Abstract—Synthesis of a new Ag⁺ ion conducting glass-polymer electrolytes (GPEs): (1-x) PEO: x [0.75(0.75AgI:0.25AgCl):0.25(Ag₂O:P₂O₅)]:0.25Ag₂O:P₂O₅], where x = 0 < x < 50 wt. (%), are reported. GPEs have been casted using hot-press techniques. The highest conducting composition: 70PEO: 30[0.75(0.75AgI:0.25AgCl):0.25(Ag₂O:P₂O₅)] with conductivity (σ) ~ 6.0 × 10⁻⁶ S.cm⁻¹ was identified from the compositional dependent conductivity studies and this has been referred to as the Optimum Conducting Composition (OCC). Approximately three orders of conductivity enhancement have been achieved in GPE OCC from that of the pure polymer PEO. The glass-polymer complexation has been confirmed by the SEM and DSC analysis. Ion transport parameters viz. ionic conductivity (σ), ionic mobility (µ) and mobile ion concentration (n) have been characterized using different experimental techniques. Solid-state polymeric batteries were fabricated using GPE OCC as electrolyte and the cell-potential discharge characteristics were studied under different load conditions.

Keywords---Glass Polymer Electrolytes, Hot-Press Method, SEM, DSC

I. INTRODUCTION

The development of new solid-state dry electrolytes with both high conductivity and limited reactivity with electrodes are great attention recently [1, 2]. Among the known electrolytes, solid polymer electrolytes (SPEs) based on high molecular weight dielectric polymer hosts, generally polyethylene oxide (PEO), seem the most suitable electrolytes for solid state device applications. Their ether groups solvate lithium-ions in the same manner as crown ethers, and confer low reactivity, increasing safety. However, the room temperature conductivities of PEO-based polymer electrolytes are in the range of 10⁻⁷ to 10⁻⁸ S.cm⁻¹ because of low effective carrier mobility in the largely crystalline material below the transition temperature [3, 4]. In a recent work, a number of glass polymer electrolytes (GPEs) have been developed for solid state device applications, which show the high ionic conductivity by stabilizing the highly conductive amorphous phase, improving the electrode–electrolyte interfacial stability by trapping residual impurities, extend shelf-life by decreasing PEO recrystallization rate and increase the lithium-ion transference number [4–7]. SPE/ NCPE/ GPE films are prepared, in general, by a traditional solution-cast method. However, recently a novel hot-press technique has been developed for casting SPE/ NCPE films [8-12].

The present paper, we reports synthesis of a new Ag⁺ ion conducting PEO-based glass polymer electrolytes (GPEs): (1-x) PEO: x [0.75(0.75AgI:0.25AgCl):0.25(Ag₂O:P₂O₅)], where x = 0 < x < 50 wt. (%), using hot-press method. The glass-polymer complexation and materials characterization is also reported with the help of SEM and DSC analysis.

II. EXPERIMENTAL

The AR grade precursor chemcials: poly (ethylene oxide) PEO (10⁵ Mw, Aldrich, USA), AgI (purity >98%, Reidel India), AgCl (>99%, Reidel India), Ag₂O (>98%, Reidel India) & P₂O₅ (>99%, Reidel India) has been used for synthesis of a new Glass Polymer Electrolytes (GPEs): (1-x) PEO: x [0.75(0.75AgI:0.25AgCl):0.25(Ag₂O:P₂O₅)], where x = 0 < x < 50 in wt. (%). Firstly, the Ag⁺ ion conducting phosphate glass: 0.8(0.75AgI:0.25AgCl):0.2(Ag₂O:P₂O₅) have been prepared using melt-ashing technique [13]. This phosphate glass was used as a host salt for synthesis of GPEs. The dry powders of pure polymer PEO and salt in appropriate wt. (%) ratios were homogeneously mixed for ~ 30 min at room temperature then heated separately ~ 70°C (close to the melting point of PEO) for ~ 30 min with mixing continued. It resulted into a soft lump/ slurry which was then pressed (~1.25 ton/ cm²) between two SS- cold blocks, giving rise to a uniform film of thickness ~ 0.013 cm. The details related to hot-press casting of other SPEs/ NCPEs have been given elsewhere in the literature [9,10,12]. Material characterizations were done with the help of SEM (model: JEOL, JXA-8100, Japan) and DSC (model: Perkin Elmer) techniques. The conductivity (σ) -measurements were carried out on different samples at a fixed frequency (i.e. 5 kHz) using an LCR- bridge (model: HIOKI 3520-01, Japan).

A new Ag⁺ ion conducting solid-state polymeric battery was also fabricated in the following cell configuration:

<table>
<thead>
<tr>
<th>Material</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode</td>
<td>Ag (Anode)</td>
</tr>
<tr>
<td>Cathode</td>
<td>(C+I₂+Electrolyte)</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>70PEO: 30[0.75(0.75AgI:0.25AgCl):0.25(Ag₂O:P₂O₅)]</td>
</tr>
<tr>
<td>(GPE OCC)</td>
<td>(C+I₂+Electrolyte)</td>
</tr>
</tbody>
</table>

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The cell performances were studied under different load conditions and the important cell parameters were calculated from the plateau of the discharge profiles.

III. RESULTS AND DISCUSSION

Fig. 1 shows the compositional dependence of room temperature conductivity for the silver phosphate glass electrolytes: [y (0.75AgI:0.25AgCl)+(1-y) (Ag₂O:P₂O₅)], where y in mol. wt. %, synthesized by melt-quenching technique [13]. The conductivity of the glass system increased initially and attained a peak value of x = 0.75, then decreased. The highest conducting composition: 0.75 [0.75AgI:0.25AgCl]: 0.25 [Ag₂O:P₂O₅] with room temperature conductivity σ ~ 5.5 x 10⁻³ Scm⁻¹ has been used as a host salt for synthesis of glass polymer electrolytes (GPEs): (1-x) PEO: x [0.75(0.75AgI:0.25AgCl):0.25(Ag₂O:P₂O₅)], where x = 0 < x < 50 in wt. %.

Fig. 2 shows the room temperature conductivity (σ) variation with different salt concentration for hot-pressed GPEs. The conductivity (σ) increased abruptly (~10² times) after the addition of salt in the host polymer. However, a moderate sized σ-maxima appeared at x = 30 wt. (%) and then decreases on further addition of salts. The GPE films beyond 50 wt. (%) salt concentration were brittle and appeared decreases on further addition of salts. The GPE films beyond 50 wt. (%) salt concentration were brittle and appeared physically less stable. GPE film: 70PEO: 30[0.75(0.75AgI:0.25AgCl):0.25(Ag₂O:P₂O₅)], with room temperature conductivity (σ ~ 6 x 10⁻⁶ S/cm), exhibited optimum conductivity and this has been referred to as Optimum Conducting Composition (OCC). The three orders of conductivity enhancement in GPE OCC are due to the increase in degree of amorphousity/ decrease in degree of crystallinity from that of the pure PEO.

The surface morphology of GPE OCC was observed by scanning electron micrograph (SEM), as shown in Fig. 3. The smooth surface morphology of GPE OCC is clearly indication of increase in degree of amorphousity/ reduction in the crystallinity of pure PEO after salt complexation. This is due to the cross-linking with polymer and the host glassy salts. The thermal properties of GPE OCC and pure PEO have been characterized with the help of very useful DSC technique. Fig. 4 shows the DSC thermograms for the pure PEO and GPE OCC. The broad endothermic peak was observed in SPE OCC at ~ 65-67 °C and it is corresponding to the melting point temperature of pure PEO. The slightly shifting in the melting point temperature towards lower side is due to the complexation of Ag⁺ ion to the ether oxygen of pure PEO and it is also indicative the formation of GPEs.

Fig. 5 shows the cell potential discharge profiles for the solid state polymeric cell under different loads viz. 100 kΩ, 50 kΩ at room temperature, as mentioned in Section 2. The Open Circuit Voltage (OCV) ~ 0.68 V obtained for both the cells. It can be clearly noticed that except for the initial potential drop, OCV value remained practically stable for ~ 35 and ~ 15 hrs. when discharged through 100 & 50 kΩ respectively (i.e. during a low current drain state). However, the cell potential decreased relatively faster when discharge through 50 kΩ load (i.e. during higher current drain states). Hence, a GPE based newly polymer battery, performed fairly satisfactorily especially under low current drains.

IV. CONCLUSION

A new Ag⁺ ion conducting glass-polymer electrolyte: 70PEO: 30[0.75(0.75AgI:0.25AgCl):0.25(Ag₂O:P₂O₅)] has been synthesized using a novel hot-press technique. Three orders of conductivity enhancement were observed in GPE from that of the pure polymer. The materials characterization has been done by SEM and DSC analysis. This GPE can be potentially used to fabricate all solid state polymer batteries.

REFERENCES


FIGURE CAPTIONS

Figure 1: ‘Log σ – y’ plots for glassy electrolytes: y [0.75AgI:0.25AgCl]: (1-y) [Ag₂O:P₂O₅] [13].

Figure 2: ‘Log σ – x’ plots for glass polymer electrolytes: (1-x) PEO: x [0.75(0.75AgI:0.25AgCl):0.25(Ag₂O:P₂O₅)].

Figure 3: SEM image of GPE OCC: 70PEO: 30[0.75(0.75AgI:0.25AgCl):0.25(Ag₂O:P₂O₅)].

Figure 4: DSC thermograms: (a) pure PEO and (b) GPE OCC: 70PEO: 30[0.75(0.75AgI:0.25AgCl):0.25(Ag₂O:P₂O₅)].

Figure 5: Cell potential discharge profile as a function of load conditions: 100 KΩ (●) and 50 kΩ (■) at room temperature.