

Structural characteristics of silver–chromate glasses and performance of silver–chromate electrochemical cells

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Silver–chromate glasses $x\text{AgI}-y\text{Ag}_2\text{O}-z\text{CrO}_3$ ($x = 64, 67$ and 70 mol % and $y/z = 1$) were prepared by rapid quenching of the melt. The microstructure of the as-quenched samples showed different surface agglomerates which led to non-uniformity in chemical distribution throughout the sample. The presence of potassium, detected by energy dispersive analysis of X-rays EDAX, was due to contamination of potassium nitrate produced during the preparation of AgI via the double decomposition of silver nitrate and potassium iodide. The battery fabricated from the glass with 70 mol % AgI contaminated with potassium showed an unstable discharge compared to the battery fabricated from glass with 70 mol % AgI of AR grade. This was attributed not only to the formation of low-conducting silver iodide but also to low-conducting potassium compounds which increased the internal resistance of the battery leading to a quick drop in cell voltage.

1. Introduction

The transport properties of silver–chromate glasses and the variation with time of OCV for silver–chromate electrochemical cells have been reported [1]. An understanding of fast-ion conduction in silver–chromate glasses via a chemical approach has also been undertaken [2]. The glassy electrolytes employed in battery fabrications are usually formed by melting the chemical constituents and rapidly quenching them to room temperature. The constituents are assumed to be well dispersed and maintain a uniform compositional distribution. However, there have been variations in the performance of the actual battery systems, which have not been well understood. There is little experimental data linking structural characteristics of the material to the battery performance [3–5]. Although many AgI-based solid electrolytes exhibiting exceptionally high conductivity have been reported, the parameters which give the best specific conductivity are not fully understood. Thin films prepared under controlled conditions of deposition temperature, operating current and film thickness gave the best specific conductivity, resulting in good battery performance [6–7]. In the present paper, electron microscopic investigations were undertaken in order to relate structural characteristics to battery performance.

2. Experimental procedure

The glasses were prepared by a rapid quenching

method in which the energy given to the system was removed rapidly so as to prevent nucleation resulting in crystalline structures. The as-quenched samples were carbon coated, and microstructure and microanalysis studies were carried out with a Philips SEM 515 equipped for energy-dispersive analysis of X-rays (Philips 9800). Several batteries were fabricated and discharged under a load of 19 k Ω .

3. Results and discussion

Fig. 1 shows a scanning electron microscopy (SEM) micrograph for the glass containing 70 mol % AgI (G1) taken at an electron accelerating voltage of 15 kV and a magnification of 2.12×10^2 . The surface exhibits different surface agglomerates with dark regions, white clusters and a greyish matrix. These surface agglomerates have different chemical content as confirmed by EDAX. The average chemical composition for several dark regions gave a silver content of 72.84%, an iodine content of 20.65% and a chromium content of 6.51%. The grey matrix exhibited an average chemical content of 69.66% silver, 28.33% iodine and 2.01% chromium. In some microregions, as much as 20.29% potassium was detected by EDAX, Fig. 2. This was attributable to contamination of AgI with KNO_3 produced during the preparation of AgI by coprecipitation of aqueous KI and AgNO_3 , possibly as a result of insufficient washing of the AgI precipitate during preparation. The occurrence of these surface

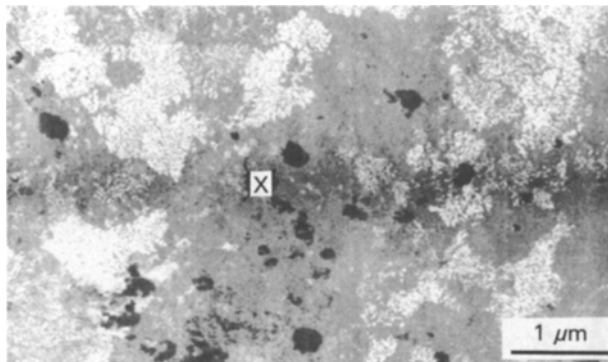


Figure 1 SEM micrograph of G1.

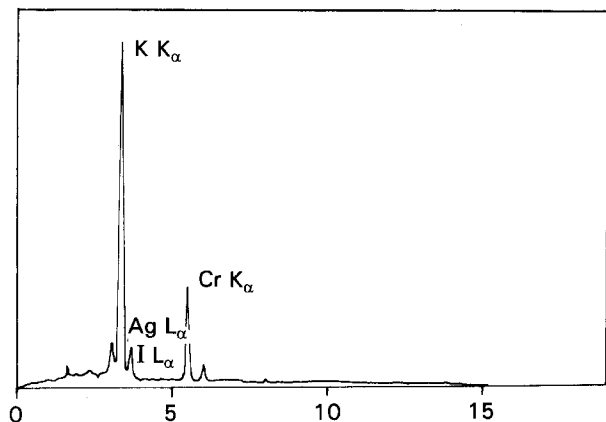


Figure 2 EDAX spectrum of G1 in the microregion containing potassium.

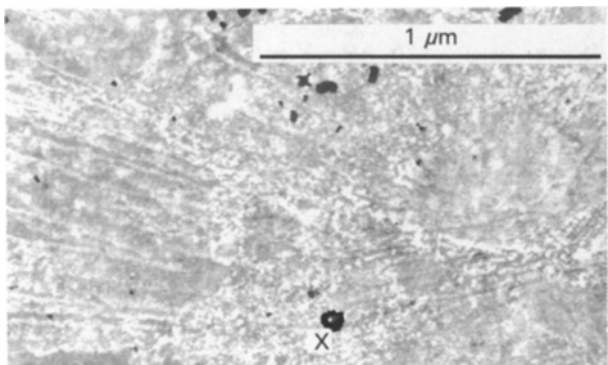


Figure 3 SEM micrograph of G1 after annealing for 15 h at 250 °C.

agglomerates in glasses is a key factor leading to the non-uniformity in chemical distribution. On the atomic level, these surface segregations could be explained in terms of the increasing competition, between the cations in the glass modifier and the cations in the glass former, to attract anions of the glass former to form clusters based on the modifier in the glassy network as the electric-field intensity of the cations in the glass modifier increases [5].

The occurrence of these surface segregations was initially attributed to the lowering of the total free energy, but in solidification phenomena, there is a separation mechanism that can produce surface segregation even when the total free energy does not favour the formation of an enriched surface layer. This is due to the solid redistribution that occurs at the

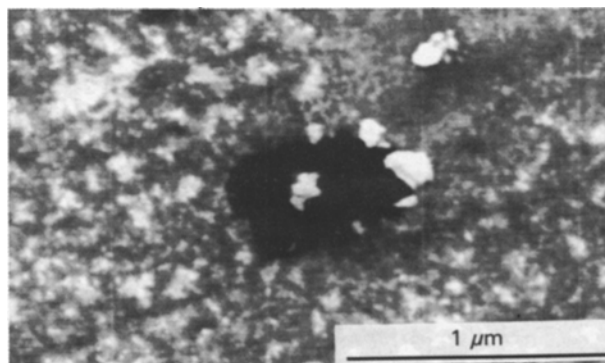


Figure 4 Magnified dark region (G1) showing polyhedral structure.



Figure 5 SEM micrograph of G2.

liquid–solid boundary, causing the solute to accumulate on the surface during freezing. In rapidly quenched glasses, the segregation behaviour is known to depend on the cooling rate. As the cooling rate increases, the quenched structures change from branch dendrites via cellular structures to featureless grains [8].

Fig. 3 shows a SEM micrograph of the same G1 sample annealed for 15 h at 250 °C. The surface morphology still consists of the same surface agglomerates, but the grey matrix exhibits planes of defects in the form of layer-like structures. The formation of these layer-like structures was attributed to the presence of silver ions in dual valency, i.e. 1 and 0. In Fig. 3, these layer-like structures cover quite a large area in the microregion scanned. EDAX revealed a slight increase in silver content for the grey matrix, and the dark regions showed an increase in potassium content suggesting that the annealing process also caused a redistribution of chemical composition apart from forming layer-like structures. Fig. 4 shows a SEM micrograph of the dark region marked “X” in Fig. 3 enlarged to a 5.7×10^3 magnification. The white spots in the dark region of Fig. 3 are believed to be polyhedral structures with open channels for ion migration, as observed for the As_2O_3 glass prepared by an open-air-crucible-melting and rapid-quenching method [8].

Fig. 5 presents the surface of the glass containing 67 mol % AgI (G2). Defect planes and different surface agglomerates were observed by EDAX revealing: 52.54 % Ag, 20.42 % I and 27.05 % Cr in the dark

regions; 73.75 % Ag, 20.19 % I and 6.06 % Cr in the grey matrix; and 56.78 % Ag, 36.12 % I and 7.1 % Cr in the white polyhedral structure.

Fig. 6 shows the morphology of a broken section of the 64 mol % AgI glass (G3) which shows many open, channel-like, structures. Fig. 7 is an enlargement of the region near "X", in Fig. 6, which more distinctively shows two channel-like structures, one above the other, extending into the bulk.

Fig. 8 represents the discharge curve of the battery fabricated from the glass with (a) 70 mol % AgI but contaminated with potassium, and (b) with 70 mol % AgI but of AR grade. The OCV of both batteries, (a) and (b), was 0.679 V. The OCV for battery (a) dropped to 0.613 V upon drawing 30 μ A from the battery using a resistance of 19 k Ω . The internal resistance of the battery was estimated to be about 1.4 k Ω . The discharge is not very stable and this was attributed to the potassium–nitrate contamination or probably other potassium salts which could increase the internal resistance of the battery. Battery (b) showed a smaller drop in voltage on applying a similar load. The internal resistance was estimated to be about 460 Ω . This shows that the potassium contamination increased the internal resistance of the battery and caused the discharge to be unstable.

4. Conclusion

AgI produced from co-precipitating AgNO₃ and KI can be contaminated by KNO₃ due to insufficient washing of the AgI precipitate although a lot of effort was spent in doing so. In the present investigation, all glasses produced by rapid quenching of the melt contain surface agglomerates which caused the chemical distribution of the glass to be non-uniform. Annealing produced defect planes in the form of layer-like structures in the glass, and caused a redistribution of the chemical composition. The battery fabricated from glass contaminated with potassium salts showed an unstable discharge characteristic.

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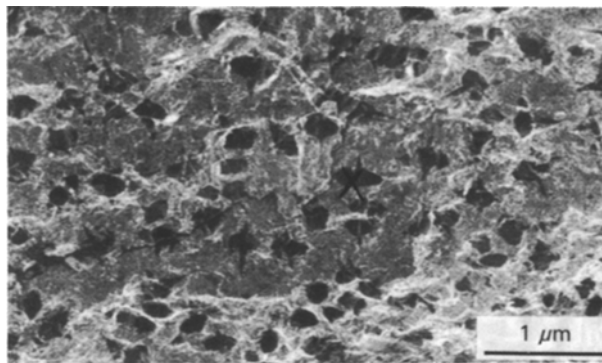


Figure 6 Structure of internal section of G3.

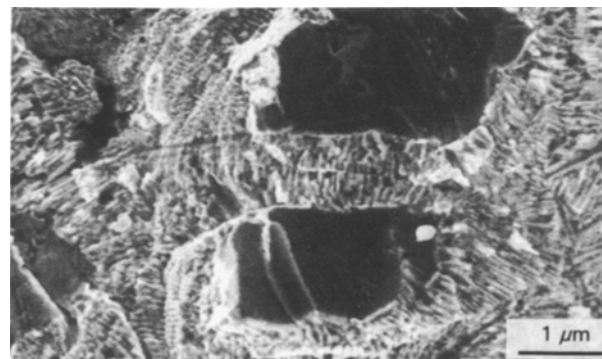


Figure 7 Enlargement of channel-like structures in G3.

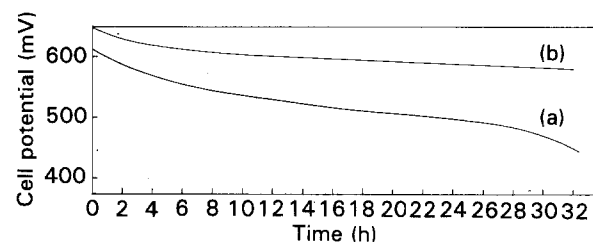


Figure 8 Discharge characteristic of silver batteries: (a) AgI produced via co-precipitation of aqueous AgNO₃ and KI, and (b) AR grade AgI.

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