CHAPTER VI

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SUMMARY

6.1. CONCLUSION

The chapter summarizes all the experimental results observed in the present investigation of silver based fast ionic conducting glassy materials and it also gives the scope of further research work & the possible electrochemical applications of FIC materials.

Fast ion conducting silver based chromovanate (SCV), chromophosphate (SCP) and chromoarsenate (SCA) systems were prepared through melt quench method in various compositions, by varying formers, modifier to former ratio and dopant salt contents. Also, silverborosilicate (SBS) glassy system was prepared through sol-gel process in various compositions, by varying formers and modifier to former ratio. All the prepared compounds of SCV, SCP, SCA & SBS systems were confirmed as glass/amorphous and also, their glass formation regions are obtained by X-ray diffraction. From the observed band positions of Infrared (IR) spectra, it is confirmed that all the SCV, SCP, SCA & SBS glassy samples are respectively composed of chromate & vanadate, chromate & phosphate, chromate & arsenate and borate & silicate ionic clusters as expected from the composition of the compounds. The DSC results of various dopant compositions of SCV, SCP & SCA samples revealed that the glass transition temperature ($T_g$) decreases with dopant content. The conductivity varies randomly with formers compositions of all SCV, SCP, SCA & SBS glassy systems and it is attributed to mixed former effect. The particular former composition $x = 0.3, 0.7, 0.2 \& 0.2$ of the SCV, SCP, SCA & SBS systems showed the high conductivity compared to the other compositions. The conductivity variation is also explained using the general conductivity expression, structural changes from IR results and the random site model.
Similarly, the variation of conductivity is observed with glass modifier to former ratio in all the SCV, SCP, SCA & SBS systems. The highest conducting m/f compositions are fixed SCV m/f = 0.5, SCP m/f = 1.75, SCA m/f = 1.75 & SBS m/f = 0.25. The variation in conductivity is explained by weak electrolyte model considering the Ag₂O as solute and glass matrix as solvent. The conduction mechanism for the conductivity variation of dopant compositions of SCV, SCP & SCA systems was explained qualitatively by correlating the general conductivity relation, IR results and the diffusion path model. The obtained highest conducting compositions for all four systems are as follows:

<table>
<thead>
<tr>
<th>Composition</th>
<th>AgI %</th>
<th>Ag₂O %</th>
<th>CrO₃ %</th>
<th>V₂O₅ %</th>
<th>Conductivity (Scm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCV</td>
<td>66.6%</td>
<td>11.1%</td>
<td>22.2%</td>
<td>0.3%</td>
<td>3.175 x 10²</td>
</tr>
<tr>
<td>SCP</td>
<td>66.6%</td>
<td>21.2%</td>
<td>12.1%</td>
<td>0.3%</td>
<td>2.364 x 10²</td>
</tr>
<tr>
<td>SCA</td>
<td>66.6%</td>
<td>21.2%</td>
<td>12.1%</td>
<td>0.8%</td>
<td>1.666 x 10²</td>
</tr>
<tr>
<td>SBS</td>
<td>20%</td>
<td>80%</td>
<td>0.2%</td>
<td>0.8%</td>
<td>1.361 x 10⁻⁷</td>
</tr>
</tbody>
</table>

The impedance measurements were carried out for all the formers, modifier to former & dopant compositions of the SCV, SCP & SCA (120 to 343K) and for all the formers and modifier to former compositions of SBS samples (413 to 480K) in the frequency range of 40Hz to 100kHz. The impedance data is analyzed and obtained the bulk resistance and equivalent circuit. The obtained equivalent circuit is the parallel combination of bulk resistance and CPE in series with CPE in the interfacial region. The a.c conductivity, σ(ω), dielectric permittivity, ε* and electric modulus, M* were calculated from the measured impedance data, Z' & Z'' and pellet dimensions respectively using their corresponding inter relations. In the impedance spectra, with increase in temperature, the intersection of the semicircle with the real axis shifts towards the origin, in turn increase in conductivity. The log (σT) vs. 1000/T plots follow Arrhenius relation and from the slope of the linear square fits, the d.c activation energy of the mobile charge carriers were calculated. The activation energy is low for the high conducting sample. The frequency dependence of
conductivity spectra were fitted to the Jonscher's power law expression and obtained $A$, $s$ & $\sigma_0$. The obtained $\sigma_0$ values are in good agreement with the dc conductivity from the impedance spectra and the $s$ is found to be temperature dependent. The hopping rate ($\omega_p$) of mobile ions is obtained from the frequency at which the dispersion starts from the dc conductivity region, where $\sigma(\omega) = 2\sigma_0$.

The real dielectric permittivity $\varepsilon'$ decreases with increase in frequency, and attains a constant value at high frequencies. The modulus spectra exhibited broadened non-Debye curve with a maximum and were fitted to the KWW decay function. The obtained stretched exponent $\beta$ and the relaxation time $\tau$ confirmed respectively the shape of the spectra is non-Debye and the samples are ionic in nature. The peak frequency at which $M''_{\text{max}}$ occurs was found to shift towards higher frequencies with increasing temperature. The relaxational activation energy were obtained from the slopes of the fits of log ($\tau$) vs. 1000/$T$ plots. The superimpossability of the normalized $M''$ spectra at different temperatures were ascribed to temperature independent mechanisms of relaxation.

The transport properties such as electronic conductivity and transport number are measured using Wagner's dc polarization technique and the electronic conductivity is found to be negligible in comparison with the total conductivity. Hence, the transport number for silver ion migration is almost found to be unity in all the systems. Solid-state batteries were fabricated using the high ionic conducting compositions of the SCV, SCP, SCA & SBS samples as solid electrolytes with different cathode compounds such as iodine (I), graphite (C) and solid electrolyte (SE) in various ratios I+C & I+C+SE. The solid state batteries are characterized by measuring the open circuit voltage (OCV), polarization and discharge characteristics. In all the cells, the OCV is observed around 687 to 675 mV, which are found to be very close to theoretical cell voltage of 687 mV. The polarization and discharge characteristics of the cells of
varying cathode compositions indicate that the cell performance is very sensitive to the composition of the cathode components. The I + C : SE = 7:3 were found to be stable, exhibit good polarization and discharge characteristics. The present battery studies suggest that the solid state batteries made up of SCV, SCP, SCA & SBS as solid electrolytes are suitable for low power source applications.

6.2. SCOPE OF FURTHER RESEARCH WORK ON FIC GLASSES

The following are the important research topics of further research work in this field. Synthesis of new high ionic conducting materials by various techniques, such as microwave preparation, sol-gel, thermal/flash evaporation, sputtering, etc. Many advanced experimental techniques like IR, EPR, NMR, TEM, SEM, EXAFS, XPS, etc., can be employed to study the microstructure of the glassy materials.

The advanced tools like Monte Carlo (MC) simulation can be used to analyze impedance data for obtaining various complicated possible configurations of various combinations of R, C & L elements of electrical behavior of the sample. The bulk conductivity and microscopic properties can be correlated using various parameters such as power law exponent, decay constant, Kroning-kramers relation, Warburg impedance parameter, etc.

High speed parallel processors are available, which can be used to simulate complicated glassy structures using various simulation techniques like Monte Carlo, molecular dynamics, percolation, etc. Also, Monte Carlo technique can be to simulate many-particle hopping models for studying transport processes in glassy materials.
FICs in thin film forms are widely used in various applications as power source devices like thin film microbatteries, etc. as they possess following advantages, like stability, miniaturization and long shelf life for energy storage.

6.3. POSSIBLE ELECTROCHEMICAL APPLICATIONS OF FIC GLASSES

The fast ionic conductors (FICs) are the future promising materials and could be used in many potential ionic device applications at ambient temperature as well as at higher temperature. The possible electrochemical applications of the FIC materials in various fields are given below. These are mainly divided into two 1) battery and 2) non-battery applications.

1) Battery Applications
   i) Solid State Batteries
      a) Primary batteries b) Secondary batteries c) Micro batteries d) Fuel cells
      ii) Thermal Batteries, etc.

2) Non-Battery Applications
   a) Coulometer b) Electrolysis separators c) Variable resistors d) Memory devices
   e) Timers and sensors f) Smart windows g) Thermometers, h) High temperature heating elements, i) redox capacitors, j) electrochemical actuators, etc.

Further, an interesting application will be concerned with the development of some circuit or devices that may be used in certain kind of computers in which ionic transport phenomena must play an important role. In hand with solid state electronics, solid state ionics may be highlighted more and more in the future.