Effect of Substitution of SIO₂ on Electrical Conductivity of LI₂O:B₂O₃ System

Prof. M.D.Mehare
Department of Applied Physics, Priyadarshini Indira Gandhi College of Engineering, Nagpur, INDIA

ABSTRACT
Solid ionic conductors are of particular interest both for basic studies of the ionic transport parameters in solid and for several practical applications like electrochemical sensor, electrochemical display devices, timers, coulometer and miniature energy storage devices employed in cardiac pacemakers, electronic calculators and many other micro-electronic appliances. Although liquid electrolytes such as fused salts have been used in electrochemical cells, their application in advanced batteries has been limited due to their chemical reactivity with electrodes and other cell components. The vast interest in solid electrolyte in recent years, is mainly because of their potential application in technological devices, as solid electrolytes, glasses shows many advantage over crystalline solids. LI₂O:B₂O₃ (40:60) composition has been reported to give the maximum conductivity, with a view to enhance this conductivity, addition of different mole of SI0₂ has been done in different mole% in composition of LI₂O:B₂O₃ system.

Keywords — Ionic transport parameter, electrochemical sensor, Electrochemical cells, Solid electrolyte glasses.

I. INTRODUCTION
A glass defined as a super cooled liquid has the same structure as that of liquid from which it is frozen [1]. The process of formation of the glassy solid differs from that of the crystalline solid the later being formed by the discontinuous solidification in which solid masses appears and grow in the liquid. From the XRD studies, a glass may be thought as a composite of microcrystallines and this implies that a glass is endowed with a specific translational order known as “short range order”. In the other wards, a glass can be visualized by a duplex mixture of ordered islands in a disordered medium and this is known as the “continuous network model” first proposed by Zachariasen [2]. This modal differs from the crystalline lattice in the sense that the probability of finding an atom at a given distance from an arbitrary central atom falls off with distance [3]. Nevertheless, in a glass the nearest neighbor Co-ordination of the crystal remains unaltered and on this picture band gap model semiconducting glasses has been visualized

1.1 CLASSIFICATION OF GLASSY ELECTROLYTE
In general classification of glassy electrolyte (Fast Ionic Conducting glasses) is broadly classified into 1. Anionic Conducting glasses and 2 Cationic Conducting glasses. Further Cationic conducting glasses is classified into 1.Sulphide glasses 2. Oxide glasses .Oxide glasses are further classified into a) Quenched glasses b) Silicate glasses c) Phosphate glasses d) Borate glasses. The two major categories of glasses depending upon the types of ions contributing to conduction are anionic conducting glasses and cationic conducting glasses.

1.2 ANIONIC CONDUCTING GLASSES.
These glasses are very few in number. Most of them belong to fluoride glass system. The conductivity enhancement factors in these glasses are: a) F- ion concentration, b) Average separation between F-M ions, c) Proportion of free volume, d) Average bond strength between M⁺ and F⁻ e) Average polarizing power or polarizability of constituent ions. Kawamotto et al [4] have investigate the correlation between the conductivity, and factor shown above in many glasses in the ZrF₄-BaF₂-MFₙ (M= various cations in the group I-V with vacancy n). Some examples of the glass system with such ions are listed in table 1.

1.3 CATIONIC CONDUCTING GLASSES
It is broadly classified further into Sulphide and oxide glasses.

SULPHIDE GLASSES:
Sulphide glasses have been studied extensively since, the lower electro negativity of sulphur atom results into a weaker bond between the alkali ion and the non-bridging sulphur. New Li⁺ conducting glasses based on Li₂S has been reported [5-7] beside the systems LiI-Li₂S-
P₂S₅ and LiI-Li₂S-P₂S₂ [8] as shown in table 1. The conductivity at 25°C of these glasses reaches the order of magnitude 10⁻⁴ S/cm which is one of the criteria for applications as solid electrolyte. Also, the Li⁺ glasses of the LiI-Li₂S-P₂S₂ system have been reported to be commercially used as electrolyte in all solid state primary cells of the type Li/glass/Tis₂.

**Table 1. Maximum Conductivity for glasses in fluoride and sulphide system**

<table>
<thead>
<tr>
<th>Glass system</th>
<th>Max.625 (S/cm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr-Ba-Cs-F</td>
<td>~ 10⁻² at 200 °C</td>
<td>10</td>
</tr>
<tr>
<td>Zr-Th-Ba-Li-F</td>
<td>~ 10⁻⁴ at 200 °C</td>
<td>5</td>
</tr>
<tr>
<td>In-Sn-Pb-F</td>
<td>~ 10⁻² at 200 °C</td>
<td>6</td>
</tr>
<tr>
<td>LiI-Li₂S-P₂S₅</td>
<td>~ 10⁻⁴</td>
<td>11</td>
</tr>
<tr>
<td>LiI-Li₂S-B₂S₃</td>
<td>~ 10⁻⁵</td>
<td>5</td>
</tr>
<tr>
<td>LiI₂S-SiS₂</td>
<td>~ 10⁻⁵</td>
<td>7</td>
</tr>
</tbody>
</table>

**OXIDE GLASSES:**

Extensively studied oxide glasses mainly consist of a network former either (B₂O₃, SiO₂ or P₂O₅), a metal oxide or network modifier such as Li₂O, Na₂O, Ag₂O, etc., the B₂O₃, SiO₂, GeO₂ and P₂O₅ readily form glass of their own and are commonly known as “Glass formers” for they provide the backbone in other mixed-oxide glasses. As₂O₃ and Sb₂O₅ are also produce glass when cooled rapidly TeO₂, SeO₂, MoO₃, WO₃, Bi₂O₅, V₂O₅ does not formed glass independently. According to Rawson, these oxide are termed as “conditional glass formers”. The network modifier as their name implies serve to include structural change in the glass network, which are reflect in many physical properties including melting point, glass transition temperature T_g, density, refractive index etc. It has been investigated that the doping with salt appears to enter the glass with little or no direct effect on the network[12]. Both the cation and the anion are accommodated interstitially with the cation contributing substantially to the ionic conductivity. Some evidence has been presented recently that this does not hold for all glasses [13-19].

**II. EXPERIMENTAL TECHNIQUE**

The present work study the effect of addition of SiO₂ on the electrical conductivity of lithium-Borate (Li₂O-SiO₂) system. A.R.Grade Li₂SO₄ (Pure 99.9% MOSCOW, USSR), B₂O₃ (pure 99.9% SISCO, INDIA) and SiO₂ was used as starting materials for the preparation of glass belonging to series with general composition 42.5Li₂O – (57.5-X) B₂O₃ – XSiO₂. The series is specified with constancy of Li₂O content given in table II.

**Table II.**

<table>
<thead>
<tr>
<th>S.No</th>
<th>Glass No</th>
<th>Y</th>
<th>Composition of mole%</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>I₁</td>
<td>0</td>
<td>42.5 57.5 0</td>
<td>For fixed n=1.35 y is varied</td>
</tr>
<tr>
<td>2</td>
<td>I₂</td>
<td>0.08695</td>
<td>42.5 52.5 5</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>I₃</td>
<td>0.1739</td>
<td>42.5 47.5 10</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>I₄</td>
<td>0.3478</td>
<td>42.5 37.5 20</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>I₅</td>
<td>0.05217</td>
<td>42.5 27.5 30</td>
<td></td>
</tr>
</tbody>
</table>

The initial ingredient were kept at kept at 100°C for 24 hours to remove the moisture and were weighted as per molar ration with an accuracy of 0.00001 g using AE136 mettler (Switzerland) monopan electronic Balance. After grinding them thoroughly in acetone for homogeneity, then dried mixture kept furnace at 400°C for 2 hour, then temperature increase to 600°C and maintain at 1 hour. After evolution of decomposition product the melt was kept at 900-1050 °C for 30 minute then viscous melt was quenched in aluminum block kept at room temperature. The quenching rate offered by the teo block was found to be approximately 10²°C/s.

The prepared sample were studied by electrical characterization. The electrical characterization has been done in three different way. 1. Complex impedance Spectroscopy (CIS). 2. AC Conductivity. 3. Transport number determination.

**II. RESULTS AND DISCUSSION**

**Complex impedance spectroscopy**

The variation of real and imaginary parts of complex impedance as a parametric function of applied electric frequency for Li₂O:SiO₂:B₂O₃ at 200°C, 250°C 300°C shown in figure.
A single depressed semicircular arc can be clearly seen at both temperature. An incline straight line is due to electrode-electrolyte interface. On the other hand, the distorted semicircular arc is the manifestation of ionic motion through solid.

V. CONCLUSION

The glasses prepared by quenching technique are found to be ionic conductors. Amongst all the sample studied, the glass with 42.5Li2O:57.5B2O3:0SiO2 composition exhibits maximum conductivity.

REFERENCES