5.1 Introduction

5.2 Results and Discussion

5.2.1 Compositional dependent studies on basic ionic parameters and characterization of ion transport properties:

(i) Solid Polymer Electrolyte (SPE) membranes:

\[(1-x)\text{PEO} : x [0.7(0.75\text{AgI}:0.25 \text{AgCl}): 0.3 \text{ M}] (M=\text{Rb, K})\]

(ii) Nano-Composite Polymer Electrolyte (NCPE) membranes:

\[(1-x) [90 \text{PEO}: 10 \text{AgNO}_3] : x \text{SiO}_2\]

5.2.2 Temperature dependent studies on basic ionic parameters:

(i) Solid Polymer Electrolyte (SPE) membranes:

\[(1-x) \text{PEO} : x [0.7(0.75\text{AgI}:0.25 \text{AgCl}): 0.3 \text{ M}] (M=\text{Rb, K})\]

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5.3 Conclusion
5.1 Introduction

As described in Chapter I, ion conducting electroactive polymeric materials have recently been attracting widespread attentions due to their tremendous technological potentials in developing all-solid-state electrochemical power sources viz. flexible/ compact/ lightweight/ leak-proof thin film micro primary/ secondary batteries of desirable shapes/ sizes [MacCollum et al 1989; Armand et al 1990; Gray et al 1991 & 1997; Croce et al 1998; Appetecchi et al 2000, 2001, 2003; Maier et al 2006; Chandra et al 2006; Hashmi et al 2008]. After the discovery of first ion conducting polymeric membrane in 1973 [Fenton et al 1973] and the demonstration of first practical thin film battery in 1979 [Armand et al 1979], a large variety of polymer electrolyte materials involving different kinds of mobile ions viz. H+, Li+, Na+, K+, Ag+ etc., as the principal charge carriers, has been discovered since then in the last ~ 3 decades. The device potentials of these polymer electrolyte membranes are constant under test at various R & D laboratories and in fact, many of these devices are presently being manufactured at the commercial scale. Polymer electrolyte membranes are usually casted by solution-cast method. However, a novel hot-press technique is recently getting wide acceptability as an alternate procedure for casting completely dry polymer electrolyte membranes. This technique has several advantageous merits over the traditional solution-cast method, as already mentioned in Chapter 2. This chapter reports the hot-press casting of two new Ag+ ion conducting polymer electrolyte membranes: (i) Solid Polymer Electrolytes (SPEs): (1-x) PEO: x [0.7(0.75AgI:0.25 AgCl):0.3 MI] and (ii) NanoComposite Polymer Electrolytes (NCPEs): (1-x) [90 PEO: 10 AgNO3 : x SiO2. As pointed out earlier, this is an additional work, other then what has been proposed in the original Ph.D. synopsis. However, this additional study has been carried out with the view to fabricate thin film all-solid-state micro-batteries using the polymer electrolyte membranes as well the electrode couples also in the film form. In fact, the newly investigated Ag+ ion conducting quaternary superionic solids: 0.7(0.75AgI:0.25 AgCl):0.3 MI (where M = Rb, K) (Chapters 3 & 4), have been used intentionally as complexing salts to cast two SPE membranes. Subsequently, all-solid-state cells have been fabricated with the polycrystalline quaternary superionic solids: [0.7(0.75AgI:0.25 AgCl):0.3 MI] and SPE membranes, in order to compare cell performances of the macro (thin film) batteries. NCPE films complexed with AgNO3 salt and dispersed with nano-size SiO2 particles were also used to fabricate micro (thin film) batteries. The details of the SPE/ NCPE film casting and the techniques used for materials/ ion transport characterizations have already been discussed in Chapter 2. The results of various experimental measurements on transport behaviour of the two newly synthesized hot-pressed polymer electrolyte membranes are presented below. With SPE/
NCPE films, exhibiting optimum conductivity thin film batteries have been fabricated and their performances have been discussed in Chapter 6.

5.2 Results and Discussion

5.2.1 Compositional dependent studies on ionic parameters and characterization of ion transport properties

(i) Solid Polymer Electrolyte (SPE) membranes:

\[(1-x)\text{PEO}: x[0.7(0.75\text{AgI}:0.25\text{AgCl}): 0.3 \text{M}] (M = \text{Rb, K})\]

Fig. 5.1 shows the variations of room temperature conductivity \((\sigma)\) as a function of salt concentration \((x)\) for the hot-pressed solid polymer electrolyte (SPE) films: \((1-x)\) PEO: \(x[0.7(0.75\text{AgI}:0.25\text{AgCl}): 0.3 \text{M}] (M = \text{Rb, K})\), where \(x = 0-50\) wt. (%). SPE films beyond 50% salt concentration were found unstable and brittle. ‘Log \(\sigma - x\)’ plots for the two systems look almost alike, as expected and followed the usual compositional dependent conductivity variations. One can note that initially \(\sigma\) increased very rapidly as the salt concentration was increased up to 30 wt. (%), then decreased on further addition of the salt. SPE compositions: 70 PEO: 30 \([0.7(0.75\text{AgI}:0.25\text{AgCl}): 0.3 \text{RbI}]\) and 70 PEO: 30 \([0.7(0.75\text{AgI}:0.25\text{AgCl}): 0.3 \text{KI}]\) exhibited highest room temperature conductivity \((\sigma) \sim 9.5 \times 10^{-7}\) and \(\sim 1.07 \times 10^{-6}\) S.cm\(^{-1}\) respectively and have been identified as Optimum Conducting Compositions (OCCs), as mentioned. A conductivity enhancement of approximately three orders of magnitude was achieved in both OCC SPEs from that of the pure PEO polymeric host with room temperature conductivity \((\sigma) \sim 3.2 \times 10^{-9}\) S.cm\(^{-1}\). The conductivity increase in both OCC SPE membranes may be due to the increase in \(n\) or \(\mu\) or both. Hence, to identify the reason for \(\sigma\) increase in the two OCC SPEs, ionic mobility \((\mu)\) as a function of \(x\) was measured at room temperature using TIC-technique, as mentioned in Chapter 2. Subsequently, mobile ion concentration \((n)\) values for different film compositions were evaluated from \(\sigma\) and \(\mu\) data.

Fig. 5.2 (a & b) shows ‘log \(\mu - x\)’ and ‘log \(n - x\)’ plots for the two SPE films: \((1-x)\) PEO: \(x[0.7(0.75\text{AgI}:0.25\text{AgCl}): 0.3 \text{M}]\). Table 5.1 lists the room temperature values of \(\sigma, \mu, n\) for the two OCC SPE films along with the ionic transference number \((t_{ion})\) and activation energy \((E_a)\) values (to be discussed below) as well as \(\sigma\)-value of pure PEO. One can clearly note from the figure that the increase in both \(\mu\) and \(n\) predominantly governed the overall enhancement in the room temperature conductivity for both the OCC SPE membranes. Increase in \(\mu\) is indicative of enhanced degree of amorphousity in the polymeric host as a result of salt complexation. The increase in \(n\) may be a consequence of some structural changes in polymeric host which might have favored facilitating more number of mobile...
Fig. 5.1: 'Log $\sigma - x$' plots of hot-pressed SPE films: (1-x) PEO: $x [0.7(0.75AgI:0.25AgCl): 0.3 RI]$ ($M = Rb, K$).
Fig. 5.2: 'Log $\mu - x$' and 'log $n - x$' plots for hot-pressed SPE films: (a) (1-x) PEO: x [0.7(0.75AgI: 0.25AgCl): 0.3 Rbl]; (b) (1-x) PEO: x [0.7(0.75AgI: 0.25AgCl): 0.3 KI].
Table 5.1: Room temperature (27 °C) values of some basic ionic parameters for the hot-pressed SPE OCCs membranes: 70 PEO:30[0.7(0.75AgI: 0.25AgCl): 0.3M] (M = Rb, K) and $\sigma$-value of pure polymer PEO.

<table>
<thead>
<tr>
<th>System</th>
<th>$\sigma$ (S cm$^{-1}$)</th>
<th>$\mu$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>n (cm$^{-3}$)</th>
<th>$t_{\text{ion}}$</th>
<th>$E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure polymer: Poly(ethylene oxide)PEO</td>
<td>3.2 x 10$^{-9}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Solid Polymer Electrolyte (SPE) OCCs:</td>
<td></td>
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</tr>
<tr>
<td>70 PEO:30[0.7(0.75AgI: 0.25AgCl): 0.3Rbl]</td>
<td>9.5 x 10$^{-7}$</td>
<td>(6.25 ± 1) x 10$^{-3}$</td>
<td>9.53 x 10$^{14}$</td>
<td>~0.98</td>
<td>~0.62</td>
</tr>
<tr>
<td>70 PEO:30[0.7(0.75AgI: 0.25AgCl): 0.3KI]</td>
<td>1.07 x 10$^{-5}$</td>
<td>(5.24 ±1) x 10$^{-3}$</td>
<td>5.01 x 10$^{15}$</td>
<td>~0.98</td>
<td>~0.86</td>
</tr>
</tbody>
</table>
Ag⁺ ions for conduction.

Fig. 5.3 shows the X-ray diffraction patterns for the pure polymeric host PEO, quaternary superionic complexing salts: 0.7(0.75AgI: 0.25AgCl):0.3 MI (M = Rb, K) (reported in Chapters 3 & 4) and both the above Ag⁺ ion conducting hot-pressed OCC SPE membranes. On closer inspection of XRD patterns of OCC SPEs, one can clearly note that some of PEO peaks became relatively broader as well as less prominent/feeble after salt complexation. This in turn, indicative of decrease in degree of crystallinity and/or increase in degree of amorhousity in PEO host. The complexation of salts in PEO host has also been confirmed in these XRD-patterns of OCC SPEs. The surface morphology of the two OCC SPE films has been studied using Scanning Electron Microscopy (SEM). Fig. 5.4 (a & b) shows SEM micrograph of the two OCC SPE films which indicated almost smooth surface morphology. This is also closely related to the reduction of crystallinity with salts, as pure PEO usually shows a rough morphology [Peter Chu et al 2003]. Fig. 5.5 shows DTA thermograms for the two newly synthesized OCC SPEs: 70 PEO: 30 [0.7(0.75AgI:0.25 AgCl): 0.3 MI] (M = Rb, K). The broad endothermic peak ~ 70 °C in both the thermograms correspond to the semicrystalline to amorphous phase transition and/or melting point temperature of PEO polymeric host.

(ii) Nano-Composite Polymer Electrolyte (NCPE) membranes:

\[(1-x) [90 \text{PEO}: 10 \text{AgNO}_3] : x \text{SiO}_2\]

To synthesise NCPE films, firstly the solid polymer electrolyte (SPE): (90PEO: 10AgNO₃), to used as 1st-phase for the dispersal of 2nd-phase dispersoid SiO₂ particles, was identified. Fig. 5.6 shows the room temperature conductivity (\(\sigma\)) as a function of salt concentration for the hot-pressed conventional solid polymeric electrolyte (SPE) membranes: (PEO: AgNO₃). In this case also, \(\sigma\) increased abruptly (> 10³ times) as AgNO₃ salt concentration increased initially up to \(x = 10\) wt. (%), then remained almost unaltered on further addition of the salt. A moderate-sized \(\sigma\) -maxima with room temperature conductivity (\(\sigma \sim 4 \times 10^6\) S.cm⁻¹) was observed at 10 wt.% of AgNO₃ (i.e. for the composition 90 PEO: 10AgNO₃). Chandra et al [1993] also synthesized the similar SPE films by usual solution cast method and reported almost analogous salt-concentration dependent conductivity variation with maximum conductivity (\(\sigma \sim 4 \times 10^7\) S.cm⁻¹) for the SPE film of the same composition: (90 PEO: 10AgNO₃). According to them, addition of salt in PEO resulted into the increase in degree of amorhousity which consequently led to an abrupt increase in the conductivity. As mentioned in Chapter 1, the dispersal of nano-size filler particles of insulating/inert compound viz. Al₂O₃, SiO₂, TiO₂ etc. into the conventional SPE materials brings substantial
Fig. 5.3: XRD patterns: (a) pure PEO; (b) I- quaternary superionic salt: 0.7[0.75AgI: 0.25AgCl]:0.3Rbl; II- OCC SPE: 70 PEO: 30 [0.7 (0.75AgI:0.25AgCl):0.3 Rbl]; (c) I- quaternary superionic salt: 0.7[0.75AgI:0.25AgCl]:0.3KI; II- OCC SPE: 70 PEO: 30 [0.7(0.75AgI: 0.25AgCl):0.3 KI].
Fig. 5.4: SEM images for OCC SPEs: (a) 70 PEO: 30 [0.7(0.75AgI:0.25AgCl): 0.3 Rbl],
(b) 70 PEO: 30 [0.7(0.75AgI:0.25AgCl) : 0.3 KI].
Fig. 5.5: DTA thermograms for OCC SPEs: (a) 70 PEO: 30 [0.7(0.75AgI:0.25AgCl): 0.3 Rbl], (b) 70 PEO: 30 [0.7(0.75AgI:0.25AgCl): 0.3 KI].
Fig. 5.6: Room temperature conductivity of hot-pressed SPE membranes: (PEO: AgNO$_3$) as a function of salt AgNO$_3$ concentration (wt. %).
improvement in several physical properties including conductivity, mechanical integrity etc. Such systems are referred to as Nano-Composite Polymer Electrolytes (NCPEs). Hence, using SPE composition: (90 PEO: 10AgNO₃) as the first phase polymeric electrolyte host and SiO₂ filler particles of 8 nm size as second phase dispersiode, NCPE films have also been casted by hot-press technique, as already described in Chapter 2. Fig. 5.7 shows SiO₂-concentration-dependent conductivity variation at room temperature for the hot-press Ag⁺ ion conducting NCPE membranes: (1-x) [90 PEO: 10 AgNO₃]: x SiO₂. As a consequence of dispersal, the room temperature conductivity of SPE host increased initially as SiO₂ ratio increased, attained a peak value at 5 wt. %, then decreased gradually. The conductivity variation of this kind has invariably been witnessed in majority of 2-phase inorganic composite electrolytes and the mechanism of conductivity enhancements in these systems could by understood by various proposed models which are principally based on space-charge double layer effect [Maier 1989; Agrawal 1999]. The increasing/ decreasing trend in the conductivity with the increase in dispersoid concentration can be understood on the basis of percolation model [Bunde et al 1985]. These models can be convincingly used to explain the mechanism of ion transport in composite polymeric (organic) electrolytes also. However, due to absence of exact structural-property correlations in these systems, a clear understanding of ion conduction phenomenon is still lacking. Nonetheless, to explain the mechanistic aspects of ion transport in micro/ nano-composite polymer electrolyte systems, a working hypothesis has been suggested. Accordingly, the dispersal of submicron size filler particles, containing large surface area, into the solid polymer electrolyte host additionally creates a high degree of amorphousity and/ or lowers the degree of crystallinity which may also be thought to be due to Lewis-acid-base interaction between ceramic surface states and polymer segments [Scrosati et al 2000; Croce 1998, 2001; Golodnitsky et al 2002]. Hence, in addition to usual space charge effects of the dispersoid particles, the increased amorphousity also supports the conductivity enhancement in terms of increased ionic mobility through amorphous phase. As a consequence of dispersal of nano-sized SiO₂ particles, a two-fold increase in the room temperature conductivity was achieved further in NCPE membrane: 95[90 PEO: 10AgNO₃] : 5 SiO₂ with σ ~ 8.8 x 10⁻⁶ S.cm⁻¹. This has been referred to as Optimum Conducting Composition (OCC) NCPE membrane. The decrease in the ionic conductivity for SiO₂ concentrations higher than 5 wt. (%) can be attributed to the usual blocking effect of the filler particles [Bunde et al 1985]. Physically, OCC NCPE film appeared relatively more stable/ flexible mechanically than the SPE-host film. Improvements in the physical properties in composite polymer electrolytes due to dispersal of filler particles
Fig. 5.7: Room temperature conductivity of hot-pressed NCPE membranes: \((1-x)\) \((90\text{ PEO}: 10\text{ AgNO}_3): x\text{ SiO}_2\), as a function of \text{SiO}_2\ concentration (wt. %).
have already been reported [Wieczorek et al 1989; Cauapno et al 1991; Croce et al 1998]. In order to identify the reason for conductivity enhancement in OCC NCPE, ionic mobility ($\mu$) was determined at room temperature using TIC technique and mobile ion concentration ($n$) was evaluated from $\sigma$ & $\mu$ data, as before. Fig. 5.8 shows the 'log $\mu$ - x' and 'log $n$ - x' plots for NCPE membranes: (1-x) [90 PEO: 10 AgNO$_3$]: x SiO$_2$. Table 5.2 lists the room temperature values of $\sigma$, $\mu$, $n$ for SPE host & OCC NCPE membranes along with $t_{on}$ and $F_a$ values (to be discussed below). One can clearly note again that the overall increase in $\sigma$ of OCC NCPE is due to a moderate increase in $\mu$ (indicative of increase in the degree of amorphousity in the polymeric electrolyte host) and increase of approximately one order of magnitude in $n$ (indicative of usual space charge double layer effect and/or dissociation of more number of Ag$^+$-ions from the salt) as a result of favorable structure acquired by the system. In order to confirm the salt complexation in the polymeric electrolyte host, X-ray diffraction analysis was done on OCC NCPE, SPE host and pure PEO film materials and the diffraction patterns are shown in Fig. 5.9. On a closer inspection, it can be noted that some of the peaks of pure PEO became relatively broader as well as less-prominent/ feeble after salt complexation/ SiO$_2$ dispersal. This is usually attributed to the increase (decrease) in the degree of amorphousity (crystallinity) and also confirmed the salt complexation as well as to some extent, dispersal of nano-SiO$_2$ in the polymeric host. However, the characteristic peaks belonging to AgNO$_3$ and SiO$_2$ could not be noticed distinctly in the XRD pattern which may probably be due to their presence in the relatively low percentage in the system as compared to PEO and/or overlapping of some of their main peaks with those of PEO. SEM micrographs, as shown in Fig. 5.10, indicated almost smooth surface morphology which is closely related to the reduction of crystallinity, as mentioned earlier. Fig. 5.11 shows the DSC thermograms for OCC NCPE: [95 (90PEO: 10AgNO$_3$): 5 SiO$_2$] which exhibits a broad endothermic peak of PEO at ~ 70 °C, as before.

5.2.2 Temperature dependent studies on the basic ionic parameters

(i) Solid Polymer Electrolyte (SPE) membranes:

(1-x) PEO: x [0.7(0.75AgI: 0.25AgCl): 0.3 M] (M ≡ Rb, K)

In order to explain the mechanism of ion transport in two OCC SPEs, temperature dependent studies on the basic ionic parameters: $\sigma$, $\mu$, $n$ have been done. Fig. 5.12 (a & b) shows the temperature dependent conductivity plots for different compositions of the two SPE films: (1-x) PEO : x [0.7(0.75AgI:0.25AgCl):0.3 M], (M ≡ Rb, K). The 'log $\sigma - 1/T$' variations can be expressed by following general Arrhenius equation:
Fig. 5.8: 'Log $\mu$ - $x$' and 'log $n$- $x$' plots for hot-pressed NCPE films: [(1-$x$) (90 PEO: 10 AgNO$_3$): $x$ SiO$_2$].
Table 5.2: Room temperature (27°C) values of some basic ionic parameters for the hot-pressed membranes of solid polymer electrolyte (SPE) host: (90 PEO: 10 AgNO₃) and nano-composite polymeric electrolyte (NCPE) OCC: 95 (90 PEO: 10 AgNO₃): 5 SiO₂ and σ-value of pore PEO.

<table>
<thead>
<tr>
<th>System</th>
<th>σ</th>
<th>μ</th>
<th>n</th>
<th>t&lt;sub&gt;ion&lt;/sub&gt;</th>
<th>E&lt;sub&gt;a&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Polymer: Poly(ethylene oxide) PEO</td>
<td>3.2 x 10⁻⁹</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SPE host:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(90 PEO: 10 AgNO₃)</td>
<td>4.03 x 10⁻⁵</td>
<td>(3.6 ± 1) x 10⁻³</td>
<td>6.99 x 10¹⁵</td>
<td>~ 0.90</td>
<td>0.38</td>
</tr>
<tr>
<td>NCPE OCC:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>95(90 PEO:10AgNO₃):5 SiO₂</td>
<td>8.8 x 10⁻⁶</td>
<td>(4.8 ±1) x 10⁻³</td>
<td>1.12 x 10¹⁶</td>
<td>~ 0.90</td>
<td>0.32</td>
</tr>
</tbody>
</table>
Fig. 5.9: XRD patterns: (a) pure PEO, (b) SPE host: (90 PEO: 10 AgNO₃), (c) NCPE OCC: [95 (90 PEO: 10 AgNO₃) : 5 SiO₂].
Fig. 5.10: SEM images for OCC NCPE: [95 (90 PEO: 10 AgNO₃) : 5 SiO₂] at two resolutions.
Fig. 5.11: DSC thermograms for OCC NCPE: [95 (90 PEO: 10 AgNO₃) : 5 SiO₂].
Fig. 5.12 (a): 'Log σ- 1/T' Arrhenius plots for SPE films with different salt concentrations (x): (1-x) PEO : x [0.7(0.75AgI:0.25AgCl):0.3Rbl; x = 10 (▲), 20 (○), 30 (●), 40 (△), 50 (○). Top inset: Variation of activation energy (E_a) as a function of x.
Fig. 5.12 (b): 'Log $\sigma - 1/T''$ Arrhenius plots for SPE films with different salt concentrations ($x$): $(1-x)$ PEO : $x$ [0.7(0.75AgI: 0.25AgCl): 0.3 KI]; $x$ = 10 ($\uparrow$), 20 ($\Box$), 30 ($\bullet$), 40 ($\Delta$), 50 ($\circ$). Top inset: Variation of activation energy ($E_a$) as a function of $x$. 
\[ \sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) \quad \text{[S.cm}^{-1}\text{]} \quad (5.1) \]

where \( E_a \) is the activation energy (in eV) involved in the thermally activated conductivity process and can be computed from the least square fitting of the data. The activation energy values for different compositions of the two SPEs are plotted as top-inset in both the figures. One can note that the activation energy \( (E_a) \) values \( \sim 0.62 \) & \( 0.86 \) eV for two OCC SPEs (also listed in Table 5.1) are minima as compared to those for other SPE film compositions. This is further indicative of a relatively easier ion migration in OCC SPEs as a consequence of increased amorphous phase.

The ionic mobility \((\mu)\) and mobile ion concentration \((n)\) of both the OCC SPEs have also been measured as a function of temperature. \( \log \mu = 1/T \) and \( \log n - 1/T \) variations for the two SPE membranes are shown in Fig. 5.13 (a & b) which can be expressed by following Arrhenius equations:

**OCC SPE: 70 PEO: 30 \([0.7(0.75\text{AgI}:0.25\text{AgCl}):0.3 \text{Rbl}]\)**

\[
\begin{align*}
\mu (T) &= 8.69 \times 10^2 \exp (-0.31/kT) \quad [\text{cm}^2\text{.V}^{-1}\text{.s}^{-1}] \\
n (T) &= 5.27 \times 10^9 \exp (-0.32/kT) \quad [\text{cm}^{-3}] 
\end{align*}
\]

**OCC SPE: 70 PEO: 30 \([0.7(0.75\text{AgI}:0.25\text{AgCl}):0.3 \text{KI}]\)**

\[
\begin{align*}
\mu (T) &= 1.55 \times 10^{-2} \exp (-0.06/kT) \quad [\text{cm}^2\text{.V}^{-1}\text{.s}^{-1}] \\
n (T) &= 1.18 \times 10^{29} \exp (-0.79/kT) \quad [\text{cm}^{-3}] 
\end{align*}
\]

where the pair of numerals: \((0.31 & 0.06)\) and \((0.32 & 0.79)\) in the arguments of exponentials are the energies in eV, involved in the two separate thermally activated processes and as before, designated as the energy of migration \((E_m)\) and energy of formation \((E_f)\) respectively. It is obvious from the figure that \( n \) increased with increasing temperature in both OCC SPEs which may be attributed to the fact that many of \( \text{Ag}^+ \) ions, loosely entangled with the polymeric chain, got themselves detached as the temperature increased and became available for conduction. \( \mu \) also increased with temperature for OCC SPE: 70PEO: 30 \([0.7(0.75\text{AgI}:0.25\text{AgCl}):0.3 \text{Rbl}]\) but remained almost unaltered for OCC SPE: 70 PEO: 30 \([0.7(0.75\text{AgI}:0.25\text{AgCl}):0.3 \text{KI}]\). Increase in \( \mu \) may be a consequence of structural expansion of the polymeric host as well as increase in the kinetic energy of mobile ions with increasing temperature. The ionic transference number \((t_{\text{ion}})\) in two OCC SPE membranes was also evaluated at room temperature and above (i.e. 30, 35, 40, 45, 50, 55, 60 °C) using d.c. polarization TIC technique, as mentioned in earlier.
Fig. 5.13: ‘Log $\mu - 1 / T$’ (○) and ‘log $n - 1 / T$’ (●) plots for OCC SPEs: (a) 70 PEO: 30 [0.7(0.75AgI: 0.25AgCl): 0.3 Rbl], (b) 70 PEO: 30 [0.7(0.75AgI:0.25AgCl) : 0.3 KI].
Figs. 5.14 (a & b) shows the ‘current vs time’ plots for OCC SPEs: 70 PEO: 30 [0.7 (0.75AgI:0.25AgC):0.3 RbI] and 70 PEO: 30 [0.7 (0.75AgI:0.25AgC):0.3 KI], obtained at different temperatures (as indicated in the parenthesis) with peak current (I_T) values. One can obviously notice that I_r-values at all temperatures decreased rapidly and then leveled-off to a minimum residual value of current. The rapid initial drop in the current has been due to the polarization of mobile Ag⁺-ions of the system subjected to a fixed external d.c. potential (~0.5 V). The extent of ionic current I_ion was known from each TIC-plot and t_00 was evaluated with the help of following equation:

\[ t_00 = \frac{I_00}{I_T} \]  \hspace{1cm} (5.6)

On substituting I_00 & I_T values, t_00 ~ 0.98 (listed in Table 5.1), obtained for both OCC SPEs at all temperatures of measurements, also indicated as top-insets in Fig. 5.14 (a & b). One can clearly note that t_00 is very close to unity, thus, indicative of the fact that the two OCC SPEs remained purely ionic in the temperature range 27 - 60 °C with ~ 98% of Ag⁺-ions in the system may probably be participating in the conduction process. As observed before, the time elapsed for I_T to approach a minimum value of the current got prolonged as the sample temperature increased. The reason for this has already mentioned, since the mobile ions would be more agitated thermally at higher temperatures, would require relatively longer, time to get polarized with a fixed value of d.c. potential applied across the sample. Also, the magnitude of peak current (I_T) increased as the sample got hot, as also observed earlier. This may be attributed to the increase in n and/or ionic drift velocity (v_d). These experimental results on t_00 was used to evaluate v_d at different temperatures, as before. Fig. 5.15 (a & b) shows ‘log v_d - 1/T’ plot for the two OCC SPEs: 70 PEO: 30 [0.7 (0.75AgI:0.25AgC):0.3 RbI] and 70 PEO: 30 [0.7 (0.75AgI:0.25AgC):0.3 KI], which can be expressed by following Arrhenius type equations respectively:

\[ v_d = 1.78 \times 10^{10} \exp (-0.30/kT) \quad [\text{cm.s}^{-1}] \]  \hspace{1cm} (5.7)

\[ v_d = 1.49 \times 10^{5} \exp (-0.06/kT) \quad [\text{cm.s}^{-1}] \]  \hspace{1cm} (5.8)

where the numerals: 0.30 and 0.06 are the energy (E_d) in eV, involved in these thermally activated process for the two OCC SPEs. As already discussed, since, v_d is directly proportional to \( \mu \) at a fixed external d.c. electric field, ‘log v_d - 1/T’ and ‘log \( \mu \) - 1/T’ variations and the energies: E_d & E_m, involved in the two separate thermally activated
Fig. 5.14 (a): ‘Current vs time’ plots for OCC SPE: 70 PEO: 30 [0.7(0.75AgI:0.25AgCl): 0.3 RbI]. Top inset: Ionic transference number (ton) values at different temperatures.
Fig. 5.14 (b): 'Current vs time' plots for OCC SPE: 70 PEO: 30 [0.7(0.75AgI:0.25AgCl) : 0.3 KI]. Top inset: Ionic transference number (t_{ion}) values at different temperatures.
Fig. 5.15: ‘Log $v_d - 1/T$’ plots for OCC SPEs: (a) 70 PEO: 30 [0.7(0.75AgI:0.25AgCl): 0.3 Rbl], (b) 70 PEO: 30 [0.7(0.75AgI:0.25AgCl) : 0.3 KI].
processes (Figs. 5.13 & 5.15) for both the OCC SPEs, are almost identical. To check again that during the d.c. polarization measurements the externally applied potential should not cause any polarization build-up effect in the sample, the applied voltages (below 0.5 V) applied across the sample were plotted against instant current values obtained. ‘I vs V’ plots, shown in Figs. 5.16 (a & b) for both the OCC SPEs clearly illustrated that the current varied linearly with applied voltage following the Ohm’s law very well and hence, indicative of no-polarization-charge build-up effects in the sample materials.

(ii) Nano-Composite Polymer Electrolyte (NCPE) membranes:

(1-x) [90PEO: 10AgNO₃] : x SiO₂

Fig. 5.17 shows the temperature dependent conductivity variations for NCPE membranes: (1-x) [90 PEO: 10 AgNO₃]: x SiO₂ as well as that of SPE host: (90 PEO: 10AgNO₃). The equations, governing the straight line portion of Arrhenius plots ‘log σ - 1/T’ for SPE host and NCPE OCC films, can be expressed as:

\[ \text{SPE host: } \sigma (T) = 1.04 \times 10^4 \exp (-0.38/kT) \quad \text{[S.cm}^{-1}\text{]} \quad (5.9) \]

\[ \text{NCPE OCC: } \sigma (T) = 2.88 \times 10^6 \exp (-0.32/kT) \quad \text{[S.cm}^{-1}\text{]} \quad (5.10) \]

where \( E_a = 0.38 \) & 0.32 eV are the activation energy values (listed in Table 5.2) for SPE host and NCPE OCC materials respectively. The activation energy values for other NCPE membranes of different SiO₂ concentrations, computed likewise from the respective ‘log \( \sigma - 1/T \)’ plots, are plotted as inset in Fig. 5.17. It can be clearly noted that the activation energy for OCC NCPE is not only minimum but has been reduced substantially from that of the pure host. This is indicative of a relatively easier ion transport in the OCC NCPE as compared to pure SPE.

Fig. 5.18 shows ‘log \( \mu - 1/T \)’ and ‘log \( n - 1/T \)’ plots for the hot-pressed NCPE OCC membrane: 95[90 PEO: 10AgNO₃] : 5 SiO₂ and can be expressed by following Arrhenius type equations:

\[ \mu (T) = 2.12 \times 10^{11} \exp (+0.49/kT) \quad \text{[cm}^2\text{.V}^{-1}.\text{s}^{-1}\text{]} \quad (5.11) \]

\[ n (T) = 3.22 \times 10^{29} \exp (-0.79/kT) \quad \text{[cm}^{-3}\text{]} \quad (5.12) \]

As mentioned before, the numerals 0.47 & 0.78 are the energies (in eV), referred to as the energy of migration (\( E_m \)) and energy of formation (\( E_f \)) respectively and the signs appeared in
Fig. 5.16: ‘$I_T$ vs $V$’ plot for the hot-pressed polymer electrolyte OCC: (a) 0.7 PEO : 0.3 [0.7(0.75AgI:0.25AgCl) : 0.3 Rbl]; (b) 0.7 PEO : 0.3 [0.7(0.75AgI:0.25AgCl) : 0.3 KI].
Fig. 5.17: 'Log $\sigma - 1/T$' plots for SPE host: [90 PEO: 10 AgNO$_3$] (■); NCPE membranes: (1- $x$) (90 PEO: 10 AgNO$_3$): $x$ SiO$_2$; $x$ = 1 ( ), 2 (Δ), 3 (□), 5 (○), 10 (+), 15 (×). Top inset: Variation of activation energy ($E_a$) as a function of $x$. 
Fig. 5.18: 'Log $\mu - 1/ T$ (○); 'log $n - 1/ T$ (●) plots for NCPE OCC: 95 (90 PEO: 10
$\text{AgNO}_3$: 5 $\text{SiO}_2$)
the argument have the usual meaning. It can be obviously noted from the Fig. 5.18 that $\mu$ (n) decreased (increased) as the temperature increased. The decrease in $\mu$ with increasing temperature, in contrast to what has been observed earlier (Fig. 5.13a) for OCC SPE: 70 PEO: 30 [0.7 (0.75AgI:0.25AgC):0.3 Rbl], may probably due to the decrease in the preferred conduction pathways and/or decrease in the degree of amorphousity at higher temperatures. The reason for the increase in n may be same as mentioned earlier for the two OCC SPEs and/or a consequence of dissociation of Ag$^+$ ions from the ionic salt AgNO$_3$ in larger number as temperature increased. The ionic transference number ($t_{ion}$) for OCC NCPE was evaluated at room temperature and above (viz. 30, 35, 40, 45, 50, 55, 60 °C) using d.c. polarization TIC technique, as before. Fig. 5.19 shows the ‘current vs time’ plots for OCC NCPE: 95[90PEO:10AgNO$_3$]: 5 SiO$_2$ at different temperatures. As observed earlier, at all temperatures of measurements $I_T$ decreased rapidly, then leveled-off to a minimum residual value. The rapid initial drop in the current is due to polarization of the mobile Ag$^+$ ions in the system subjected to a fixed external d.c. potential (~ 0.5 V). Substituting ionic current $I_{ion}$ and the total current $I_T$ values in eq. (5.6), $t_{ion} \sim 0.98$ for OCC NCPE at all temperatures, as also shown as inset in Fig. 5.19. $t_{ion}$ is very close to unity, hence, indicative of OCC NCPE remaining purely ionic at least in the temperature range 27 - 60 °C and also approximately 98% of Ag$^+$ ions in the system might be involved in the conduction process. As before, the results of $t_{ion}$ measurements were used to evaluate ionic drift velocity $v_d = I_{ion}/A n q$, at different temperatures where $I_{ion}$ & n-data were obtained from Fig. 5.19 and Fig. 5.18 respectively. Fig. 5.20 shows ‘log $v_d$ - 1/T’ plot for OCC NCPE: 95[90 PEO: 10AgNO$_3$] : 5 SiO$_2$ which can be expressed by following Arrhenius type equation:

$$v_d = 1.03 \times 10^{-4} \exp (0.46/kT) \quad [cm.s^{-1}]$$  \hspace{1cm} (5.13)\\

where 0.46 in eV is the energy ($E_d$), involved in the thermally activated process. As already pointed out, at fixed external d.c. field, $v_d \propto \mu$, both ‘log $v_d$ - 1/T’ and ‘log $\mu$ - 1/T’ plots look alike and the energies: $E_d$ & $E_m$ are fairly close to each other. As mentioned, in this d.c. polarization measurements on ionic/ superionic systems, including polymer electrolytes, it has been always assumed that the initial total current $I_T$, obtained in the ‘current-time’ TIC plots, would be directly proportional to the applied d.c. voltage (V) i.e. the Ohm’s law would be valid and hence, the effect of polarization charge build-up would be negligible during the measurements. ‘$I_T$ vs V’ plot for the OCC NCPE, as shown in Fig. 5.21, clearly indicated that the current varies linearly with applied voltage and hence, the effect of polarization charge build up has been negligible.
Fig. 5.19: 'Current vs time' plots for NCPE OCC: 95 (90 PEO: 10 AgNO$_3$) : 5 SiO$_2$. Top inset: Ionic transference number ($t_{\text{ion}}$) values at different temperatures.
Fig. 5.20: 'Log $v_d - 1/T$' plot for the OCC NCPE: 95 (90 PEO: 10 AgNO$_3$) : 5 SiO$_2$. 
Fig. 5.21: $I_T$ vs $V$ plot for the NCPE OCC: 95 (90 PEO: 10 AgNO$_3$) : 5 SiO$_2$. 
5.3 Conclusion

Two new Ag\textsuperscript{+} ion conducting polymer electrolyte systems viz. Solid Polymer Electrolyte (SPE): 70 PEO: 30 [0.7(0.75AgI:0.25AgCl):0.3MI] (M \equiv Rb, K); Nano-Composite Polymer Electrolyte (NCPE): 95[90 PEO: 10AgNO\textsubscript{3}] : 5 SiO\textsubscript{2} have been synthesized employing a novel hot-press/ solvent free/ dry technique. Material characterization/ phase identification and the mechanism of ion transport have been studied. The ionic transference number measurements by d.c. polarization clearly indicated the fact that both the polymeric electrolyte membranes are almost pure ion conducting materials with majority of Ag\textsuperscript{+} ions take part in conduction process. Hence, both the polymeric electrolyte membranes may prove to the suitable candidates for fabricating all-solid-state thin film battery, as discussed in the subsequent chapter.