

Short Communication

Solid-state batteries using silver-based fast ionic conducting glassy electrolytes

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Abstract

The highest conducting composition of silver molybdovanadate (SMV) and silver molybdoarsenate (SMA) fast ionic conducting glassy systems are used as solid electrolytes (SEs) for battery studies. Solid-state primary cells of the type Ag+SE/SMA (or) SMV/I (iodine)+C+SE have been developed. Polarization and discharge characteristics of cells with different cathode compositions are studied. The performance of these cells is analysed with respect to the application of SMV and SMA glassy systems in the development of solid-state batteries.

Introduction

Solid-state primary and secondary batteries have many advantages such as long shelf life, miniaturization, durability, etc. [1, 2]. Solid-state cells based on silver-ion conductors are promising designs for low energy-density battery applications [3]. Though the high cost of silver-based materials restrict their commercial utility, active research continues because of the material's advantage of very high electrical conductivity, stability (i.e., long shelf life), and the possibility of micro-battery development [3, 4]. Also, silver-ion conducting glasses have many other benefits, e.g., ease in preparation, flexibility of shape, inert to moisture, for electrochemical applications [2, 3].

In the present paper, the silver-ion conducting glasses: (i) silver molybdovanadate (SMV): $\text{AgI-Ag}_2\text{O}-(\text{MoO}_3 + \text{V}_2\text{O}_5)$, and (ii) silver molybdoarsenate (SMA): $\text{AgI-Ag}_2\text{O}-(\text{MoO}_3 + \text{As}_2\text{O}_5)$ are investigated as solid electrolytes for primary batteries.

Experimental

Glass preparation and transport properties

Analar grade chemicals were mixed in appropriate proportions and the product was melted (at 600 °C for the SMV system, at 500 °C for the SMA system) in silica

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crucibles. The glasses were prepared by rapidly quenching the molten liquid in liquid nitrogen. The glasses were characterized by X-ray diffraction. To select the best conducting composition of the SMV and SMA glassy systems, compounds differing both in the content of the glass former (F) ($x\text{F}_1:(1-x)\text{F}_2$, $x=0.1$ to 1.0) and in the glass modifier ($\text{M}=\text{Ag}_2\text{O}$) to glass former ratio ($\text{M:F}=0.5$ to 3.0) and dopant salt (AgI) content (20% to 80%) were prepared and their electrical properties studied [5, 6]. Measurements of the total conductivity and the electronic conductivity (by Wagner's polarization method) were carried out on these samples. Table 1 lists the highest conducting composition in the SMV and SMA systems together with the transport parameters. Both systems exhibit very high ionic conductivity (of the order of $10^{-2} \Omega^{-1} \text{cm}^{-1}$) with negligible electronic conductivity. Hence, SMV and SMA glassy systems are suitable for battery applications. Further details of these experiments are published elsewhere [5, 6].

Galvanic cell

The glass compositions, given in Table 1, have been chosen as solid electrolytes (SEs) for the fabrication of cells with the design:

anode/solid electrolyte (SE)/cathode

$\text{Ag} + \text{SE} (1:1)/\text{SMV}$ or $\text{SMA}/((\text{I} + \text{C}) + \text{SE}) + \text{TAAI}$

where, I = iodine; C = graphite, and TAAI = tetraalkylammonium iodide. A mix of silver and glassy electrolyte in the weight ratio 1:1 is used as the anode material. Cells are fabricated with various cathode compositions. To select the best cathode composition, with good cell parameters, the weight ratios of the cathode constituents are varied according to the following scheme. Initially, I+C is chosen as the cathode material and the performance of cells with various I:C ratios is evaluated. For the best I:C composition, SE is added in various weight ratios as (I+C):SE and, finally, TAAI is added.

Anode/electrolyte pellets are prepared by pressing the finely ground powders of electrolyte and anode mix at an optimum pressure of 5000 kg cm^{-2} . The diameter of the pellet is 10 mm and the thickness is about 1.5 mm. The cathode pellets are prepared separately (diameter: 15 mm, and thickness: ~ 1.0 mm). The cell is assembled by sandwiching the anode/electrolyte and cathode pellets between graphite discs and copper foils in a holder assembly, as shown in Fig. 1. The cells are then sealed with

TABLE 1

Highest conducting composition and transport parameters of silver molybdovanadate and silver molybdoarsenate systems

	Silver molybdovanadate ^a	Silver molybdoarsenate ^b
Conductivity at 30 °C $\sigma(\Omega^{-1} \text{cm}^{-1})$	1.9×10^{-2}	1.65×10^{-2}
Activation energy $E(\text{eV})$	0.33	0.35
Heat of transport $q(\text{eV})$	0.34	0.37
Ion transport number t_i	0.999	0.999

^a(60 wt.% AgI, 24 wt.% Ag_2O , 16 wt.% (0.1 $\text{MoO}_3 + 0.9 \text{V}_2\text{O}_5$).

^b(60 wt.% AgI, 25.5 wt.% Ag_2O , 14.5 wt.% (0.6 $\text{MoO}_3 + 0.4 \text{As}_2\text{O}_5$).

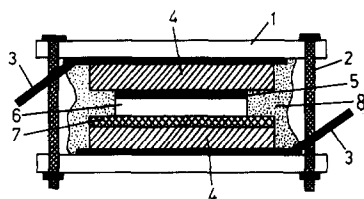


Fig. 1. Cross-sectional view of cell assembly: (1) hylem holder disc; (2) screw; (3) copper foils; (4) graphite discs; (5) anode; (6) solid electrolyte; (7) cathode, and (8) epoxy sealing.

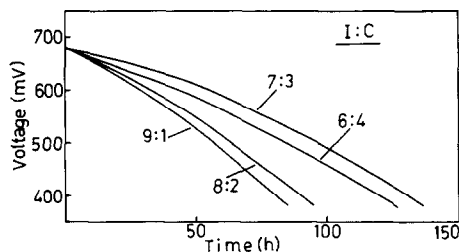


Fig. 2. Discharge curves for cells with SMV system (at $50 \mu\text{A cm}^{-2}$) with different I:C cathode compositions, at 30°C .

epoxy resin and stored under ambient conditions. A set of similar cells are fabricated and their open-circuit voltage (OCV), polarization and discharge performance is measured.

Results and discussion

Table 2 summarizes the results obtained for the two sets (SMV and SMA) of battery studies. The OCV of cells with different I:C cathode compositions is 687 mV. The current drain for a drop in voltage of 0.4 V is about 2 to 5 mA; the composition I:C=7:3 exhibits the maximum current drain of 5 mA. The cathode composition 6:4 also gives a current equal to that of 7:3, but the cathode pellet is highly brittle and this composition is therefore not suitable for practical use. Discharge characteristics for a current density of $50 \mu\text{A cm}^{-2}$ for these cells are shown in Fig. 2. It is clear that the best I:C composition is 7:3.

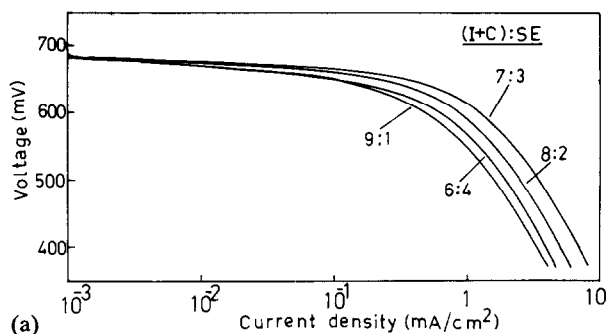
The polarization and discharge characteristics of cells with a varying (I+C):SE cathode composition (with I:C=7:3) are presented in Figs. 3(a) and (b). All these cells display almost similar polarization characteristics and yield around 5 mA of current. The cell with the cathode composition (I+C):SE=7:3 exhibits excellent discharge characteristics with an energy density of 2.9 Wh kg^{-1} . Thus, the addition of SE improves the discharge characteristics appreciably and the energy density of this cell is high compared with that of cells with other cathode compositions. The cathode composition (I+C):SE=7:3 is used for further studies that involve the addition of TAAI.

Tetraalkylammonium iodide (TAAI) (alkyl=methy or ethyl) is added to reduce the activity of the iodine in the cathode. The parameters of these batteries are given in Table 2, and the polarization and discharge characteristics are shown in Figs. 4(a) and (b). The addition of TMAI and TEAI improves the current drain of the battery, but degrades the discharge profile. Also, the addition of alkylammonium iodide improves the cell storage properties and provides better stability for the cells.

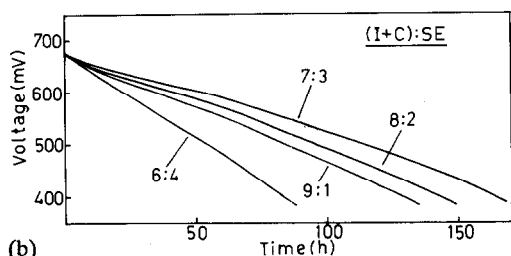
The highest conducting composition of the SMA glassy system is used for battery fabrication with the cathode composition (I+C):SE=7:3. The parameters of the cells based on the SMA systems are listed in Table 2; the polarization and discharge characteristics are presented in Figs. 4(a) and (b), respectively. These cells provide a current drain of about 7.5 mA cm^{-2} with an (I+C):SE cathode and 20 mA cm^{-2}

TABLE 2
Cell parameters of silver molybdovanadate and silver molybdoarsenate glassy electrolytes at room temperature, 30 °C

Cathode composition	OCV (mV)	Current drain 0.4 V (mA)	Operating time for OCV to 0.4 V (h)	Discharge capacity at 50 μ A cm ⁻² (mAh)	Energy density (Wh kg ⁻¹)	OCV after 1 year (mV)
(a) Electrolyte: silver molybdovanadate						
I:C variation						
10:0	687	0.01	2			
9:1	687	2.0	80	3.1	1.42	
8:2	687	4.0	90	3.5	1.6	
7:3	687	5.0	130	5.1	2.3	610
6:4	687	5.0	120	4.7	2.1	
(I+C):SE variation						
9:1	687	3.5	130	5.1	2.3	
8:2	687	5.0	140	5.5	2.5	
7:3	685	7.0	160	6.3	2.9	630
6:4	683	4.0	80	3.1	1.4	
((I+C)+SE):TAAI variation						
TMAI-9:1	675	9.0	102	4.0	1.8	652
TEAJ-9:1	673	16.0	50	2.0	0.9	650
(b) Electrolyte: silver molybdoarsenate						
(I+C):SE = 7:3						
(with I:C = 7:3)	686	7.5	150	5.9	2.7	630
TMAI-9:1	670	10.0	106	4.2	1.8	656
TEAJ-9:1	660	20.0	60	2.4	1.0	653

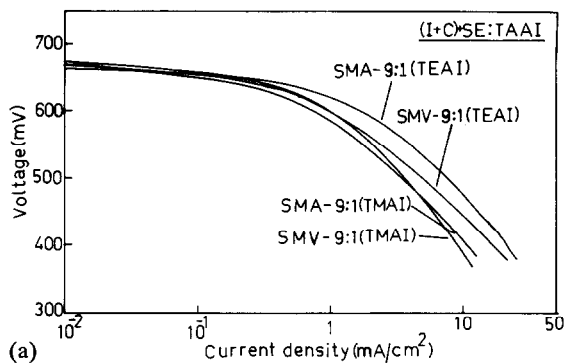


(a)

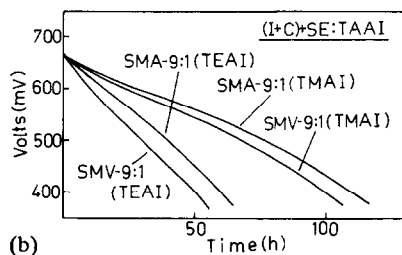


(b)

Fig. 3. (a) Cell voltage as a function of current density for different (I+C):SE cathode composition (SE=SMV). (b) Discharge curves for cells of SMV system (at $50 \mu\text{A cm}^{-2}$) with different (I+C):SE cathode compositions, at 30 °C.



(a)



(b)

Fig. 4. (a) Cell voltage as a function of current density for different ((I+C)+SE):TAAI cathodes in SMV and SMA systems. (b) Discharge curves for cells with ((I+C)+SE):TAAI cathode in SMV and SMA systems.

with ((I+C)+SE)+TEAI cathode. The SMA system gives a greater current than cells based on the SMV system.

Conclusions

Studies of SMV and SMA glasses as solid electrolytes have shown that these two glassy systems are suitable for solid-state battery applications. Results for cells with different cathode compositions, (I+C):SE, indicate that the electrical performance is very sensitive to this composition. The present study assists the choice of a suitable composition for the cathode constituents. The stability of the cell is improved by the addition of polyalkylammonium iodides. The test battery systems provide an OCV of about 687 to 670 mV, a drain current of 5 to 20 mA cm⁻², and an energy density of 0.5 to 3.0 Wh kg⁻¹. These cells are therefore suitable for low-power devices. The operational parameters of production-type cells are expected to be even better.

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