ELSEVIER

Journal of Power Sources 62 (1996) 15–19

JOURNAL OF POWER SOURCES

Fabrication and characterization of silver-based solid-state primary batteries

M. Venkateswarlu [a], N. Satyanarayana [b,*]

[a] Department of Physics, Osmania University, Hyderabad 500 007, India
[b] Department of Physics, Pondicherry University, R.V. Nagar, Pondicherry 605 014, India

Received 8 December 1995; accepted 29 January 1996

Abstract

Solid-state primary batteries are fabricated using the highest conducting composition of $AgI–Ag_2O–(SeO_2+V_2O_5)$ (SSV) quarternary glassy compound with different cathode materials such as I:C, (I+C):SE, and [(I+C)+SE]:TAAI=9:1 (I: iodide; C: graphite; SE: solid electrolyte; TAAI: tetraalkyl ammonium iodide, and A: methyl, ethyl and butyl). Various sets of batteries are fabricated with the following configuration: anode/glassy solid electrolyte/cathode. The performance of the batteries made up of SSV glass is evaluated in terms of the measured open-circuit voltage, polarization and discharge characteristics.

Keywords: Solid-state batteries and characteristics; Glass; Silver

1. Introduction

The importance of solid-state batteries (SSBs) has been increasing considerably due to their application as new electrical power sources for advanced technological devices such as calculators, watches, cameras, measuring meters, computers, bio-medical devices, space, military equipment, etc. [1–3]. Further, batteries made with solid electrolytes (SEs) will overcome the many limitations of the conventional liquid-electrolyte batteries (LEBs) such as leakage, corrosion, instability towards temperature variation, short shelf-life [1–3]. In view of these advantages, various types of SEs have been synthesized [4,5] to achieve high ionic conductivity comparable with that of the liquid electrolytes.

Among the available SEs, silver-based SEs display high ionic conductivity and more stability towards temperature. Hence, we have chosen the silver selenovanadate (SSV) glassy system and studied its transport properties to determine the highest conducting composition of the SSV glassy system for SSB applications [6,7]. Recently, it has been found [5,8–10] that the SSB characteristic parameters are very sensitive to the chemical composition of the cathode material. Hence, in this paper, we report the design, fabrication and characterization of solid-state primary batteries using the highest conducting SSV glass with different cathode materials. The performance of SSBs is analysed in terms of the measured open-circuit voltage (OCV), polarization and discharge characteristics.

2. Experimental

2.1. Preparation and characterization of battery material

Analar grade AgI, Ag_2O, SeO_2 and V_2O_5 chemicals are chosen to prepare the following highest conducting 66.67% $AgI–23.07\%Ag_2O–10.26\%[0.8SeO_2+0.2V_2O_5]$ composition of SSV glassy system obtained from our earlier studies [6,7].

According to the molecular weight percentages, appropriate quantities of chemicals are placed in a quartz crucible and melted at 550 °C. The molten liquid is quenched into liquid nitrogen to form the glass. The resulting bulk compound is ground into fine powder and this is used for characterization and battery studies. The SSV compound is examined by X-ray diffraction (XRD). Its glassy nature is confirmed by the observed peak-free XRD spectrum. The various transport parameters of the highest conducting composition of the SSV glass, obtained from our earlier studies, are listed in Table 1.

2.2. Design and fabrication of solid-state primary batteries

The highest conducting composition of the SSV glassy material is used as SE for the fabrication of solid-state primary

* Corresponding author.

PII S0378-7753(96)02392-0

Table 1
Highest conducting composition and transport parameters of SSV glassy systems

High conducting composition of SSV glass [a]			
Conductivity at 30 °C (S/cm)	Activation energy (eV)	Heat of transport, q^* (eV)	Ion transport number (t_i)
2.63×10^{-2}	0.22	0.23	= 1 (0.9999)

[a] SSV: 66.67%AgI-23.07%Ag_2O-10.26%(0.8 SeO_2 + 0.2 V_2O_5).

batteries. It is observed that the battery performance is very sensitive to the chemical composition of the constituents of the cathode material [8–10]. Hence, various sets of solid-state primary batteries have been fabricated using SSV glassy compounds with different cathode compositions.

The following solid-state primary batteries, with different cathode compositions, have been fabricated and studied systematically in order to estimate the performance of the cells

anode (Ag + SE) / solid electrolyte (SSV) / cathode

{[(I + C) + SE] + TAAI}

where Ag is silver powder, SE the SSV solid electrolyte, I iodide, C graphite, and TAAI tetraalkyl ammonium iodide (A = methyl, ethyl and butyl). According to this battery configuration, analar grade silver powder and the SSV glass mixer (1:1 weight ratio) are used as a anode. The SE is added to the silver powder to improve the interfacial contacts. Different compositions of the cathode compounds are made by varying the weight ratios of the iodide, graphite, SE and TAAI. Addition of graphite to the iodine increases the electronic conductivity and, hence, it acts as a good current-collector. The addition of SE improves the interfacial properties and the added TAAI will react with AgI and form a better conducting layer or compound to reduce the activity of the iodide at the interface [5,8–10].

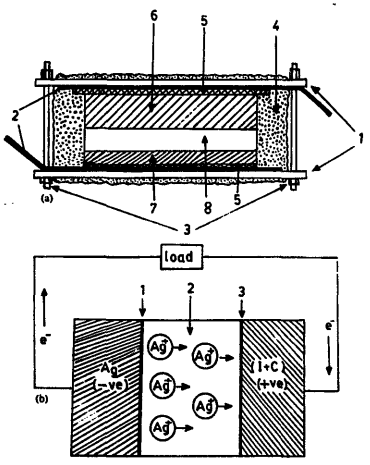

Fig. 1. (a) Cross-sectional view of solid-state primary battery with ebonite material: (1) ebonite sheets; (2) copper leads; (3) bolts and screws; (4) resin; (5) graphite sheets; (6) cathode pellet; (7) anode; (8) electrolyte. (b) Discharge process of silver-ion conducting, solid-state electrolyte cell: (1) anode and electrolyte interface; (2) silver-ion conducting electrolyte; (3) cathode and electrolyte interface.

Using the above design, the solid-state primary batteries were constructed in the following. The finely ground powders of the anode mixture and SSV electrolyte layers were pressed at an optimum pressure of 5000 kg cm^{-2} to form a pellet of 10 mm diameter and about 1.5 to 2.0 mm in thickness. Also, finely ground powder of the cathode mixture alone was pressed to make pellets of 10–12 mm diameter and about 1 mm in thickness. The anode/electrolyte/cathode pellets were sandwiched between graphite discs, copper foils were used over the two graphite discs, as leads, to form a solid-state primary battery. The battery assembly together with an outer jacket made up of ebonite material are shown in Fig. 1(a). Immediately after fabrication, all the batteries were sealed with epoxy resin to provide isolation from atmospheric effects. Systematically, various sets of solid-state primary batteries were fabricated using SSV glass with different cathode mixtures. Laboratory-scale studies were made of their temperature dependence of the OCV, the polarization and discharge characteristics in order to estimate the performance of each battery. The typical discharge process of the silver-ion conducting, solid-state electrolyte cell is shown in Fig. 1(b).

The following sets of batteries were constructed:

(Ag + SE = 1:1)/66SSV82/(I:C)	batteries V1
(Ag + SE = 1:1)/66SSV82/[(I + C):SE]	batteries V2
(Ag + SE = 1:1)/66SSV82/[(I + C) + SE]:TMAI = 9:1	battery V3
(Ag + SE = 1:1)/66SSV82/[(I + C) + SE]:TEAI = 9:1	battery V4
(Ag + SE = 1:1)/66SSV82/[(I + C) + SE]:TBAI = 9:1	battery V5

One set of batteries (V1) have been fabricated with different weight ratios of iodide and graphite (I:C) mixtures as the cathode material. From studies of the battery characteristics, the best cathode composition is determined for further studies. The SSV SE material is added in various weight ratios to the best cathode (I:C) composition and a set of solid-state primary batteries (V2) is fabricated with different (I + C):SE cathode compositions. Again, the performance of batteries is estimated and the best cathode composition, i.e. (I + C):SE, is selected. Next, 10% of tetraalkyl (methyl, ethyl and butyl) ammonium iodide is added to the best [(I + C) + SE] cathode composition to reduce the iodide

activities and the corresponding sets of batteries are fabricated (V3 to V5).

3. Results and discussion

3.1. Temperature dependence of open-circuit voltage

The first characteristic parameter of the battery is the OCV. The OCV was measured at room temperature for various (I+C) compositions of the cathode and was found to be 687 mV for SSV glassy SE. The measured OCV is equal to the thermodynamically calculated theoretical voltage. The temperature dependence of OCV was measured for various cathode compositions, see Fig. 2. For a set of batteries, the OCV increases with temperature. The variation of OCV with temperature decreases progressively for cells made of: (I+C), (I+C)+SE and [(I+C)+SE]+(TMAI/TEAI/TBAI) cathodes. It is found that the addition of C, SE, and TAAI to the iodide stabilizes the cells to provide an uninterrupted constant voltage source in the tested 27–60 °C temperature range.

3.2. Polarization and discharge characteristics of solid-state primary batteries

Polarization (cell voltage versus current density) measurements were made for different cathode I:C compositions by applying different loads, see Fig. 3. The cell voltage for I:C = 7:3 displays better performance than the other I:C cathode compositions. For all the I:C cathode compositions, the cells give the same OCV of 687 mV; this is equal to the theoretical voltage of an AgI-based cell (687 mV). A particular load (corresponding to 100 μA cm^{-2}) is applied and allowed to discharge the cells. Fig. 4 shows the resulting discharge characteristics of cells with different I:C cathode compositions. The battery made up of SSV glassy material

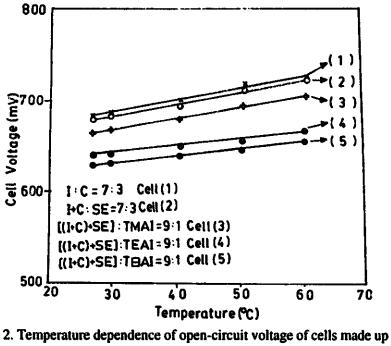

Fig. 2. Temperature dependence of open-circuit voltage of cells made up of SSV glass with various cathode maerials I:C, (I+C):SE and [(I+C)+SE]:TAAI (A = methyl, ethyl and butyl).

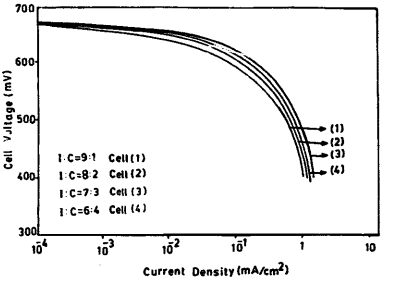

Fig. 3. Polarization characteristics of cells made up of SSV glass with various I:C compositions.

with a cathode composition of I:C = 7:3 displays the best shelf-life.

The OCV for the I:C cathode composition is found to be 687 mV, which is equal to the thermodynamically calculated theoretical voltage (687 mV). For various current densities, a fall in OCV of up to 60% of its initial value (687 mV) is observed for all the cathode compositions. As shown in Fig. 3, for such a fall in OCV, the current drain is about 1.2 to 4.85 mA and the maximum current drain is obtained for the battery with an I:C = 7:3 cathode composition. From the data given in Fig. 4, it is clear that the battery with a 7:3 cathode composition yields the higher discharge capacity and specific energy. The cathode pellet with a 6:4 composition is found to be brittle, while the pellets with higher percentages of graphite exhibit cracks. Hence, the cathode pellet with I:C = 7:3 gives the best performance and it was selected for further studies.

A set of batteries were fabricated with different cathode compositions ((I+C):SE; SE = SSV glass) and their polarization and discharge characteristics were examined. The polarization characteristics are given in Fig. 5. For a drop in OCV of up to 60% of the initial voltage (687 mV), the current drain is about 5 mA. The discharge characteristics with a current density of 100 μA cm^{-2} are presented in Fig. 6.

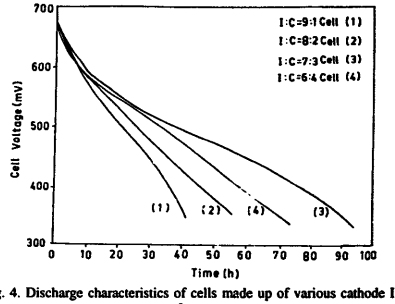

Fig. 4. Discharge characteristics of cells made up of various cathode I:C compositions; load = 100 μA cm^{-2}.

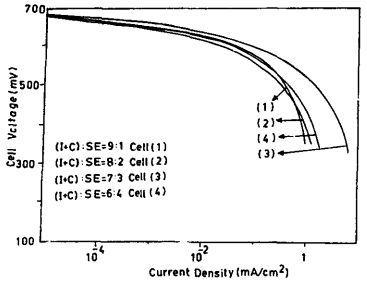

Fig. 5. Polarization characteristics of cells made of SSV glass with various cathode (I+C):SE compositions.

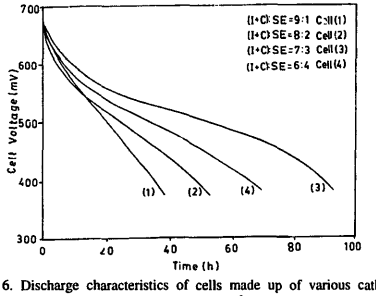

Fig. 6. Discharge characteristics of cells made up of various cathode (I+C):SE compositions; load = 100 μA cm^{-2}.

Batteries with a (I+C):SE=7:3 cathode composition give the best performance with an energy density of 3.21 Wh kg^{-1}. The addition of SE to (I+C) reduces the resistance at the interface. Thus, the addition of SE improves both the discharge capacity and the energy density. Finally, a set of batteries were made with different cathode compositions {[(I+C)+SE]:TAAI=9:1}. The cell parameters measured for all the batteries made with SSV glass and different cathode materials are summarized in Table 2.

The polarization characteristics for the batteries made with different cathode compositions are shown in Fig. 7. The current drain obtained from the various batteries is improved progressively by the addition of TMAI, TEAI and TBAI to the cathode. The current drain for a drop in voltage of up to 60% of the OCV for batteries with SSV glass is 8.5, 12 and 18 mA, respectively, for the cathode materials TMAI, TEAI and TBAI. It is found that the addition of TAAI to the cathode reduces the iodine activity at the electrode/electrolyte interface [5,8–10]. At the interface, the TAAI reduces the iodine activity by forming a strong complex $(CH_3)_4NI$, which avoids the tarnishing actions of molecular iodine with the electrolyte and, hence, increases the specific energy. Also, the ionic conductivity of the reaction product $[(CH_3)_4N]_2Ag_{13}I_{15}$ is highly conducting and offers good charge-transfer continuity [5]. Hence, the improvement in polarization characteristics of these cells is attributed to reduced internal resistance (*IR*) drop (even at higher current densities) compared with cells of (I+C+SE) cathodes. This is due to the formation of a complex with higher conductivity than AgI [5].

The discharge characteristics at a current density of 100 μA cm^{-2} for batteries with different cathode compositions are shown in Fig. 8. These batteries display better discharge capacities than the other cells, cf., Figs. 4 and 6. Taking into consideration all the cell parameters (summarized in Table 2), the batteries made of [(I+C)+SE]:TAAI; A = methyl,ethyl and butyl) cathode compositions exhibit better discharge performance.

Table 2
Cell parameters measured at room temperature (303 K) for batteries made up of SSV glassy electrolyte compound [a] studied with different cathode materials

Cathode composition	OCV (mV)	Current drain (mA)	Discharge time (h)	Discharge capacity (mAh)	Specific energy (Wh kg^{-1})
a) *I:C variation*					
9:1	687	1.20	34	2.67	1.18
8:2	687	2.62	43	3.37	1.56
7:3	687	4.85	75	5.89	2.62
6:4	686	3.21	57	4.48	1.98
b) *(I+C):SE*					
9:1	687	1.16	33	2.59	1.15
8:2	687	2.82	48	3.77	1.67
7:3	687	8.20	92	7.22	3.21
6:4	684	3.60	65	5.10	2.26
c) *[(I+C)+SE]:TAAI* = 9:1					
TMAI	676	8.50	122	9.58	4.29
TEAI	663	12.0	98	7.69	3.40
TBAI	652	18.0	68	5.34	2.32

[a] 66.67% AgI–23.07%Ag_2O–10.26%(0.8 SeO_2 + 0.2 V_2O_5). I: iodide, C: graphite, SE: solid electrolyte, TAAI = tetraalkylammonium iodide (A = methyl, ethyl and butyl).

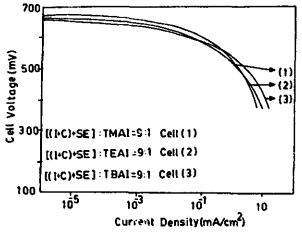

Fig. 7. Polarization characteristics of cells made of SSV glass with various cathode [(I+C)+SE]:TAAI (A = methyl, ethyl and butyl) compositions.

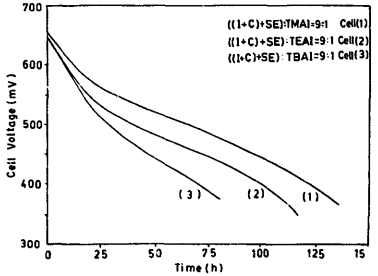

Fig. 8. Discharge characteristics of cells made of various cathode [(I+C)+SE]:TAAI (A = methyl, ethyl and butyl) compositions.

4. Conclusions

The glassy nature of the highest conducting composition of the SSV compound prepared by the melt-quenching method is confirmed by XRD analysis. The compound is chosen as the SE material for the fabrication of SSBs. The primary cells are fabricated using the SSV glass with varying cathode compositions. A high OCV of around 687 mV is obtained for cells made up of SSV glassy material, which suggests that the fabricated batteries are suitable for electrochemical applications. The battery performance is very sensitive to the composition of the cathode and the present study assists the choice of the best composition for the cathode constituents. A set of batteries has provided current drains of about 1.2–8.2 mA and specific energies of about 1.1–3.2 Wh kg^{-1}. The stability of these cells is improved appreciably by the addition of TAAI to the cathode. Further, the polarization characteristics of these cells are also improved by the addition of TAAI to the cathodes. A set of SSBs exhibit OCVs between 676 and 652 mV, current drains of 8.5–18 mA, and specific energies between 2.3 and 4.29 Wh kg^{-1}. These results suggest that cells fabricated with SSV glassy material as SE are suitable for low-power, ionic device applications that require long shelf-lives.

Acknowledgements

One of the authors (N.S.) is grateful to Department of Science and Technology, Government of India, for financial support in the form of research project (SP/S2/M-57/90).

References

[1] D. Linden (ed.), *Handbook of Batteries and Fuel Cells*, Mc-Graw Hill, New York, 1984.
[2] C.A.C. Sequeria and A. Hooper (eds.) *Solid State Batteries, NATO Advanced Study Institute Series*, Martinus Nijhof, Dordrecht, 1935.
[3] R.T. Foley, *J. Electrochem. Soc., 116* (1969) 13.
[4] C.C. Liang, *Appl. Solid State Sci., 116* (1969) 95.
[5] B.B. Owens, *Adv. Electrochem. Electrochem. Eng., 8* (1971) 1.
[6] M. Venkateswarlu and N. Satyanarayana, *Radiat. Effects Defects Solids*, submitted for publication.
[7] M. Venkateswarlu, K. Narasimha Reddy and N. Satyanarayana, *Solid State Ionics*, (1996) in press.
[8] P.S.S. Prasad and S. Radhakrishana, *J. Power Sources, 25* (1989) 287.
[9] A. Karthikeyan and N. Satyanarayana, *J. Power Sources, 51* (1994) 457.
[10] M. Venkateswarlu and N. Satyanarayana, *Solid State Ionics*, (1996) in press.