

Solid-state batteries using silver-based glassy materials

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Abstract

A new, fast ion-conducting, silver seleno molybdate (SSM), glassy electrolyte has been synthesized. Solid-state primary cells of the design anode/solid electrolyte/cathode have been fabricated with the highest conducting composition of the SSM glass as the solid electrolyte. The polarization and discharge characteristics of the cells are studied with different compositions of the cathode material. The effect of adding the solid electrolyte and tetraalkylammonium iodide (alkyl = methyl, butyl) to the cathode on the cell performance is investigated. The cell parameters are evaluated and the results are compared with a cell of the type Ag/AgI/(iodine + graphite) (I+C) that is fabricated using polycrystalline AgI as the solid electrolyte.

Keywords: Electrolytes; Silver seleno molybdate; Solid-state batteries

1. Introduction

The discovery of fast ion-conducting (FIC) solids and the consequent application of these materials in the fabrication of solid-state, primary cells have overcome a number of inherent disadvantages with liquid-state cells [1,2]. In recent years, various types (crystalline, polycrystalline, glasses, composites, and polymers) of FICs have been discovered and characterized [3–5]. The glassy or amorphous versions have gained more importance due to their high ionic conductivity and very low electronic conductivity. The discovery of amorphous/glassy electrolytes has now opened up the possibility of realizing electrochemical devices using these materials. Among the fast ionic-conducting glasses, silver-ion conducting glasses were the first solid electrolytes to be used in solid-state electrochemical devices [6]. Although electrochemical cells based on such glasses are suitable only for low energy-density applications [7], increasing research activities are continuing because of the good stability of the material and the possibility of microbattery applications [7,8].

This study presents the performance of solid-state cells of the configuration:

anode/solid electrolyte/cathode

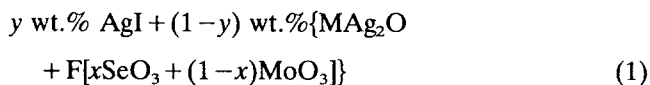
and the effect on battery performance of adding the solid electrolyte (SE) and tetraalkylammonium iodide

(TAAI) to the cathode. The study was carried out for various compositions of the cathode material at ambient temperature.

2. Experimental

2.1. Solid electrolyte preparation and transport studies

Analar grade chemicals of high purity were mixed in their respective molar weight ratio according to the general formula:



where Ag_2O is a glass modifier (M); SeO_3 (F1) and MoO_3 (F2) are glass formers; AgI is a dopant salt; x is the glass former composition. The mixture was melted in a silica crucible for about 1 h at 650 °C. The molten liquid was then quenched to liquid nitrogen temperature to form a glass. Since one of the starting materials used in the glass preparation, viz., H_2SeO_4 is highly hygroscopic, the entire preparation was performed inside a glove box under a controlled atmosphere of argon. To select the glass composition with the highest conductivity, compounds were prepared first by varying: the composition (x) of the glass formers from 0.0 to 1.0; the glass-modifier/glass-former ratio (M/F) from

0.5 to 3.0; the dopant salt composition (y) from 20 to 80 wt.%. The prepared compounds were characterized by X-ray diffraction (XRD), infrared (IR) and scanning electron microscopy (SEM) studies to identify their glassy nature. The glass composition 60 wt.% AgI + 26.67 wt.% Ag_2O + 13.33 wt.% ($0.4\text{SeO}_2 + 0.6\text{MoO}_3$) (termed: 60SSM46) exhibited the highest ionic conductivity of $3.12 \times 10^{-2} \text{ S cm}^{-1}$. The compound 60SSM46 was therefore selected and produced in a large quantity for the fabrication of solid-state cells. Details of the sample preparation and the conductivity studies have been published elsewhere [9,10]. The electronic conductivity of the highest conducting composition is measured by the e.m.f. method [11] and is found to be $4.72 \times 10^{-7} \text{ S cm}^{-1}$.

2.2. Construction of solid-state cells

Solid-state cells of the following type have been fabricated using 60SSM46 as the solid electrolyte are given in Table 1.

The solid-state cells, C1–C5, have been prepared with various cathode materials and for different cathode compositions. Initially, (I + C) was used as the cathode material and cells of type C1 with various I:C ratios were made and the best I:C ratio was selected. Solid electrolyte was added to the best I:C ratio and cells of type C2 were constructed. Either TMAI or TBAI was added to the best (I + C):SE to produce cells of type C3 and type C4, respectively. The cell of type C5 was fabricated to provide a benchmark for the performance of cells C1–C4.

An anode/electrolyte pellet of diameter 10 mm and thickness 1.5 mm was formed by pressing a mixture of 0.05 g of Analar Grade silver powder and 0.05 g of finely powdered SE into one disc, and 0.5 g of SE as another disc, under a pressure of 5000 kg cm^{-2} . The SE is added to the anode material in a 1:1 ratio to obtain an optimized performance through providing a large surface area for the interfacial contact. The cathode pellet was made separately by pressing a 0.225 g mixture of cathode material. The diameter and thickness of the cathode pellet were 12 mm and 2.0 mm, respectively.

Table 1
Construction of solid-state cells^a

Cell type	Construction
C1	Ag + SE (1:1)/60SSM46/(I + C)
C2	Ag + SE (1:1)/60SSM46/(I + C) + SE
C3	Ag + SE (1:1)/60SSM46/((I + C) + SE) + TMAI
C4	Ag + SE (1:1)/60SSM46/((I + C) + SE) + TBAI
C5	Ag + SE (1:1)/AgI/(I + C)

^a I = iodine, C = graphite, TMAI = tetramethylammonium iodide and TBAI = tetrabutylammonium iodide.

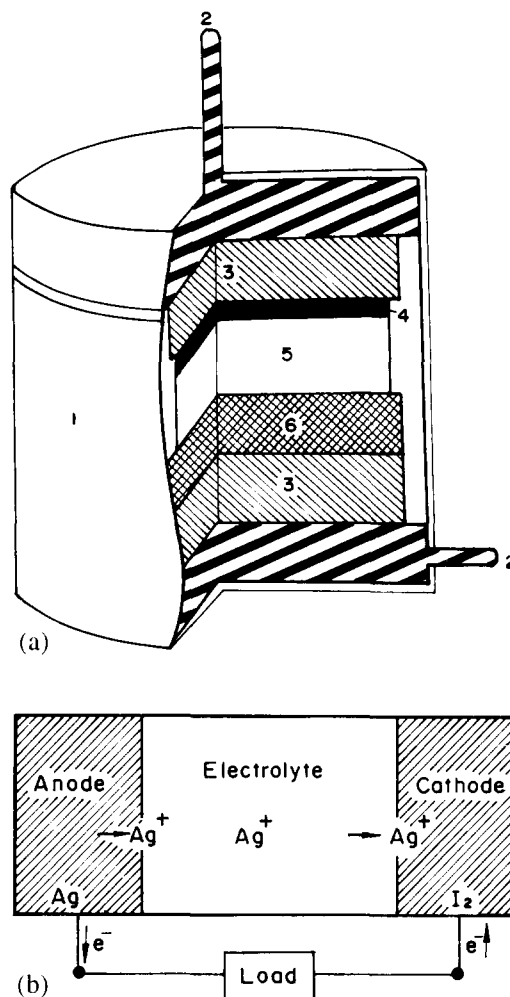


Fig. 1. (a) Cross-sectional view of silver ion, solid-state battery: (1) Teflon block; (2) silver leads; (3) graphite discs; (4) anode; (5) solid electrolyte, and (6) cathode. (b) Schematic diagram of cell when providing power to an external circuit.

The cells were assembled by sandwiching the anode/electrolyte and cathode pellets between the graphite discs inside a Teflon box. The bottom and top faces of the box were fitted with silver electrodes for external connections. A cross-sectional view of the assembled cells is given in Fig. 1(a). Immediately after the cells were fabricated, the open-circuit voltage (OCV) was measured with a high-impedance microvoltmeter (Keithley, Model 228A). A schematic diagram of the cell providing power to an external circuit is shown in Fig. 1(b).

3. Results and discussion

Fig. 2(a) gives the variation of cell potential versus discharge-current density of type C1 cells with different I:C ratios. The potentials were recorded 60 s after connecting the respective load. The maximum current drain is obtained for an I:C = 7:3. The cathode com-

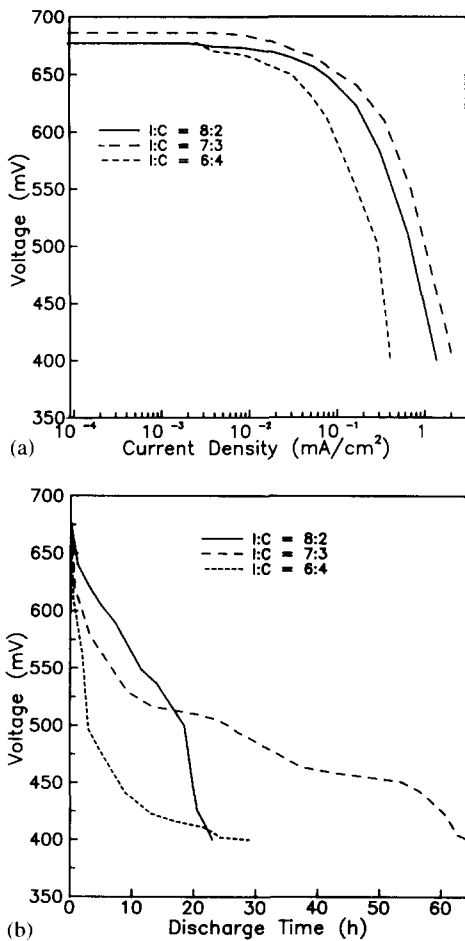


Fig. 2. (a) Polarization curves of cell type C1. (b) Discharge characteristics of cell type C1 at 100 µA cm⁻².

position I:C = 6:4 is found to be brittle, while cathode pellets of still higher graphite content develop cracks on the surface and, hence, are not suitable for practical use.

The C1 cells were discharged at ambient temperature under constant-current density (100 µA cm⁻²). The

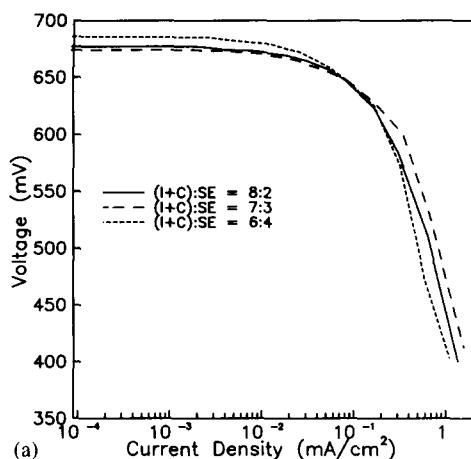
discharge was terminated when the cell potential dropped to 0.4 V. The discharge curves are presented in Fig. 2(b). During the discharge process, Ag⁺ ions released from the anode migrate to the I₂ cathode through the electrolyte to form AgI at the cathode/electrolyte interface. The compound AgI is poorly conducting and as the battery discharge occurs continuously, the amount of discharge product (AgI) at the interface increases and hence the internal resistance of the cell increases. The values of OCV, discharge capacity and the energy density for various I:C ratios are listed in Table 2. It is clear that the cell with an I:C ratio = 7:3 exhibits the best performance.

After selecting the best cathode composition (i.e., I + C = 7:3), cells of type C2 are fabricated with varying (I + C):SE values and the OCVs were measured. The discharge and polarization characteristics are given in Fig. 3(a) and (b). The cell with the cathode composition (I + C):SE = 7:3 is found to have the best performance with an energy density of 3.08 Wh kg⁻¹, see Table 2. The addition of SE to the cathode improves both the discharge capacity and the energy density of the cell. This is because the addition of SE to the cathode (I + C) reduces the resistance to charge transfer at the electrolyte/cathode interface.

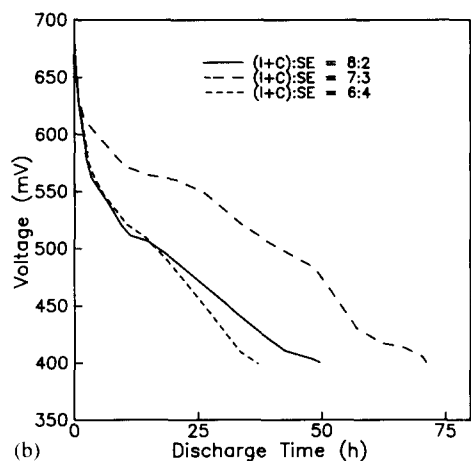
The type C2 cell with cathode composition (I + C):SE = 7:3 was discharged under different current drains (50 to 150 µA). Fig. 4 shows the effect on the discharge efficiency of successively heavier drains. The rapid drop in voltage observed in the initial stage is due to ohmic polarization and this is followed by a gradual decrease in voltage due to discharge. It is clear from the data of Fig. 4 that the discharge is the same for all drains during the initial period of discharging but, thereafter, increases with the current drain. The rapid decrease in cell potential at high current drain (150 µA) may be due to disruption of the (Ag + SE)/solid-electrolyte interface.

Table 2
Parameters of silver-ion cells at room temperature

Cell type	Cathode composition	OCV (mV)	Current drain at 0.4 V (mA)	Operating time for 0.4 V (h)	Discharge capacity at 100 µA cm ⁻² (mAh)	Energy density (Wh kg ⁻¹)
C1	8:2	677	1.07	21	1.65	0.83
	7:3	677	1.44	68	5.34	2.67
	6:4	687	0.86	25	1.96	0.99
C2	8:2	684	1.12	50	3.93	2.17
	7:3	686	1.61	71	5.58	3.08
	6:4	677	0.94	37	2.91	1.60
C3	9:1	652	1.63	96	7.54	4.24
C4	9:1	654	1.96	118	9.27	5.22
C5	7:3	686	0.16	14	1.10	0.55



(a)



(b)

Fig. 3. (a) Polarization curves of cell type C2. (b) Discharge characteristics of cell type C2 at $100 \mu\text{A cm}^{-2}$.

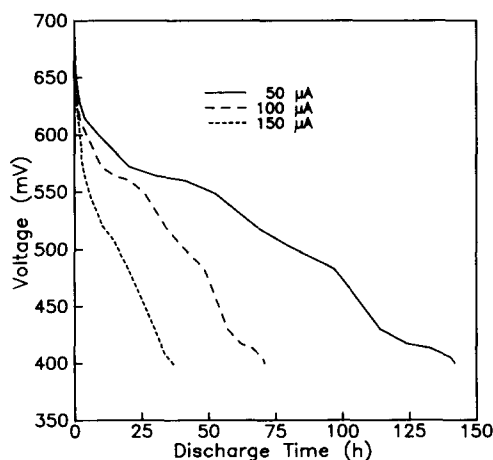
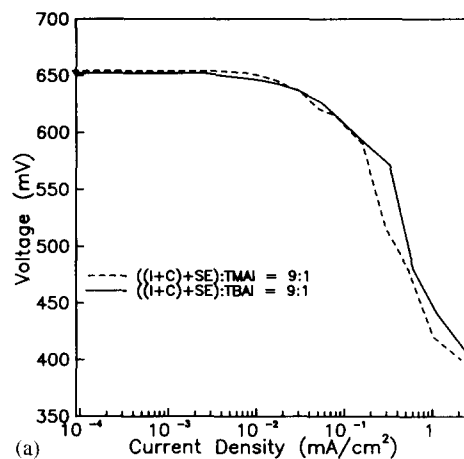
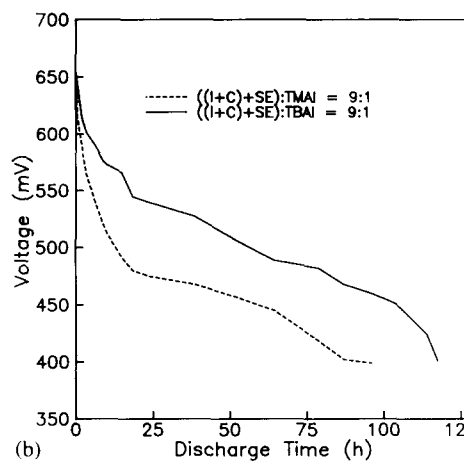


Fig. 4. Discharge curves of cell type C2 under various current drains.

Cells of type C3 and C4 were fabricated to study the effect of adding tetraalkylammonium iodide (alkyl = ethyl and methyl) to the cathode [(I+C):SE = 7:3]. The tetraalkylammonium iodide is added to the cathode structure to reduce the iodine activity. This use of tetraalkylammonium iodide has been highlighted based on the fact that the iodine activity was reduced by



(a)



(b)

Fig. 5. (a) Cell voltage as a function of current density of cell types C3 and C4. (b) Discharge curves for cell types C3 and C4 at $100 \mu\text{A cm}^{-2}$.

forming a complex with $(\text{CH}_3)_4\text{NI}$ and $(\text{C}_4\text{H}_9)_4\text{NI}$. These complexes reduce the tarnishing action of molecular iodine with the electrolyte and increase the energy density. Further, the ionic conductivity of the reaction products, namely, $((\text{CH}_3)_4\text{N})_2\text{Ag}_{13}\text{I}_{15}$ and $((\text{C}_4\text{H}_9)_4\text{N})_2\text{Ag}_{13}\text{I}_{15}$, is high and, therefore, offers good continuity of charge transfer [12]. The polarization and discharge curves for cells C3 and C4 are presented in Fig. 5(a) and (b), respectively. The observed decrease in the OCV of cells C3 and C4 can be attributed to the reduced activity of molecular iodine in the organic tetraalkylammonium iodide. Since the iodide is complexed in the cage-like structure of these materials, the OCV – which arises from the energy of formation of the cell reaction – was found to decrease as the weight, stability and the complexing ability of the cathode material increase.

Fig. 6(a) and (b) show the polarization and discharge curves of cells of type C5 along with similar curves for cell types C1, C2, C3 and C4 with the best cathode composition for comparison. From these curves, it is clear that the current drain of cells C1–C4 that are

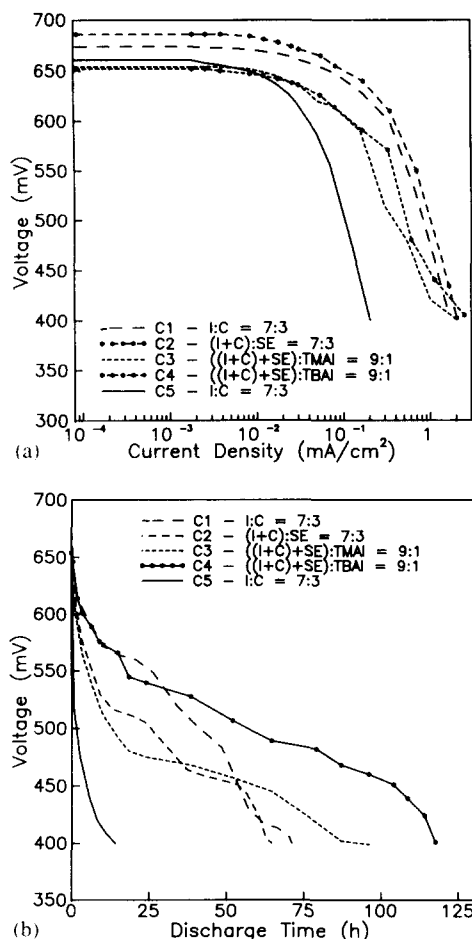


Fig. 6. (a) Cell voltage as a function of current density for best cathode composition of cell types C1, C2, C3, C4 and C5. (b) Discharge curves for cell types C1, C2, C3, C4 and C5 at $100 \mu\text{A cm}^{-2}$ for best cathode composition.

developed using glassy solid electrolyte is about an order of magnitude higher when compared with the cell type C5, where polycrystalline AgI was used as the electrolyte. Further, the discharge capacity of cell type C5 is very small because of the high internal resistance that results from the poor ionic conductivity of the polycrystalline AgI at ambient temperature. Therefore, an amorphous solid electrolyte with very high ionic conductivity is more suitable for solid-state cell/battery applications than its crystalline counterpart.

4. Conclusions

The set of solid-state cells exhibits OCV values between 686 and 650 mV, current drains of 0.8 and 1.96 mA, and an energy density between 0.8 and 5.0 Wh kg⁻¹. These results support the conclusion that cells fabricated using the present glassy system, 60SSM46, as a solid electrolyte are suitable for application in low-power devices. The studies also reveal that the cell parameters are very sensitive to the cathode composition and the cathode materials. The addition of TAAI to the cathode improves both the performance and the stability of the cells. Electrochemical studies confirm the superiority of these amorphous solid electrolytes for solid-state cell/battery applications compared with their crystalline counterparts.

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