Preparation of some metal chloride doped silver phosphate glass electrolytes–Application to solid state batteries

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Silver phosphate glasses doped with various compositions (0, 1, 5, 10 and 15 wt%) of some metal chlorides, viz, lithium, sodium, magnesium, lead and copper are prepared by melt quenching technique. These glasses are characterized by X-ray diffraction analysis, FTIR spectra, transference number measurements and electrical conductivity studies. The glasses exhibiting maximum electrical conductivity are used as solid electrolytes for the fabrication of solid-state batteries with the cell configurations: Ag ∥ $Ag_2O – P_2O_5 – MCl_y$ ∥ (C + I_2) (where $y = 1$ when M is Li or Na; $y = 2$ when M is Mg, Pb or Cu). The open circuit voltage (OCV) and discharge characteristics of all the fabricated batteries have been studied. The addition of metal chlorides to silver phosphate glass matrix results in a substantial increase in the OCV. The cell with the configuration Ag ∥ $Ag_2O – P_2O_5 – (15\%)$ Li Cl ∥ (C + I_2) gives the best performance. The results have been discussed on the basis of FTIR and electrical conductivity studies.

Keywords: Silver phosphate glass, Solid state battery, Glass electrolyte, Ion conducting glasses

Fast ion conducting (FIC) glasses are interestingly useful materials for developing solid-state batteries and other ionic devices[1-3]. Among FIC glasses of different kinds phosphate glasses are more important because they can be easily prepared, possess simple composition, exhibit high ionic conductivity and have diverse applications[4,5]. They have attracted greater attention of the electrochemical research communities[6-12].

During the past few years, a number of Li^{+}, Na^{+}, Ag^{+} and Cu^{2+} fast ion conducting phosphate glasses which exhibit high ionic conductivity at ambient temperatures have been synthesized and studied[3,13-16]. Among them, Ag^{+} ion based glasses have recently attracted widespread attention mainly due to their high ionic conductivity at ambient temperatures, better stability and potential applications in the development of several electrochemical devices especially solid-state batteries[8,9,15,17]. Very recently Bhattacharya and Ghosh[18-23] have reported the role of Ag^{+} ions in $(AgI)_x – (AgPO_3)_{1-x}$, $xAg_2O – (1–x)$ TeO_2, Ag_2S doped $AgPO_3$, superionic iodomolybdate glass composites doped with nanoparticles of zinc oxide, AgI doped silver vanadate and AgI doped silver molybdate superionic glasses. The results of their investigation are highly important in order to reveal the role of the mobility of Ag^{+} ions for enhancement of the conductivity and ion transport behaviour in fast ion conducting glasses. Therefore, much effort has been made to synthesize fast ion-conducting silver based glassy electrolytes[17,24,25] which could be used in the fabrication of solid-state batteries with better discharge characteristics. Solid state batteries with FIC glassy materials as solid electrolytes are very interesting and competitive in comparison to other batteries due to the absence of any possible liquid leakage or gassing, a very long shelflife and the possibility of a wide temperature range operation. The possibility of miniaturisation makes them suitable for use in implantable electronic instruments such as cardiac pacemakers and physiological monitoring. In order to obtain new glassy electrolytes with enhanced conductivity and increased stability at ambient temperatures, attempts have also been made to add some other metal ions such as lithium, sodium, magnesium, lead and copper in the phosphate glass matrix[6,13,14,16,26]. However, limited studies have been done to use them as electrolytes for the fabrication of solid-state batteries[14,27].

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In view of the above, several samples of silver ion conducting phosphate glasses doped with various compositions of Li, Na, Mg, Pb and Cu chlorides have been synthesized to attain high ionic conductivity in our laboratory. Solid-state cells were fabricated by using those glasses which exhibited maximum electrical conductivity as solid electrolytes.

The present paper reports the results of our investigation on the newly fabricated solid state batteries with the following cell configurations:

$$Ag \parallel Ag_2O - P_2O_5 - MCl_y \parallel (C + I_2)$$
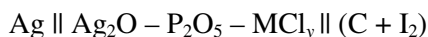
[where $y = 1$ when M = Li or Na ; $y = 2$ when M = Mg, Pb, or Cu]

A battery using undoped silver phosphate glass as electrolyte with the cell configuration:

$$Ag \parallel Ag_2O - P_2O_5 \parallel (C + I_2)$$
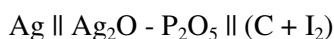
was also fabricated to observe the effect of the dopant Li^+, Na^+, Mg^{2+}, Pb^{2+} and Cu^{2+} ions on the open-circuit voltage and discharge characteristics of the cells.

Experimental Procedure

All the chemicals used in the preparation of metal chloride doped silver phosphate glass as electrolytes were of analytical grade. Silver nitrate (Merck), ammonium dihydrogen phosphate (Merck), lithium chloride (BDH), sodium chloride (Merck), magnesium chloride (Merck), lead chloride (Merck) and copper chloride (Merck) were used as such.

All the phosphate glasses were prepared by the melt quenching technique in a way similar to that reported earlier[8]. Doped and undoped glasses were prepared simultaneously in two different platinum dishes. Undoped silver phosphate glass was produced by heating a 1:1 molar mixture of silver nitrate and ammonium dihydrogen phosphate. Similarly, for preparing silver phosphate glasses doped with metal chlorides appropriate amounts of Li/Na/Mg/Pb/Cu chloride were added to a 1:1 molar mixture of silver nitrate and ammonium dihydrogen phosphate. Both the mixtures were first heated slowly in an oven at 150-200°C, care being taken that the material did not spurt out in the initial stages when frothing occurred due to brisk evolution of ammonia, oxides of nitrogen, and water vapour. After the frothing subsided, the platinum dishes were placed in a muffle furnace, which was preheated to the desired temperature in the range 800-900°C. The melts were heated in the muffle furnace for a period of 4 h and then quenched to yield glassy products. These glass electrolytes were then dried in an oven at 100°C, placed in sample tubes, and stored in a desiccator.

X-ray diffraction studies of the synthesized undoped and metal chloride doped silver phosphate glasses were carried out on a Philips PW 3020 X-ray powder diffractometer using Cu-K_α radiation.

The FTIR spectra of glasses were recorded on a SHIMADZU 8201 PC FTIR spectrometer in the range 4000-400 cm^{-1} using KBr pellets.

The ionic transference numbers of all the glassy samples were determined by Wagner's polarization technique[28] as described earlier[8].

The electrical conductivities were determined by means of a HIOKI 3520 LCR tester at different temperatures which ranged from room temperature to 200°C at a frequency of 100 kHz in a manner similar to that reported earlier[29].

All chemicals used in the preparation of solid-state batteries were of analytical grade. Graphite (Eltecks), iodine (Merck) and synthesized silver phosphate glasses both undoped and doped with Li, Na, Cu, Mg and Pb chlorides were used as such without further purification.

In the present investigation, six batteries were fabricated. In all these, silver metal was used as the anode, silver phosphate glass as the electrolyte, and a mixture of graphite and iodine in 1:1 weight ratio as the cathode. The glasses were powdered and pressed in a pelletizing die to give the desired electrolyte pellets[30].

The materials used as the cathode were ground into fine powders, mixed, poured into the die and pressed into a pellet. In all the cases, a pressure of 5 ton cm^{-2} was applied to produce pellets of electrolytes and cathode. The dimensions of electrolyte pellets were kept the same (diameter 0.76 cm and thickness is 0.50 cm). The electrolyte pellet was kept between the cathode pellet and the silver metal anode in a sample holder to give the desired batteries with the following cell configurations

$$Ag \parallel Ag_2O - P_2O_5 \parallel (C + I_2)$$

$$Ag \parallel Ag_2O - P_2O_5 - Li / \text{ or } NaCl \parallel (C + I_2)$$
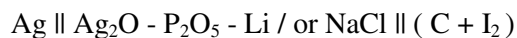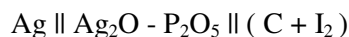
and

$Ag \parallel Ag_2O$ - P_2O_5 - Mg / Pb / or Cu $Cl_2 \parallel$ ($C + I_2$)

For characterizing the cells, the OCVs and discharge characteristics were monitored at room temperature (27°C) with a humidity level of 45%.

The OCVs of all the cells were measured immediately after their fabrication by means of a digital multimeter (Scientific multimeter-4022).

The discharge characteristics of all the cells were monitored under a constant load of 100 kΩ. For the same load resistance, the voltage (*V*) was measured as a function of time[31]. The schematic circuit diagram for studying discharge characteristic of a cell is shown in Fig. 1.

Results and Discussion

The glassy nature of all the samples prepared as electrolytes for preparation of solid-state batteries were confirmed by employing X-ray diffraction technique. The X-ray diffraction studies for all the samples show broad diffused peaks in the diffractogram which indicates the amorphous nature of all the glasses and absence of any crystalline regions in them.

The FTIR spectral studies of the doped and all undoped silver phosphate glasses yielded nearly similar spectra. Figure 2 shows a typical spectra of Ag_2O–P_2O_5 glassy systems doped with different metal chlorides (15% LiCl, 15% NaCl 5% $MgCl_2$, 5% $PbCl_2$ and 5% $CuCl_2$) in the frequency range 2000-450 cm^{-1}. The comparison of spectral bands suggests that all the characteristic bands found in the spectra of the undoped silver phosphate glass are also present in the
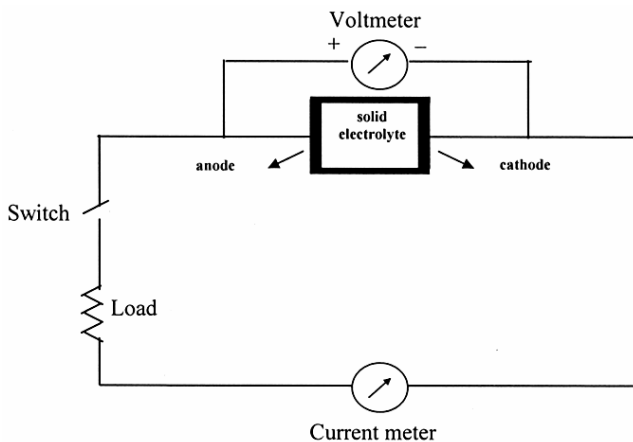
metal chloride doped glasses with very slight shift (5-25 cm^{-1}) in their peak frequencies.

The absorption bands in all the IR spectra of the glasses appearing in the range 1633-1599 cm^{-1} may be attributed to the δ (H_2O) in – plane bending vibrational modes of physisorbed water molecules[32,33]. The absorption bands appearing in the range 1347-1351 cm^{-1} in all the metal chloride doped glasses may be attributed to the stretching mode of P = O double
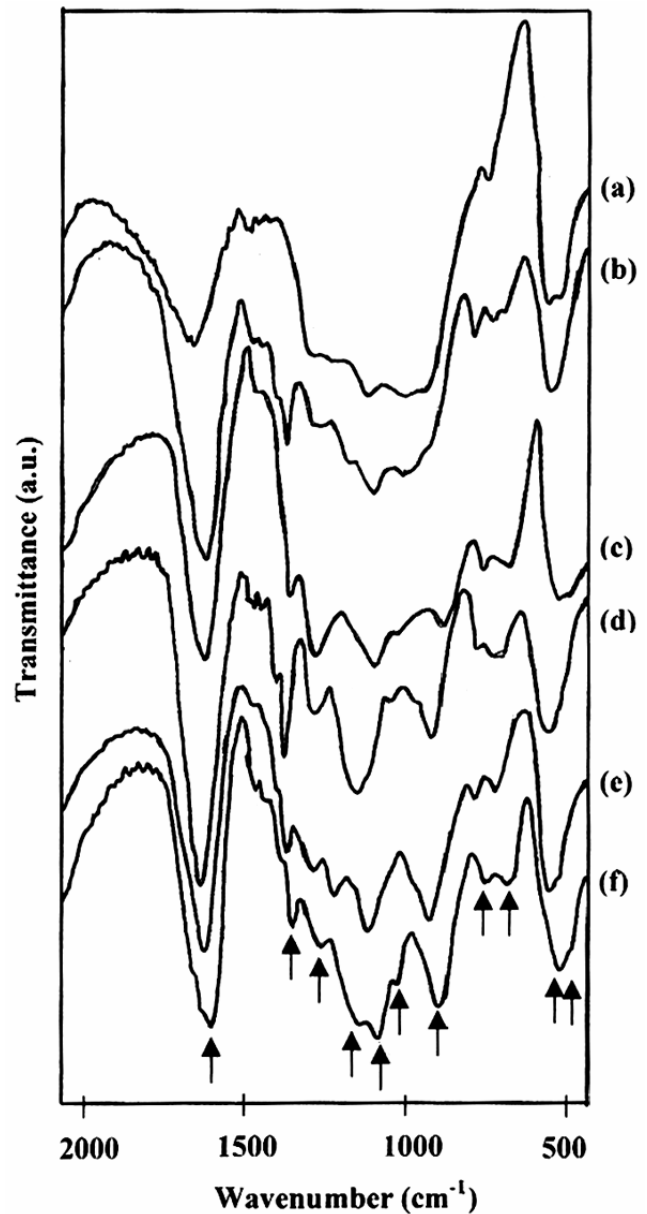

Fig. 2—FTIR spectra of metal chloride doped silver phosphate glasses in the range 450 – 2000 cm^{-1} (a) Ag_2O – P_2O_5, (b) Ag_2O – P_2O_5 – (15%)LiCl, (c) Ag_2O –P_2O_5 – (15%) NaCl, (d) Ag_2O – P_2O_5 – (5%) $MgCl_2$, (e) Ag_2O – P_2O_5 – (5%) $PbCl_2$ and (f) Ag_2O – P_2O_5 – (5%) $CuCl_2$

Fig. 1—Schematic circuit diagram for studying discharge characteristics of a cell

bonds[34,35]. However, in the undoped glass, a weak shoulder is present at ~1390 cm^{-1}. The strong intense bands in the region 1250-1278 cm^{-1} can be ascribed to the asymmetric stretching of PO$_2$ terminal groups, υ_{asy}(PO$_2$)[35,36]. The weak bands appearing at 1122-1145 cm^{-1} are assigned to the PO$_2$ symmetric stretching mode, υ_{sym}(PO$_2$) of the two non-bridging oxygens[36,37]. The absorption bands near 1100 cm^{-1} and 1000 cm^{-1} have been assigned to P – O$^-$ groups, the phosphate non- bridging oxygen portion of PO$_4$ tetrahedra in a chain structure[7]. In the present investigation such bands have been found in the range 1080-1103 cm^{-1} and 965-1020 cm^{-1} respectively confirming the presence of P – O$^-$ groups in all the glassy systems. The absorption bands appearing in the range 888-910 cm^{-1} could be assigned to the asymmetric stretching modes of the in-chain P – O – P linkages, υ_{asy}(P – O – P), while the two bands observed in the range 760-770 cm^{-1} and 690-720 cm^{-1} suggest the presence of symmetric stretching modes of the linear P – O – P groups, υ_{sym} (P – O – P)[33,34]. The two weak bands appearing in the range 526-538 cm^{-1} and 460-495 cm^{-1} have been assigned as the bending vibrations of δ (O = P – O) and δ (O – P – O) respectively[7,33].

On the basis of FTIR spectral studies, it may be inferred that the network of the phosphate glass consists of PO$_4$ tetrahedra with three bridging (P – O – P) and one non– bridging (P = O) oxygen atoms. On the addition of Ag$_2$O into the PO$_4$ network of the phosphate glass, the three-dimensional network is converted into linear phosphate chains[33] and the P – O – P bridging oxygens are replaced by P⋯O$^-$– Ag$^+$ linkages. When metal chloride is added in the undoped silver phosphate glass, formation of P – O – M bonds (where M = Li, Na, Mg, Pb or Cu) occur in the glass structure[32]. In the case of monovalent lithium and sodium chloride doped silver phosphate glasses, the metal ions (Li$^+$/Na$^+$) get attached to the negative ends of the P – O$^-$ of the phosphate chain. On the other hand, in the case of divalent metal chlorides, the Mg^{2+}, Pb^{2+} and Cu^{2+} ions serve as ionic cross-links between the non-bridging oxygen of two phosphate chains of the silver phosphate glass[32].

The T_g values of all the glassy systems, as obtained by DSC are reported in Table 1. The T_g values show a systematic increase as the dopant chloride is changed from lithium to copper and the following sequence in T_g values is observed

T_g (-LiCl) < T_g (-NaCl) < T_g (Ag$_2$O – P$_2$O$_5$) < T_g (-MgCl$_2$) < T_g (-PbCl$_2$) < T_g (-CuCl$_2$)

The T_g value of phosphate glass is related to its chain length, cross-link density and bonding strength of the phosphate chains[7]. In the case of divalent metal chlorides as dopants the T_g values are high which reflects an increase in cross-link strength of the glass network. This is because of formation of P – O – M type linkages between two chains of the phosphate glasses. However, in the case of monovalent metal chlorides doped glasses, the low values of T_g could be attributed due to the loosening of the glass structure[38,39]. The monovalent Li$^+$ or Na$^+$ ions do not increase the cross-link density by interconnecting two liner chains of silver phosphate glass.

The percent ionic transference number (t_i) of all the glass electrolyte and their conductivities at room temperature (27°C) and at 200°C are reported in Table 1. The (% t_i) values lie in between 93.3-98.3 for all the glass electrolytes. This indicates that the charge transport in these glasses is mainly through the ions. However, a part "electronic" conductivity cannot be fully ruled out. The inhererent limitation of Wagner's polarization method[28] lies in the true identifications of initial current (I_T) because some polarization does get set in before the reading of I_T can be recorded. So, in

Table 1—Glass transition temperature (T_g), percent ionic transference number (% t_i) and conductivity (σ) values of various silver phosphate glass electrolytes

S.No.	Glassy system	Glass transition temperature (T_g), °C	% ionic transference number (% t_i)	Conductivity (σ), S. cm^{-1}	
				at room temp. (30°C)	at 200°C
1	Ag$_2$O – P$_2$O$_5$	208.8	95.4	8.51×10^{-7}	2.69×10^{-4}
2	Ag$_2$O – P$_2$O$_5$ – (15%) LiCl	184.2	98.3	8.91×10^{-5}	4.16×10^{-3}
3	Ag$_2$O – P$_2$O$_5$ – (15%) NaCl	185.9	98.0	6.45×10^{-5}	4.16×10^{-3}
4	Ag$_2$O – P$_2$O$_5$ – (5%) MgCl$_2$	213.6	94.1	8.12×10^{-6}	8.70×10^{-4}
5	Ag$_2$O – P$_2$O$_5$ – (5%) PbCl$_2$	215.6	93.8	7.41×10^{-6}	7.76×10^{-4}
6	Ag$_2$O – P$_2$O$_5$ – (5%) CuCl$_2$	221.8	93.3	3.80×10^{-6}	6.76×10^{-4}

general t_{ion} from this method comes out to be slightly lower than 1 even for pure ionic conductor. But such an error makes $t_{ion} \approx 0.97$-0.99 instead of 1. But the present values of $t_{ion} \sim 0.93$-0.98 lies slightly below the above value. So there is a possibility of partial "electronic" conduction in $Mg/Pb/CuCl_2$ doped silver phosphate glasses. However, these glasses with t_{ion} values 0.941, 0.938 and 0.933 respectively could be treated principally as ionic conductors[40].

The electrical conductivity values of all the glasses measured from room temperature to 200°C at 100 kHz frequency are reported in Table 1. The electrical conductivity of undoped Ag_2O - P_2O_5 glass is less than all the metal chloride doped glassy systems. The room temperature σ values for monovalent lithium and sodium chloride doped glasses are greater than those of divalent Mg. Pb and Cu chloride containing glasses. Out of all the synthesized glasses, the σ values of (15 wt%) LiCl/NaCl, and (5 wt%) Mg, Pb and $CuCl_2$ doped silver phosphate glasses exhibited the maximum conductivities in their respective series, both at room temperature and at 200°C. Therefore, they were used as electrolytes for fabricating the solid-state batteries. The configuration of six batteries and their corresponding OCV values are given in Table 2. The discharge curves (voltage versus time) of the cells at a load resistance of 100 kΩ are shown in Figs 3 and 4.

The results of OCV values suggest that when the dopant salt in the glass electrolyte $Ag_2O – P_2O_5 – MCl_y$ changes from LiCl (cell II) to $CuCl_2$ (cell VI), the OCV value decreases from 0.668 V (LiCl) to 0.588 V ($CuCl_2$). When undoped glass $Ag_2O – P_2O_5$ is used as the electrolyte (cell I), the OCV value is as low as 0.298 V. In between, there are values of 0.653 V for NaCl (cell III), 0.611 V for $MgCl_2$ (Cell IV) and 0.597 V for $PbCl_2$ (cell V). These results clearly indicate that the addition of Li/Na/Mg/Pb/Cu chloride in silver phosphate glass increases markedly the OCV value in the order:

OCV (-LiCl) > OCV (-NaCl) > OCV (-$MgCl_2$) > OCV (-$PbCl_2$) > OCV (-$CuCl_2$)

The explanation for higher OCV values in doped silver phosphate glasses may be given in the following manner. The OCV value of undoped silver phosphate glass is 0.298 V. On doping the silver phosphate glass with metal chlorides the OCV values increase. The results of FTIR studies suggest that in the undoped silver phosphate glass, when metal ions are added, a few Ag^+ ions are replaced by the dopant metal ions from the main chain of the silver phosphate glass[32]. This causes an increase in the concentration of free Ag^+ ions in the glass matrix which eventually leads to significant increase in the OCV values of the cells containing doped glasses as electrolytes. The results show that the OCV values of the cells containing glassy electrolytes doped with monovalent lithium and sodium ions are higher than those cells in which the glassy electrolytes are doped with divalent magnesium, lead and copper ions. This could be explained on the basis of increase in cross-links in Mg/Pb/ or $CuCl_2$ doped glasses. When Mg/Pb/ or $CuCl_2$ are added as dopants, formation of $P – O^- – M^+$ linkages occur in the PO_4 tetrahedra and the doped bivalent metal cations (Mg^{2+}, Pb^{2+} or Cu^{2+}) serve as ionic cross-links between the non-bridging oxygen of two different phosphate chains. This leads to an increase in the cross-link density of the glassy network[32,41]. The mobility of free replaced Ag^+ ions is thus restricted and hence the OCV values of the cells IV, V and VI are low. On the contrary, in glasses doped with monovalent chlorides, the Li^+ or Na^+ ions get attached to the negative ends of P–O^- groups of the phosphate glass chain by replacing Ag^+ ions. In this case, since no cross-linking between two different phosphate chains takes place, the movement of free replaced Ag^+ ions is not restricted. This eventually leads to higher OCV values in cells II and III.

The discharge times of cells I , II , III , IV, V and VI with $C + I_2$ as cathode obtained from the discharge curves (Figs 3 and 4) are nearly ~6h, ~26 h, ~19 h, ~ 10 h, ~8 h and ~8 h respectively. The cell II with the configuration Ag ‖ Ag_2O - P_2O_5 - (15%) LiCl ‖ ($C + I_2$) gives the best OCV (0.668 V) and discharge time

Table 2—Open circuit voltage (OCV) values for various cells using doped and undoped silver phosphate glasses as electrolytes

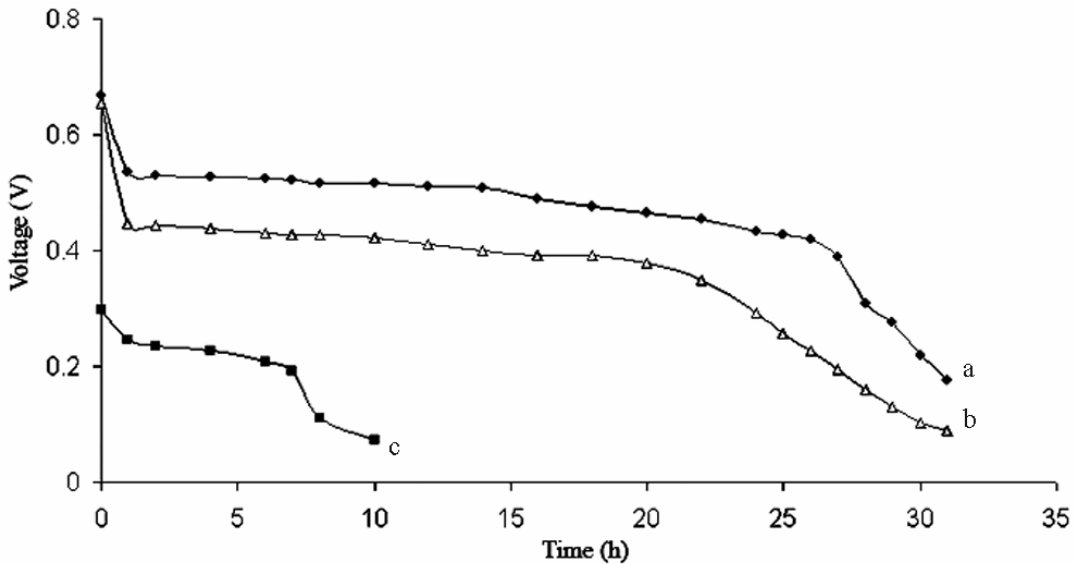| Cell No.	Anode	Electrolyte	Cathode	OCV (V)
I	Ag	$Ag_2O – P_2O_5$	$C + I_2$ (1:1)	0.298
II	Ag	$Ag_2O – P_2O_5 – (15\%)$ LiCl	$C + I_2$ (1:1)	0.668
III	Ag	$Ag_2O – P_2O_5 – (15\%)$ NaCl	$C + I_2$ (1:1)	0.653
IV	Ag	$Ag_2O – P_2O_5 – (5\%)$ $MgCl_2$	$C + I_2$ (1:1)	0.611
V	Ag	$Ag_2O – P_2O_5 – (5\%)$ $PbCl_2$	$C + I_2$ (1:1)	0.597
VI	Ag	$Ag_2O – P_2O_5 – (5\%)$ $CuCl_2$	$C + I_2$ (1:1)	0.588

Fig. 3 — Discharge curves (voltage vs time) at load resistance 100 kΩ for (a) Cell II, (b)   Cell III and (c) Cell I
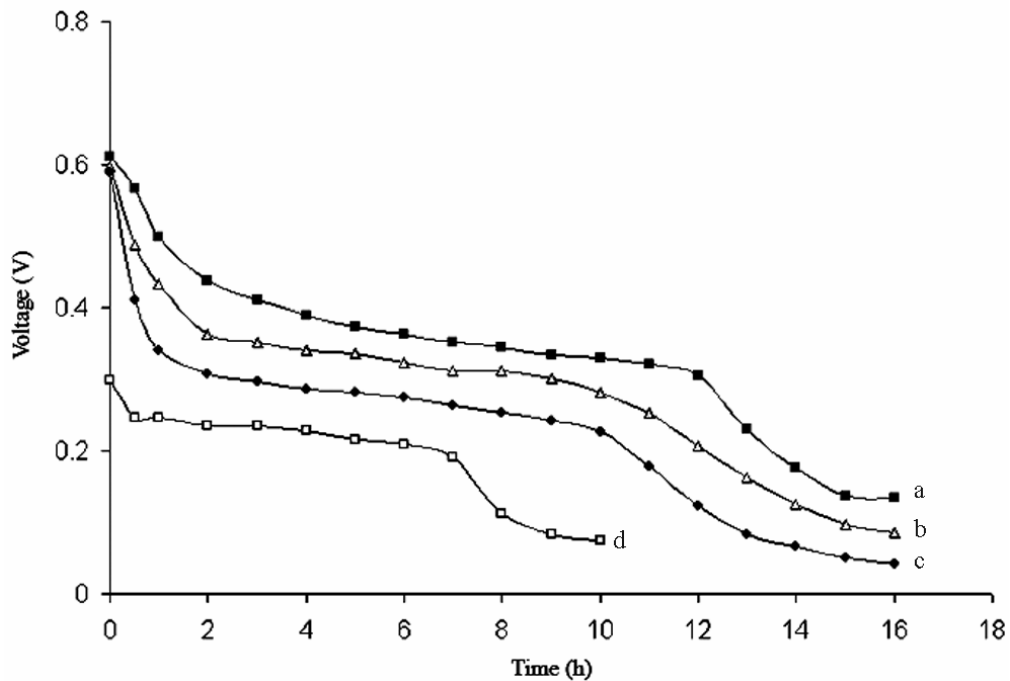

Fig. 4 — Discharge curves (voltage vs time) at load resistance 100 kΩ for (a) Cell IV, (b) Cell V, (c) Cell VI and (d) Cell I

(~ 26 h) compared with all other cells. The OCV value (0.653V) and discharge time (~ 19 h) of cell III having cell configuration Ag ‖ Ag$_2$O – P$_2$O$_5$ – (15%) NaCl ‖ (C + I$_2$) is also quite satisfactory. The measured OCV values of cell II and cell III are in good agreement with the theoretically calculated OCV value (0.687 V) of a silver solid-state battery using iodine as cathode[30]. Thus, these Li/Na chloride doped silver phosphate

glasses could be used as interesting model systems for the development of solid-state batteries.

The high OCV values and lives (discharge times) of the cells using metal chloride doped silver phosphate glasses as electrolytes could be explained in the following manner. The dopant metal chloride in all probability reacts with Ag$_2$O to form AgCl and metal oxide during glass formation:

$$Ag_2O + x\,M\,Cl_y = \quad 2\,AgCl + M_xO$$
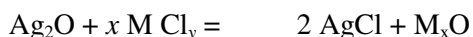
where $y = 1$; $x = 2$ when M is Li or Na and $x = 1$; $y = 2$ when M is Mg, Pb or Cu. Due to this reaction, the glass electrolyte $Ag_2O – P_2O_5 – MCl_y$ changes to the pseudo-quaternary system $AgCl – Ag_2O – P_2O_5 – MCl_y$. Since a part of this system $AgCl – Ag_2O – P_2O_5$ possesses high electrical conductivity and falls into the category of fast ion conducting glasses[42], a high OCV value and long cell life is obtained for the cells containing doped glasses as electrolytes.

The observed decreasing trend in the OCV values and lives of the cells also seems to depend on the electrode potential values of the metal ions[43]. The Li^+ having highest electrode potential can replace more Ag^+ ions from the main glassy chain of silver phosphate glass in comparison to other metal ions having lower electrode potential values. Thus, cell II with $Ag_2O – P_2O_5 – LiCl$ glass as an electrolyte shows the maximum OCV value and life while cell VI with $Ag_2O – P_2O_5 – CuCl_2$ glass as an electrolyte, exhibits the lowest OCV and minimum life since Cu^{2+} has the lowest electrode potential. The OCV values and lives of the cells with $Ag_2O – P_2O_5 – NaCl$, $Ag_2O – P_2O_5 – MgCl_2$ and $Ag_2O – P_2O_5 – PbCl_2$ as electrolytes fall in between cells II and VI according to the electrode potential values of Na^+, Mg^{2+} and Pb^{2+}.

Conclusions

On the basis of ion transport and cell discharge characteristics studies reported in this paper, it can be concluded that silver phosphate glasses doped with Li/NaCl are potential electrolytes for the fabrication of solid-state batteries. Among the monovalent Li/NaCl doped silver phosphate glasses, viz, $Ag_2O – P_2O_5 – (15\%)\,LiCl$ and $Ag_2O – P_2O_5 – (15\%)\,NaCl$ when used as electrolytes in cells yield high OCV values and long cell lives. However, when the glassy systems containing divalent metal chlorides are used as electrolytes, the OCV values and cell lives of the resultant cells decrease markedly.

Acknowledgements

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