Ion Transport Property Studies on New Ag⁺ Ion Conducting
Quaternary Solid Electrolyte Systems:

\[ x [0.75 AgI:0.25 AgCl]: (1-x) KI \]

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4.3 Conclusion
4.1 Introduction

This chapter discusses the results of the second Ag⁺-ion conducting quaternary systems: x [0.75AgI: 0.25AgCl]: (1-x) KI synthesized identically using the alternate host: [0.75AgI: 0.25AgCl] instead of the traditional host salt AgI. The routes of sample preparation adopted have been similar to the preceding quaternary solid electrolyte systems, as described in Chapter 2. The highest conducting composition, referred to as the Optimum Conducting Composition (OCC) for this quaternary system, has also been identified from the compositional-dependent conductivity studies. The well-known ternary superionic solid KAg₄I₅ has been prepared in the identical manner for direct comparison of the room temperature conductivity behaviour with that of the newly synthesized quaternary OCC. The materials characterization/phase identification studies as the quaternary OCC sample have also been done using X-ray Diffraction (XRD) and Differential Thermal Analysis (DTA) techniques. The basic ionic parameters viz. conductivity (σ), mobility (μ), mobile ion contraction (n), transference number (t_on), drift velocity (v_d) etc. have been determined with the help of the techniques already mentioned. The temperature dependent measurements on these ionic parameters have also been carried out and the ion transport behavior in the newly synthesized quaternary systems: x [0.75AgI: 0.25AgCl]: (1-x) KI has been explained as before. As expected, both the quaternary solid electrolyte systems exhibited identical ion transport characteristics.

4.2 Results and discussion

4.2.1 Compositional dependent studies on some basic ionic parameters of quaternary solid electrolyte systems: x [0.75AgI: 0.25AgCl]: (1-x) KI

Fig. 4.1 shows ‘log σ – x’ variations at room temperature for the quaternary solid electrolyte systems: x [0.75AgI: 0.25AgCl]: (1-x) KI, prepared by routes #1, 2, 3. Akin to quaternary solid electrolyte systems of Chapter 3, three plots look almost alike and exhibit the usual variation. A conductivity maxima has been found at x = 0.7 for all the samples prepared by the three routes and a minima at x = 0.8. As before, σ – values for the quaternary composition: 0.7[0.75AgI: 0.25AgCl]: 0.3KI, prepared by route #4 and for the ternary composition: 0.8AgI: 0.2KI, prepared by routes #1, 2, 4 (as mentioned in Section 2) have also been plotted in Fig.4.1, for direct visualization. The significant features of these studies are outlined below:
Fig. 4.1: 'Log $\sigma - x$' plots for quaternary systems: $x[0.75\text{AgI}:0.25\text{AgCl}]$: $(1-x)$ KI prepared by routes #1 (■), #2 (▲), #3 (●). The conductivity values for quaternary OCC: $0.7[0.75\text{AgI}:0.25\text{AgCl}]$: 0.3 KI prepared by route #4 (•) and ternary system: $0.8\text{AgI}:0.2\text{KI}$ prepared by routes: #1(●), #2(○), #4(+) are also plotted. (Refer to the text for details).
• For the quaternary system i.e. the solid solution of the alternate host: [0.75AgI: 0.25AgCl] with KI, the molar composition at $x = 0.7$ prepared by route #1, exhibited highest conductivity $\sigma \sim 5.9 \times 10^{-3}$ Scm$^{-1}$ at room temperature (27°C). This has been referred to as the Optimum Conducting Composition (OCC). The solid solution reactions of the same composition involving prolonged heating of the melt (routes ##2 & 4) as well as the sample prepared by simple physical mixing (route #3) resulted into the quaternary systems of relatively lower conductivity values.

• As a matter of fact, for the ternary systems: $x$ AgI: $(1-x)$ KI, the composition at $x = 0.8$ results into the well-known superionic solid KAg$_4$I$_5$ with highest room temperature conductivity [Owens and Argue 1967, Bradely and Greene 1967]. The solid solution reactions for this ternary composition: 0.8AgI: 0.2KI have been carried following routes ##1, 2, 4, as mentioned. The conductivity results of solid solution ternary solids prepared by three different routes have been just other way round from those for the above quaternary system. The highest conducting superionic solid: KAg$_4$I$_5$ could be prepared only when a prolonged (~1 week, i.e. route #4) heating has been carried out, akin to what has been reported in the literature [Owens and Argue 1967, Bradely and Greene 1967] as well as to the preceding quaternary OCC (Chapter 3). The ternary superionic solid: KAg$_4$I$_5$, prepared by # 4, exhibited conductivity $\sigma \sim 1.1 \times 10^{-2}$ Scm$^{-1}$ at 27°C, approximately one order of magnitude lower than that reported in the literature. This may be due to the same reasons i.e. use of the precursor chemicals of relatively lower purities. Nevertheless, these chemicals are relatively much cheaper and hence, cost effective. The ternary system: 0.8AgI: 0.2KI, prepared by other two routes (## 1, 2), exhibited of much lower conductivity values. This is probably due to the insufficient heating and hence, incomplete solid solution reaction.

The conductivity of the newly synthesized quaternary OCC: 0.7[0.75AgI: 0.25AgCl]: 0.3KI has been approximately one-half that of the ternary KAg$_4$I$_5$. However, as noticed for the quaternary solid electrolyte system of Chapter 3, the conductivity of this quaternary system also remained almost stable for more than 100 hrs. in the prevailing ambient conditions. While the conductivity of KAg$_4$I$_5$ decreased from $10^{-2} \rightarrow 10^{-5}$ in the order of magnitude in this duration. The conductivity-stability plot for the two systems are shown in Fig. 4.2. As already pointed out in the preceding chapter for RbAg$_4$I$_5$, the instability in $\sigma$-value KAg$_4$I$_5$ has been due to its being thermodynamically unstable around room temperature particularly in the humid ambience as it gets dissociated into following low conducting compounds:

$$2 \text{KAg}_4\text{I}_5 \rightarrow \text{K}_2\text{AgI}_3 + 7 \text{AgI}$$
Fig. 4.2: Conductivity-stability plot for quaternary electrolyte OCC: 0.7[0.75AgI: 0.25AgCl]: 0.3 KI (●) and ternary superionic solid: KAg₄I₅ (▲).
In order to identify the reason for $\sigma$-maxima at $x = 0.7$ in \(\log \sigma - x\) plot of Fig. 4.1, giving rise to the quaternary solid electrolyte OCC, $\mu$ and $n$ measurements have been carried out at room temperature for different compositions ($x$). Fig. 4.3 shows $\log \mu - x$ and $\log n - x$ plots for the quaternary systems: $x [0.75\text{AgI}: 0.25\text{AgCl}]: (1-x) \text{KI}$ prepared by route #1. One can obviously note that $\mu$ remained almost unaltered for different compositions (except for a moderate peak at $x = 0.7$), while $\log n - x$ followed the variation almost analogous to $\log \sigma - x$, with $n$-maxima appearing at $x = 0.7$. Table 4.1 lists the room temperature values of these ionic parameters for the quaternary OCC as well as those of the pure host salt [Agrawal et al. 1994] along with the values of ionic transference number ($t_{on}$) and activation energy ($E_a$) (to be discussed below). The data, listed in the table for the pure host and the quaternary superionic OCC, are self explanatory. One can clearly identify that the overall increase in $\sigma$ for the quaternary electrolyte OCC is predominantly due to the increase in $n$. This, in turn, indicated the fact that a relatively larger number of mobile ions got available for conduction in the OCC composition and probably the structural factor has again been responsible for this increase in $n$, akin to preceding quaternary OCC: $0.7[0.75\text{AgI}: 0.25\text{AgCl}]: 0.3\text{Rbl}$.

### 4.2.2 Phase identification and materials characterization studies

Fig. 4.4 shows X-ray diffraction patterns for the quaternary OCC: $0.7[0.75\text{AgI}: 0.25\text{AgCl}]: 0.3\text{KI}$, host salt: 'a quenched/ annealed [0.75\text{AgI}: 0.25\text{AgCl}] mixed system/ solid solution' and pure KI. Table 4.2 lists $d$-values and relative intensities for some prominent diffraction peaks. These results clearly indicate the formation of a new compound and also confirm the existence of polycrystalline phase in OCC. The DTA thermogram for the newly synthesized quaternary OCC: $0.7[0.75\text{AgI}: 0.25\text{AgCl}]: 0.3\text{KI}$ is shown in Fig. 4.5. A small shallow endothermic peak $\sim 140 ^\circ C$ is indicative of fractional presence of unreacted host salt, while the second endothermic peak $\sim 250 ^\circ C$ may be attributed to the melting point of the new compound.

### 4.2.3 Temperature dependent studies on ionic parameters: $\sigma$, $\mu$, $n$, $t_{on}$ $v_d$ of quaternary solid electrolyte systems: $x [0.75\text{AgI}: 0.25\text{AgCl}]: (1-x) \text{KI}$

Fig. 4.6 shows $\log \sigma - 1/T$ plots for different compositions of the quaternary solid electrolyte systems: $x [0.75\text{AgI}: 0.25\text{AgCl}]: (1-x) \text{KI}$ synthesized through route #1. Similar plot for the pure quenched host: [0.75\text{AgI}: 0.25\text{AgCl}] has been reproduced in Fig. 4.6 for direct comparison [Agrawal et al. 1994]. One can obviously note the gradual increase in conductivity as the temperature increased. No abrupt changes from the straight line behavior were observed in $\log \sigma - 1/T$ plots of all the compositions. This is indicative of stabilization.
Fig. 4.3: 'Log $\mu - x$' and 'log $n - x$' plots for quaternary solid electrolyte systems: $x$ \([0.75\text{AgI} : 0.25\text{AgCl}] : (1-x) \text{KI}\).
Table 4.1: Room temperature (27 °C) values of some important ion transport parameters of the pure host: 0.75AgI:0.25AgCl [Agrawal et al 1994]; fast Ag⁺ ion conducting quaternary solid electrolyte OCC: 0.7[0.75AgI:0.25AgCl]:0.3KI.

<table>
<thead>
<tr>
<th>System</th>
<th>σ (S cm⁻¹)</th>
<th>μ (cm² V⁻¹ s⁻¹)</th>
<th>n (cm⁻³)</th>
<th>t&lt;sub&gt;ion&lt;/sub&gt;</th>
<th>E&lt;sub&gt;a&lt;/sub&gt; (eV)</th>
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</thead>
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<tr>
<td>Host salt: [0.75AgI: 0.25AgCl]</td>
<td>3.1x10⁻⁴</td>
<td>(2.4±1)x10⁻²</td>
<td>8.0x10¹⁶</td>
<td>~ 1</td>
<td>0.23</td>
</tr>
<tr>
<td>Newly synthesized quaternary electrolyte OCC: 0.7[0.75AgI: 0.25AgCl]: 0.3KI</td>
<td>5.9x10⁻³</td>
<td>(7.6±1)x10⁻²</td>
<td>4.87x10¹⁷</td>
<td>~ 1</td>
<td>0.11</td>
</tr>
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</table>
Fig. 4.4: XRD patterns for: (a) quaternary electrolyte OCC: 0.7[0.75Agl:0.25AgCl]: 0.3 KI, (b) pure host: [0.75Agl:0.25AgCl], (c) pure KI.
Table 4.2: XRD diffraction data (d-value & relative intensity) for pure host: [0.75AgI:0.25AgCl], KI and quaternary solid electrolyte OCC: 0.7[0.75AgI:0.25AgCl]: 0.3 KI.

<table>
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<tr>
<th>Host d</th>
<th>I/I₀</th>
<th>KI d</th>
<th>I/I₀</th>
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Fig. 4.5: DTA thermogram for quaternary solid electrolyte OCC: 0.7[0.75AgI; 0.25AgCl]; 0.3 KI.
Fig. 4.6: 'Log $\sigma-1/T$' Arrhenius plots for different molar compositions of quaternary solid electrolyte systems: $x$ [0.75AgI:0.25AgCl] : (1-$x$) KI, prepared by route # 1; $x = 0.1$ (■), 0.2 (▲), 0.3 (×), 0.4 (Δ), 0.5 (●), 0.6 (+), 0.7 (○), 0.8 (-), 0.9 (□) and pure quenched host (○). Top inset: Activation energy ($E_a$) as a function of $x$. 
of the host as well as formation of new compounds. XRD analysis on OCC sample confirmed the formation a new compound in the polycrystalline phase. The conductivity values of OCC remained almost temperature independent and fairly high from that of other compositions at all temperatures. However, a slight upward change in the slope was observed around 130-140 °C, which was also been reflected in the DTA thermogram of Fig. 4.5 and as discussed above this is due to the fractional presence of unreacted host. The Arrhenius equation governing the thermally activated conductivity process in the quaternary superionic OCC: 0.7[0.75AgI: 0.25AgCl]: 0.3KI can be expressed as:

\[ \sigma(T) = 5.7 \times 10^1 \exp \left( -0.11 \right) \frac{\text{S.cm}^{-1}}{\text{kT}} \]  

where \( E_a = 0.11 \) eV is the activation energy computed by least square fitting of the data and listed earlier in Table 4.1. Similar equations have been set-up for other ‘log \( \sigma/\text{T} \)’ Arrhenius plots and the computed activation energy \( (E_a) \) values are plotted as a function of \( x \), as inset in Fig. 4.6. It can be clearly noticed that the activation energy for the quaternary superionic OCC is minimum as well as substantially lower than that of the pure host (Table 4.1). This is indicative of a relatively easier ion transport in quaternary superionic solid system. \( \mu \) and \( n \) values for the quaternary solid electrolyte OCC: 0.7[0.75AgI:0.25AgCl]: 0.3KI have also been determined at different temperatures. ‘log \( \mu /\text{T} \)’ and ‘log \( n/\text{T} \)’ plots are shown in Fig. 4.7. One can note a substantial rise in \( \mu \) and a slight decrease in \( n \) as the temperature increased. The increase in \( \mu \) may be attributed as a consequence of lattice expansion as well as increase in the kinetic energy of the mobile ions as a result of heating, while decrease in \( n \) may be due to some kind of association of mobile ions in the crystal lattice. The equations governing the Arrhenius type variations of \( \mu \) and \( n \) can be expressed as:

\[ \mu(T) = 5.75 \times 10^1 \exp \left( -0.173 \right) \frac{\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}}{\text{kT}} \]  

\[ n(T) = 1.33 \times 10^{17} \exp \left( +0.043 \right) \frac{\text{cm}^{-3}}{\text{kT}} \]

As mentioned before, the numerals: 0.173 and 0.043 in the arguments of the exponential terms correspond to migration \( (E_m) \) and formation \( (E_t) \) energies in eV respectively, involved in the two separate thermally activated processes and the (-) ve/ (+) ve signs have the same meaning. The ionic transference number \( t_{\text{ion}} \) measurements have also been carried out at various temperatures using d.c. polarization method. Fig. 4.8 shows the ‘current vs time’ plots for quaternary OCC: 0.7[0.75AgI:0.25AgCl]: 0.3KI recorded at various temperatures.
Fig. 4.7: ‘Log $\mu - 1/T$’ (□) and ‘log $n - 1/T$’ (●) plot for quaternary solid electrolyte OCC: 0.7[0.75AgI: 0.25AgCl]: 0.3 KI.
Fig. 4.8: 'Current vs time' plot for quaternary solid electrolyte OCC: 0.7 [0.75 AgI: 0.25 AgCl] : 0.3 KI at different temperatures. Top inset: Ionic transference number (t_{ion}) values at different temperatures.
As for the previous quaternary OCC, the current ($I_T$) finally approached to zero which is indicative of the fact that the system remained purely ionic at all temperatures of measurements with $t_{on} \geq 1$. However, as observed earlier, the time taken for $I_T$ to approach zero has been relatively longer for the samples at higher temperatures which is due to the same reason mentioned for the preceding quaternary solid electrolyte system, i.e. at high temperatures, the mobile ions were more thermally agitated and hence, required longer time to get polarized. Using the values of the peak current ($I_T$) in Fig. 4.8 and mobile ion concentration ($n$) data from Fig. 4.7, the ionic drift velocity ($v_d$) has been calculated at different temperatures, as before. Fig. 4.9 shows ‘log $v_d - 1/T$’ plot for the quaternary OCC: 0.7[0.75AgI:0.25AgCl]: 0.3 KI, which can be expressed by following Arrhenius type equation:

$$v_d = 6.81 \times 10^5 \exp (-0.190/kT) \quad [\text{cm.s}^{-1}] \quad (4.4)$$

where $E_d \sim 0.190$ eV is the energy involved in this thermally activated process. As mentioned, since $v_d$ is directly proportional to $\mu$, if the external dc electric field applied across the sample, is held constant. Consequently, the temperature variation of both the parameters ($\mu$ & $v_d$) would be analogous and the energies involved in the two thermally activated processes would be identical. Comparing the two Arrhenius type plots of Figs. (4.7 & 4.9), one can be clearly note that two variations looks almost analogous, also the two energy values are in very good agreement with each other. Similarly, $I_T$ vs V plot for the OCC, shown in Fig. 4.10, clearly indicates that the current varies linearly with applied voltage obeying the Ohm’s law for this system also. Hence, the $I_T$-values used for calculating $v_d$ correspond approximately to the true values free from the effects of instant polarization charge build-up due to applied dc voltage, as mentioned before.

### 4.3 Conclusion

Another new fast Ag$^+$ ion conducting quaternary solid electrolyte system: 0.7 [0.75 AgI: 0.25 AgCl]: 0.3 KI, has been investigated in place of the well-known ternary superionic solid: KAg$_3$I$_5$. An alternate host salt: ‘a quenched/ annealed [0.75AgI:0.25AgCl] mixed system/solid solution’, has been used in place of the traditional host AgI. Although, the room temperature conductivity of the newly synthesized quaternary electrolyte system is slightly lower than that of KAg$_3$I$_5$, synthesized at the present laboratory. However, the conductivity of the quaternary solid electrolyte system remained practically stable for very long time in
Fig. 4.9: 'Log $v_d - 1/T$' plot for quaternary solid electrolyte OCC: 0.7[0.75AgI: 0.25AgCl]: 0.3 KI.
Fig. 4.10: \( \text{I}_T \text{ vs } V \) plot for quaternary solid electrolyte OCC: 0.7[0.75AgI:0.25AgCl] : 0.3 KI.
the prevailing ambient conditions, while that of the ternary superionic solid KAg$_4$I$_5$ decreased by more than two orders of magnitude in 24 hrs. Moreover, the new fast Ag$^+$ ion conducting quaternary electrolyte system can be prepared much quicker than KAg$_4$I$_5$. XRD analysis confirmed the formation of a new solid solution compound in the polycrystalline phase. The ion transport behavior in the quaternary solid electrolyte system has been characterized on the basis of various ionic parameters viz. $\sigma$, $\mu$, $n$, $v_{\text{ion}}$, $v_d$ etc. Hence, based on various experimental studies it can be concluded that the newly investigated fast Ag$^+$ ion conducting quaternary solid electrolyte system exhibits far superior electrolytic properties than the ternary superionic solid KAg$_4$I$_5$, hence, it can be proved to be a better choice for solid state electrochemical device applications. All solid state batteries using this electrolyte system have been fabricated and the cell performances have been presented in Chapter 6.