Chapter 2

Materials Synthesis and Characterization Techniques
2. Materials Synthesis and Characterization Techniques

Variety of preparatory routes have been adopted to synthesis the solid state ionic materials. The characterization of the materials and ion transport properties are done using different experimental techniques. Ideally, these materials should exhibit very high ionic conductivity comparable to that of the aqueous/liquid electrolytes. As already mentioned in Chapter 1, a large number of solid state ionic materials, in variety of phases and involve different kinds of mobile ion species, discovered so far exhibit room temperature conductivity in the range of \( \sim 10^{-1} \) - \( 10^{-4} \) S/cm. Since, the present work focused on to synthesis of a few new superionic solids in glassy/amorphous phase, hence, the routes adopted during preparation of glassy electrolyte materials have only been discussed in this chapter along with the techniques commonly employed for characterization of the materials and transport properties. The experimental methods, used in general for characterization of superionic glasses viz. the phase/structural identification include: X-ray Diffraction (XRD) and Differential Thermal Analysis (DTA) or Differential Scanning Calorimetry (DSC). For the characterization of ion transport properties, investigations on some basic ionic parameters viz. ionic conductivity \( (\sigma) \) and ionic mobility \( (\mu) \), mobile ion concentration \( (n) \), ionic transference number \( (t_{\text{on}}) \), ionic drift velocity \( (v_d) \) etc. are done employing a.c. impedance spectroscopy (IS) and de polarization method viz. Transient current (TIC) technique. A detail discussion on the materials synthesis and characterization procedures has been presented below in the following sub-sections.

2.1 Materials Synthesis

The amorphous materials are generally synthesized by solidifying the liquid melt through rapid cooling techniques. Depending upon the nature of the constituent materials, different rates of cooling, ranging from: \( 10^1 \) - \( 10^3 \) K/s, are adopted which results into the formation of glassy/amorphous phase. The rapid quenching techniques, commonly used for the preparation of superionic glasses, include: drop and/or twin-roller quenching methods [Prasad & Radhakrishan 1998; Chowdari et al 2000; Nogami et al 2001; Tatsumisago et al 2001; Kumar et al 2004; Varsamis et al 2004; Jayaseelan et al 2005; Akhiko et al 2006; Karthikeyan et al 2006]. However, glasses can also be formed by evaporation or sputtering technique in which the liquid phase is bypassed. Sol-gel process and mechanochemical ball-milling are few other techniques also employed for the preparation of amorphous solid electrolytes [Morimoto et al 1999, 2000; Dalvi & Shahi 2001, 2003; Hayashi et al 2003; Murdainedaran et al 2004; Uma et al 2005; Tang et al 2005]. In the present work, the fast Ag+ ion conducting glasses were formed by twin-roller quenching method and the
characterization of ion transport behavior was done by the usual techniques, as mentioned. In addition to this, as already mentioned earlier in the preceding chapter, Section 1.6, the present thesis also reports the preparation of Ag⁺-ion conducting solid polymeric electrolyte (SPE) and nano composite polymer electrolyte (NCPE) membranes employing a novel dry/hot-press method as well as the characterization of ion transport properties of these systems. The Ag⁺ ion conducting glasses and polymeric electrolytes are synthesized with a view to fabricate solid state macro/micro batteries and study their cell performances. The routes adopted during the preparations of these samples are discussed below separately.

(i) Fast Ag⁺ ion conducting glassy electrolytes:
As mentioned, fast ion conducting glassy electrolyte systems are formed when the molten mixture of a host salt (MX), a glass modifier (M₂O) and a glass former (AₓOᵧ) in appropriate mol. wt (%) composition is cooled very rapidly. The general compositional formula has already been expressed earlier in Chapter I as:

\[ \text{MX: } M_2O: A_xO_y \]

For the formation of Ag⁺ ion conducting superionic glasses, AgI has traditionally been used as host salt with a common glass modifier: Ag₂O and any one of the oxide glass formers, mentioned in Chapter I. Attempts have also been made to mix two or more glass formers to study the ‘Mixed Former Effect’ on \( \sigma \) - values. In the present work, however, an alternate host salt: ‘a quenched [0.75 AgI: 0.25 AgCl] mixed system/ solid solution’, discovered at the present research laboratory in 1994 [Agrawal et al 1994], has been used in place of the traditional host salt AgI. The detailed investigations related to the synthesis and characterization of the new host material as well as discovery of some new fast Ag⁺ ion conducting solid electrolyte systems, in glassy/amorphous, two-phase composite and polycrystalline phases at the present laboratory using the alternate host salt have been published elsewhere and hence, reference may be made to the original papers by Agrawal and coworkers [Agrawal et al 1994, 1995; Agrawal & Kumar 1994, 1996; Agrawal & Gupta 1995, 1997; Agrawal et al 1996, 1998, 2000, 2002, 2004(a), 2004(b), 2005; Agrawal et al 2006]. The present investigation is an extension of the activity pursued at this research laboratory by earlier workers. Based on the alternate host, following two new Ag⁺ ion conducting glass systems have been prepared by rapidly cooling the molten mixtures of different mol (wt%) composition (x) in a twin-roller with a rate of quenching \( \sim 10^2 \) K/s:
x [0.75 AgI : 0.25 AgCl] : (1 – x) [Ag2O : P2O5]
• x [0.75 AgI : 0.25 AgCl] : (1 – x) [Ag2O : V2O5]

The twin - roller quenching machine was designed and fabricated at the present laboratory. The precursor AR grade chemicals: AgI (purity > 98%), AgCl (> 99%), Ag2O (> 98%), P2O5 (> 99%), V2O5 (99%), supplied by M/s Reidel (India) Ltd. were used without further purification for the preparation of the alternate host salt as well as glass systems. For direct comparison of the ionic conductivity of the newly synthesized glasses at room temperature, following two glass systems were also synthesized in the identical manner using the traditional host salt AgI:

• x AgI : (1 – x) [Ag2O : P2O5]
• x AgI : (1 – x) [Ag2O : V2O5]

The constituent chemicals in different mol. wt. compositions were thoroughly mixed, kept in separate silica test tubes, and then heated well above the melting point (i.e. ~ 700°C). The molten mixtures were shaked well before pouring the melt in between twin - rollers revolving at ~ 3000 rpm. The final finished products, in the thin solid flake form, were thoroughly ground and pressed at ~ 2 ton/cm² to form the pellet of dimension: thickness ~ 1 - 3 mm, diameter ~ 1.185 cm. Conducting colloidal silver and graphite paints were applied on to the well polished surfaces of the pellet for measurements by IS as well as for the direct determination of \( \mu \) and \( t_{\text{on}} \) by TIC technique. \( n \) and \( v_d \) values were evaluated subsequently from these data, as discussed below. The sample pellets were also used as electrolytes for the fabrication of solid state batteries by sandwiching them in between appropriate cathode and anode materials.

(ii) \( \text{Ag}^+ \) ion conducting solid polymer electrolyte (SPE) and nano - composite polymer electrolyte (NCPE):

\( \text{Ag}^+ \) ion conducting PEO - based solid polymer electrolyte (SPE) membranes: (PEO: AgI) of different salt concentrations by wt (%), were casted employing a novel hot - press technique, as mentioned. Normally, SPE membranes are prepared by usual solution - cast technique. The highest conducting SPE composition was identified from the salt - composition - dependent conductivity studies. Using this SPE composition as 1st - phase polymeric electrolyte host and nano-sized particles (size ~ 8 nm) of SiO\(_2\) as 2nd - phase dispersoid, \( \text{Ag}^+ \) ion conducting nano - composite polymeric electrolyte (NCPE) membrane : \((1 - x)[\text{PEO : AgI}] : x \text{SiO}_2\), where \( x = 0, 2, 3, 5, 10, 15 \) (wt %), were casted by similar hot - press procedure. As a consequence of
dispersal of nano-size particles of SiO₂ in SPE - host a further enhancement in the room temperature conductivity could be achieved for a particular SiO₂ concentration. The additional precursor chemicals used for the preparation of SPE and NCPE membranes are: Poly (ethylene oxide) PEO (10⁵ MW, Aldrich, USA) and SiO₂ (> 99.8%, Sigma, USA). The hot-press technique is a completely dry/solution-free procedure which is recently receiving widespread acceptability to form polymeric electrolyte films. It is an inexpensive and quicker procedure as compared to the solution cast method. For the preparation of SPE film by hot-press technique, dry powders of PEO and AgI, in different salt concentrations viz. 10, 20, 30, 40, 50, 60, 70, 80 (wt. %), were thoroughly mixed at room temperature in an Agate mortar & pestle for ~30 min and then heated separately at ~70°C in the open ambience for about 15 min to form the homogeneously mixed slurry. The slurry, so obtained, was quickly hot-pressed (~1.25 ton/cm²) between two cold SS blocks. This, in turn, resulted into As a result, mechanically stable yellowish thin membranes of SPE having thickness ~0.03 - 0.035 cm. As mentioned, the highest ion conducting SPE film composition was identified from the salt-composition dependent conductivity studies. Using this polymer-salt composition of SPE as 1st phase polymeric-electrolyte host matrix, NCPE films were casted in the identical manner by dispersing the nano sized SiO₂ particles in different wt (%) as the 2nd phase dispersoid, as mentioned above. The optimum conducting composition (OCC) of NCPE film was further identified from the SiO₂ - concentration dependent conductivity measurements. The ion transport characterization studies on NCPE membrane were done employing usual techniques. Using NCPE OCC film as electrolyte, thin film micro-batteries were fabricated and the cell performances were studied under different load conditions.

2.2 Materials Characterization

2.2.1 X-Ray Diffraction (XRD) analysis

X-Ray diffraction (XRD) technique is widely used as an experimental tool for the characterization of structural and materials properties in crystalline/polycrystalline solids. XRD analysis is also very useful to identify the formation of glassy/amorphous phases in the solid state ionic materials. The formation of glassy phase is usually confirmed on the basis of presence of broad/hollow diffused peaks in place of well defined sharp diffraction peaks in XRD pattern normally obtained in case of crystalline/polycrystalline solids. The absence of sharp well-defined XRD diffraction peaks in amorphous solids is mainly due to the reasons mentioned earlier in Chapter I. Glass/amorphous solids contain microscopically disordered structures, lacking 3-D periodicity as well as long range order arrangements. However, in crystalline solids there exists a 3-D regular periodic lattice and long-range ordered structural
arrangements. The X-rays incident on such solids gets reflected from the set of atomic planes, as shown in Fig. 2.1. The outgoing diffracted rays from the set of parallel planes interfere constructively after satisfying the well-known Braggs criterion:

\[ 2d \sin \theta = n\lambda \]  

Consequently, a well-defined XRD pattern containing sharp reflection peaks is obtained. In the case of mixed glassy/polycrystalline solids, XRD pattern contains sharp peaks as well as the broad diffused peaks. However, for pure glassy/amorphous solids only a few broad/diffused pattern is obtained. Hence, the presence of broad-diffused peak in the XRD pattern confirms the formation of the glassy/amorphous phase. In the present investigations, XRD analysis was done on the optimum conducting composition (OCC) samples only to confirm the existence of the glassy/amorphous phases. An XRD unit: Seifert (Germany), operated at 30 KV with Cu K\(_\alpha\) wavelength was used.

2.2.2. Differential Thermal Analysis (DTA)/Differential Scanning Calorimetry (DSC)
Differential Thermal Analysis (DTA) and/or Differential Scanning Calorimetry (DSC) are commonly used for thermal characterization of superionic solids. Some of the important characteristic thermal parameters which can be determined fairly accurately by these techniques include: phase transition temperature (T\(_c\)), glass-transition temperature (T\(_g\)), crystallization temperature (T\(_p\)), heat enthalpy, degree of amorphosity and/or crystallinity etc. A schematic experimental arrangement for DTA/DSC study is shown in Fig. 2.2. The test sample and an inert reference material are heated together simultaneously. The physical/chemical changes viz. phase transition change in the latent/specific heat, chemical/decomposition reactions etc. in the test material, as a consequence of heating, can be recorded in terms of electrical signal, i.e., a change in the thermo emf, with the help of a thermocouple with two junctions in thermal contact with the test and reference materials respectively. A typical DTA/DSC thermogram for a test sample is shown in Fig. 2.3. The physical/chemical changes in the test sample are observed in terms of endothermic and/or exothermic peak responses in the thermogram, which reflect the absorption and/or liberation of heat energy respectively. Alumina (Al\(_2\)O\(_3\)) is most widely used as reference material due to the fact that no physical/chemical changes occur in it well up to 1000°C.

2.3 Ion Transport Property Characterization
The ion transport mechanism in ionic/superionic solids can be understood on the basis of variety of experimental measurements on some basic ionic parameters viz. ionic conductivity
Bragg's Criterion: $2dsin\theta = n\lambda$

Fig. 2.1: Schematic representation of diffraction of X-rays by a crystal; atomic planes
Figure 2.2 Schematic arrangement for DTA/DSC analysis.
Figure 2.3: Typical DTA/DSC Thermal response of a test sample with exothermic and endothermic peaks.
(σ), ionic mobility (μ), mobile ion concentration (n), ionic transference number (t_ion), ionic drift velocity (v_0) etc. The temperature dependence studies on these ionic parameters, which usually follow Arrhenius type variations, provide informations regarding the energies involved in different thermally activated processes. These energy values are computed from the linear least square fittings of the straight line portion of the slope of Arrhenius plots. Variety of experimental techniques, commonly used to measure these ionic parameters, are discussed below in following subsection.

### 2.3.1 Ionic Conductivity (σ) by Impedance Spectroscopy (IS)

The conductivity measurements in ion conducting solids by d.c. potentials usually lead to erroneous results due to instant polarization of the mobile ions. The polarization effects are more dominant in the fast ion conducting systems. Hence, the conductivity measurements in the superionic systems are generally carried out using a.c. signals. Impedance Spectroscopy (IS) is an a.c. technique, extensively used for the ionic conductivity measurements in ionic/superionic samples. [Randles 1947; Baurele 1969; Macdonald 1976, 1987; Gabrieli 1984; Mellander and Lunden 1986; Paisttic 1986; Badwal 1988; Garbarczyk et al 2000, 2003; Machowski et al 2003]. IS, actually, refers to study the impedance response of the solid state ionic materials under a small amplitude sinusoidal (ac) signal of varying frequencies ranging from few mHz to several MHz. This technique has several advantages over the d.c. measurements. Some of the definite advantages include: absence of polarization effects, true bulk resistance of the test sample can be separated out from the other resistance contributions viz. grain boundary resistance, electrode - electrolyte interfacial resistance etc. A series of small amplitude ac signal in a broad range frequency, as mentioned, is applied across the sample and the absolute magnitude of impedances (|Z|) as well as phase angles (θ) are measured. With the help of |Z| and θ data, the real and imaginary impedances: Z' (σ) = |Z| cosθ and Z''(σ) = |Z| sinθ, respectively, are evaluated at different frequencies. In fact, the complex impedance Z is expressed in terms of real and imaginary impedances by following well known equation:

\[ Z = Z'(\omega) - j Z''(\omega) \]  \hspace{1cm} (2.2)

The plot between Z' and Z'' at varying frequencies is called 'complex impedance plot'. Some typical Z' - Z'' complex impedance plots for a pure resistance (R)/ capacitance (C) and their series/parallel combinations are shown in Fig. 2.4. A pure resistance (R) is frequency independent parameter, hence, it gives a single point on the real Z'-axis which exactly corresponds to the true value of the bulk resistance. For a pure capacitance C, the capacitive
Figure 2.4: Complex impedance plots for some elementary R, C and RC circuits.
reactance \((=1/\omega C)\) varies infinitely with increasing frequency and hence, coincides with the imaginary \(Z''\) - axis, having phase angle \(\theta = 90^\circ\). When, R & C are connected in series, the complex impedance plot is a line parallel to imaginary \(Z''\) - axis intersecting the real \(Z'\) - axis at the value of R; when R and C are connected in parallel, \(Z' - Z''\) plot is a semicircle intersecting the real \(Z'\) - axis at the value of R, as shown. Based on these simple circuit analysis, one can easily analyses more complicated complex impedance plots and draw the possible equivalent circuits for the test sample. For the electrochemical cells consisting of a test sample pallet, sandwiched between blocking/ non-blocking electrodes, the typical complex impedance \((Z' - Z'')\) responses and corresponding ideal equivalent circuits are shown in Fig. 2.5. The true bulk resistance \((R_b)\) can be known from the intersection of the semicircle on the real impedance axis, as shown. As mentioned, apart from true bulk resistance \((R_b)\), there exists several other resistive components viz. grain boundary \((R_{gb})\), electrode/ electrolyte interfacial \((R_{ed})\) resistances which may also contribute to the total resistance. Since these resistive components respond at different regions of frequency spectrum and depicted by different semicircles, hence, the true bulk resistance \((R_b)\) can be accurately separated out in the complex - impedance plot, as shown in Fig. 2.6.

In the present investigation, the conductivity \((\sigma)\) measurements were carried out at room temperature and above using IS technique in the frequency range 40 Hz to 100 KHz. A computer controlled multifrequency LCR Bridge (Model HIOKI 3520 - 01, Japan) was used during these measurements. The sample pallet was placed in a spring - loaded electrode holder, as shown in Fig. 2.7. The true bulk resistance \((R_b)\) values were obtained from the \(Z' - Z''\) complex impedance plots for different samples and the conductivity values were determined with the help of following equation:

\[
\sigma = G l / A \tag {2.3}
\]

where \(G \left( = 1/R_b \right)\) is the conductance, \(l\) and \(A\) are the thickness and cross sectional area of the sample pallet respectively. The temperature dependent conductivity measurement was also carried out on different samples and the activation energy \((E_a)\) involved in the thermally activated process was computed from the least - square linear fitting of \('\log \sigma - 1/T'\) plot, expressed by following Arrhenius equation:

\[
\sigma = \sigma_0 \exp (-E_a / kT) \tag {2.4}
\]
Figure 2.5: Typical electrochemical cells and their equivalent circuits along with responses in $Z' - Z''$ complex impedance plots with: (i) non-blocking electrode and (ii) blocking electrodes.
Figure 2.6: Typical electrochemical cells and their equivalent circuits along with responses in $Z'-Z''$ complex impedance plots with: (i) non blocking electrode and (ii) blocking electrodes.
Figure 2.7: Schematic experimental arrangement for electrical conductivity measurements.
2.3.2 Ionic Mobility ($\mu$), mobile ion concentration ($n$), ionic transference number ($t_{ion}$), ionic drift velocity ($v_d$) by d.c. polarization techniques

It is one of the established facts that the conduction phenomenon in the ion conducting solids is strongly dependent on two basic ionic parameters: the ionic mobility ($\mu$) and the mobile ion concentration ($n$). The three ionic parameters are related with each other by following well-known equation [see also eq. (1.25), Chapter 1]:

$$\sigma = n q \mu$$  \hspace{1cm} (2.5)

where $q$ is the charge associated with mobile ion species. In order to understand the conduction mechanism in the ionic/superionic systems, it is very essential to estimate the values of $\mu$ and $n$. As mentioned, a d.c. polarization method called: ‘Transient Ionic Current (TIC)’ technique, has been developed and widely employed in the recent times for the direct determination of $\mu$ [Watanabe et al 1985; Chandra et al 1988; Agrawal & Kumar 1994; Agrawal et al 1994]. Further, $n$ values can subsequently be evaluated with the help of $\sigma$ and $\mu$ data using the above equation. Another ionic parameter having paramount importance is the ionic transference number ($t_{ion}$). The magnitude of $t_{ion}$ in ionic/superionic solids quantitatively provides the information regarding the extent of ionic contribution to the overall conduction process. The ionic transference number can be expressed as:

$$t_{ion} = \frac{\sigma_{ion}}{\sigma_T} = \frac{I_{ion}}{I_T}$$  \hspace{1cm} (2.6)

where $\sigma_{ion}$ and $I_{ion}$ are the ionic conductivity and current contributions respectively, $\sigma_T$ and $I_T$ are the total (ionic + electronic) conductivity and current respectively. Since, the superionic solids are usually pure ion conducting systems i.e. the sole charge carriers are the ions only, hence, $\sigma_{ion} = \sigma_T$ and/or $I_{ion} = I_T$ and thus, $t_{ion} \geq 1$. In case of mixed (ionic + electronic) systems, $t_{ion}$ varies in the range: 1 - 0, where $t_{ion} = 0$ and/or $t_{e,h} = 1$ corresponds to the electronic transference number in a pure electron conducting system. $t_{ion}$ measurements in superionic solids can also be done with the help of TIC technique as well as Wagner’s d.c polarization method [Wagner and Wagner 1957]. An other important ionic parameter viz. the ionic drift velocity ($v_d$), providing an additional insight to understand ion conduction phenomenon in superionic solids, can also be determined with the help of data received in the above measurements. The basic experimental arrangement used during d.c polarization studies (TIC and/or Wagner’s methods) is shown in Fig. 2.8. In TIC technique, the test sample pellet
Figure 2.8: Basic experimental set-up for d.c. polarization measurements: TIC technique with both the electrodes blocking, Wagner's method with a blocking and non-blocking electrodes (see text)
of thickness: \( d \), area of cross section: \( A \), is sandwiched between two blocking electrodes (e.g. graphite (C) acts as blocking electrode for Ag\(^+\) ion conducting superionic solids), while in the Wagner's method one of the electrodes is replaced by a non-blocking (reversible) electrode (e.g. silver metal acts as non-blocking electrode for Ag\(^+\) ion conducting solids). The direct determination of \( \mu \) by TIC technique can be done on the sample pellet, sandwiched between blocking electrodes and subjected to an external d.c. potential (viz. \( V \sim 0.5 \) V for Ag\(^+\) ion conducting solids) for sufficiently long time to ensure that a state of complete polarization has been attained in the sample i.e. all the mobile ions of the sample got accumulated/ blocked at the electrolyte/ (-) ve electrode interface. At this stage, the polarity of the externally applied potential is then reversed and instantly, the current in the external circuit is monitored simultaneously as a function of time with the help of an x - y- t recorder. As a result of polarity reversal, the polarized ion cloud instantly starts traveling back across sample thickness towards the opposite electrode/ electrolyte boundary. As soon as the polarized ion cloud reaches the other end, a peak occurs in the 'current vs. time' plot. A typical 'current vs. time' TIC plot is shown in Fig. 2.9. The peak in TIC - plot corresponds to the time of flight (\( \tau \)) for the mobile ion cloud to cross the thickness \( d \) of the sample pallet. If the sample pallet contains more than one ion as mobile species, then in TIC plot we obtain corresponding numbers of peaks, each belonging to the times of flights of one kind of mobile ion. Eventually, the ionic mobility (\( \mu \)) can be evaluated with help of following equation:

\[
\mu = \frac{d^2}{V \tau} \quad [\text{cm}^2\text{V}^{-1}\text{s}^{-1}]
\]  

The ionic mobility (\( \mu \)) measurements can also carried out at different temperatures. In the present study, an x - y - t recorder (Model Graphtec WX 2300 - IL, Japan) was used for monitoring the ionic current as a function of time. Since, all the solid electrolyte systems, investigated in the present work, involved only Ag\(^+\) ions as the sole charge carries, hence, one single peak was obtained in all the TIC plots. Using \( \mu \) and \( \sigma \) data, the number of mobile ions (\( n \)) was subsequently determined at different temperatures, as mentioned above. Since, Both \( \mu \) and \( n \) are temperature dependent ionic parameters, and hence, they obey usual Arrhenius type variations expressed by following equations:

\[
\mu = \mu_0 \exp \left( \frac{+E_m}{kT} \right) \quad (2.8)
\]

\[
n = n_0 \exp \left( \frac{+E_d}{kT} \right) \quad (2.9)
\]
Figure 2.9: A typical TIC plot for ionic mobility measurements in a superionic solid with a single mobile ion species.
where \( \mu_0 \) and \( n_0 \) are the pre-exponential factors, \( E_m \) and \( E_f \) have been designated as energies of migration and formation respectively and can be computed from the slopes of \( \log \mu - 1/T \) and \( \log n - 1/T \) straight line plots. The (-) ve and (+) ve signs appearing in the arguments of the two exponentials indicate the increase and decrease respectively of the factor on the left hand side (LHS) of the equation with increasing temperature. As mentioned, the ionic transference number \( (t_{\text{on}}) \) can also be determined by TIC technique, besides usual Wagner's d.c. polarization method. In fact, in the later method, the sample pellet is sandwiched between a blocking and a non-blocking electrode and subjected to external d.c. potential with (+) ve and (-) ve polarities connected appropriately. In case of cation conductivity systems, the positive polarity is connected to the blocking (say graphite) electrode and negative polarity to non-blocking (say silver metal for Ag\(^+\) ion conducting solid) electrode. As a result, the mobile cations travel towards the non-blocking electrode and get dissolved ultimately into it with the lapse of time. Typically, two kinds of 'current vs. time' plots are expected in this experiment, as schematically illustrated in Fig. 2.10. Plot 1 belongs to a pure ionic system in which the initial total current \( (I_T) \) finally approached to zero with time. Hence, \( I_T \approx I_{\text{on}} \) and \( t_{\text{on}} \approx 1 \). Plot 2 corresponds to the current - time response for a mixed (ionic/ electronic) system in which the initial peak current \( (I_T) \) levels off to a final residual current value. This residual value indicates the extent of electronic current contribution due to the motion of electrons and/or holes in the sample. In such a mixed system, ionic transference number is estimated as:

\[
t_{\text{on}} = 1 - (t_{\text{eh}} / I_T)
\]

where the second term is equivalent to the electronic transference number \( (t_{\text{eh}}) \). The ionic transference number in solid electrolyte systems can also be determined alternatively using 'electrochemical cell potential' method, to be discussed in the next section.

Further, for a single ion conducting superionic solid, the ionic drift velocity \( (v_d) \) can also be estimated with the help of following equation [Agrawal and Kumar 1994, 1996; Agrawal & Gupta 1995; Agrawal et al 2004a, 2004b; Kumar et al 2005]:

\[
v_d = I_T / A.n.q
\]

where \( I_T \) is the initial total peak current obtained in TIC and/or Wagners current - time plot, \( n \) is the number of mobile ions obtained from \( \sigma \) & \( \mu \) data, as mentioned, \( A \) is the area of cross section of the sample pellet and \( q \) is the charge on the mobile ion. The accuracy of \( v_d \) measurements, depends upon how accurately \( I_T \) and \( n \) values are evaluated. \( v_d \) measurement
Figure 2.10: Transference number measurements using Wagner's d.c. Polarization method
can also be carried out as a function of temperature and hence, the temperature dependence of \( v_d \) also obeying the usual Arrhenius type variation, can be expressed by following equation:

\[
v_d = v_{do} \exp \left( \frac{\mp E_d}{kT} \right)
\]

(2.12)

where \( v_{do} \) is the usual pre-exponential factor and \( E_d \) is the energy involved in this thermally activated process. At a fixed value of applied d.c. field, \( v_d \) is directly proportional to \( \mu \). Hence, 'log \( v_d \) - 1/T' and 'log \( \mu \) - 1/T' variations should be exactly analogous and the two energy (\( E_d \) and \( E_m \)) values would be the same. For the number of fast Ag\(^+\) ion conducting solids, discovered by Agrawal and co-workers [Agrawal & Kumar 1994, 1996; Agrawal 1995], it has been observed that the two Arrhenius type plots are almost analogous and the two energy values are excellently close to each other. In the present investigation, based on the temperature dependent ionic transference number (\( t_{ion} \)) measurements, the ionic drift velocity (\( v_d \)) values were calculated at different temperatures for the optimum conducting composition (OCC) samples only.

2.4 Electrochemical Device Characterization

2.4.1 Solid State Battery fabrication and study of cell potential discharge performances

As mentioned, solid state ionic materials can be potentially used as electrolytes to fabricate solid state electrochemical devices viz. batteries, fuel cells, supercapacitors, memory & ECD devices. Depending upon the power requirements and energy demands, variety of batteries in a very wide energy range: 0.1 mWh to 100 MWh are being manufactured employing liquid/aqueous electrolyte and/or alternatively the solid state ionic materials, as discussed in Chapter 1. Batteries mainly consist of the following three basic active components:

- **Electrolyte**: A perfectly ion conducting and a perfect electron separator medium.
- **Cathode**: A positive current collecting metallic electrode, capable of getting readily reduced after combining with a free electron.
- **Anode**: A negative current collecting metallic electrode, capable of getting readily oxidized by the release of an electron.

Batteries work on very simple principle of reduction-oxidation (redox) reactions at the interfaces of the two electrochemically different electrodes (anode & cathode) separated by a pure ion conducting electrolyte. The solid state battery can have following three possible configurations:
A typical solid state cell is shown in Fig. 2.11. The solid electrolyte MX with $M^+$ - mobile ions, is sandwiched between $M$ - anode and $X$ - cathode of different chemical potentials: $\mu_1$ and $\mu_2$ respectively. Typically, the reactions, involved in this solid state electrochemical cell, can be expressed as:

**At the anode:**  
$M - e = M^+$  
(dissolved in MX)

**At the cathode:**  
$X + e = X^-$  
(remained at cathode/ electrolyte interface)

**Hence, overall cell reaction:**  
$M^+ + X^- = MX$  
(At cathode/ electrolyte interface)

Thermodynamically, as a consequence of redox reactions at the two electrode/ electrolyte interfaces, an electromotive force (emf) is generated across the cell due to the usual Gibbs free energy involved in the above chemical reactions and can be expressed by the following equation [Chandra & Agrawal 1980]:

$$E = \frac{1}{|Z|F} \int_{\mu_1}^{\mu_2} \frac{I_{\text{hon}} d\mu}{|\mu|F} = \frac{I_{\text{hon}}}{|Z|F} \Delta G$$  (2.13)

where $I_{\text{hon}}$ is the ionic transference number ( =1 for a pure ionic solid), $F$ is Faraday’s constant, $|Z|$ is the charge valancy on the mobile ion, $\Delta G (= \mu_2 - \mu_1)$ is the Gibbs’ free energy. Larger is the difference in the chemical potentials of the two electrode materials, higher would be $\Delta G$ and hence, greater would be the emf. Thus, an appropriate choice of electrode couple is very essential for generating high emf [= Open Circuit Voltage (OCV) in the open circuited condition]. Using the newly investigated fast $Ag^+$ ion conducting solids i.e. glassy and polymer electrolytes solid state batteries were fabricated in the following cell configuration using Ag/ I$_2$ electrode couple:

$$Ag (\text{Anode}) | \text{Fast Ag}^+ \text{ion conducting solid (Solid Electrolyte)} | (C+I_2) (\text{Cathode})$$

The cathode is a mixture of elemental iodine (I$_2$) and conducting graphite (C) in 1:1 wt (%).

The details related to the cell reaction involved in the above batteries will be discussed later in Chapter 5. In the open circuited condition, emf is equivalent to the Open Circuit Voltage.
Figure 2.11: A typical solid state cell
(OCV), as mentioned. However, in the closed circuited condition, i.e. when a load (resistance) is connected across the two electrodes in the outer circuit, the electrons flow from anode to cathode and the cell starts discharging by doing some electric work on the load. During discharge, a current I flows through the load resistance and the voltage V progressively decreases from the maximum theoretical OCV (i.e. emf) value. The variation of V during discharge can be expressed by the following equation:

\[ V = E_{\text{theo}} - \eta - I_r \]  

where \( \eta = [(\eta_{\text{ct}} + \eta_{\text{ed}}) - (\eta_{\text{a,ct}} + \eta_{\text{a,d}})] \) is the charge transfer (ct)/diffusion (d) overpotentials at both the cathode and anode/electrolyte contacts, \( I_r \) is the ohmic overpotential with \( r_i \) as the internal resistance of the cell. The potential distribution of an electrochemical cell under the external load condition is shown in Fig. 2.12 and the cell potential polarization profile, representing the above equation is shown in figure Fig. 2.13. During low current drain state, the charge-transfer overpotential losses dominate; at higher drain current \( I_r \) losses dominate; at a still higher current drain mass transfer (diffusion overpotential) losses give rise to a rapid decrease in the cell potential. The performance of the cell is often characterized by the discharge behavior of the cell potential under varying load conditions. The discharge profile of a typical cell under the different current drain states are shown in Fig. 2.14. It is obvious from the figure that cell discharges very rapidly under high current drain state i.e. through a low load resistance. To specify the figure of merit and the performance of the battery, following basic cell parameters are determined in the plateau region of the discharge profile:

- Electric Power: \( P = VI = I^2R = V^2/R \) [W]
- Electric Energy: \( E = V \times t = qV \) [Wh]
- Current Density: \( J = I/A \) [Amp/cm²]
- Discharge Capacity: Current \times Discharge Time [Ah]
- Energy density (or Volume Capacity): Electric Energy/ Battery Volume [Wh/ cc]
- Specific Energy (or Weight Capacity): Electric Energy/ Battery Weight [Wh/ kg]
- Specific Power: Electric Power/ Battery Weight [W/ kg]

As mentioned in the proceeding subsection, the electrochemical cell potential method can be alternatively used to determine the ionic transference number (t_ion). Hence, \( t_{\text{ion}} \) can be
Fig. 2.12: Potential distribution in a typical electrochemical cell. $E_{\text{theo}}$ (= OCV): potential at open circuited condition; $V$: potential during discharge through a load resistance.

Figure 2.13: A typical cell under two different current drain states.

Figure 2.14: A typical cell under two different current drain states.
calculated for the fast Ag\(^+\) ion conducting solids kept in the intimate contact with Ag - anode and (C+I\(_2\)) cathode in the form of solid state battery.

If \(E\) and \(E'\) are the theoretical and measured values of emf, then \(t_{\text{ion}} = t_{\text{Ag}^+}\) can be known with the help of following equation:

\[
t_{\text{Ag}^+} = \frac{E'}{E}
\]  

(2.15)

The results obtained by this method can compared with those obtained earlier through d.c. polarization methods. In all the cell potential measurements, high internal impedance digital voltmeter (Philips, Model PM 2518) was used.