron Microscopy (SEM)

The scanning electron microscope gives useful analysis of surface structure and morphology of heterogenous organic and inorganic materials [54]. SEM was carried out with the Philips 515 scanning electron microscope. Since its invention in the early sixties, SEM has been utilised in many surface science studies. The layout of a scanning electron microscope is as shown in Figure [2.3] Electrons will escape from the tungsten filament of the electron gun by

thermionic emission. The electrons are accelerated by a high negative voltage (between 2 to 25 kV) so that they will not be recaptured by the filament in its attempt to maintain electrical neutrality. The filament is enclosed in a metal cylinder called the wehnelt cylinder or cathode which shapes the diameter of the electron beam electrostatically to a size between 10 and 50μm. A vacuum system prevents the scattering of electrons by air or gas molecules in the column casing. As the electron beam enters the electron lens system, its diameter is reduced to ≈ 5 nm. The electron lens system acts in an opposite manner to optical lenses. The electron lens system consists of a coil to wire with its axis aligned along the beam's path. A cross-section of the electron gun is as shown in Figure [2.4].

This coil of wire is partially enclosed in a cylindrical iron case, figure [2.5]. When current is passed through the coil an electromagnet is produced. The magnetic lines of force will converge the electron beam to focal point (f) below the lens. A single focus point will be produced if all of the electrons have the same energy and to ensure this, the accelerating voltage of the electron gun must be very stable. Otherwise, 'chromatic' aberration will occur. The focal length of the lens can be changed by varying the current through the coil. The objective lens ensures that the beam will have its smallest diameter when it hits the specimen.
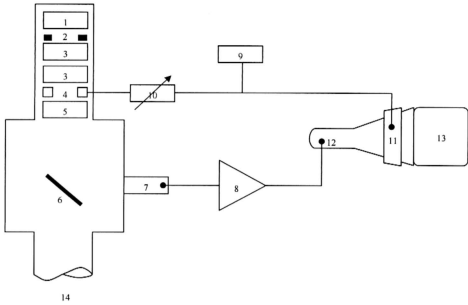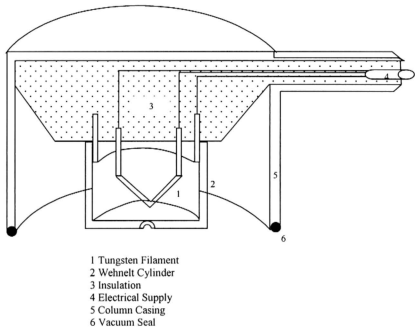
Electron Optical Column

1. Electron Gun
2. Anode disc
3. Condenser lens
4. Scan coils
5. Objective lens
6. Specimen
7. Detector

Display/electronics

8. Signal amplifier
9. Waveform generator
10. Magnification coil
11. Scan coils
12. CRT brightness control
13. CRT dsplay screen
14. Vacuum cconnection

Fig[2.3]: Layout of scanning electron microscope

When the beam hits the specimen surface, electrons are emitted from the surface of the sample. The electrons are collected by a detector which converts them into a small electrical signal. This signal contains a lot of information about a single point on the sample surface. The process of forming an image of the sample surface requires a large number of points to be scanned over an area.

1 Tungsten Filament
2 Wehnelt Cylinder
3 Insulation
4 Electrical Supply
5 Column Casing
6 Vacuum Seal

Fig[2.4]: Cross section of electron gun in SEM

The electron beam traverses the sample surface point by point along the line and back-scattered electrons (BSE) signal is collected. After completing a line of 1000 points the beam is moved quickly back to the start of the line where it is shifted one line down before repeating the scan of another 1000 points. One complete scan consisting of one thousand lines, each of one thousand points is called a 'frame' [55].
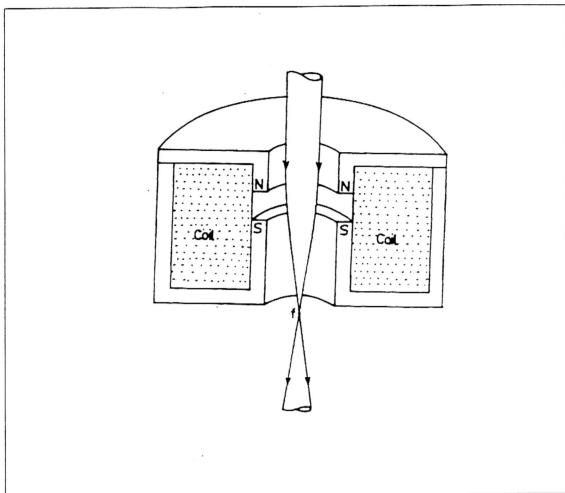
Fig[2.5]: Partially enclosed coil of wire in a cylindrical iron case.

2.5 Energy Dispersive Analysis of X-Rays (EDAX)

EDAX was performed with a Philips 9800 equipment to analyse the chemical composition of the sample surface. X-ray microanalysis can be considered as a quantitative and non-destructive technique that allows insitu detection of elements as low as 10^{-19}g. Its limitations are that it cannot distinguish between ionic, non-ionic and isotopic species and EDAX in particular cannot detect the low atomic number elements. EDAX fitted with beryllium window detectors cab detect elements with $Z>11$ while EDAX with windowless detection can detect elements with $Z>5$. EDAX is a surface analytical technique and because of the vacuum requirements of the SEM, it is not suitable for

hydrated samples. To explain X-ray production, consider figure [2.6].
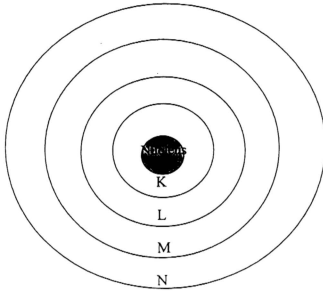
Fig[2.6]: energy shells for orbiting electrons.

The orbiting electrons are arranged in distinct energy bands or shells. In X-ray work, these shells are designed as K,L,M,N etc. The electrons in the innermost K shell will need the most energy compared to the electrons in the L,M,N etc. Shells to be removed from the atoms.

If an incident electron from the electron gun knocks one of the K shell electrons a vacancy is created in the K shell of the silver atom. Since the vacancy is created at a higher energy, an electron from an outer shell L, M, N, etc. can fill in this vacancy, restoring the atom of the 'ground' or non-excited state. An amount of energy equal to the difference in energy between the shells involved in the transition is released as a photon of electromagnetic radiation. If the ejected electron was from an inner shell (K,L,M) then the energy is such that the photon is an X-ray.

Although shells have distinct energies, within these shells the energy of the electron differs with the atomic number. This is because the positive charge on the nucleus is also dependent on the atomic number. Even between elements of adjacent atomic number this variation in energy is significant. Hence whenever an electron transition occurs the energy released is characteristic for each atomic number and therefore characteristic to each element.

X-rays are also produced when incident beam electrons are slowed down or stopped as they pass through the electrostatic field, close to the atomic nuclei and inner electron shells. In doing so they give up some or all of their energy to produce X-rays. These X-rays are called the X-ray continuum or bremsstahlung ('braking radiation'). As far as micro analysis is concerned, the continuum is undesirable since it represents a background signal on which the useful characteristic X-rays are superimposed. Some possible electron transition producing these characteristic X-rays are shown in figure [2.7].
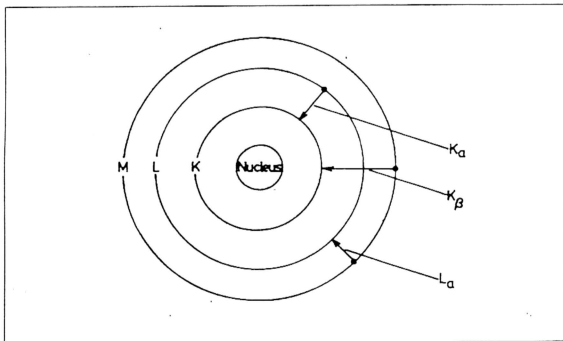
Fig[2.7]: Possible electron transition and x-rays produced.

A K_α X-ray is produced when a K shell vacancy is filled by an L shell electron. A K_β X-ray is produced when a K shell vacancy is filled by an M shell electron. An L_α X-ray is produced when an L shell vacancy is filled by an M shell electron. These characteristic X-rays strike the detector of the EDAX system which produces a current pulse. The current pulse is them preamplified at liquid nitrogen temperatures so that the signal to noise ratio will be improved. The signal is then passed through the main amplifier and electronic processors and finally into a multichannel analyser which separates the pulses according to their amplitude, counts them and store the results. The results are then displayed in a variety of ways.

The techniques for quantifying results is called ZAF. ZAF is an acronym from three separate effects, atomic number (Z), absorption (A) and fluorescence (F) which the method compensates for. An incident electron may undergo elastic scattering in which case it may reemerge before it has excited any x-rays. X-rays may also not be generated because the electrons lose energy so rapidly that it could not eject an inner core electron. These effects depend on the atomic number of the elements in the sample and if left uncorrected could cause errors greater than 10%.

Absorption corrections must take into account many factors e.g., the incident electron accelerating voltage, take off angle, mean atomic number and mean atomic mass of the specimen. In very thin samples absorption effect is almost negligible.

X-rays produced within the specimen may interact with some of the inner shell orbital electrons, producing further secondary x-rays. The effect causes

abnormally high counts in the lower energies. Fluorescence can cause errors as large as 15% when analysing elements of adjacent atomic numbers.

For consistency of the results in the present study, not less than five difference locations were analysed, accumulating more than 3000 counts per element. The sample for observation was mounted on a stub using conductive carbon cement which provided the necessary electrical connections between the sample and holder. The sample was also carbon coated to prevent surface charging which may cause defects [56].

2.6 Impedance spectroscopy

Theory of AC measurements.

AC method represents the most popular approach to the determination of the electrical properties of polymer electrolytes. This is because, simple cells using inert blocking electrodes are used to determine bulk electrolyte properties, even though the theory to interpret the measurements are more complex.

Impedance spectroscopy refers to the measurement of real and imaginary part of the impedance over a wide range of frequencies. This helps in separating out the true bulk conductivity from the conduction due to grain boundaries and electrode-electrolyte interfacial impedance [57] and hence is more accurate than impedance measurements made at one particular frequency.

In impedance spectroscopy, a sinusoidal signal of low voltage amplitude is applied across the cell. The output signal which is also a sinusoidal wave is compared with the input signal to determine impedance modulus and phase shift. It is because the impedance frequency is dependent, that we can extract

information about the different electrical properties of the cell. The result is presented in the form of a complex impedance plot [58]. The result of an ac experiment can also be presented in any one of three additional complex formalism; admittance Y, permittivity ε or electric modulus M.

$$Y = 1/Z = J\omega C_o \varepsilon \tag{2}$$

$$M = 1/\varepsilon = j\omega C_o Z \tag{3}$$

The response of any cell to an ac signal can be represented by an equivalent electrical circuit consisting of resistors and capacitors, which individually represent charge migration and polarization occuring within the cell [23].

Let us look at some of the theoritical models that can be used to interpret the data.
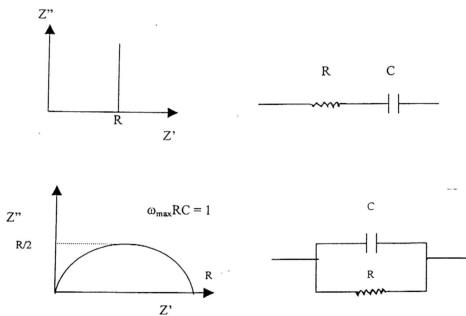
Fig[2.8]: Complex impedance plots in an RC circuit in a)series and b)parallel

- A resistor and capacitor in series.

- The plot defines a vertical spike displaced to distance R along the real axis. As frequency is increased, the impedance of the capacitor is reduced.

- A resistor and capacitor in parallel.

If we consider a parallel combination, total admittance is given by

$$Y_{tot} = 1/R + j\omega C \qquad (4)$$

$$Z_{tot} = R[1/\{1+(\omega CR)^2\}] - jR[\omega RC/1+(\omega RC)^2] \qquad (5)$$

This defines a semicircle with diameter R extending along the real axis from the origin. The maximum of the semicircle obey the relationship below:

$$\omega_{max}RC = 1 \qquad (6)$$

In a.c. work, the resistance R is replaced by the impedance Z, which is the sum of the resistance and the reactance. The reactance has 2 components, a capacitative term and an inductive term and in this type of work the latter is normally neglected and will therefore be omitted from this treatment. The capacitative term is $-j/\omega C$ where $j = (-1)^{1/2}$, ω is the angular frequency and C is the capacitance. Thus,

$$Z = R - j/\omega C = R + 1/j\omega C = Z' - Z'' \qquad (7)$$

Z is the complex quantity [59].

The importance of Z transform to polymer electrolytes is that frequency dependent measurements are made of the real and imaginary parts (denoted by Z' and Z") and the results are normally displayed on a complex plane port. The real part is plotted on the horizontal axis and the imaginary part is plotted as the vertical axis. The diagram is upside down compared with Argand diagrams used by electrical engineers, because for them indictive terms are in the upper and capacitative terms are in the lower right hand quadrants. Inverting the diagram enables the dominant capacitative terms to be shown on a graph of more conventional appearance). The full curve would be shown as in figure [2.9], but only a part of the curve falls within the 'frequency window' of the measuring equipment, typically $10-10^5$ Hz for blocking electrode measurements. The top of the semicircular portion of the impedance plot is at $\omega CR=1$, so that as the electrolyte is studied at higher temperatures at which R is lower and consequently ω is higher, the window moves towards the direction of the spike and the semicircle may not be shown [60]. However in this current work, temperature variation of AC measurements were not carried out.
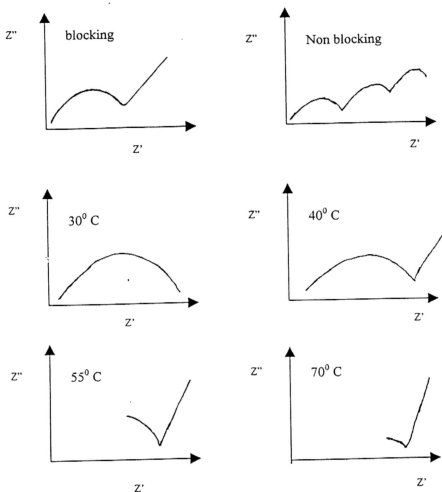
Fig[2.9]: Windows in impedance plots

Electrical measurement was done using a HIOKI 3250-01 LCR Hi Tester which is interfaced to a microcomputer. The frequency range was from 100 Hz to 100 Khz. The electrode area was 1.0 cm^2. Very thin polymer films were sandwiched between 2 stainless steel electrodes. The experimental setup is as shown above in figure [2.10].
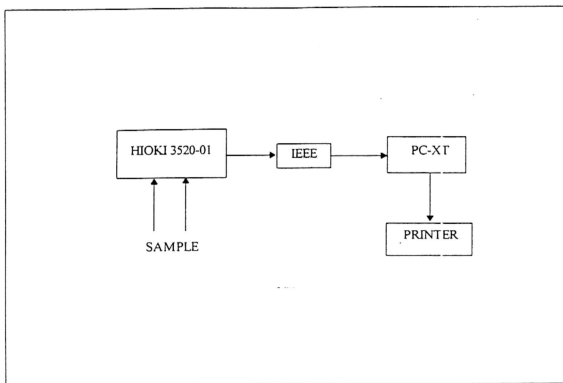
Fig[2.10]: Experimental setup for impedance measurement [61].

A new type of circuit element, the constant phase angle element, cpe, is needed to account for semi-circle flattening and spike tilting. It may be thought of as conceptually as a leaky capacitor, the physical origin of which for polymer electrolytes is perhaps related to the presence of crystalline non-conducting regions interwoven with conducting amorphous material within the spherulites. Its impedance, Z_{cpe}, is given by

$$Z_{cpe} = k(j\omega)^{-p} \text{ where } 0 \le p \le 1 \qquad (8)$$

When $p = 0$, Z is frequency independent and k is just the resistance R whereas when $p=1$, $z=k/j\omega=-j/\omega(k^{-1})$, the constant k^{-1} now corresponding to the capacitance C. When p is in between 0 and 1, the cpe acts in a way intermediate between a resistor and a capacitor. To incorporate Z_{cpe} into an expression that can

be used to model equivalent circuits so that the experimental complex plane plots can be interpretted, equation (8) can be recast using de Moivre's theorem, i.e.

$$Z_{cpe} = k \left[\cos(p\pi/2) - j \sin(p\pi/2)\right]/\omega^p \qquad (9)$$

The cos term contributes to Z' and the sin term to Z". The use of series cpe terms tilts the spike and parallel cpe terms depress the semi-circle, as shown in figure [2.11]. The value obtained at the intersection of the flattened semicircle and the tilted spike is the bulk resistance, R_b, of the electrolyte. This is related to the conductivity by

$$Gl/A = l/R_bA \qquad (10)$$

Where G is conductance, l is thickness and A is the cross-sectional area. The thickness varies with temperature, however, and this is not always taken into account. Experiments are done in triplicate to ensure accuracy of the results and the small changes in conductivity are not within experimental errors.
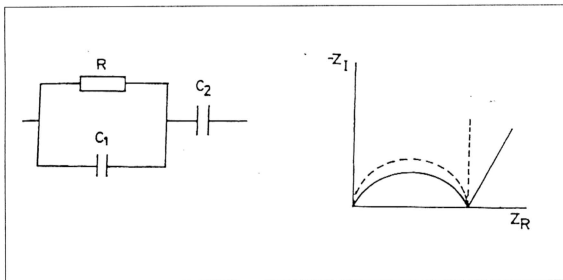

Fig [2.11]: Depression of semi-circle and tilting of spike caused by replacing capacitors by constant phase elements. [62]