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Short communication

Characterization of solid-state batteries using a silver selenoarsanate glass system

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Abstract

The highest conducting composition of the silver selenoarsanate (SSA) compound was prepared by a melt-quenching method and its glassy nature was confirmed by X-ray diffraction. Primary cells with the configuration: anode (Ag + (solid electrolyte, SE))/SE glass (SSA)/cathode ((iodide, I) + (graphite, C) + SE + (tetra-alkylammonium iodide, TAAI)) were fabricated. Their characteristics were examined in order to estimate the life time. In particular, a study was made of the open-circuit voltage (OCV), polarization and discharge behaviour of three different sets of primary batteries made up of SSA glassy compound with various cathode materials. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Silver glass; Solid-state batteries; Open-circuit voltage polarization; Discharge characteristics

1. Introduction

It is well known that conventional electrochemical cells, made up of liquid electrolytes (LEs), have many limitations such as short shelf-life, leakage, instability towards temperature variations, etc. [1]. Many of these difficulties can be eliminated if the electrochemical cells employ solid electrolytes (SEs) [2–6]. SEs can be made in the form of thin films, bulk material, sheets, etc. and, hence, can provide new electrical power sources for advanced micro- and macro-technological applications such as, highly reliable long shelf-life micro-batteries used in cardiac pacemakers, certain integrated circuit devices, space, missile, and electrical vehicles [7–11]. In this paper, we report the fabrication and the laboratory-scale study of the open-circuit voltage (OCV), polarization and discharge characteristics of three sets of primary batteries made up of 60 wt.% AgI–26.67 wt.% Ag_2O–13.33 wt.% (0.5 SeO_2 + 0.5 As_2O_5) glass, which is selected from our earlier studies [12], with various cathode materials.

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2. Experimental

2.1. Material preparation and characterization

Appropriate quantities of analar grade AgI, Ag_2O, SeO_2 and As_2O_5 chemicals were placed in a quartz crucible and melted at 500°C. The molten liquid was poured into liquid nitrogen to form the glass. The glassy nature of the silver selenoarsanate (SSA) compound was confirmed by X-ray diffraction. The electrical conductivity (σ) of the SSA glass measured at 1 KHz was 1.65×10^{-2} S cm^{-1}; detailed conductivity studies are reported elsewhere [12]. The electronic conductivity (σ_e) was measured using the DC polarization technique of Wagner and Wagner [13], and was found to be 5.78×10^{-7} S cm^{-1}. This is five orders of magnitude less than the total conductivity (1.65×10^{-2} S cm^{-1}) of the SSA glass. Hence, the conductivity data suggest that the prepared SSA glass is useful for electrochemical applications [2–6,10,14]. High purity silver powder, glassy SE, graphite sheets, analar grade iodide, and tetr-alkylammonium iodide (TAAI) (A = methyl, ethyl and butyl) were used to prepare anode and different compositions of cathode compounds.

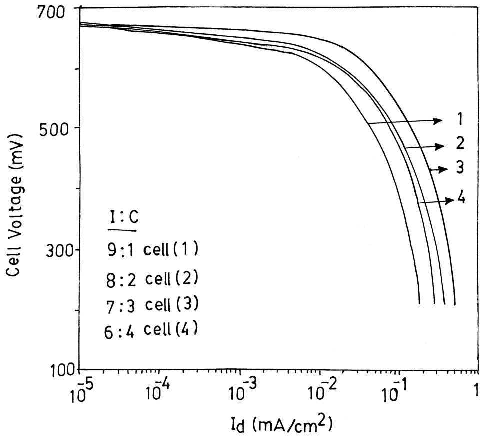

Fig. 1. Polarization characteristics of cells made with SSA glass and various cathode (I:C) compositions.

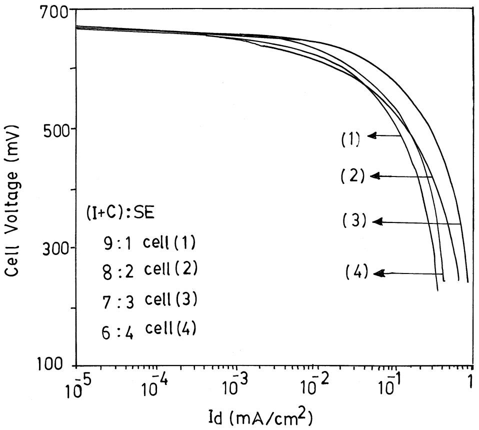

Fig. 3. Polarization characteristics of cells made with SSA glass and various cathode (I + C:SE) compositions.

2.2. Fabrication of solid-state primary batteries

Recently, it has been found that the characteristics of solid-state batteries are very sensitive to the chemical composition of the constituents of the cathode materials [6,14,15]. Hence, to obtain improved performance, various mixtures of cathode material were used in the fabrication of the battery system: anode (Ag + SE)/SE SSA/cathode (I + C + SE + T*A*AI), where: Ag is silver powder; I is iodide; C is graphite; T*A*AI is tetra-alkylammonium iodide (T*A*AI) (A = methyl, ethyl or butyl). Analar grade silver powder and the SSA glass (1:1 weight ratio) were used as an anode. The SE was used to reduce the interfacial resistance. The finely ground anode mixture and SSA electrolyte layers were pressed at an optimum pressure of 5000 kg cm^{-2} to form a pellet of 10-mm diameter and 1.5 to 2.0 mm in thickness. Different compositions of cathode compounds were made by varying the weight ratio of iodide, graphite, SE and T*A*AI and these were used as different cathode mixtures to improve the electrolyte and cathode interfacial properties [6,14,15]. Finely ground cathode mixture alone was pressed to an optimum pressure of 2000 kg cm^{-2} to form a pellet of 10-mm diameter and 1.0 to 1.5 mm in thickness. Finally, the anode/electrolyte and cathode pellets were sandwiched between graphite discs. Copper foils were used over the graphite discs as current leads. The outer jacket of the battery assembly was made up of two ebonite plates with nuts and bolts. The details of the battery assembly are reported elsewhere [15]. After the fabrication of the battery, the whole assembly was sealed immediately with epoxy resin to isolate the battery from the atmosphere.

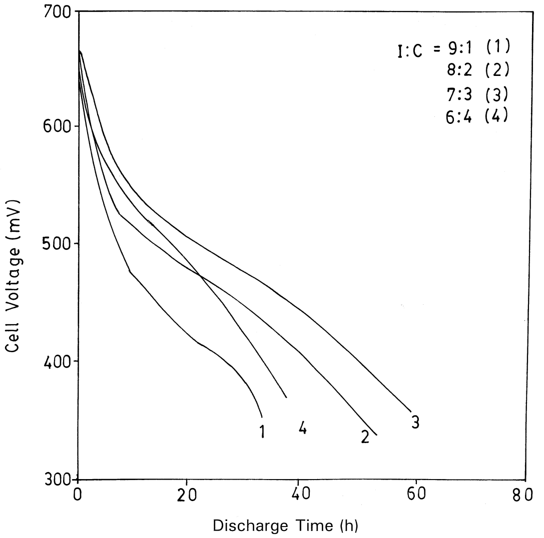

Fig. 2. Discharge characteristics of cells made with SSA glass and various cathode (I:C) compositions.

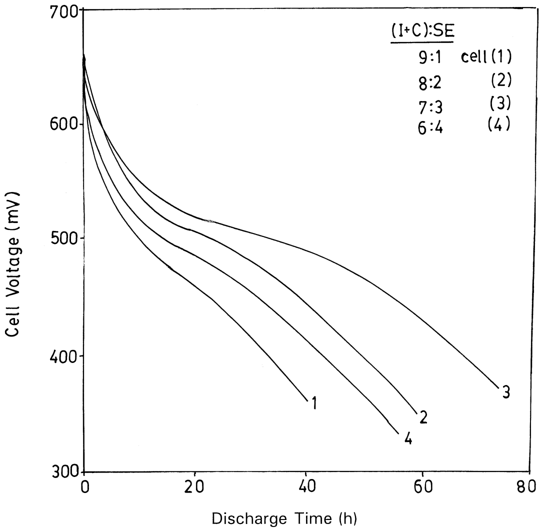

Fig. 4. Discharge characteristics of cells made with SSA glass and various cathodes (I + C:SE) compositions.

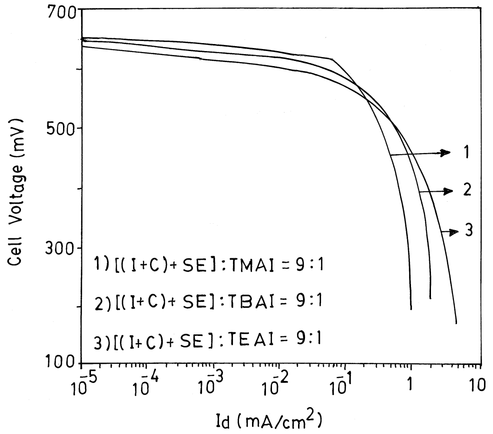

Fig. 5. Polarization characteristics of cells made with SSA glass and various cathodes (I + C + SE:TAAI = 9:1; *A* = methyl, ethyl or butyl).

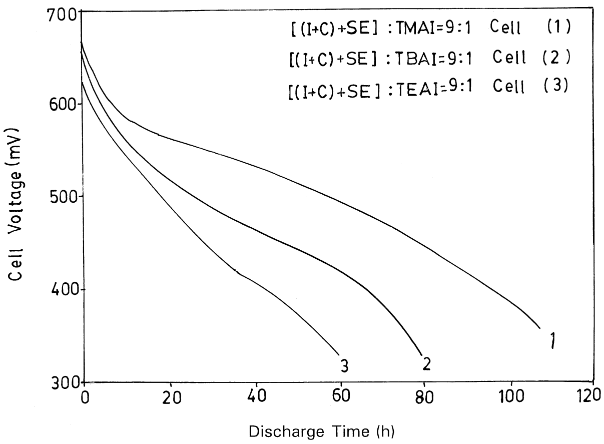

Fig. 6. Discharge characteristics of cells made with SSA glass and various cathodes (I + C + SE:TAAI = 9:1; *A* = methyl, ethyl or butyl).

3. Results and discussion

The following structured types of primary batteries were fabricated using SSA glassy material with different cathode mixtures.

Ag + SE (1:1)/60 SSA55/I:C	cells A1
Ag + SE (1:1)/60 SSA55/(I + C):SE	cells A2
Ag + SE (1:1)/60 SSA55/(I + C + SE):TMAI	cell A3
Ag + SE (1:1)/60 SSA55/(I + C + SE):TMEI	cell A4
Ag + SE (1:1)/60 SSA55/(I + C + SE):TMBI	cell A5

3.1. Open-circuit voltage

The OCV was measured for different cathode compositions. The OCV was found to decrease from 684 to 626 mV, for the cells of A1 to A5. The OCV of the cells A1 with I:C cathodes is close to the theoretical voltage (687.3 mV) [4].

3.2. Polarization and discharge characteristics

The polarization (voltage vs. current density) characteristics of various SSA-based batteries with different cathode (I:C) compositions are shown in Fig. 1. For a drop of OCV up to 0.4 V, the current drain varies from 0.1 to 0.2 mA and the maximum drain is obtained for the cell with I:C = 7:3 cathode composition. The discharge characteristics at a current density of 50 μA cm^{-2} for cells made up of SSA glassy materials with different cathode (I:C) compositions are presented in Fig. 2. It is clear that the cell with a I:C = 7:3 cathode composition gives the higher discharge capacity and specific energy. Hence, this cathode composition was chosen for further studies.

Table 1
Cell parameters measured at room temperature (303 K) for three different sets of solid-state batteries made with SSA[a] glass

Cathode composition	Open-circuit voltage (mV)	Discharge time (h)	Discharge capacity (mA h)	Specific energy (W h/kg)
I:C variation				
9:1	684	28	1.10	0.50
8:2	684	44	1.73	0.79
7:3	684	53	2.08	0.95
6:4	683	34	1.33	0.61
(I + C):SE variation				
9:1	684	36	1.42	0.64
8:2	684	58	2.27	1.03
7:3	684	69	2.70	1.23
6:4	684	46	1.80	0.82
(I + C + SE):TAAI variation				
9:1 (TMAI)	663	98	3.85	1.70
9:1 (TEAI)	656	65	2.55	1.12
9:1 (TBAI)	626	43	1.69	0.70

[a] 60 wt.% AgI–26.67 wt.% Ag_2O–13.33 wt.% [0.5 SeO_2 + 0.5 As_2O_5].

The polarization and discharge characteristics of cells with different cathode (I + C):SE compositions are given in Figs. 3 and 4, respectively. The results show that the battery with a (I + C):SE = 7:3 cathode composition gives the best performance with a current drain of 0.5 mA and a specific energy of 1.23 W h/kg. Hence, the addition of the SE to the (I + C) cathode improves the discharge capacity and the specific energy of batteries made with the same SSA glassy material.

Using the cathode with the best performance, viz., (I + C):SE = 7:3, a set of batteries were made with different cathode compositions [{(I + C + SE):T*A*AI} (*A* = methyl or ethyl or butyl)] and their polarization and discharge characteristics were studied, see Figs. 5 and 6. It was found that the current drain for a drop in OCV of up to 0.4 V varies from 0.5 to 2.0 mA; the highest current drain, viz., 2.0 mA, was obtained for the cathode composition of (I + C + SE):TBAI = 9:1. Table 1 lists the values of the OCV, discharge time, capacity and specific energy of all the abovementioned cells made from SSA glass with different cathode materials. Recently, it has been found that the addition of T*A*AI to the cathode (I + C + SE) composition reduces the iodide activity by forming a high-conducting complex at the electrode/electrolyte interface [6,14,15]. Hence, the improved polarization and discharge characteristics of the cells studied here, i.e., cells made of SSA glass with alkylammonium iodide, are attributed to a lower internal resistance (IR) drop, even at high current densities.

4. Conclusions

Using the best conducting SSA glassy compound, three different sets of primary batteries with different cathode compositions have been fabricated and studied in terms of their OCV, polarization and discharge characteristics. The highest OCV (684 mV) was obtained for the cells with a (I + C) cathode combination; the value is very close to the thermodynamically calculated theoretical value. The results show that the battery performance is very sensitive to the cathode composition. The present study assists the choice of suitable compositions for the cathode constituents. Finally, the battery results suggest that systems with SSA glass, as SE, are suitable for application in low-power, electrical devices.

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