

## Short Communication

---

### Application of Silver Boromolybdate Glasses as Electrolytes in Solid-state Cells

R. V. G. K. SARMA and S. RADHAKRISHNA

*Department of Physics, Indian Institute of Technology, Madras 600 036 (India)*

(Received February 5, 1990; in revised form March 30, 1990)

#### *Summary*

A silver boromolybdate system with composition yielding the highest ionic conductivity is used as an electrolyte for a solid-state cell with the configuration: anode/amorphous electrolyte/cathode. The discharge and polarization characteristics are examined for different anodes and cathodes to evaluate the applicability of these cells as power sources for low-energy applications.

#### *Introduction*

Over the last twenty years, technological progress has increased the demand for lightweight, compact power sources capable of storing electrical energy. In particular, miniaturization of electronics has encouraged the development of solid-state cells and batteries. The conductivity of quaternary superionic conducting glasses is greater than that of ternary glasses [1 - 3]. Moreover, glasses have many advantages over their polycrystalline counterparts including: higher conductivity, absence of grain boundaries, an ability to be shaped into various forms, inertness to iodine atmosphere, etc. [4]. In the present work, an investigation has been made of silver-ion conduction in the system  $\text{AgI-Ag}_2\text{O-B}_2\text{O}_3\text{-MoO}_3$ ; the glass formation and transport properties have been reported elsewhere [5]. Recently, our laboratories reported the suitability of silver molybdotungstate glasses as electrolytes with charge transfer complexes as cathodes [6]. In this communication, we assess the corresponding feasibility of silver boromolybdate glasses.

#### *Experimental*

##### *Sample preparation*

AnalaR grade  $\text{AgI}$ ,  $\text{Ag}_2\text{O}$ ,  $\text{B}_2\text{O}_3$  and  $\text{MoO}_3$  chemicals were used to prepare the various quaternary glasses. The mixture of the individual components was heated to 650 °C in a quartz crucible. The melt was then

quenched onto a plate maintained at liquid nitrogen temperature. Other details of the sample preparation and electrical conductivity measurements are discussed elsewhere [5].

### *Anodes*

Silver powder (200 mesh), and silver powder mixed with electrolyte (1:1 ratio) were used for the anodes. This choice was dictated by the fact that silver ions are the mobile species in the electrolyte.

### *Cathodes*

Four types of cathodes were used in the present study: iodine ( $I_2$ );  $I_2$  + carbon (1:1);  $I_2$  + carbon + electrolyte (5:1:5);  $I_2$  + carbon + electrolyte + tetramethylammonium iodide (TMAI) (5:1:5:1).

The anode and electrolyte materials were formed into one pellet and the cathode material was formed into a second pellet. The two pellets were pressed together and sealed with epoxy resin to avoid the effect of atmosphere on the behaviour of the formed cell. Four types of cells were constructed:

cell 1: Ag/electrolyte/ $I_2$

cell 2: Ag/electrolyte/ $I_2$  + C

cell 3: Ag + electrolyte/electrolyte/ $I_2$  + C + electrolyte

cell 4: Ag + electrolyte/electrolyte/ $I_2$  + C + electrolyte + TMAI

The cells were discharged at various currents and the voltages and currents were measured using a Keithley electrometer.

## *Results and discussion*

### *Ionic and electronic conductivity*

For the AgI-Ag<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub>-MoO<sub>3</sub> system, a composition of 66.67AgI-14.29Ag<sub>2</sub>O-19.04[0.1B<sub>2</sub>O<sub>3</sub>-0.9MoO<sub>3</sub>] exhibited the highest ionic conductivity ( $\sim 10^{-2}$  S cm<sup>-1</sup>) at room temperature (305 K) [5]. The corresponding electronic conductivity was 10<sup>-9</sup> S cm<sup>-1</sup>. The transport number of the silver ions calculated from the ionic and electronic conductivities was close to unity (0.99). Thus, glass with this composition can be used as an electrolyte for a solid-state cell or battery.

## *Galvanic cell*

### *Open-circuit voltage*

The electrochemical cells were activated by pressing together the anode/electrolyte and cathode pellets. After sealing in an ebonite case with epoxy resin, the measured open-circuit voltage (OCV) was, respectively, 686, 685, 683 and 640 mV for cells 1 - 4. The OCV values remained constant over a period of 6 months. This implies that the intrinsic electronic conductivity is negligible and, hence, the cell has a long shelf life. The low OCV of cell 4 is due to the reduced activity of iodine in the presence of the alkyl group; this enhances battery shelf-life.

### Polarization and discharge characteristics

It was found that the potentials of the four cells remained constant under no-load conditions. Polarization was not observed for any of the cells at low current densities. The polarization losses were mainly due to the bulk resistance and the nucleation at the electrode/electrolyte interface. The polarization characteristics can be improved by using an electrolyte of higher conductivity or by reducing the interfacial resistance. The capacities of cells 1 - 4 were 2.5, 3.5, 7, and 11 mA h, respectively, as determined from Fig. 1. Thus, the use of TMAI as a cathode in a silver/electrolyte/iodine cell causes a four-fold increase in capacity.

The discharge profiles for cells 1 - 4 are shown in Fig. 1 up to 400 mV at  $50 \mu\text{A}$ . The initial drop in the cell potential is due to the formation of a poorly conducting AgI layer at the cathode/electrolyte interface. The decline in the potential of cell 4 was less rapid than that for cell 1 over the same period. This is because the cage-like structure of the alkyl group traps iodine [7]. The lower value of the internal resistance of cell 4 compared with that of cell 1 is due to the formation of highly conducting tetraalkylammonium iodide-silver iodide double salts [8].

Figure 2. presents the discharge profiles of cell 4 at the following current densities: 50, 100, 150, and 200  $\mu\text{A}$ . It can be seen that the cell is capable of delivering 150  $\mu\text{A}$  without any serious polarization.

### Conclusions

A silver boromolybdate system, with composition yielding the highest conductivity, has been used as an electrolyte in the fabrication of solid-state cells. The polarization and discharge characteristics have been studied. The

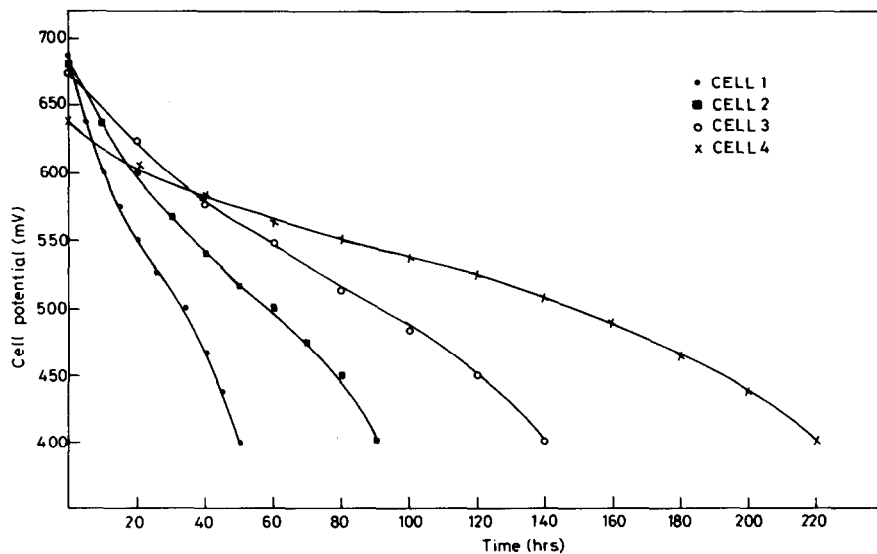


Fig. 1. Cell potential vs. time for cells 1 - 4 at  $50 \mu\text{A}$ .

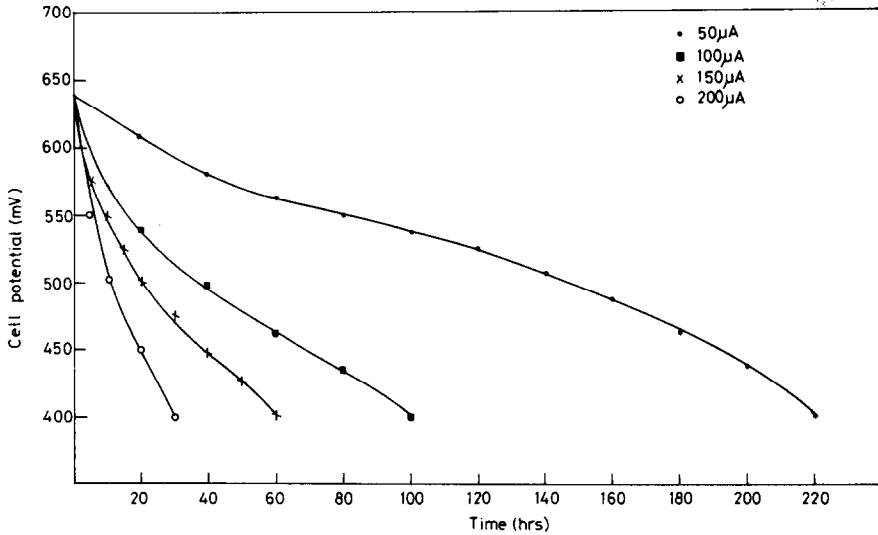


Fig. 2. Constant-current discharge curves at 32 °C for cell 4.

progressive improvement in the cell performance with change in anode and cathode materials has been attributed to an improved surface area of contact between the electrode and the electrolyte.

### References

- 1 A. Magistris, G. Chiodelli and M. Duclot, *Solid State Ionics*, 9/10 (1983) 611.
- 2 R. V. Salodkar, V. K. Deshpande and K. Singh, *J. Power Sources*, 25 (1989) 257.
- 3 V. K. Deshpande, A. Pradel and M. Ribes, *Mater. Res. Bull.*, 23 (1988) 379.
- 4 T. Minami, M. Tanaka and Y. Takuma, *J. Electrochem. Soc.*, 124 (1977) 1659.
- 5 R. V. G. K. Sarma and S. Radhakrishna, *Mater. Sci. Eng., B.*, submitted for publication.
- 6 P. S. S. Prasad and S. Radhakrishna, *J. Power Sources*, 5 (1989) 287.
- 7 M. Derossi, G. Pistoia and B. Scrosati, *J. Electrochem. Soc.*, 116 (1969) 1642.
- 8 B. B. Owens, *J. Electrochem. Soc.*, 117 (1970) 1536.