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Short communication

Characteristics of solid-state batteries with zinc/cadmium halide-doped silver phosphate glasses as electrolytes

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Abstract

Several samples of ion-conducting silver phosphate glasses doped with zinc/cadmium halides are prepared and subjected to X-ray diffraction analysis, transference number measurement, and electrical conductivity studies. The percentage transference numbers of these glasses are found to lie between 98.3 and 99.3, which suggests that the glasses are essentially ionic conductors. The conductivity values range from 1.66×10^{-2} to 8.66×10^{-2} S cm^{-1} at 300 °C. Solid-state batteries using these glassy systems as electrolytes with the cell configurations $Ag||Ag_2O–P_2O_5–(20\%)Zn/CdX_2||(C + I_2)$ and $Ag||Ag_2O–P_2O_5–(20\%)Zn/CdX_2||(C + I_2 + \text{electrolyte})$ (where X is Cl, Br or I) have been fabricated and their discharge characteristics studied. Cells with undoped silver phosphate glasses as electrolytes have also been prepared and studied. The addition of Zn/CdX_2 to silver phosphate glass results in a substantial increase in the open-circuit voltage in the order $MI_2 > MBr_2 > MCl_2$ (where M is the dopant cation). Cells with $Ag||Ag_2O–P_2O_5–(20\%)Zn/CdI_2||(C + I_2 + \text{electrolyte})$ deliver the best performance.

Keywords: Silver phosphate glass; Solid-state battery; Glass electrolyte; Open-circuit voltage; Silver-ion conductors; Zinc/cadmium halides

1. Introduction

Research on solid-state batteries and technological applications of solid-state ionics have been reviewed by several authors [1–4]. The main objective of such studies is to find and develop suitable materials for solid-state batteries that can be operated at normal ambient temperatures. Superionic glasses [5–7] are of great technological interest because of their potential use in the fabrication of microbatteries in heart pacemakers and microchip devices. A number of Li^+, Na^+, Ag^+ and Cu^+ ion-conducting glasses which exhibit high ionic conductivity at ambient temperatures are known [8]. Ag^+ ion-conducting glasses [9–12] have attracted special attention due to their ease of preparation in different forms and their high values of conductivity at room temperature. Silver ion-conducting glasses are also interesting from an academic point of view and can be used as model systems for the development of solid-state batteries [13]. Therefore, much effort has been devoted to the preparation of silver-based solid electrolytes [14–16]. Zn/Cd halide-doped silver phosphate glasses with high values of ionic conductivities (1.66×10^{-2} to 8.66×10^{-2} S cm^{-1} at 300 °C) have recently been synthesized in our laboratory [17]. It was considered worthwhile to fabricate/develop solid-state batteries using these new silver phosphate glasses as electrolytes. The present communication reports studies on the fabrication and the characterization of solid-state batteries with following cell configurations:

$$Ag||Ag_2O–P_2O_5–(20\%)Zn/CdX_2||(C + I_2)$$

$$Ag||Ag_2O–P_2O_5–(20\%)Zn/CdX_2||(C + I_2 + \text{electrolyte})$$

where X is Cl, Br or I. In the second cell configuration, a small amount of the glassy electrolyte was also added to the cathode to examine its effect on cell performance.

Batteries using undoped silver phosphate glass as electrolyte with the cell configurations:

$$Ag||Ag_2O–P_2O_5||(C + I_2)$$

$$Ag||Ag_2O–P_2O_5||(C + I_2 + \text{undoped electrolyte})$$

were also fabricated to observe the effect of dopant salts Zn/CdX_2 on the open-circuit voltage (OCV) and discharge characteristics of the cells. The effect of two different cathode configurations on OCVs and discharge characteristics of the cells have also been discussed.

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2. Experimental

2.1. Preparation of glass electrolytes

All the chemicals used in the preparation of Zn/Cd halide-doped silver phosphate glass electrolytes were of analytical grade. $AgNO_3$, ammonium dihydrogen phosphate, $ZnCl_2$, $ZnBr_2$, ZnI_2, $CdCl_2$, $CdBr_2$ and CdI_2 were used as received for preparing the glasses.

Silver phosphate glasses were prepared by the melt quenching technique [18,19]. Undoped silver phosphate glasses were produced by heating a 1:1 molar mixture of silver nitrate and ammonium dihydrogen phosphate in a platinum dish. Similarly, for preparing silver phosphate glasses doped with 20 wt.% zinc/cadmium halide, appropriate amounts of zinc or cadmium halide were added to a 1:1 molar mixture of silver nitrate and ammonium dihydrogen phosphate in a second platinum dish. Both the mixtures were first heated slowly in an oven at 150–200 °C and care was 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 700–800 °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.

2.2. X-ray diffraction studies

X-ray diffraction studies of the synthesized undoped and doped (with 20 wt.% zinc/cadmium halide) silver phosphate glasses were carried out on an automatic X-ray powder diffractometer.

2.3. Transference number measurements

The ionic transference number of all the glassy samples was determined by the Wagner's polarization method [20].

2.4. Electrical conductivity measurements

Electrical conductivities were determined by means of a HIOKI 3520 LSR tester [21] at different temperatures which ranged from room temperature to 300 °C, and at a frequency of 100 kHz.

2.5. Battery fabrication

All chemicals used in the preparation of the solid-state batteries were of analytical grade. Graphite (Reidel, India) silver (Qualigens), iodine (Glaxo) and synthesized silver phosphate glasses, both undoped and doped with (20 wt.%) MX_2 (where M is Zn or Cd and X is Cl, Br or I), were used as such without further purification.

In the present investigation, 10 batteries were fabricated. In seven of these, silver was used as the anode, silver phosphate glass as the electrolyte, and a mixture of graphite and iodine in the ratio 9:1 as the cathode. In the remaining three cells, the anode was unchanged but a mixture of graphite, iodine and silver phosphate glass electrolyte in the ratio 8:1:1 was used as the cathode. These three components were powdered and successively pressed in a pelletizing die to give the desired battery [22]. The material used as the anode was ground into fine powder, poured into the die, and pressed into a pellet. Similarly, the powdered cathode material and the powdered electrolyte were converted into pellets.

In all the cases, a pressure of 5 t cm^{-2} was applied to produce pellets of anode, electrolyte and cathode. The dimensions of the electrolyte pellets were kept the same (diameter 0.76 cm, thickness 0.50 cm). The electrolyte pellet was located between the cathode and the anode in a sample holder to yield the desired cell configurations, viz.

$$Ag||Ag_2O{-}P_2O_5{-}Zn/CdX_2||(C + I_2)$$

$$Ag||Ag_2O{-}P_2O_5{-}Zn/CdX_2||(C + I_2 + \text{electrolyte})$$

2.6. Battery characterization

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

2.6.1. Open-circuit voltage

The OCVs of all cells were measured immediately after fabrication by means of a high impedance multimeter (Phillips model PM 2718). The values were monitored for 24 h. The OCVs took some time to stabilize (∼12 h). The measurement of OVC value was conducted after 24 h for all cells.

2.6.2. Discharge characterisitcs

The discharge characteristics of all cells were monitored under a constant load of 1 MΩ. For the same load resistance, the current (μA) and voltage (V) were measured as a function of time [15].

3. Results and discussion

The X-ray diffraction patterns for all samples show that the prepared glasses were amorphous in nature with hardly any crystalline regions.

The configurations of the 10 different batteries that were fabricated by using undoped and 20 wt.% Zn/CdX_2 doped silver phosphate glasses as electrolytes with two different types of cathodes are given in Table 1. The corresponding OCV values are also listed. The discharge curves (voltage versus time) of the cells at a load resistance of 1 MΩ are

Table 1
Different cell configurations and open-circuit voltage (OCV) values for various cells using doped and undoped silver phosphate glasses as electrolytes

Cell	Anode	Electrolyte	Cathode	OCV (V)
I	Ag	Ag_2O–P_2O_5–ZnI_2	C + I_2 (9:1)	0.613
II	Ag	Ag_2O–P_2O_5–$ZnBr_2$	C + I_2 (9:1)	0.511
III	Ag	Ag_2O–P_2O_5–$ZnCl_2$	C + I_2 (9:1)	0.463
IV	Ag	Ag_2O–P_2O_5–CdI_2	C + I_2 (9:1)	0.593
V	Ag	Ag_2O–P_2O_5–$CdBr_2$	C + I_2 (9:1)	0.456
VI	Ag	Ag_2O–P_2O_5–$CdCl_2$	C + I_2 (9:1)	0.352
VII	Ag	Ag_2O–P_2O_5	C + I_2 (9:1)	0.261
VIII	Ag	Ag_2O–P_2O_5–ZnI_2	C + I_2 + electrolyte[a] (8:1:1)	0.670
IX	Ag	Ag_2O–P_2O_5–CdI_2	C + I_2 + electrolyte[b] (8:1:1)	0.643
X	Ag	Ag_2O–P_2O_5	C + I_2 + electrolyte[c] (8:1:1)	0.342

[a] Ag_2O–P_2O_5–(20%)ZnI_2.
[b] Ag_2O–P_2O_5–(20%)CdI_2.
[c] Ag_2O–P_2O_5.

shown in Figs. 1–4. Similar curves were obtained by plotting current density versus time.

The percent ionic transference number ($\%t_i$) of all the glass electrolytes and their conductivities at room temperature (27 °C) and at 300 °C are reported in Table 2. The $\%t_i$ values lie between 98.3 and 99.3 for all the glass electrolytes. This indicates that the electrolytes are essentially ionic conductors. The range of conductivity values (1.44×10^{-2} to 8.66×10^{-2} S cm^{-1} at 300 °C) compares favourably with that obtained by Minami et al. [23] for AgI–Ag_2O–P_2O_5 glasses. This is a clear indication of their potential for use in the fabrication of solid-state batteries.

For the cell configuration Ag‖Ag_2O–P_2O_2–Zn/CdX_2-‖(C + I_2), when the dopant salt in the glass electrolyte Ag_2O–P_2O_5–ZnX_2 changes from ZnI_2 (cell I) to $ZnCl_2$ (cell III) the OCV value decreases from 0.613 V (ZnI_2) to 0.463 V ($ZnCl_2$) (Table 1). In between, there is a value of 0.511 V for $ZnBr_2$ (cell II). The same trend is observed with CdX_2-doped glass electrolytes. The OCV values for CdI_2, $CdBr_2$ and $CdCl_2$-doped glass electrolyte cells are 0.593, 0.456 and 0.352 V, respectively. When undoped glass Ag_2O–P_2O_5 is used as the electrolyte (cell VII), the OCV value is as low as 0.261 V. This clearly suggests that the addition of zinc and cadmium halides in silver phosphate glass increases markedly the OCV value in the order:

$$\mathrm{OCV}(\mathrm{MI_2}) > \mathrm{OCV}(\mathrm{MBr_2}) > \mathrm{OCV}(\mathrm{MCl_2})$$

where the dopant cation M is Zn or Cd. The results also show a decreasing trend in the OCV value of the cell as the halogen of the dopant salt changes from iodine to chlorine.

On addition of Zn/CdX_2 to the silver phosphate glassy network, it is likely that Ag^+ ions are replaced by the transition metal cations (Zn^{2+}/Cd^{2+}) from the main chain of the silver phosphate glass. These replaced silver ions, randomly present in the phosphate glass matrix, are free to move through the glass structure towards the cathode and hence the OCV value increases markedly.

The decreasing trend in OCV values of MI_2, MBr_2 and MCl_2 may be explained on the basis of the size of the halide ion: the larger the halide ion, the greater is the loosening of the network structure. The iodide, being the largest in size

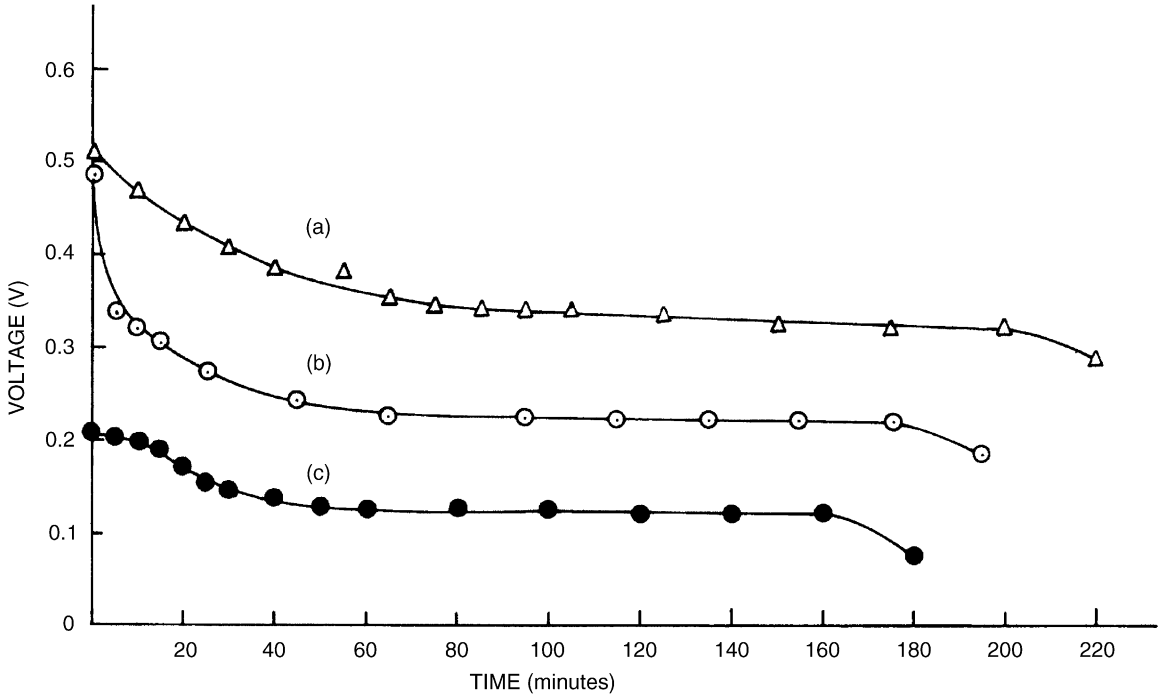

Fig. 1. Discharge curves (voltage vs. time) at load resistance 1 MΩ for (a) cell I, (b) cell II and (c) cell III.

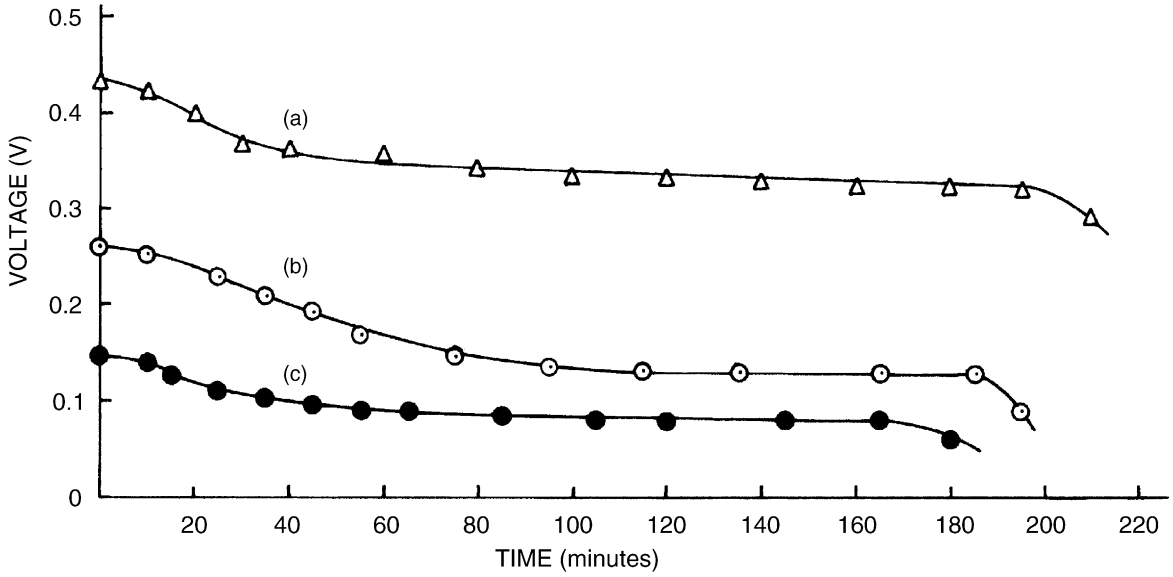

Fig. 2. Discharge curves (voltage vs. time) at load resistance 1 MΩ for (a) cell IV, (b) cell V and (c) cell VI.

[24], will loosen the glassy network to a maximum and, therefore, the transport of the free silver ions will be facilitated more towards that cathode.

A comparison of the results obtained for glass samples doped with Zn halide with those for Cd halide-doped samples shows that the OCV values of the former are higher than those of the latter. It appears that because Zn^{2+} has a higher electrode potential [24] (0.76 V) than Cd^{2+} (0.60 V) it replaces more Ag^{+} ions from the silver phosphate glass chains. These free Ag^{+} ions are then available for transport through the glassy electrolyte towards the cathode and thus the OCV value increases. The $\%t_i$ values of the Zn/Cd halides as reported in Table 2 further support this observation.

The OCV values of three other cells which were fabricated with other cathode configurations are also given in Table 1.

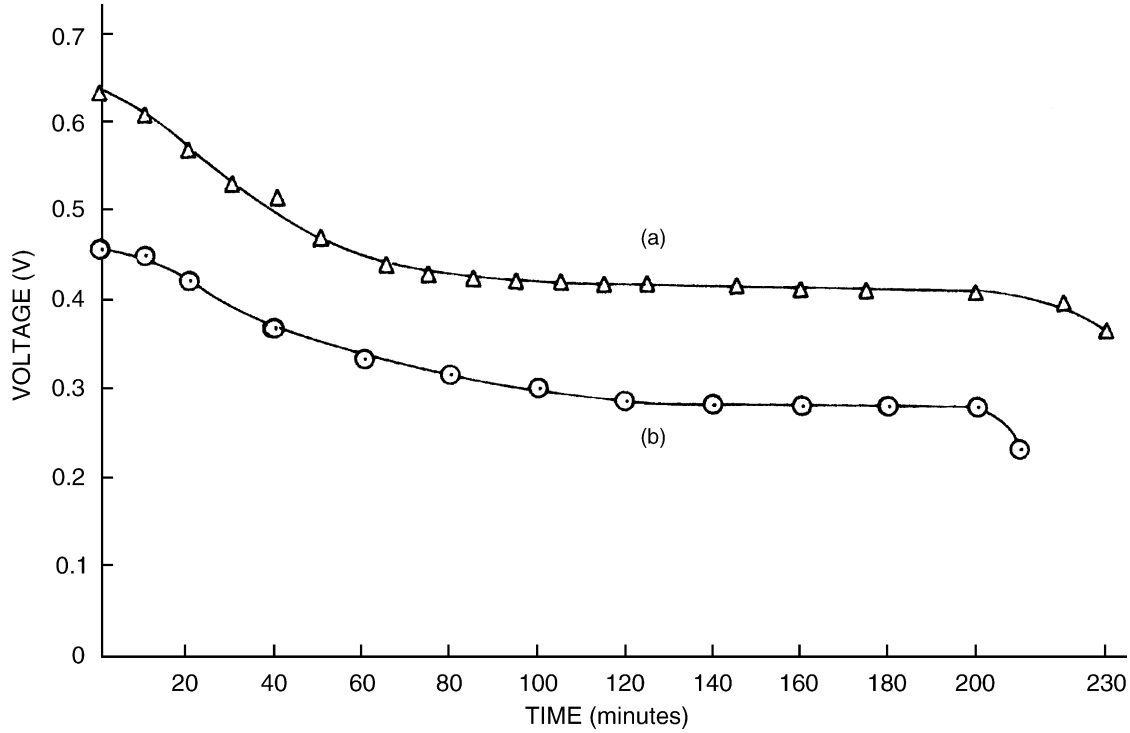

Fig. 3. Discharge curves (voltage vs. time) at load resistance 1 MΩ for (a) cell VII and (b) cell IX.

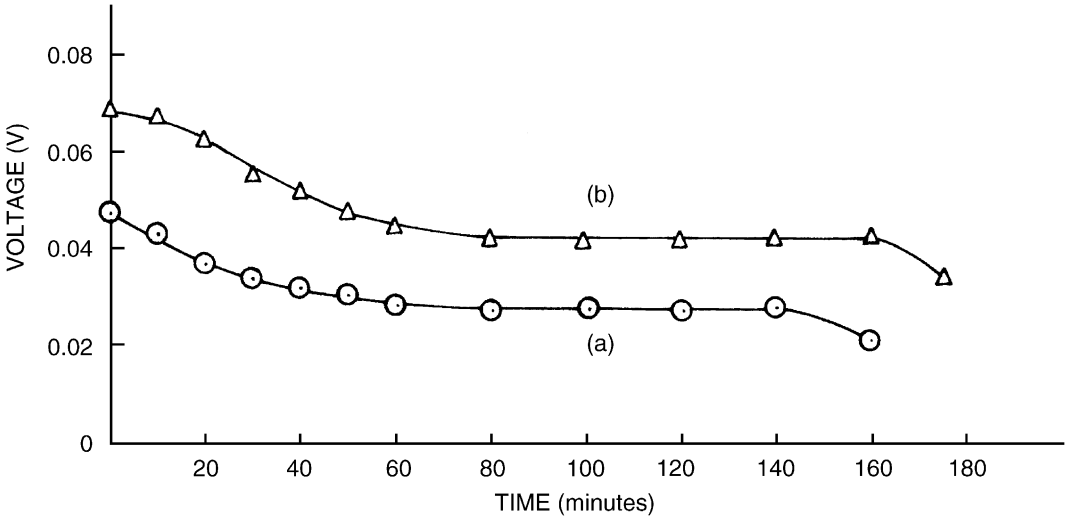

Fig. 4. Discharge curves (voltage vs. time) at load resistance 1 MΩ for (a) cell VII and (b) cell X.

Table 2
Percent ionic transference number ($\%t_i$) and conductivity (σ) values of various silver phosphate glass electrolytes

Sample	Glass electrolyte	Ionic transference number ($\%t_i$)	Conductivity (σ) (S cm^{-1})	
			Room temperature (27 °C)	300 °C
1	Ag_2O–P_2O_5	95.4	3.75×10^{-6}	3.97×10^{-3}
2	Ag_2O–P_2O_5–(20%)$ZnCl_2$	98.3	9.05×10^{-5}	1.66×10^{-2}
3	Ag_2O–P_2O_5–(20%)$ZnBr_2$	98.8	9.72×10^{-5}	6.84×10^{-2}
4	Ag_2O–P_2O_5–(20%)ZnI_2	99.3	6.22×10^{-4}	8.66×10^{-2}
5	Ag_2O–P_2O_5–(20%)$CdCl_2$	98.5	4.64×10^{-5}	1.47×10^{-2}
6	Ag_2O–P_2O_5–(20%)$CdBr_2$	98.7	1.17×10^{-4}	6.65×10^{-2}
7	Ag_2O–P_2O_5–(20%)CdI_2	98.8	1.25×10^{-4}	8.53×10^{-2}

An OCV value of 0.670 V is obtained for cell VIII with the configuration $Ag||Ag_2O + P_2O_5 + (20\%)ZnI_2||(C + I_2 +$ electrolyte). On the other hand, the OCV value for cell IX, $Ag||Ag_2O + P_2O_5 + (20\%)CdI_2||(C + I_2 +$ electrolyte), is found to be 0.643 V. The OCV value for cell X with undoped silver phosphate glass as cell electrolyte with the configuration $Ag||Ag_2O + P_2O_5||(C + I_2 +$ undoped electrolyte) is as low as 0.342 V.

According to these results, mixing of even a small amount of synthesized glass electrolyte with graphite and iodine-($C : I_2 :$ electrolyte $= 8 : 1 : 1$) in the cathode invariably leads to an increase in OCV in all the three cells compared with cells in which the cathodes were simply a mixture of graphite and iodine. The addition of glass electrolyte in the cathode appears to provide a better electrodelelectrolyte contact and minimizes polarization. Thus, the transport of ions through electrolytes increases which, in turn, increases the OCV. This results of ion transport studies (Table 2) corroborate this explanation.

The discharge curves of the cells described in Table 1 are given in Figs. 1–4. Cell I with $C + I_2$ as cathode has a discharge time of around 220 min. When the electrolyte (Ag_2O–P_2O_5–(20%)ZnI_2) is mixed with the cathode ($C + I_2$), the discharge time of the cell (cell VIII) increases to more than 230 min. Cell I with $C + I_2$ as cathode has the maximum life (discharge time 220 min). When the electrolyte (Ag_2O–P_2O_5–ZnI_2) is mixed with $C + I_2$ the discharge time of cell VIII further increases, viz. >230 min. The cell with configuration $Ag||Ag_2O$–P_2O_5–$ZnI_2||(C + I_2 +$ electrolyte) gives the best OCV and discharge time compared with all other cells (I–X). Its measured OCV (0.670 V) is in good agreement with the theoretically calculated OCV (0.687 V) of a silver solid-state battery using iodine as cathode [22].

It is interesting to note that the cells using iodides, whether of Cd or Zn, as dopants in the silver phosphate glass electrolyte, give higher OCV values and life than those employing chlorides and bromides. Also, zinc iodide-doped electrolyte yields higher OCV values (0.670 V) and life (>230 min) than the corresponding cadmium iodide-doped electrolyte (OCV ∼ 0.643 V; life ∼ 220 min).

The high OCV values and lives of the cells using iodide-doped glasses may be explained in the following manner. The dopant Zn/Cd iodide in all probability reacts with Ag_2O to form AgI and metal oxide, i.e.

$$Ag_2O + MI_2 \rightarrow 2AgI + MO \quad (1)$$

where M represents Zn or Cd. Due to this reaction the electrolyte Ag_2O–P_2O_5–MI_2 changes to the pseudo-quaternary

system AgI–Ag_2O–P_2O_5–MO. Since AgI–Ag_2O–Ag_2O–P_2O_5, which now becomes a part of the this system, is known as the best ion-conducting glass system [25], a high OCV value and long cell life is the end result.

4. Conclusions

On the basis of the ion transport and battery characterization studies reported above, it can be concluded that silver phosphate glass doped with Zn/CdX_2 are potential electrolytes for the fabrication of solid-state batteries. Among the glassy systems investigated, Ag_2O–P_2O_5–(20%)ZnI_2 and Ag_2O–P_2O_5–(20%)CdI_2 when used as electrolytes in cells give the highest OCV and long life. When these glassy systems are mixed with the cathode ($C + I_2$), the OCV value and life of the resultant cells are further increased.

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