CHAPTER 2
EXPERIMENTAL TECHNIQUES

This chapter describes the preparation of various proton conducting polymer electrolyte membranes studied in this thesis and experimental techniques used for their characterization, and fabrication and characterization of proton batteries.

2.1 Preparation of Polymer Electrolyte Membranes

The solution casting technique has been used to prepare the polymer electrolyte systems in the form of films. In this technique, the starting materials, a polymer host and the ion donating salt(s), are dissolved in appropriately chosen solvent separately. Then they are mixed together to prepare a homogeneous solution. The homogeneous solution is poured in petri dishes to form films as a result of evaporation of the solvent. This technique is well known and widely used by polymer electrolyte community to prepare electrolyte films. The steps involved in the preparation are shown by a flow chart in figure 2.1.

Figure 2.1: Schematic representation of different steps, in general, involve in the solution casting technique.
The following polymer electrolyte systems have been prepared in our case:

1. **Polyethylene oxide (PEO) based SPEs**
   - (a) PEO-NH$_4$PF$_6$ complex
   - (b) PEO-NH$_4$PF$_6$ complex plasticized with ethylene carbonate (EC) and ethylene carbonate (EC): propylene carbonate (PC) (1:1 volume ratio)
   - (c) PEO-NH$_4$PF$_6$ complex plasticized with polysorbate 80 (tween 80)

2. **Blend gel polymer electrolyte system**: 35 wt% \([(100-x) \text{ PMMA} + (x) \text{ PVdF-HFP}] + 65 \text{ wt% } [1\text{M NH}_4\text{SCN in EC:PC (1:1 v/v)}\text{], where } x = 0, 25, 50, 75, 85, 90, 95, 100.\]

3. **Nanocomposite blend gel polymer electrolyte system**: \[35 \{(25 \text{ PMMA} + 75 \text{ PVdF-HFP}) + x \text{ SiO}_2\} + 65 \{1\text{M NH}_4\text{SCN in EC+PC}\text{], where } x = 0, 1, 2, 4, 6, 8, 10 \text{ and 12.\]

4. **Blend gel polymer electrolyte system**: \[\text{[PVdF-HFP]/ PVP} + x\text{BMImHSO}_4, \text{ where } x= 50, 60, \text{ and 70.}\]

The preparation conditions of the above systems are given in table 2.1.

**Table 2.1: Preparation conditions for various polymer electrolyte systems.**

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Polymer electrolyte system</th>
<th>Solvent</th>
<th>Stirring Temp./Time</th>
<th>Drying Temp./Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Solvent-free PEO - NH$_4$PF$_6$</td>
<td>Acetonitrile</td>
<td>RT/20 hours</td>
<td>RT/ 72 hours</td>
</tr>
<tr>
<td>2</td>
<td>PEO - NH$_4$PF$_6$ - EC/EC:PC</td>
<td>Acetonitrile</td>
<td>RT/14 hours</td>
<td>RT/72 hours</td>
</tr>
<tr>
<td>3</td>
<td>PEO - NH$_4$PF$_6$ - Polysorbate 80</td>
<td>Acetonitrile</td>
<td>RT/14 hours</td>
<td>RT/72 hours</td>
</tr>
<tr>
<td>4</td>
<td>[x \text{ PMMA} + (100-x) \text{ PVdF-HFP}] + liquid electrolyte [1\text{M NH}_4\text{SCN in EC:PC}\text{]</td>
<td>THF + Acetone</td>
<td>RT/10 hours</td>
<td>RT for first 48 hours, then at 50 °C for 5 hours</td>
</tr>
<tr>
<td>5</td>
<td>[(25\text{PMMA} + 75\text{PVdF-HFP}) + x \text{ SiO}_2] + liquid electrolyte [1\text{M NH}_4\text{SCN in EC:PC}\text{]</td>
<td>THF + Acetone</td>
<td>RT/12 hours</td>
<td>RT for first 48 hours, then at 50 °C for 5 hours</td>
</tr>
<tr>
<td>6</td>
<td>[100-x) \text{[90 PVdF-HFP} +10 \text{PVP}] + x \text{BMImHSO}_4\text{]</td>
<td>DMF</td>
<td>60°C/12 hours</td>
<td>70°C/48 hours</td>
</tr>
</tbody>
</table>
2.2 Characterization Membranes

2.2.1 Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR spectroscopy is based on the fact that vibrational modes of different chemical functional groups absorb infrared light at different wavelengths. Thus an infrared spectrum represents a fingerprint of a sample with absorption bands corresponding to the frequencies of vibrational motion of the atoms in the functional group. By interpreting the infrared absorption spectrum, the chemical bonds in a molecule can be determined.

A fourier transform of IR provides simultaneous and almost instantaneous recording of the entire IR spectrum then converts the scanning results into a wavelength (or equivalently wavenumber) versus absorbance/transmitted spectra [345]. The relative simplicity of the FTIR technique makes it a widely used technique for the analysis of a wide range of materials. Figure 2.2 shows schematic diagram of FTIR spectrophotometer.

![Schematic diagram of FTIR technique.](image)

The basis of all quantitative analysis in FTIR spectroscopy is Beer’s law, which relates absorbance (A) to the concentration of the sample according to the following relation:

\[ A = \upsilon \psi C_S \]  

\( \psi \) is absorptivity, \( \psi \) is the path length and \( C_S \) is the concentration of the sample with respect to a reference.
The transmittance ($T$) is defined as:

$$T = \frac{I}{I_o} \quad \ldots (2.2)$$

where $I$ and $I_o$ are the intensity of the beams with and without sample respectively.

IR instruments can be operated in either the transmittance or reflectance mode. In the past, Absorption/Transmittance was often limited by the thickness of the samples, sample shape, and the sample’s quantity. These limitations have been largely overcome by the use of adapter that changes the presentation of the samples to the IR beam. Attenuated Total Reflectance (ATR) and Diffuse Reflectance accessories allow the analysis of the surface of the coatings and allow comparison of the bulk properties with the surface properties of a material. The ATR measures the changes that occur when a totally internally reflected IR beam comes into contact with the sample. Figure 2.3 shows the schematic diagram of ATR arrangement in FTIR spectrophotometer.

![Figure 2.3: shows the schematic diagram of ATR arrangement in FTIR spectrometer.](image)

In the ATR mode, there must be good contact between the sample and the ATR crystal surface. The properly placed sample and crystal are then placed in the IR beam in such a position that the IR beam enters the crystal at an angle and go through multiple reflections along with the length of the sample. The IR energy leaving from the other end of the crystal is measured versus the respective wavenumber.
In the present work, the FTIR spectra of the polymer electrolyte membranes were recorded to investigate ion-polymer interaction, plasticizer’s effect, polymer-polymer interaction and the dispersion of the filler particles in the polymer electrolytes. The FTIR spectra were recorded by Perkin-Elmer FTIR spectrophotometer (Model: Spectrum BX) in the wavenumber range 4000 – 650 cm\(^{-1}\) in ATR mode at room temperature.

### 2.2.2 X-Ray Diffraction (XRD)

X-ray powder diffraction (XRD) is a powerful technique for determining the crystal structure and the orientation of the crystals. Various informations like phase identification and quantification, crystallinity, crystallite size, lattice constants, molecular orientations and structure etc. can be obtained from x-ray scattering technique.

The three-dimensional structure of non-amorphous materials is defined by regular, repeating planes of atoms that form a crystal lattice. When a focused X-ray beam interacts with these planes of atoms, part of the beam is transmitted, part is absorbed by the sample, part is refracted and scattered, and part is diffracted. W. H. Bragg and W. L. Bragg developed a simple way of understanding and predicting diffraction phenomena from a crystal using optical analogy to crystallographic planes as shown in figure 2.4. A set of crystallographic lattice planes with distances \(d_{hkl}\) is irradiated by plane wave x-rays incident on the lattice planes at an angle \(\theta\). The inter-planar spacing, \(d_{hkl}\), sets the difference in path length for the ray scattered from the top plane and the ray scattered from the bottom plane. Figure 2.4 shows that this difference in path lengths is \(2d \sin \theta\). Constructive interference for the reflected wave, however, can only be achieved when the difference in path length for the top and bottom rays is an integral multiple of wavelength \(\lambda\). This is described by Bragg’s equation:

\[
2d \sin \theta = n\lambda \quad \text{...(2.3)}
\]

where integer \(n\) is the order of the diffracted beam. The condition for maximum intensity is contained in Bragg’s law which allows calculating details about the crystal structure. Figure 2.5 shows the schematic diagram of basic arrangement of X-ray diffractometer.
In the present work, XRD studies on the polymer electrolyte membranes have been carried out using XRD-6000 SHIMADZU, Japan. The diffraction data were recorded at room temperature using CuKα irradiation with varying Bragg angles (2θ).
2.2.3 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is widely used technique to investigate the structure, morphology and crystallite size. In this technique, an electron beam is produced by heating the tungsten filament and then focused across the surface of a sample through magnetic field in high vacuum. The zone, in which such interaction occurs and different signals are produced, is called "interaction volume" or "electron – diffusion cloud". Depending on the energy of the incident electrons and properties of the sample material, various phenomena, like reflection of high-energy electrons by elastic scattering, emission of secondary electrons (SE) by inelastic scattering and the emission of electromagnetic radiation and several other radiations, take place during the interaction of electron beam with sample, as shown in figure 2.6.

![Figure 2.6: Schematic diagram showing different scattering processes when the beam of high energy electrons interacts with the sample](image)

The electron beam, which typically has an energy ranging from 0.5 keV to 40 keV, is incident on the solid surface of the sample and gives signals as shown in the figure 2.6. Out of the various signals shown, backscattered electrons, secondary electrons and transmitted electrons provide information about the microstructure of the sample. Auger electrons, ejected electrons and X-ray...
beam energies, are specific to the element from which they are coming. These signals provide information about the chemical identification and composition of the sample. Figure 2.7 shows the schematic diagram of a scanning electron microscope.

Figure 2.7: Schematic diagram of a scanning electron microscope

Backscattered electrons and secondary electrons are predominantly important for SEM application. For backscattered electrons, the contrast in the produced image is determined by the atomic number of the elements in the sample and the image shows the distribution of different chemical phases in the sample. The emission of these electrons occurs from the depth of the sample and because of that, the resolution in the image is not as good as for secondary electrons. The low–energy secondary electron technique is the most common method. The primary electron beam with energy of 0.5–40 keV enters to the surface of specimen and generates many low–energy secondary electrons. The intensity of these secondary electrons is governed by the surface
topography of the sample. The image of the sample is constructed by measuring secondary electron intensity as a function of the position of the scanning primary electron beam.

In the present work, the morphology of the prepared polymer electrolyte membranes has been observed by SEM (Model: LEO 435 VP). In order to prepare conducting surface, each sample was coated with gold through sputtering before taking the images.

2.2.4 Differential Scanning Calorimetry (DSC) Studies

In order to study thermal stability, thermal transitions and phase changes in a material, DSC is a valuable technique. It is a thermo-analytical technique in which the difference in heat flow (power) to a sample and a reference (usually alumina) is monitored with time or temperature in a specified atmosphere. Both the sample and reference are maintained at the same temperature throughout the experiment. The sample and reference are placed in identical environments, metal pans on individual bases, where each base contains a thermocouple (or platinum resistance thermometer) and a heater. Schematic drawing of DSC measurement technique is shown in figure 2.8.

In this experiment, energy is introduced simultaneously into both sample cell and a reference cell which is, generally, an empty pan. The amount of energy, which has to be supplied (endothermic
process) or withdrawn from the sample (exothermic process) to maintain zero temperature differential between the sample and the reference, is the experimental parameter displayed as the ordinate of the analysis curve.

In general, the temperature program for a DSC analysis is designed to ensure that temperature of the sample holder increases linearly as a function of time. This technique is highly efficient to study the properties like, temperatures of phase transitions, enthalpies of phase transitions, phase diagrams, polymer phase changes, glass transition temperatures ($T_g$), melting temperature ($T_m$), crystallization temperature ($T_c$) etc [346, 347]. (Figure 2.9)

![Figure 2.9: Schematic drawing illustrating glass transition temperature ($T_g$), crystallization temperature ($T_c$) and crystalline melting point ($T_m$).](image)

In the present thesis, the DSC studies of the prepared polymer electrolyte systems were carried out with DSC of Mettler Toledo (Model: DSC 822) and of TA Instrument (Model: Q100) at a heating rate of 10 °C/min⁻¹.

2.2.5 Electrical Measurements and Ion Transport Studies

2.2.5.1 A.C. Impedance Spectroscopy and Ionic Conductivity

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The ionic conductivity of polymer electrolyte is an important parameter which is inversely proportional to the resistivity of the material. The ionic conductivity can be expressed as:

$$\sigma = \frac{1}{d} \frac{d}{R A}$$

...(2.4)

where, R is the resistance, d is the thickness of the sample and A is the area of the electrodes.

A.C. impedance technique is the most popular approach for determining the electrical properties of ion conducting solids. The data obtained from this technique carry not only the information about the long-range migration of ions but also provides information about polarization phenomena occurring within the cell comprising electrolyte sandwiched between electrodes. In this technique, response of the cell to a sinusoidal signal is analyzed and the data is obtained in the form of impedance as a function of frequency of the applied signal. This technique is broadly referred as “Electrochemical Impedance spectroscopy (EIS)”.

EIS technique enables us to evaluate and separate the contribution of different mechanisms and domains contributing to the overall resistance, like, electrode reaction at the electrode/electrolyte interface and migration of ions through the bulk and the grain boundaries within the electrolytes [348-352].

In EIS technique, as mentioned above, a low amplitude a.c. signal (sinusoidal) is applied to cell (electrode/electrolyte/electrode) and obtained output is compared with the input signal to determine impedance modulus $|Z|$ and phase shift ($\theta$). Randles [351] demonstrated that various electrical processes occurring within the cell could be represented as an equivalent circuit comprising resistors, capacitors, inductors and their combinations in parallel and in series.

Figure 2.10: Equivalent circuit model for impedance measurement of a solid state electrochemical cell.
Figure 2.11: Impedance plots for various R-C circuits [352].
Practically, the equivalent circuit consists of resistors and capacitors referring the charge migration and polarization occurring in the cell. One charge polarization or migration process can be represented as parallel combination of resistance (R) and capacitance (C). Hence, an equivalent circuit for a cell comprising a solid electrolyte sandwiched between two electrodes can be signified as three parallel RC circuits connected in series, which represent the contribution of bulk properties of the solid electrolyte material, grain boundary and electrode/electrolyte interface in the overall conduction process at different frequency regions [348, 352] (figure 2.10).

Figure 2.11 shows some typical complex impedance (Z’- Z”’) plots for elementary circuits containing elements like R, C and RC (series & parallel) combinations [352].

The behavior of the cell and hence its equivalent circuit depends on the type of electrode, reversible or non reversible and the type of electrolyte i.e. whether having single mobile species as in conventional solid electrolyte or two mobile species (cation and anion both) as in liquid and polymer electrolytes. This can be described as follows:

1. **Irreversible electrodes (or blocking electrodes)**

Figure 2.12 shows schematic impedance response of a single ion conducting electrolyte within the irreversible electrodes.

![Figure 2.12: Typical impedance plot for the cell carrying electrolyte sandwiched between irreversible electrodes. The corresponding equivalent circuit is shown in the inset.](image-url)
The semicircle observed in the high frequency range reflects the bulk polarization and ion migration in the electrolyte and it corresponds to the parallel combination of bulk resistance \( R_b \) and the geometrical capacitance \( C_g \). The spike parallel to the imaginary axis \( (Z'') \) at the low frequency range is attributed to the double layer capacitance \( C_e \), which builds up due to the charge accumulation at electrode/electrolyte interface. Hence, the high frequency response in the impedance data gives the characteristic properties of electrolyte, whereas the low frequency carries information about the electrode/electrolyte interface. This shows that the impedance data may be utilized to obtain the magnitude of all the fundamental electrical properties of the cell.

2. **Reversible electrodes (or non-blocking electrodes)**

The reversible electrodes imply the presence of finite non-blocking reversible electrode reaction which allows the dissolution of mobile species in the electrode itself. Figure 2.13 shows the schematic representation of the impedance plots of the cell consisting of (a) single ion conducting electrolyte, and (b) both the cation and anion conducting electrolyte. The corresponding equivalent circuits are shown in the insets.

Similar to the behavior of the cell with blocking electrodes, semicircle is observed for single ion conducting electrolyte, as shown in the figure, the high frequency semicircle is observed due to the parallel combination of \( R_b \) and \( C_g \). This is further followed by another semicircle in the middle frequency region which is attributed to the contribution of electrode/electrolyte interface. This may be represented as a parallel combination of a finite charge-transfer resistance \( R_{ct} \) and charging discharging double layer capacitance \( C_e \). In the case when both cation and anion are mobile in the electrolyte, a third semicircle comes into existence which corresponds to the diffusion impedance \( (Z_d) \) due to the concentration gradient of anions introduced at sufficiently low frequency region (Figure 2.13). However, all these three features may not be necessarily observed in all the cases practically [352].

Practically in the polymer electrolytes, the impedance data obtained from the experiments deviate from the ideal equivalent circuit model and a significant flattening in the semicircular pattern and tilting of spike is observed. This may be due to the presence of crystalline non-conducting regions interwoven with the conducting amorphous materials within the structure of a polymer electrolyte system and the cell behaves like a “leaky capacitor”. This effect may also be
attributed to the physical phenomena like, multiple or coupled reaction sequences, roughening of electrode, and frequency dependent ohmic resistances due to non-uniform charging of the double layer.

Figure 2.13: Typical impedance plots for the cells comprising reversible (or non-blocking) electrodes with (a) single ion conducting electrolyte, and (b) both the cation and anion conducting electrolyte (e.g. liquid/polymer electrolyte). The corresponding equivalent circuits are shown in the insets [351].
Reference to these effects, a generalized impedance element, known as “constant phase element (cpe)” is introduced into the equivalent circuit model. The impedance of this constant phase element may be given as:

$$Z_{cpe} = k (j\omega)^{-p}, \quad 0 \leq p \leq 1$$  \hspace{1cm} (2.5)

In the present thesis the electrical conductivity measurements of the prepared polymer electrolyte membranes were carried out by ac impedance spectroscopy technique using a HIOKI 3522-50 LCR HiTESTER in the frequency range 50 Hz - 100 kHz with a signal level of 10 mV. For conductivity measurements, free standing polymer electrolyte membranes were placed between two stainless-steel (SS) blocking electrodes of 1 cm$^2$ area. The electrode-electrolyte arrangement is shown in figure 2.14.

**Figure 2.14:** Schematic diagram of cell configuration (SS/sample/SS) for electrical measurements.

We have also used the EIS technique to confirm the protonic conduction in the prepared polymer electrolyte membranes. The impedance measurements have been carried out on the symmetrical cell; Zn+ZnSO$_4$.7H$_2$O |gel electrolyte| Zn+ZnSO$_4$.7H$_2$O, whereas the pellets of Zn+ZnSO$_4$.7H$_2$O act as the reversible electrodes (the proton source).

In order to have insight of ion conduction process in the PEO based solid polymer electrolytes following frequency dependent parameters have also been obtained using the impedance modulus $|Z|$ and phase shift ($\theta$), obtained from the EIS technique:

1. **Complex permittivity (dielectric constant):** The complex dielectric behavior of a polymer electrolyte system can be expressed as:
\[ \varepsilon^* = \varepsilon' - j \varepsilon'' \] 

...(2.6)

where \( \varepsilon' \) and \( \varepsilon'' \) are real and imaginary parts of complex permittivity. These parameters can be obtained from impedance modulus \(|Z|\) and phase shift (\(\theta\)) using following relations:

\[ \varepsilon' = \frac{(-Z'')}{\omega C_o (Z'^2 + Z''^2)} \] 

...(2.7)

\[ \varepsilon'' = \frac{(Z')}{\omega C_o (Z'^2 + Z''^2)} \] 

...(2.8)

where \( Z' \) and \( Z'' \) are real (= \( Z \cos \theta \)) and imaginary (= \( Z \sin \theta \)) part of impedance, \( \omega \) is the angular frequency (\( \omega = 2\pi f; f = \) applied ac frequency in Hz) and \( C_o \) is the geometrical capacitance.

2. **Loss tangent** (tan \( \delta \)):

Loss tangent (tan \( \delta \)) has been obtained using the equation:

\[ \tan \delta = \frac{\varepsilon''}{\varepsilon'} = -\frac{Z'}{Z''} \] 

...(2.9)

3. **A.C. conductivity** (\( \sigma_{ac} \)):

The frequency dependent ac conductivity (\( \sigma_{ac} \)) of the electrolyte systems has been determined from the following relation:

\[ \sigma_{ac} = \varepsilon' \varepsilon_o \omega \tan \delta \] 

...(2.10)

where \( \varepsilon_o \) is the vacuum permittivity having value of 8.8514 x 10\(^{-14}\) Farad cm\(^{-1}\).

### 2.2.5.2 Ion Transference Number (\( t_{ion} \)) Measurement

The total ionic transport number (\( t_{ion} \)), which measures the contribution of ions to the total charge transport through the polymer electrolytes, was measured by dc polarization method [353]. In this method, a dc potential of \(~1\text{V}\) was applied across the cell, SS/polymer electrolyte/SS, and the current was recorded as function of time till the complete polarization of the samples. The experimental circuit of dc polarization method is shown in figure 2.15. The complete polarization was decided by the constant current observed for a comparatively longer time. A typical current vs. time plot is shown in figure 2.16.
The total ionic transport number was calculated by the equation:

\[ t_{\text{ion}} = \frac{(I_T - I_e)}{I_T} \]  \hspace{1cm} \text{(2.11)}

where, \( t_{\text{ion}} \) is the total ionic transference number, \( I_T \) is total (ionic + electronic) current and \( I_e \) is residual electronic current.

**Figure 2.15:** Experimental setup for dc polarization technique.

**Figure 2.16:** Typical current vs time plot obtained from dc polarization technique.
2.2.6 Cyclic Voltammetry

Cyclic voltammetry is a popular technique for acquiring information about the electrochemical reactions in a cell. It also provides the working potential range or electrochemical potential window (ESW) of polymer electrolyte systems. This technique has the ability to provide information on the thermodynamics of redox processes and the kinetics of heterogeneous electron transfer reactions [354, 355]. The cyclic voltammetric process consists of scanning the potential linearly of a stationary working electrode, using a triangular potential waveform (figure 2.17). In this case, the voltage is swept between two values ($V_1$ and $V_2$) at a fixed rate, and when the voltage reaches $V_2$, the scan is reversed and swept back to $V_1$. Depending on the information required, the experiment can be performed for a number of cycles. During the potential sweep, the potentiostat measures the current from the applied voltage. The resulting current-potential (I-V) plot is referred to as cyclic voltammogram.

![Figure 2.17: Potential-time excitation signal in a cyclic voltammetric experiment](image)

When the potential of the working electrode is more positive than that of a redox couple present in the electrolyte, the corresponding species may be oxidized, i.e., electrons go from the electrolyte to the electrode and produce an anodic current. Similarly, on the return scan, as the working electrode potential becomes more negative than the reduction potential of a redox couple, reduction (i.e., electrons flowing away from the electrode) may result in a cathodic current. It is known that the anodic currents are positive and cathodic currents negative.
Figure 2.18: The expected response of a reversible redox couple during a single potential cycle

Figure 2.18 illustrates the expected response of typical reversible redox couple during a single potential cycle. The scan shown in the figure starts at a slightly negative potential, point A, up to some positive switching value, point D, at which the scan is reversed back to the starting potential. The current is first observed to peak at $E_{pa}$ with value $i_{pa}$ indicating that an oxidation is taking place and then drops due to depletion of the reducing species from the diffusion layer. During the return scan the processes are reversed (reduction is now occurring) and a peak current is observed at $E_{pc}$ with corresponding $i_{pc}$ value.

In the present thesis, cyclic voltammetry studies have been carried out on a cell comprising polymer electrolyte membranes sandwiched between two stainless-steel (SS) blocking electrodes of 1 cm² area, using electrochemical analyzer (CHI 608C, CH Instrument, USA).

2.3 Fabrication of All-Solid-State Proton Batteries and Measurement of its parameter

Proton batteries have been fabricated using the optimized compositions of the electrolyte systems described in chapter 3-6, in the following cell configuration:

$$\text{Zn} + \text{ZnSO}_4.7\text{H}_2\text{O} \mid \text{polymer electrolyte (PE) membrane} \mid \text{PbO}_2 + \text{V}_2\text{O}_5 + \text{C} + \text{PE}$$
The details of the preparation of anode and cathode pellets are described in chapter 7. The cell performance characteristics for the proton cells have been evaluated through following studies:

(a) Open circuit voltage (OCV) measurement as a function of time.
(b) Discharge characteristics at varying load conditions.
(c) Charge-discharge characteristics

The open circuit voltage (OCV) and the discharge characteristic measurements have been carried out using Keithley 2000 multimeter. From the discharge characteristics, various cell performance parameters have also been evaluated. These are given as below:

(i) **Internal resistance** ($R_{in}$): $R_{in}$ is evaluated using the formula:

$$R_{in} = \left(\frac{OCV - V}{V}\right)R_L$$

...(2.12)

where, $V$ is the instantaneous voltage reading and $R_L$ is the externally applied load resistance. The internal resistance is expressed in ohm ($\Omega$).

(ii) **Power density**: The power density of the battery is defined as the capacity of a battery to deliver power per unit weight of the battery. It can be obtained by using the formula:

$$\text{Power density} = \frac{V^2}{R_{in}W}$$

...(2.13)

Where $W$ is the total weight of the battery in kilograms (kg) and $R_{in}$ is the internal resistance in ohm ($\Omega$). The power density is expressed as $W\text{kg}^{-1}$.

(iii) **Energy density**: It is defined as the product of power density and the discharge time (in plateau region) and can be expressed as;

$$\int_0^t VI_d dt$$

$$\text{Energy density} = \frac{\int_0^t VI_d dt}{W}$$

...(2.14)

Where, $I_d$ is the discharge time. The energy density is expressed in terms of Wh kg$^{-1}$.

In order to carry out the charge-discharge studies of the fabricated proton batteries, battery tester of Arbin Instrument (BT2000), USA, has been used. The charge-discharge experiment was
performed by measuring voltage as a function of time at constant currents (10 µA and 50 µA). The charge-discharge characteristics of the cells have also been used to evaluate the discharge capacity.