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CHAPTER I

INTRODUCTION

1.1. GENERAL INTRODUCTION

The field of solid state ionics, an interdisciplinary area of physics, chemistry, material science, engineering and technology, comprises a certain new class of materials exhibiting high ionic conduction order of liquid electrolytes with negligible electronic conduction termed as fast ionic conductors (FICs) or superionic conductors (SICs) or solid electrolytes (SEs) [1-3]. FIC materials are synthesised by various techniques such as melt quench, sol-gel process, solid state reactions, thermal evaporation sputtering, etc. in different forms like bulk, powder, thin films, etc. FICs are classified based on their mobile ionic species as cationic (Ag⁺, Cu⁺, Li⁺, Na⁺, etc.) and anionic (F⁻, O²⁻, etc.) conductors and, also based on their microstructures, FICs are classified as single/ polycrystalline, glass/amorphous, composites and polymers[3-7].

For the past four decades, the study of FIC materials gained considerable importance in science & technology respectively because of their high ionic conducting nature & due to their potential applications in various electrochemical devices such as solid state batteries, membranes in ion-selective electrodes, gas sensors, electrochromic display capacitors, analog memory devices, miniature cells, power storage devices, etc [1-19].

In addition, FICs are also fascinating for physicists in understanding the high ionic conduction process by establishing a relationship between ionic conductivity & local atomic structure [1-25]. Many theoretical models have been proposed to explain their transport properties. All the above features lead to the interest of the scientists and technologists to develop new solid electrolytes suitable for particular requirements.
1.2. GENERAL FEATURES OF IONIC SOLIDS

In general, ionic conduction takes place when the field is applied across the sample, where the randomly oriented ions direct towards the applied electric field. The conduction may take place due to the presence of imperfections or defects in solids and based on the defect concept, ionic solids can be classified into two types; a) Point defects & b) Molten defects. In the point defect type of solids, ion transport is through Frenkel or Schottky defects and hence, the conductivity increases with temperature [1, 26]. These solids are called normal ionic conductors (NICs). In molten sub-lattice type of solids, all ions are available for conduction, since the number of defect or void sites in the sub-lattice are more than the number of ions and so ions can move freely from one position to another with low activation energy possessing high conductivity [1]. The other method of classification is based on the mobile ions and defects concentration (n) as a) dilute point defects, n ≤ 10^{18} cm^{-3}, considered to be normal ion conductors and b) extended defects, n = 10^{20} cm^{-3} & c) liquid-like molten sublattice, n = 10^{22} cm^{-3} considered to be fast ionic conductors.

1.3. CLASSIFICATION OF IONIC CONDUCTING SOLIDS

1.3.1. Normal ionic conductors (NICs)

NICs have low ionic conductivity of the order of 10^{-14} to 10^{-12} Scm^{-1} at ambient temperature. The ionic conduction in these compounds is mainly due to the defects such as, vacancies and interstitial ions, which are created thermally and the activation process involves both energy due to defect formation (h_d) as well as due to ion migration (h_m) [1, 26, 27]. Attempts have been made to increase the conductivity of NICs by incorporating impurities, in which ionic defects are introduced to maintain charge neutrally. The following relation gives the temperature dependence of conductivity.
\[ \sigma = \sigma_0 \exp \left( -\frac{h_f}{2kT} \right) \exp \left( -\frac{h_m}{kT} \right) \]  \hspace{1cm} (1.1)

where \( \sigma_0 \) is the pre-exponent factor and given by

\[ \sigma_0 = e^2 \nu_0 f \lambda^2 N x / k \]  \hspace{1cm} (1.2)

where \( e \) charge of the mobile ion, \( \nu_0 \) jump frequency, \( f \) correlation factor, \( \lambda \) jump distance of the charge carriers, \( N \) charge carrier density, \( x \) fraction of mobile charge carriers, \( T \) absolute temperature, \( k \) Boltzmann's constant, \( h_f \) energy of defect formation, \( h_m \) energy of defect migration.

### 1.3.2. Fast ionic conductors (FICs)

Compounds having high ionic conductivity, negligible electronic conductivity at room temperature as well as at high temperatures are called fast ionic conductors that exhibit a characteristic ionic conductivity more typical of liquid electrolytes, ranging from \( 10^{-6} \) to \( 10^{-1} \) S cm\(^{-1} \) [1]. The structure and the properties of the FICs are alike the liquid electrolytes.

The carrier ion concentration is high and almost temperature independent i.e., there is no thermally generated defects and hence, no energy is required for the formation of defects \((h_f = 0)\). Thus, conductivity equation 1.1 for the fast ionic conductors is modified according to the relation

\[ \sigma = \frac{\sigma_0}{T} \exp \left[ -\frac{h_m}{kT} \right] \]  \hspace{1cm} (1.3)

Fig.1.1 shows the plots of ionic conductivity as a function of inverse of temperature of NICs, crystalline and glassy fast ionic conductors and table 1.1 gives the comparison between the various properties of NICs and FICs.
Fig. 1.1. $\log \sigma$ vs. $1000/T$ plots of some NICs, crystalline and glassy FICs
Faraday discovered the silver sulfide $\text{Ag}_2\text{S}$ for the first time as a fast silver ion conductor [28]. Later in 1899, Nernst found that the oxygen ion exhibits high conductivity at high temperature in Yttria stabilized zirconia [29]. In 1913, Tubandt and Lorentz measured the conductivity of silver halide, which lead to the interest in search for new silver ion conductors [27]. In 1932, Tubandt reported the high ionic conductivity at high temperatures in $\text{Ag}_2\text{Se}$ and $\text{Ag}_2\text{Te}$ compounds similar to the $\text{Ag}_2\text{S}$ [30]. Till 1960, only stabilized Zirconia and silver iodide (above 420K) were known to have very...
high ionic conductivities. The conductivity of AgI abruptly increases to 0.1 S cm\(^{-1}\) at 147\(^\circ\)C, due to change in structural phase transition from \(\beta\) to \(\alpha\) phase and it is found to be more than three orders of magnitude compared to its conductivity at ambient temperature. The transition from the low conducting \(\beta\)-phase to the high conducting \(\alpha\)-phase is considered to be a breakthrough in the physics of fast ionic conductors [31,32]. Real development of fast ionic conductors is known for the past four decades due to their importance and advantageous properties in the application of various electrochemical devices. During 1966, Ag\(_2\)S\(_2\)I was found to exhibit high silver ion conductivity at room temperature [33]. In 1967, the discovery of fast ion conduction in \(\beta\)-alumina and silver ion conductors of MAg\(_4\)I\(_5\) (M= K, Rb, NH\(_4\)) were reported [34]. Bradley & Greene [20] and Owens & Argue [21] independently synthesized RbAg\(_4\)I\(_5\) that found to have very high ionic conductivity of the order of 0.3 S cm\(^{-1}\) at room temperature. Later, various kinds of cation and anion conductors, exhibiting high ionic conductivity at ambient as well as at high temperatures have been synthesized.

### 1.5. CLASSIFICATION OF FAST IONIC CONDUCTORS

Fast ionic conductors have been classified into different groups based on the type of the mobile ions (i) Anion & (ii) Cation conductors and also, these FICs are classified in different forms as, single / polycrystalline, glasses, composites and polymers [1-3].

#### 1.5.1. Anionic Conductors

In the anionic conductors, the high ionic conduction is due to the negatively charged mobile ions. Further, the high anion conducting solids are classified into fluoride and oxide ion conductors. Some of the oxide and fluoride ion conductors are given in table 1.2.
Oxygen ion Conductors (O²⁻)

Most of the oxide solid electrolytes developed based on Bi₂O₃, CeO₂, ThO₂, HfO₂ and ZrO₂, on doping with aliovalent impurities like Ca²⁺, Y³⁺, Sr²⁺, etc., have crystal structures of either fluorite type (CeO₂, ThO₂) or distorted fluorite types (Bi₂O₃, HfO₂ and ZrO₂), which are strongly temperature dependent. In CaO doped ZrO₂ system, 12 to 13 mole% of CaO content showed the maximum conductivity of 5.5 x 10⁻² Scm⁻¹ at 1273K [35]. The MgO oxide doped ZrO₂ system, 20 mole% of MgO content, showed the conductivity of 3.8 x 10⁻² Scm⁻¹ at 1273K [36]. In CaO doped ThO₂ system, 7mole% of CaO content showed the conductivity of 2 x 10⁻³ Scm⁻¹ at 1273K [37]. Also, several works have attempted by Takahashi et al. to stabilize the fluorite phase by adding various oxides such as CaO, SrO, Y₂O₃, WO₃, MoO₃, Cr₂O₃, V₂O₅, Nb₂O₅, etc.[15] The Y₂O₃, doped Bi₂O₃ system showed the conductivity as high as 1.3 x 10⁻² Scm⁻¹ at 723K [38].

Table 1.2. Some examples of oxide and fluoride ion conductors

<table>
<thead>
<tr>
<th>Type of FICs</th>
<th>Conductivity (Scm⁻¹)</th>
<th>Temp (K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen Ion Conductors</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZrO₂- Y₂O₃</td>
<td>1.2 x 10⁻¹</td>
<td>1273</td>
<td>41</td>
</tr>
<tr>
<td>Bi₂O₃-WO₃</td>
<td>1.0 x 10⁻¹</td>
<td>1023</td>
<td>42</td>
</tr>
<tr>
<td>Bi₂Ni₀.1V₀.₉O₅.₃₅</td>
<td>3.05x10⁻⁴</td>
<td>773</td>
<td>43</td>
</tr>
<tr>
<td>Bi₂Zn₀.₁V₀.₉O₅.₃₅</td>
<td>1.28x10⁻⁴</td>
<td>773</td>
<td>43</td>
</tr>
<tr>
<td>Fluoride Ion Conductors</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>β-PbF₂</td>
<td>-1.5</td>
<td>600</td>
<td>44</td>
</tr>
<tr>
<td>CaF₂</td>
<td>-3 x 10⁻⁶</td>
<td>600</td>
<td>45</td>
</tr>
<tr>
<td>LaF₃</td>
<td>2x10⁻²</td>
<td>1000</td>
<td>46</td>
</tr>
<tr>
<td>Zr-Ba-Cs-F</td>
<td>1.0x10⁻⁵</td>
<td>473</td>
<td>47</td>
</tr>
<tr>
<td>Zr-Th-Ba-Li-F</td>
<td>1.0x10⁻⁴</td>
<td>473</td>
<td>48</td>
</tr>
</tbody>
</table>
Fluoride ion conductors (F⁻)

In the fluoride ion conductors, the mobile charge carriers are Fluorine ions and possess high conductivity, since F⁻ has the smallest size & lowest charge. Some of the fluoride ion conductors are β-PbF₂, CaF₂, BaF₂, MgF₂ and KBiF₄. The 58.7ZrF₄ - 31.3BaF₂ - 10ThF₄ system found to have conductivity of 7.1 x 10⁻⁶ S cm⁻¹ at 473K [39]. The 60ZrF₄ - 33BaF₂ - 7YF₃ system showed the conductivity of 3 x 10⁻⁵ S cm⁻¹ at 523K [40].

1.5.2. Cationic Conductors

In cationic conductors, the high ionic conduction is due to the positively charged mobile ions. Some of the cationic conductors of monovalent cations are Ag⁺, Li⁺, Na⁺, K⁺, Cu⁺, divalent cations are Ca²⁺, Ba²⁺, Cd²⁺, trivalent cations are Nd³⁺, Eu³⁺, Er³⁺, etc. [1, 2, 17]. Of the above, the cationic conductors with monovalent ions exhibit high conductivity. The order of conductivity of various monovalent ionic species of glassy FlCs are in the following sequence σ (Ag) > σ(Cu) > σ (Li) > σ (Na) & others at room temperature [49].

Silver ion conductors

Silver ion conductors are mostly based on AgI and are synthesized by substituting either cation or anion or both sites of AgI. Some of the silver based ionic conductors are given in table 1.3. The best reported silver ion conductor at room temperature is RbAg₄S [20,21]. In 1973, first, Kunze had reported the high ionic conduction in AgI-Ag₂SeO₄ glassy system [50]. The multiphase AgI-Al₂O₃ composite is obtained, when Al₂O₃ was added to AgI, in which the dispersed second phase particles neither reacted nor dissolved in the matrix, enhancing ionic conductivity. Similarly, Ag based polymers like (PEO)-KAg₄S are synthesized.
Table 1.3. Examples of Silver based fast Ion Conductors

<table>
<thead>
<tr>
<th>Type of silver FICs</th>
<th>Conductivity (Scm⁻¹)</th>
<th>Temp (K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single / polycrystalline</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-Agl</td>
<td>1</td>
<td>420</td>
<td>27,30,30</td>
</tr>
<tr>
<td>RbAg₄I₅</td>
<td>0.27</td>
<td>298</td>
<td>20,21</td>
</tr>
<tr>
<td>α-Ag₂Si</td>
<td>2</td>
<td>513</td>
<td>33</td>
</tr>
<tr>
<td>Glasses</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60Agl-30Ag₂O-10B₂O₃</td>
<td>8.5x10⁻³</td>
<td>298</td>
<td>51</td>
</tr>
<tr>
<td>55Ag₅S-45GeS₂</td>
<td>1.4x10⁻³</td>
<td>298</td>
<td>52</td>
</tr>
<tr>
<td>55Ag₅S-45P₂S₅</td>
<td>2.68x10⁻⁵</td>
<td>298</td>
<td>52</td>
</tr>
<tr>
<td>66.7Ag₅S-33.3As₂S₃</td>
<td>1x10⁻⁴</td>
<td>298</td>
<td>52</td>
</tr>
<tr>
<td>70AgPO₃-30Ag₂SO₄</td>
<td>5.0x10⁻⁶</td>
<td>298</td>
<td>53</td>
</tr>
<tr>
<td>60Agl-24Ag₂O-6PbO-10B₂O₃</td>
<td>9x10⁻³</td>
<td>298</td>
<td>54</td>
</tr>
<tr>
<td>30Ag₂O-28B₂O₃-42TeO₂</td>
<td>2.8x10⁻⁶</td>
<td>373</td>
<td>55</td>
</tr>
<tr>
<td>Composites</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Agl-Fly Ash</td>
<td>1.2x10⁻⁵</td>
<td>298</td>
<td>56</td>
</tr>
<tr>
<td>Agl- Al₂O₃</td>
<td>1.0x10⁻³</td>
<td>298</td>
<td>56</td>
</tr>
<tr>
<td>Polymers</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(PEO)-KAg₄I₅</td>
<td>2.0x10⁻³</td>
<td>298</td>
<td>57</td>
</tr>
</tbody>
</table>

Lithium ion conductors

Lil is a simple Lithium ion conductor and shows the highest conductivity of 5.5 x 10⁻⁷ Scm⁻¹ than any other lithium based halide at moderate temperature [58]. The intrinsic lithium ion conductivity of pure Li₃N in polycrystalline form exhibit high ionic conductivity in the range of 2-4 x 10⁻⁴ Scm⁻¹ at room temperature [59]. The crystalline Li₁.₄Ti₁.₆In₀.₄P₃O₁₂ showed the maximum conductivity of 5.5 x 10⁻² Scm⁻¹ at 573K [60]. At room temperature, the 10P₂S₅-23B₂S₃-67Li₂S glass showed the conductivity of 1.41 x 10⁻¹ Scm⁻¹
with activation energy of 0.40 eV [61]. Lithium based polymeric solid electrolyte of 1:5 mole ratio (MEEP/PE0)-0.07(LiClO4) showed the conductivity of 1.2 x 10^{-5} Scm^{-1} at room temperature [62]. In 1973, C.C.Liang first observed a remarkable ionic conductivity enhancement in LiI, when Al2O3 was added to it to form the LiI-Al2O3 composite. Some of the lithium ion conductors are shown in table 1.4.

Table 1.4. Examples of lithium based fast ion conductors

<table>
<thead>
<tr>
<th>Type of lithium FICs</th>
<th>Conductivity (Scm^{-1})</th>
<th>Temp.(K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single / polycrystalline</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiTa3O8</td>
<td>1.5 x 10^{2}</td>
<td>723</td>
<td>63</td>
</tr>
<tr>
<td>Li2CdI4</td>
<td>1.0 x 10^{-1}</td>
<td>543</td>
<td>64</td>
</tr>
<tr>
<td>Glasses</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30LiI-70LiPO3</td>
<td>1 x 10^{-6}</td>
<td>298</td>
<td>65</td>
</tr>
<tr>
<td>15Li2O-70LiF-15Al(PO3)3</td>
<td>1.3 x 10^{-3}</td>
<td>493</td>
<td>66</td>
</tr>
<tr>
<td>33Li2S-66P2S5</td>
<td>1.1 x 10^{-4}</td>
<td>298</td>
<td>67</td>
</tr>
<tr>
<td>37Li2S-45LiI-18P2S5</td>
<td>1 x 10^{-3}</td>
<td>298</td>
<td>68</td>
</tr>
<tr>
<td>Composites</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiI-Al2O3</td>
<td>1.0 x 10^{-4}</td>
<td>298</td>
<td>69</td>
</tr>
<tr>
<td>Li2SO4-CaSO4</td>
<td>1.0 x 10^{-3}</td>
<td>773</td>
<td>70</td>
</tr>
<tr>
<td>Li2SO4-MgSO4</td>
<td>3.6 x 10^{-3}</td>
<td>673</td>
<td>71</td>
</tr>
<tr>
<td>Polymers</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(PEO)-LiClO4</td>
<td>10^{-6}</td>
<td>298</td>
<td>72</td>
</tr>
<tr>
<td>(PEO)-LiCF3SO4</td>
<td>5.5 x 10^{-4}</td>
<td>298</td>
<td>73</td>
</tr>
<tr>
<td>(PPO)-LiCF3SO4</td>
<td>10^{-6}</td>
<td>298</td>
<td>74</td>
</tr>
<tr>
<td>(PVAc)-LiSCN</td>
<td>10^{-9}</td>
<td>313</td>
<td>75</td>
</tr>
<tr>
<td>(MEEP/PPO)-(LiClO4)</td>
<td>10^{-7}</td>
<td>298</td>
<td>76</td>
</tr>
<tr>
<td>(bis-amino PEO/PPO)-(LiClO4)</td>
<td>3 x 10^{-5}</td>
<td>298</td>
<td>77</td>
</tr>
</tbody>
</table>
Copper ion conductors

Copper ion is similar to that of silver ion in size and coordination number, but the known copper ion based conductors are very few in reports. Some of copper ion conductors are given in table 1.5. In the lattice of CuCl, an introduction of Rb⁺ and I⁻ ions simultaneously resulted in the formation of Rb₄Cu₁₆Cl₁₃₋ₓIₓ (0.2 ≤ x ≤ 0.5) which showed conductivity of 3.7 to 2.8 x 10⁻¹ S cm⁻¹ at room temperature and it is found to be the highest [78]. The mixed cation conduction in partially copper substituted RbAg₄I₅ having the composition RbCu₄Ag₄₋ₓI₅ showed its room temperature conductivity.

Table 1.5. Examples of copper based fast ion conductors

<table>
<thead>
<tr>
<th>Type of copper FICs</th>
<th>Conductivity (S cm⁻¹)</th>
<th>Temp (K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polycrystalline</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-Cul</td>
<td>9 x 10⁻²</td>
<td>723</td>
<td>79</td>
</tr>
<tr>
<td>KCu₄I₅</td>
<td>0.6</td>
<td>553</td>
<td>79</td>
</tr>
<tr>
<td>α-Cu₂Se</td>
<td>0.11</td>
<td>423</td>
<td>80</td>
</tr>
<tr>
<td>Rb₄Cu₁₆I₇Cl₁₃</td>
<td>0.34</td>
<td>298</td>
<td>81</td>
</tr>
<tr>
<td>Glasses</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuI-Cu₂O-P₂O₅</td>
<td>1.0x10⁻²</td>
<td>298</td>
<td>82</td>
</tr>
<tr>
<td>CuI-Cu₂O-MoO₃</td>
<td>1.0x10⁻²</td>
<td>298</td>
<td>83</td>
</tr>
<tr>
<td>CuI-Cu₂MoO₄-Cu₃PO₄</td>
<td>1.0x10⁻²</td>
<td>298</td>
<td>84</td>
</tr>
<tr>
<td>Composites</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuCl₂Al₂O₃</td>
<td>5.0x10⁻⁶</td>
<td>298</td>
<td>85</td>
</tr>
<tr>
<td>Polymers</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(PEO)-CuI</td>
<td>10⁻⁶</td>
<td>303</td>
<td>86</td>
</tr>
</tbody>
</table>
Sodium & Potassium ion conductors

Sodium β-alumina is one of the most important solid electrolytes among sodium ion conductors. The maximum conductivity of the composition of Na$_3$Zr$_2$PO$_4$(SiO$_4$)$_2$ is $2 \times 10^{-2}$ at 573K, which is equivalent to that of Na β-Al$_2$O$_3$ conductivity [87]. Sodium based polymer electrolytes like PPO$_{12}$-NaCF$_3$SO$_3$ showed a high ionic conductivity $10^{-6}$ Scm$^{-1}$ at RT [74]. Potassium ion conducting compounds of K$_{1.6}$Al$_{1.6}$Ti$_6$O$_{16}$ has showed conductivity in the order of $10^{-4}$ Scm$^{-1}$ at 673K [88]. Some of the examples of sodium and potassium ion conductors are given in tables 1.6. a and 1.6. b.

Table. 1.6. a. Examples of sodium based fast ion conductors

<table>
<thead>
<tr>
<th>Type of sodium FICs</th>
<th>Conductivity (Scm$^{-1}$)</th>
<th>Temp (K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single or polycrystalline</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na β-Al$_2$O$_3$</td>
<td>$1.4 \times 10^{-2}$</td>
<td>298</td>
<td>89</td>
</tr>
<tr>
<td>Na$<em>{1.62}$Mg$</em>{0.71}$Al$<em>{10.39}$O$</em>{17}$</td>
<td>$2.4 \times 10^{-1}$</td>
<td>643</td>
<td>90</td>
</tr>
<tr>
<td>Na$<em>{1.2}$Pr$</em>{0.07}$Mg$<em>{0.77}$Al$</em>{10.39}$O$_{17}$</td>
<td>$4.5 \times 10^{-2}$</td>
<td>643</td>
<td>90</td>
</tr>
<tr>
<td>Na$<em>{2.2}$Al$</em>{0.1}$YbZr$<em>{0.9}$Si$</em>{0.1}$P$<em>{2.9}$O$</em>{12}$</td>
<td>$5.89 \times 10^{-2}$</td>
<td>673</td>
<td>91</td>
</tr>
<tr>
<td>Sodium Glasses</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na$_2$O-SiO$_2$</td>
<td>$2.8 \times 10^{-5}$</td>
<td>373</td>
<td>92</td>
</tr>
<tr>
<td>39Na$_2$O-8Y$_2$O$_3$-53SiO$_2$</td>
<td>$3.39 \times 10^{-3}$</td>
<td>573</td>
<td>93</td>
</tr>
<tr>
<td>60Na$_2$S-40GeS$_2$</td>
<td>$1.5 \times 10^{-4}$</td>
<td>373</td>
<td>94</td>
</tr>
<tr>
<td>Polymers</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(PEO)$_{19}$-NaI</td>
<td>$10^{-4}$</td>
<td>298</td>
<td>95</td>
</tr>
<tr>
<td>(PPO)$_{12}$-NaCF$_3$SO$_3$</td>
<td>$10^{-6}$</td>
<td>298</td>
<td>74</td>
</tr>
<tr>
<td>(PEO)$_{4.5}$-NaSCN</td>
<td>$3 \times 10^{-7}$</td>
<td>298</td>
<td>74</td>
</tr>
<tr>
<td>(MEEP)$_{24}$-NaCF$_3$SO$_3$</td>
<td>$10^{-5}$</td>
<td>298</td>
<td>96</td>
</tr>
</tbody>
</table>
Table 1.6.b. Examples of potassium ion conductors

<table>
<thead>
<tr>
<th>Type of potassium FICs</th>
<th>Conductivity (Scm(^{-1}))</th>
<th>Temp (K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single or polycrystalline</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K(_2)O-Ga(_2)O(_3)</td>
<td>(1 \times 10^{-3})</td>
<td>573</td>
<td>97</td>
</tr>
<tr>
<td>K-β-alumina</td>
<td>(6.5 \times 10^{-5})</td>
<td>573</td>
<td>98</td>
</tr>
<tr>
<td>K(_2)O-6FeO(_3)</td>
<td>(1.5 \times 10^{-3})</td>
<td>573</td>
<td>99</td>
</tr>
<tr>
<td>Glass</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10K(_2)O-90SiO(_2)</td>
<td>(1.9 \times 10^{-9})</td>
<td>748</td>
<td>100</td>
</tr>
<tr>
<td>Polymers</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(PEO)-Kag(_4)I(_5)</td>
<td>(2.0 \times 10^{-3})</td>
<td>298</td>
<td>101</td>
</tr>
<tr>
<td>(PEO)(_{1000})-(NKSO(_2)Me(_2))</td>
<td>(8.5 \times 10^{-6})</td>
<td>298</td>
<td>102</td>
</tr>
</tbody>
</table>

Proton conductors

In protonic conductors, ionic transport is not only due to H\(^+\) motion but also complex ion groups like NH\(_4^+\), H\(_3\)O\(^+\), OH\(^-\), etc. [103]. Some of the proton conducting materials are listed in the table 1.7.

Table 1.7. Examples of proton conductors

<table>
<thead>
<tr>
<th>Type of proton FICs</th>
<th>Conductivity (Scm(^{-1}))</th>
<th>Temp (K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystalline</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HUO(_2)PO(_4):4H(_2)O</td>
<td>(4 \times 10^{-3})</td>
<td>298</td>
<td>104</td>
</tr>
<tr>
<td>Sb(_2)O(_5):4H(_2)O</td>
<td>(3 \times 10^{-4})</td>
<td>298</td>
<td>105</td>
</tr>
<tr>
<td>Polytungsticacid (PWA)</td>
<td>(1.7 \times 10^{-1})</td>
<td>298</td>
<td>57</td>
</tr>
<tr>
<td>Polymers</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(PVA)-H(_3)PO(_4)</td>
<td>(10^{-5})</td>
<td>298</td>
<td>106</td>
</tr>
<tr>
<td>(PEO)-NH(_4)SCN</td>
<td>(10^{-5})</td>
<td>298</td>
<td>107</td>
</tr>
<tr>
<td>(PEO)-NH(_4)I</td>
<td>(10^{-5})</td>
<td>303</td>
<td>108</td>
</tr>
</tbody>
</table>
1.6. REVIEW ON SILVER ION CONDUCTORS

The first observed crystalline fast ionic conductor is silver iodide (AgI), whose ionic conductivity increases with temperature up to 420K and at 420K, there is a sudden increase in conductivity by more than three orders of magnitude, which is due to the structural transformation. The high conducting phase is known as the α-Agl (bcc) and the low conductivity phase is β-Agl (Wurzite) [31, 32]. The α-Agl has a body centered cubic anion (I⁻) arrangement with cationic (Ag⁺) structural disorder. Strock first reported the existence of cationic disorder in α-Agl [109] and Hoshino confirmed it [110]. Fig.1.2.a shows the structure of bcc unit cell of high conducting α-Agl in which the two silver ions are statistically distributed over 42 sites, 6 octahedral, 12 tetrahedral and 24 trigonal bipyramidal. The neutron diffraction studies by Buhrer & Halg [111] and Wright & Ferder [112] indicated that silver ions are preferentially found in oblong ellipsoidal regions of space centered at the tetrahedral sites and extending in the directions of the neighboring octahedral sites as shown in the fig.1.2.b. This extended region of the cation site occupancy is responsible for the large amplitude of anharmonic and anisotropic vibrations of the cations, which is a general feature of all liquid-like-structured fast ionic solids [1, 113].

Many attempts were made to stabilize the high conducting α-Agl phase at ambient temperature by substituting foreign ions. According to Owens, the AgI conductors are substituted with anion, cation and mixed ions. The best reported silver ion conductor at room temperature is RbAg4I5, which is obtained by the cation substitution Rbl+4AgI [20, 21]. In 1913, the high conducting silver based glassy materials have been prepared by Kunze [50]. Since then numerous binary and ternary Ag conducting glasses are synthesized. Minami et al. investigated several ternary AgI-Ag2O-MoO3, AgI-Ag2O-P2O5, etc. systems, their glass forming regions and ionic conductivity [114]. In 1998, M.Tatsumisago et al. investigated the AgI-Ag2O-B2O3 FIC glasses with incorporation of large
Fig. 1 2. a) Structure of $\alpha$-AgI, $\bigcirc$ octahedral site, $\square$ tetrahedral site, $\triangle$ trigonal bipyramidal site and b) silver ion occupancy sites in $\alpha$-AgI.
amount of silver iodide into the glassy matrix [115]. Malugani et al. investigated
glass formation in the systems AgX-AgPO3 (X= I, Br, Cl). At room temperature,
the ionic conductivity increased linearly with increasing radius of the halogen
ion and it is associated with the higher polarizability of the larger ions [116].
Similarly, Ml2-AgPO3 (M = Cd, Hg, Pb) systems showed that the introduction of I:
resulted in the rapid rise in conductivity of these glasses [117]. Silver based
chalcogenide i.e. Ag2X, X= S, Se, Te, etc. glasses were also synthesized and
found to have high conductivity. In general, sulfide glasses exhibit more
conductivity than that of their corresponding oxide glasses [118]. Quaternary
silver compounds are prepared to enhance the ionic conductivities following the
pioneering work by Chiodelli et al. Some of silver ion conducting glassy samples
were summarized in the table 1.8 [119-130]. Fig.1.3 shows the temperature
dependence of conductivity of some silver ion conductors.

Table 1.8. Some of silver ion conducting glassy samples

<table>
<thead>
<tr>
<th>Silver ion conducting glasses</th>
<th>Conductivity (S cm⁻¹)</th>
<th>Temp. (K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>58AgI-19Ag₂O-23WO₃</td>
<td>3.1x10⁻²</td>
<td>298</td>
<td>124</td>
</tr>
<tr>
<td>50AgI-25Ag₂O-25B₂O₃</td>
<td>2.7x10⁻³</td>
<td>298</td>
<td>51</td>
</tr>
<tr>
<td>33AgI-33Ag₂O-33GeO₂</td>
<td>1.3x10⁻⁴</td>
<td>298</td>
<td>119</td>
</tr>
<tr>
<td>60AgI-40Ag₂SeO₄</td>
<td>3.1x10⁻³</td>
<td>298</td>
<td>119</td>
</tr>
<tr>
<td>75AgI-25Ag₂MoO₄</td>
<td>1.4x10⁻²</td>
<td>298</td>
<td>125</td>
</tr>
<tr>
<td>80AgI-20Ag₂CrO₄</td>
<td>1.5x10⁻²</td>
<td>296</td>
<td>127,128</td>
</tr>
<tr>
<td>66.7AgI-25Ag₂O-8.3V₂O₅</td>
<td>2.6x10⁻³</td>
<td>298</td>
<td>120</td>
</tr>
<tr>
<td>50AgI-25Ag₂O-25P₂O₅</td>
<td>8.0x10⁻³</td>
<td>298</td>
<td>121</td>
</tr>
<tr>
<td>75AgI-12.5Ag₂O-12.5As₂O₅</td>
<td>3.0x10⁻³</td>
<td>298</td>
<td>119</td>
</tr>
<tr>
<td>60AgI-25.5Ag₂O-8.7MoO₃-5.8As₂O₅</td>
<td>1.65x10⁻²</td>
<td>298</td>
<td>122</td>
</tr>
<tr>
<td>60AgI-23.3Ag₂O-10(0.8 SeO₂-0.2V₂O₅)</td>
<td>1.87x10⁻²</td>
<td>303</td>
<td>123</td>
</tr>
<tr>
<td>60AgI-24Ag₂O-1.6MoO₃-14.4V₂O₅</td>
<td>1.91x10⁻²</td>
<td>298</td>
<td>126</td>
</tr>
<tr>
<td>60AgI-16.8Ag₂O-11.4B₂O₃-11.4 MoO₃</td>
<td>4.42x10⁻²</td>
<td>305</td>
<td>129</td>
</tr>
<tr>
<td>66.7AgI-23Ag₂O-3SeO₂-7.2P₂O₅</td>
<td>2.93x10⁻²</td>
<td>303</td>
<td>130</td>
</tr>
</tbody>
</table>
Fig. 1.3. Log $\sigma$ vs. 1000/$T$ plots of some silver based glassy FICs
1.7. THEORIES OF IONIC CONDUCTION IN GLASSES

The ionic transport in glassy materials is complex and difficult to understand than that of the crystalline materials. In case of glasses, it is not simple to explain the transport properties because of the lack of reference of a perfect lattice and hence, the definition of defect becomes rather arbitrary. The complete structural information and relation of structure to the ionic transport can be made from the theoretically predicted models rather than only from experimental results. Many theories have been proposed to give explanation to the behavior of the conductivity possessed by the glass samples.

1.7.1. Weak Electrolyte Model

Ravine and Souquet have proposed a theory of the weak electrolyte model to explain the ion transport in FIC glasses [131,132]. In this model, it is considered that a fraction of the total ions, mobile, that contribute to the conduction & other ions are less mobile having the same higher free-energy sites. In this model, carrier mobility is considered to be independent of the glass composition and hence, the structure. A correlation between ionic conductivity and thermodynamic activity is the basis for the weak electrolyte model. The dependence of conductivity on the thermodynamic activity ‘a’ of the glass is given by \( \sigma = K [a]^{1/2} \) where K is the dissociation constant. Ravine and Souquet [131,132] have correlated ionic conductivity to activity in silica based glasses and Tomozawa et al. [133] in germanate glasses.

1.7.2. Random site Model

In Random site model, all the ions of a particular type are treated as potential carriers with a gaussian distribution of activation energies, the width of the distribution varies with glass composition [134,135]. In general, the
variation in carrier concentration with glass composition is almost constant and hence, the conductivity variation with glass composition is affected by changes in the activation energy. This model was successful in explaining the composition dependence of conductivity in solid solutions having the fluorite structure.

1.7.3. Diffusion Path Model

Minami et al. [119, 136] had proposed a model based on the spectroscopic studies of Ag$^+$ ions conducting glasses. They suggested that there exist two types of Ag ion populations in the glass network: mobile and less mobile. The Ag ions located in the iodine surroundings are found to be mobile and those associated with the oxyanions are considered to be less mobile [137, 138]. Minami had explained the dependence of mobility and carrier concentration with the glass composition. Minami suggested that, in these glasses, partial covalency exist between silver and non-bridging oxygen ions, which gives rise to the less mobile silver ion population. Minami also postulated that the wide and shallow potential is formed by the interaction of silver ions with the iodide anions, while the narrow and deep one is formed by the interaction of silver ions with the oxide anions. The silver ions surrounded by the halide ions are considered to be mobile and contribute to the carrier concentration. The increase in the silver halide concentration increases the mobile ion concentration and hence the conductivity. Several experimental results support the existence of mobile and immobile silver ions in these types of glasses [139-141]. However, the NMR experiment leads to a contradictory conclusion on the existence of distinct populations of Ag$^+$ ions [142, 143].
1.7.4. Anderson and Stuart Model

Anderson and Stuart have proposed a model for the microscopic transport mechanism of ions in glasses [144-146]. Accordingly, ionic transport in glasses occurs by means of diffusive motion of ions between energetically stable sites located in the glass structure. The activation energy associated with such motion arises from two contributions i) coulombic term associated with the removal of an ion from its countervailing charged environment at one site to a position midway between two neighboring sites and ii) associated with the strain energy encountered by the ion when it passes through the gateway formed by the fully bonded bridging ion sites. The AS model allows estimation of both the contributions to the activation energy in a number of silicate glasses. Later, several modifications have been made in the AS model and this provides a highly useful semi-quantitative explanation for the ion transport phenomenon in glasses.

1.7.5. Cluster Bypass Model

Ingram et al. proposed the cluster bypass model by considering the glass as a congelation of ordered microdomains or clusters [147,148]. On cooling the glass below $T_g$, the residual liquid that initially surrounds the clusters solidifies to give a highly disordered phase, which is also referred to as connective tissue. The essence of cluster bypass model is that the preferred pathways for ion migration lie outside the cluster but lie within the connective tissue. This model, besides explaining the ion transport in various glasses, provides a simple explanation for the mixed alkali effect in ionic conducting glasses.
1.7.6. Diffusion Controlled Relaxation (DCR) Model

Elliott et al. proposed a microscopic model known as the DCR model for the ac response of modified glasses [149,150]. According to this model, there are energetically stable sites (NBOs) for the mobile ions to reside in the oxide glassy matrix. Ionic transport occurs by means of diffusive motion between the equivalent sites resulting in the primary relaxational event with a characteristic microscopic relaxation time τ. However, when another cation hops into one of the vicinal equivalent sites result in the creation of double occupancy known as interstitialcy effect on instantaneous relaxation process. The DCR model assumes the applicability of an Anderson-Stuart type of description for ion transport in glasses. In addition to the coulombic and strain energy contributions to the activation energy for diffusion motion, the polarization (a.c) conductivity can be attributed to the double occupancy effect has also been considered. This model explains the frequency dependence of conductivity that where the diffusion triggered relaxation is together responsible for (dielectric) relaxation. The changeover from non-exponential (KWW) behavior to Debye-like (single relaxation) behavior both for very small ion concentrations and at high temperatures, can be readily explained by this model.

1.7.7. Dynamic Structure Model

Bunde et al. has suggested a model based on the creation of fluctuating pathways, within a dynamically determined structure, for ion transport in glasses [151,152]. The main features of this model are i) the ion transport is a hopping process ii) the mobile ions are active in creating glass structure and iii) the glass structure continues to change at a local level even far below Tg. By coupling together the process of ion-hopping with local structural relaxation, Bunde et al proposed that when a ion moves on from its own site, the memory of the cation persists, and so a empty site remains there for sometime, τ. Such
empty site constitutes the preferred pathways for ion migration. This is termed as the site memory effect with the presumption that ion hopping rates are determined primarily by the available empty sites. It is also argued that this is inconsistent with the view that ion transport processes in glass are fully decoupled from the process of structural relaxation which freezes at or just below $T_g$. The success of this model includes the discovery of a simple power law ($\sigma = cv$) operative in single cation glasses and the quantitative elucidation of many features of the mixed alkali effect. The main feature of this model is that the glass structure must persist for time scales much longer that the inverse hopping rates of individual cations.

1.7.8. Jump Relaxation Model

Funke proposed the jump relaxation model, considering the glass is assumed to contain many empty equivalent sites and the ion can jump into the neighboring sites with equal probability [153-155]. When the ion jumps from its initial to final site, the equivalence of the sites disappear as the coulombic energy is added in. Immediately after the ion has jumped, ion feels the higher energy site, which tends to move back to its initial site. If this happens, the jump is described as unsuccessful or it stays. If the other ions readjust themselves to its presence, the coulombic cage potential moves across and a new absolute potential minimum is created at that site and results in the successful jump.

1.7.9. Unified site Relaxation Model

Funke, Ingram, Bunde have developed a unified site relaxation model based on the jump relaxation model and dynamic structure model [156]. The basic idea of the model is that the ion transport is strongly influenced by their mutually repulsive coulomb interactions. As a consequence, their hopping
motion is not a random process, but features a strong preference for so-called correlated forward-backward hopping sequences. If an initial forward jump of an ion is followed by a correlated backward jump, the former can be regarded as unsuccessful. If however the ion manages to stay at the new site and neighboring ions rearrange themselves causing site relaxation, then the initial forward hop is called successful. The later relaxation process (coulomb relaxation) causes a shifting of the coulomb cage potential felt by the central ion and thereby initiates the site relaxation. Contrary to the jump relaxation model, which assumes that all sites are geometrically alike, the unified site relaxation model (like the dynamic structure model) considers at least two kinds of site.

1.8. APPLICATION OF FAST IONIC CONDUCTORS

For the first time, Oxygen ion conducting material is used as a solid electrolyte to make ionic device in the determination of thermodynamic properties of materials at high temperature [3,9-16]. In 1967, Yao and Kummer applied the sodium β-alumina as solid electrolyte, in the high energy density batteries at the Ford Motor Co., [34]. Later, different types of new FICs have been prepared and applied in fabrication of various ionic devices [3,149]. The technology of preparation and designing newer ionic devices with more efficiency is being referred as ‘Solid State Ionics’ (SSI). The term SSI was first used by Prof. Takehiko Takehashi, Nagoya University, analogous to solid state electronics [1,3]. Some of the ionic device applications are solid state batteries [SSBs], fuel cells, gas and humidity sensors, pressure gauges, timers, oxidation catalysis, thermometers, thermoelectric generators, capacitors, coulometer, electrochromic displays etc. Table 1.9 gives some examples of application of different class of solid electrolyte materials [157-162].
Table 1.9. Examples of application of Fast ionic Conductors

<table>
<thead>
<tr>
<th>Materials</th>
<th>Application</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgI-Ag₂O-WO₃ glass with LaF₃ Thin films</td>
<td>Oxygen sensor</td>
<td>124</td>
</tr>
<tr>
<td>Polythiophene film - AgI-Ag₂O-WO₃ glass</td>
<td>Chemical sensor</td>
<td>124</td>
</tr>
<tr>
<td>LiAlF₄&amp; LiNbO₃</td>
<td>Smart windows</td>
<td>159</td>
</tr>
<tr>
<td>AgI-Ag₂O-WO₃ glass</td>
<td>Electron beam recording materials</td>
<td>124</td>
</tr>
<tr>
<td>LiI</td>
<td>Microfabricated solid state secondary battery</td>
<td>160</td>
</tr>
<tr>
<td>(EC-PC)-(LiClO₄)-(PMMA)</td>
<td>Solid state supercapacitors</td>
<td>161</td>
</tr>
<tr>
<td>Gel membranes matrix</td>
<td>Sensors</td>
<td>162</td>
</tr>
<tr>
<td>Al₂TiO₅, WC and SiC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Second phase β-Al₂O₃</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1.9. PRESENT INVESTIGATIONS

The important features of the fast ion conductors in the field of solid state ionics inspired to investigate the synthesis of silver based fast ionic conducting glassy samples. In the present investigation, the following four silver based FIC glassy systems are undertaken for various studies.

SYSTEM

<table>
<thead>
<tr>
<th>System</th>
<th>PROCESS</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgI  -  Ag₂O  -  CrO₃  -  V₂O₅</td>
<td>SCV</td>
</tr>
<tr>
<td>silverchromovanadate</td>
<td>melt quench</td>
</tr>
<tr>
<td>AgI  -  Ag₂O  -  CrO₃  -  P₂O₅</td>
<td>SCP</td>
</tr>
<tr>
<td>silverchromophosphate</td>
<td>melt quench</td>
</tr>
<tr>
<td>AgI  -  Ag₂O  -  CrO₃  -  As₂O₅</td>
<td>SCA</td>
</tr>
<tr>
<td>silverchromoarsanate</td>
<td>melt quench</td>
</tr>
<tr>
<td>Ag₂O  -  B₂O₃  -  SiO₂</td>
<td>SBS</td>
</tr>
<tr>
<td>silverborosilicate</td>
<td>sol-gel</td>
</tr>
</tbody>
</table>
For all the four systems, by varying molecular weight percentages of various constituents, different compositions of glassy compounds are prepared by using melt quench and sol-gel methods. The XRD, DSC, FTIR and the electrical conductivity studies are used to characterize all the synthesized compounds of SCV, SCP, SCA & SBS systems. The impedance studies are carried to find out the high conducting composition of the glass in each system along with their appropriate equivalent circuits. The observed conductivity results in these glasses are analyzed using the existing theoretical models to find out the type of mobile species exist in the glass and the distribution of relaxation time.

From the impedance and transport studies, the high ionic with negligible electronic conducting composition of the compound is chosen from each the SCV, SCP, SCA & SBS glassy system for the solid state battery (SSB) applications. The SSBs are fabricated using highest conducting composition of SCV, SCP, SCA & SBS samples as solid electrolytes with different compositions of cathode materials. Various sets of solid state batteries are fabricated using the following type of structure.

Anode (Ag + SE) / SE (SCV or SCP or SCA) / Cathode (I+C+SE)

The cell performance of the fabricated solid state batteries are studied by the open circuit voltages, polarization and discharge characteristic measurements.
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