

Short Communication

Factors affecting the internal resistance of silver/silver molybdate/iodine cells

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Abstract

A silver molybdate glass with the mol% stoichiometry of $60\text{AgI}-20\text{Ag}_2\text{O}-20\text{MoO}_3$ is prepared by liquid nitrogen temperature quenching of the melt. The glassy nature of the phase has been confirmed by powder X-ray diffraction. The conductivity of the glass from impedance spectroscopy is of the order $10^{-3} \text{ S cm}^{-1}$ at 300 K. The phase is an electrolyte and has been used to fabricate several iodine/silver electrochemical cells in which silver is mixed in different proportions with the solid electrolyte for the anode of the cells. The cathode consists of a fixed ratio of iodine, electrolyte and carbon. It is found that, if the cathode disc is placed over the electrolyte surface of the anode/electrolyte disc and clamped between two copper current collectors, the cell with a 1:1 weight ratio of silver powder and the electrolyte shows the lowest internal resistance. A second cell has been fabricated with this anode composition, but the anode, electrolyte and cathode are pressed together to form a single solid disc so as to eliminate cathode/electrolyte interfacial resistance that also contributes to the total internal resistance of the cell. For the cells with a composition of 1:1 silver powder and electrolyte weight ratio, the internal resistance of the cell decreases from 2.3 k Ω when the cathode and anode/electrolyte layers of the cell are pressed separately to 0.15 k Ω for a cell with the anode, electrolyte and cathode pressed together. The value of 0.15 k Ω is in reasonable agreement with the bulk resistance of the electrolyte as obtained from the impedance plot.

Introduction

One area of research that is currently of great interest is the application of solid electrolytes to solid-state electrochemical cells [1–4]. The most important criterion in developing such cells has been to identify solid-state ionically-conducting materials with adequate conductivity to serve as the cell electrolyte. Some solid-electrolyte cells have also been designed for operation at elevated temperatures because of the high internal resistance that emanates from the electrolyte. Although many cells have been fabricated, little information is given regarding factors that affect the internal resistance of the cell.

The main objectives of this work are to study how the electrolyte content in the anode affects the magnitude of the internal resistance and to investigate the contribution of the electrolyte/cathode interface contact to the cell internal resistance. Silver molybdate glass has been chosen as the electrolyte material for the solid-state electrochemical cells. MoO_3 has been reported [5] to add n-type conduction to glass semiconductor properties. This would introduce a deleterious effect to the present investigation if MoO_3 is used as a glass former in the solid electrolyte for application in solid-state cells. Studies [6, 7] have shown that silver molybdate glasses are ionic conductors but explanations for this behaviour have differed. It has been suggested [6] that silver molybdate glass consists of dense clusters that are connected by low-density tissues that serve as pathways for high ionic conduction. Alternatively, the ionic conductivity has been attributed [7] to the existence of channel-like structures that are formed as a result of corner sharing MoO_6 octahedra through which the silver ions flow. From transference number measurements performed via the e.m.f. method [8], we have shown in the work reported here that the majority charge carriers in the silver molybdate glass are ions.

Experimental

Electrolyte preparation

AgI , Ag_2O and MoO_3 were mixed in the mol% stoichiometric ratio of 60AgI-20 Ag_2O -20 MoO_3 . The resulting mixture was placed in a crucible and melted in a Carbolite furnace at 800 °C. The melt was then quenched rapidly to form a glass in a stainless-steel container that was kept at liquid nitrogen temperature.

X-ray diffraction analysis

To confirm the glassy nature of the sample, powder X-ray diffraction (XRD) analysis was performed. The X-ray diffractogram was recorded on a Shimadzu XD-5 diffractometer using $\text{Cu K}\alpha$ radiation of wavelength 1.542 Å.

Conductivity studies

1 g of the powdered silver molybdate sample was pelletized under a 2-ton pressure to form a 1.0 cm disc, coated with silver paint on both surfaces, and mounted between two silver electrodes. These electrodes were then connected to a HIOKI LCR Bridge (model 3520) that was operated in the frequency range 100 Hz to 100 kHz at 300 K.

Cell fabrication and characterization

The electrochemical cell comprised: (Ag + electrolyte)/electrolyte/(iodine + electrolyte + carbon). The anode consisted of different silver and electrolyte mixtures whilst the cathode composition was kept identical with an iodine:electrolyte:carbon ratio of 5:5:1. Both the anode/electrolyte layer and the cathode layer were compacted under a 2-ton pressure to form a disc of 1.0 cm diameter. The cathode layer was then placed on the electrolyte and both pellets were clamped between two current collectors made of copper plates.

To measure the internal resistance, each cell was connected in series to a resistance box (initially adjusted to maximum resistance) and a digital ammeter. A digital voltmeter was also connected across the cell. With reduction of the resistance of the resistance box, the corresponding readings of the voltmeter and the ammeter were registered.

After several readings were obtained, a dry cell of higher e.m.f. was connected to the fabricated cell (the '+' terminal of the dry cell was connected to the cathode of the fabricated cell). The rest of the circuit remained unchanged. The current in the circuit was now reversed. For an increase in negative current, an increase was observed in the voltage registered by the voltmeter. The data voltages and currents were plotted. The data obeyed the relationship $V = E - IR$ where V is the voltage of the cell when a current I is drawn, E is the open-circuit voltage (OCV), and R is the internal resistance. The gradient of the graph thus gave the internal resistance of the cell.

Using the best anode composition (i.e., that with the lowest internal resistance), another cell was constructed with the same cathode composition but the anode, electrolyte and cathode were all pressed together at a 2-ton pressure to form a solid 1.0 cm diameter disc. The internal resistance was then calculated from the voltage-current characteristics of the cell. Care was taken to ensure that the cells would not be short-circuited during fabrication. The transference numbers of the cells were obtained by the e.m.f. method [8]. Finally, all cells were discharged at $30 \mu\text{A}$.

Results

Figure 1 shows the amorphous hump and peak-free XRD pattern of the sample. The electrical conductivity value of the silver molybdate glass from the impedance plot of Fig. 2 is $2 \times 10^{-3} \text{ S cm}^{-1}$ at 300 K.

The voltage-current characteristics for all the fabricated cells are presented in Fig. 3. The internal resistances of these cells are listed in Table 1.

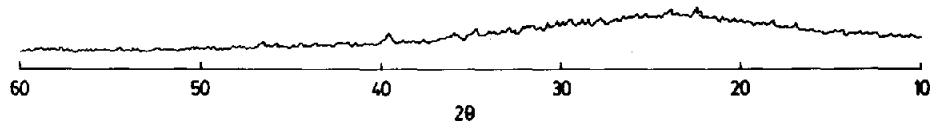


Fig. 1. X-ray diffraction pattern of silver molybdate glass.

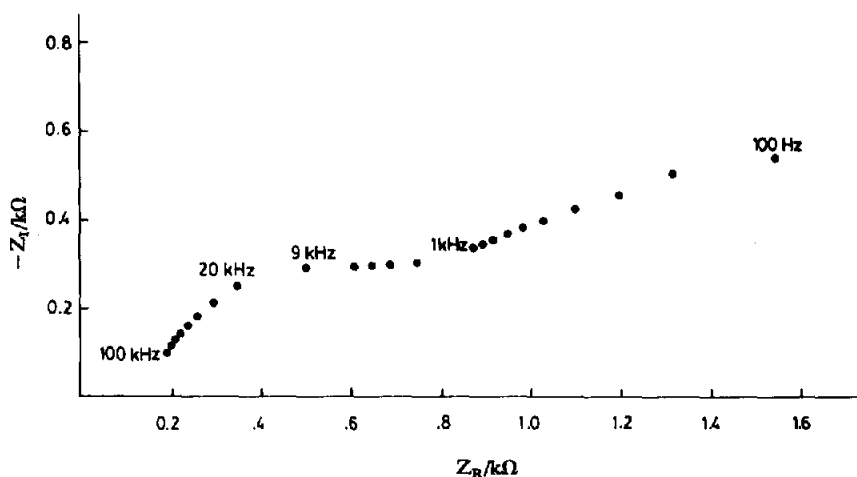


Fig. 2. Impedance spectroscopic plot.

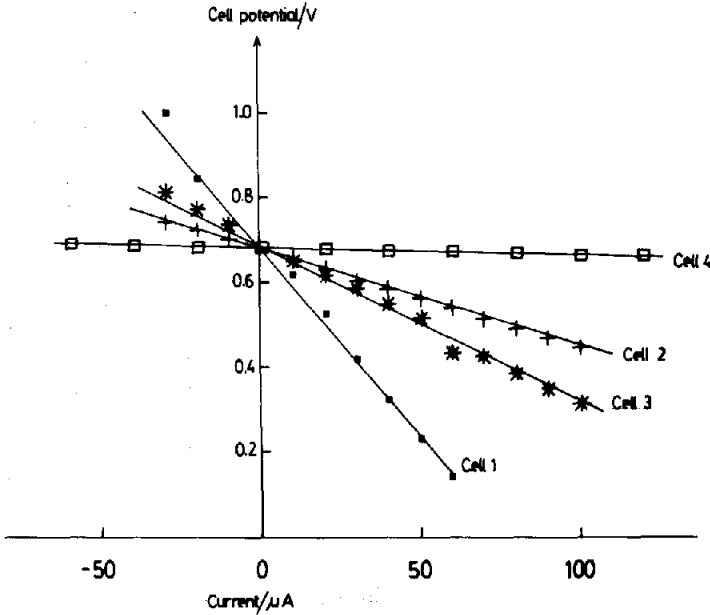


Fig. 3. Voltage-current characteristics of cells 1 to 3 (cathode and anode/electrolyte layers pressed separately) and cell 4 (anode, electrolyte and cathode pressed together).

TABLE 1

Internal resistance of cells 1, 2 and 3, in which the cathode and anode/electrolyte layers are pressed separately, and cell 4 in which the anode, electrolyte and cathode were pressed together

Cell	1	2	3	4
Ag:electrolyte (weight ratio)	1:0	1:1	1:2.5	1:1
Internal resistance (k Ω)	9.3	2.3	3.8	0.15

Figure 4 shows the discharge characteristics of cells 1 to 4 at a constant load current of 30 μ A. The OCV for all cells are the same, namely, about 0.680 V. This gives a transference number of almost unity since the theoretical e.m.f. is 0.687 V [9].

Discussion

Although it is known that MoO₃ adds n-type conduction to glass semiconductor properties, it is obvious that from the transference number (0.99) the main charge carriers in the phase are ions. Thus, silver molybdate glass is an ionic conductor and this should make it suitable for electrolyte application in solid-state cells.

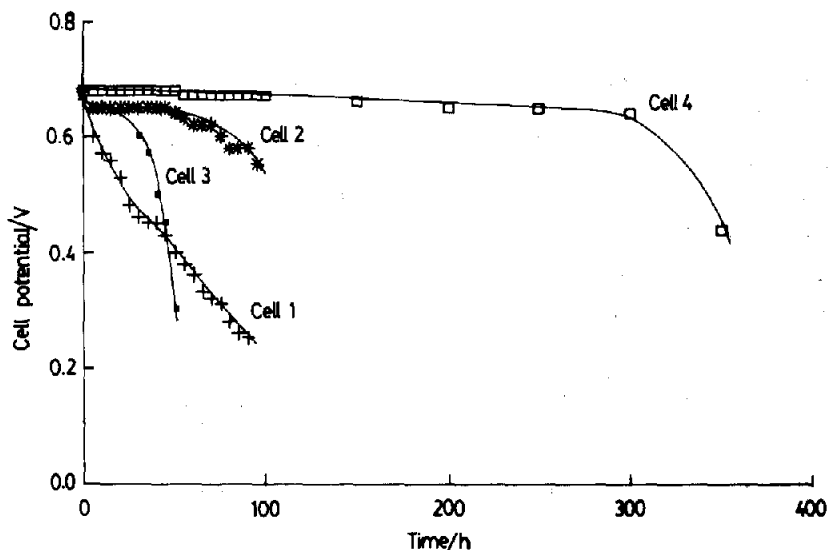


Fig. 4. Comparison of the discharge performance of cells 1 to 4 for a constant load current of $30 \mu\text{A}$.

Ideally, the internal resistance of the cell should be contributed by the electrolyte impedance only since the materials used in the anode (e.g., silver) and in the cathode (e.g., carbon) are all good conductors and possess negligible resistance. In cells employing solid electrolytes, however, the contacts between anode/electrolyte and cathode/electrolyte are not as good as the contacts in cells using liquid electrolytes. From the results presented here, the internal resistance of the cell is observed to depend on the anode composition. As silver is consumed during the discharge, contact between the silver and the electrolyte will decrease and, hence, will increase the internal resistance. This, in turn, will lead to a faster drop in cell voltage. As was observed for the cell in which the anode is purely silver (cell 1), the voltage decreases faster with time compared with cells 2 and 3. For cell 3, although the anode contains electrolyte, the silver activity is reduced. Consequently, upon consumption of the silver atoms, the anode/electrolyte contact decreases and, thereby, increases the internal resistance of the cell. This again results in a faster loss in cell potential. A 1:1 weight ratio of silver powder and electrolyte in the anode maintains a better contact between the anode and electrolyte, as indicated by cell 2. Thus, anode/electrolyte contact contributes to the internal resistance of the cell.

The interface between a solid anode and a solid electrolyte during discharge has been examined by Jow and Liang [10, 11] for a $\text{Li}/\text{Li}(\text{Al}_2\text{O}_3)/\text{PbI}_2, \text{Pb}$ solid-state galvanic cell. It was found that one of the failure modes during discharge of the cell was attributable to the loss of the interface contact between the lithium anode and the $\text{Li}(\text{Al}_2\text{O}_3)$ solid electrolyte. The loss was a result of void formation at the interface during discharge. In this work, it has been shown that the anode composition can influence the anode/electrolyte interface and, therefore, can contribute to the high internal resistance of the cell.

The internal resistance of a cell is defined as the drop in potential (i.e., open-circuit voltage minus voltage upon current drawn) divided by the current drawn from

the cell. In the case of cell 1, the drop in potential is 0.040 V when a current of 5 μA is drawn from the cell. This gives an internal resistance of 8 k Ω . For the same current, the drop in potential of cells 2 and 3 is 0.010 and 0.016 V, respectively, and the corresponding internal resistances are 2.0 and 3.2 k Ω . These values are comparable with those given in Table 1, but are still much higher than the electrolyte impedance. Since the internal resistance of cell 2 (with a 1:1 weight ratio of silver powder and electrolyte in the anode) was lowest in the present study, it was assumed that the anode/electrolyte contact resistance was almost negligible. Hence, the difference between the cell internal resistance of 2.0 k Ω and the electrolyte impedance must be attributed to the electrolyte and cathode interfacial resistance. This is confirmed from the voltage-current characteristics and discharge curve of cell 4 in which the cathode/electrolyte interfacial resistance was eliminated by compacting the anode, electrolyte and cathode together as one solid disc. Upon comparing the internal resistance of cells 2 and 4, it can be deduced that the electrolyte/cathode interfacial resistance can be of the order of several k Ω . From the measurements reported here, the voltage dropped by about 5 mV when a current of 30 μA was drawn from cell 4. This provides an internal resistance of 150 Ω which is comparable with the electrolyte impedance.

Conclusions

Although MoO_3 is known to add n-type conduction to glass semiconductor properties, transference number measurements in the present work have shown that silver molybdate is an ionic conductor and, therefore, is suitable for use as an electrolyte in electrochemical cells. Unlike cells employing liquid electrolytes, the internal resistance of a solid-state cell is contributed to by the anode/electrolyte and cathode/electrolyte interfacial resistances, as well as by the electrolyte impedance. The anode/electrolyte interfacial resistance can be eliminated by using equal weights of silver and electrolyte in the anode, and the cathode/electrolyte interfacial resistance can be eliminated by pelletizing the anode, electrolyte and cathode together as one solid disc.

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