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Electrochemical properties of a new solid electrolyte in the system silver iodide - silver dichromate

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A new silver solid electrolyte in the system AgI–$Ag_2Cr_2O_7$ has been characterized in terms of total and electronic conductivity, silver transport number and activation energy. The electrolyte undergoes a water-catalyzed decomposition reaction but, if kept in dry conditions, may be successfully used for the development of solid-state power sources capable of operating at room temperature.

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1. Introduction

Silver solid electrolytes, based on the combination of silver iodide with silver oxyacid salts have been recently described by Takahashi and co-workers [1, 2] in the systems AgI–Ag_3PO_4, AgI–$Ag_4P_2O_7$ and AgI–Ag_2WO_4 and by Chiodelli *et al.* [3] in the systems AgI–Ag_2CrO_4 and AgI–Ag_2MoO_4. In our laboratories we have investigated the systems AgI–Ag_3AsO_4 and AgI–Ag_3VO_4, finding, also in these cases, intermediate compounds having high specific ionic conductivity [4], as shown in Table 1, where typical properties of the electrolytes of the silver iodide–silver oxyacid salt type are summarized.

Since these electrolytes are of interest for practical applications such as the development of solid-state devices [2, 4], we have considered it important to extend the study also to the system AgI–$Ag_2Cr_2O_7$. A highly conductive phase, at about 85 mol % of AgI, has in fact been identified by conductivity and differential thermal analysis (DTA) studies. The electrochemical properties of this new solid electrolyte have been investigated and the results are reported in this paper.

2. Experimental

The preparation of silver iodide has already been described [4]. Silver dichromate was obtained by gradually adding a solution of $K_2Cr_2O_7$ to a hot solution of $AgNO_3$, acidified with HNO_3. After cooling, $Ag_2Cr_2O_7$ precipitated in the form of red brilliant laminae. The material was washed with distilled water and acetone and finally dried under purified nitrogen. The X-ray patterns of $Ag_2Cr_2O_7$ obtained in this way agreed with those reported in the literature [5].

The silver iodide–silver dichromate system was investigated by melting, under vacuum or nitrogen, intimate mixtures of weighed amounts of the two components and subsequently cooling them at room temperature (or, alternatively, quenching them in liquid nitrogen). The resulting products were ground and pressed at about 2500 kg cm^{-2} into pellets of 1·26 cm^2 surface for the electrochemical measurements.

The total conductivity was determined using as electrodes mixtures of silver and electrolyte (1/2 weight ratio) according to a procedure generally adopted in solid electrolyte technology to reduce contact polarizations. The resistance of the resulting symmetrical cells of the type

silver, electrolyte/electrolyte/silver, electrolyte (I)

was then measured with a 1 kHz impedance bridge.

The electronic conductivity was checked using Wagner's method and analysis [6], polarizing the cell

silver/electrolyte/graphite (II)

under voltages less than the decomposition

Table 1. Properties of silver iodide–silver oxyacid salt electrolytes at 25° C

System	*Composition* (mol% AgI)	*Total conductivity* $(\Omega\,cm)^{-1}$	*Activation energy* $(kcal\,mol^{-1})$	*Reference*
$AgI–Ag_3PO_4$	80	0·019	3·8	[1]
$AgI–Ag_3AsO_4$	80	0·004	4	[4]
$AgI–Ag_3VO_4$	80	0·007	4	[4]
$AgI–Ag_2WO_4$	80	0·047	3·6	[2]
$AgI–Ag_2CrO_4$	80	0·015		[3]
$AgI–Ag_2MoO_4$	80	0·006		[3]
$AgI–Ag_4P_2O_7$	93	0·09	3·3	[1]

potential of the electrolyte, with the graphite acting as the blocking electrode.

The silver transport number in the new solid conductor was obtained by Tubandt's method [7], using multilayered cells. Also in this case, to reduce contact resistance, electrodes formed by a mixture of silver and the electrolyte were used.

The solid state batteries were assembled by pressing the electrolyte and a thin layer of the cathode into a single pellet. This pellet was placed in a plastic container, having gold plated terminals, to which was then added a mixture of silver and the electrolyte (anode) also in the form of a pressed pellet. The cathode was a mixture of iodine and graphite or an iodine–perylene (I_2–P) charge transfer complex, obtained by a procedure already described [8]. The polarization and discharge curves were obtained and registered using standard equipment.

The X-ray data were obtained with a JEOL Difractometer, mod. JDX-8s with a CuK radiation at 30 kV and 20 mA. The DTA were performed with a Perkin Elmer differential calorimeter, mod. DSC 1B.

3. Results and discussion

Fig. 1 shows the conductivity-composition curve for the system $AgI–Ag_2Cr_2O_7$. The presence of an intermediate compound, having high specific conductivity, is indicated by the maximum at about 85 mol % AgI.

Attempts to confirm the conductivity results by X-ray analysis were unsuccessful since the spectra showed only few peaks over a rather broad base line, thus possibly indicating a glass-like structure for this electrolyte. A structure of this type has already been hypothesized by Kunze [9] for the $AgI–Ag_2SeO_4$ system. It also appears to be possible for other electrolytes of the silver iodide–silver oxyacid salt type discovered in our laboratories [4].

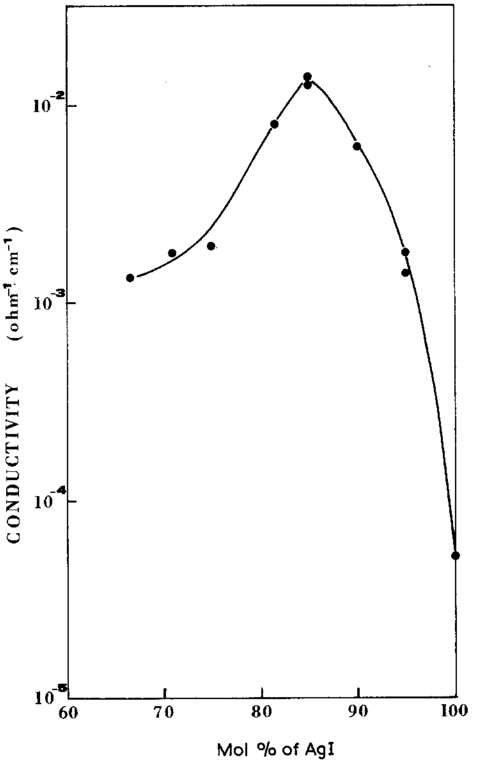

Fig. 1. Composition dependence of the specific conductivity in the system $AgI–Ag_2Cr_2O_7$ at 25° C.

In the particular case of the electrolyte described here, the amorphous character of the material becomes clear when the samples are obtained by quenching the melt in liquid nitrogen. The related X-ray spectra, in fact, do not show reflections, but only a very irregular base line.

In the X-ray spectrum of an aged sample, however, peaks related to silver iodide and to another unknown phase appear. This indicates a partial

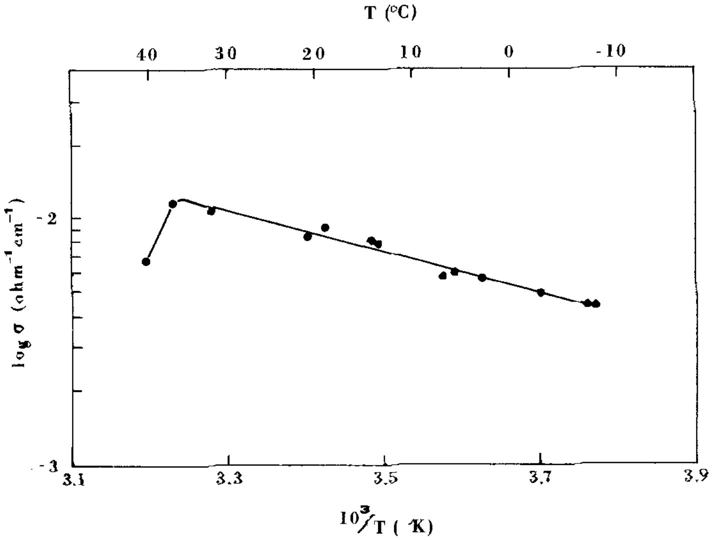

Fig. 2. Temperature dependence of the specific conductivity of 4·25AgI–0·75$Ag_2Cr_2O_7$ electrolyte.

decomposition of the electrolyte, as is also confirmed by the DTA results. DTA curve of an unreacted mechanical mixture of AgI and $Ag_2Cr_2O_7$ (85 mol % AgI), showed on heating a peak at about 150° C, ascribable to AgI, and a peak at about 170° C, due to the melting of the mixture. On fast cooling, 16° C min^{-1}, no traces of AgI are shown, thus indicating that the reaction between the two components has proceeded to completion. The DTA curve of an aged electrolyte, however, shows a broad exothermic peak, which may be related to decomposition, followed by a peak ascribable to silver iodide, an unidentified peak and, finally, the melting peak.

The X-ray and DTA results on the system examined in this work are further confirmed by conductivity measurements. In fact the Arrhenius plot, shown in Fig. 2, is linear up to about 40° C, and then falls to much lower values; this may undoubtedly be related to a decomposition into poorly conductive compounds. From the slope of the linear portion, an activation energy of about 3.9 kcal mol^{-1} is obtained, a value which is typical of solid conductors having an 'averaged' structure, in which the mobile ions are statistically distributed over a large number of sites in the lattice.

The results described indicate that in the system AgI–$Ag_2Cr_2O_7$ there is indeed a conductive phase at about 85 mol % AgI, but this electrolyte is thermodynamically unstable. Instability at various temperatures of solid silver conductors has already been noticed by Takahashi [1] and Chiodelli *et al.* [3] for the silver iodide–silver oxyacid salt electrolytes and by Topol and Owens [10] for silver rubidium iodide. On the basis of our results we may only state that the electrolyte here examined undergoes a decomposition reaction, characterized by a kinetic which becomes relatively fast at temperatures higher than 40° C and which produces two scarcely conductive compounds, one of which is silver iodide. More detailed thermodynamic studies and the phase diagram determination are in progress to fully characterize the reaction.

The decomposition reactions of solid electrolytes are frequently catalyzed by water. To investigate this in the present case, we have examined the time dependence (at 25° C) of the resistance of two cells similar to (I), one maintained open in an atmosphere of about 70% humidity and the other kept in a dry box. The results, shown in Fig. 3, show that humidity plays an important role in the decomposition, even at room temperature and, therefore, that the electrolyte has to be stored and examined under moisture-free conditions.

The total resistance of the electrolyte was measured at 1000 Hz using a cell similar to (I). The values obtained with various electrolyte thicknesses are shown in Fig. 4. Extrapolation to the origin indicates that for the configuration adopted in cell (I), the contact resistance is about 0·8 Ω. From the

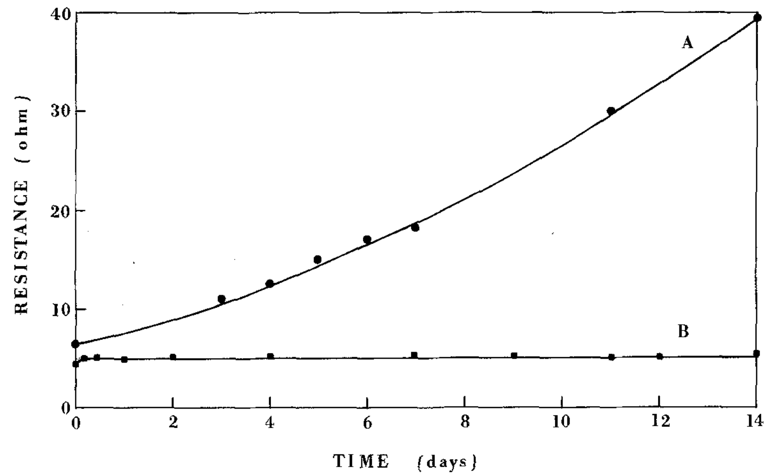

Fig. 3. Time dependence of the resistance of cells of type (I) where curve A refers to a cell maintained in 70% humidity and curve B to a cell kept in a dry box.

Table 2. Typical silver transport number results for $4{\cdot}25AgI\text{–}0{\cdot}75Ag_2Cr_2O_7$ electrolyte at 25° C

Current density (mA cm^{-2})	*Experimental changes in mass* (mg)	*Silver deposited in coulometer* (mg)	*Silver transport number*
0·16	12·1	12·5	0·971
0·16	13·1	12·5	1·051
0·24	8·5	8·45	1·006
			1·01 ± 0·03

Table 3. Properties of $4{\cdot}25AgI\text{–}0{\cdot}75Ag_2Cr_2O_7$ electrolyte at 25° C

Colour	Dark brown
Density (at 2·5 kg cm^{-2}), g cm^{-3}	4·9
Melting point, ° C	173
Total conductivity, (Ω cm)$^{-1}$	0·017 ± 0·002
Electronic conductivity, (Ω cm)$^{-1}$	$< 10^{-7}$
Silver transport number	1·01 ± 0·03
Activation energy, kcal mol^{-1}	3·9
Decomposition potential, V	~ 0·7

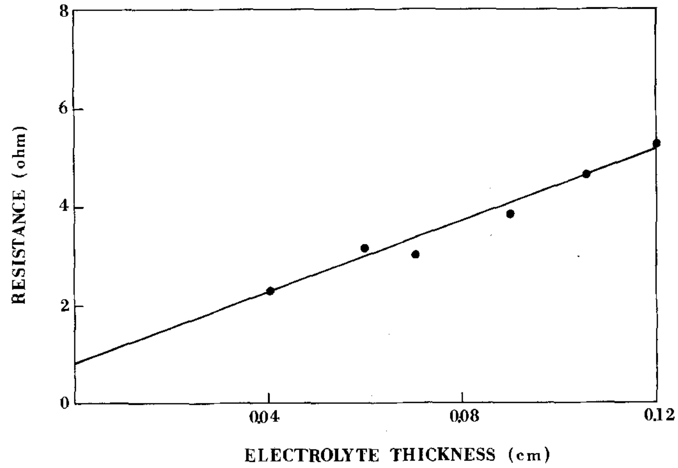

Fig. 4. Determination of the resistance of cells similar to (I) at 25° C.

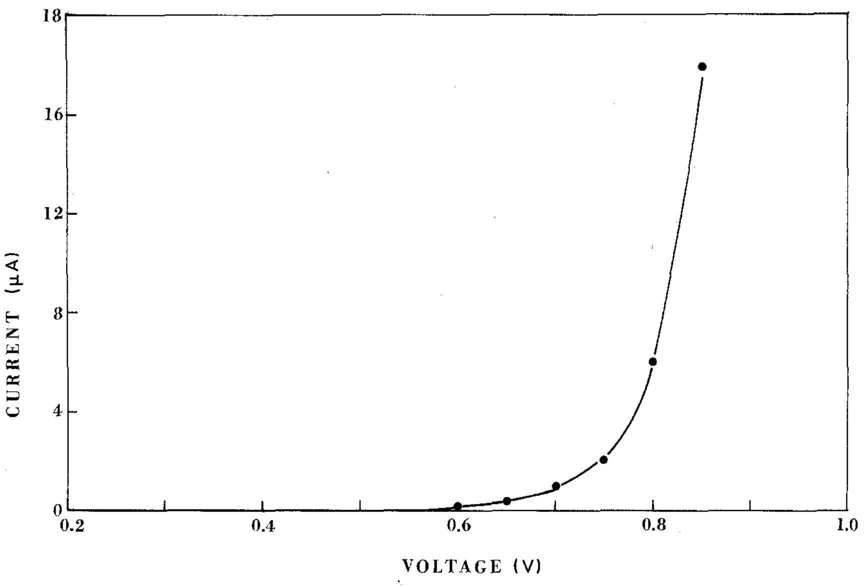

Fig. 5. Decomposition potential of $4{\cdot}25AgI–0{\cdot}75Ag_2Cr_2O_7$ at 25° C.

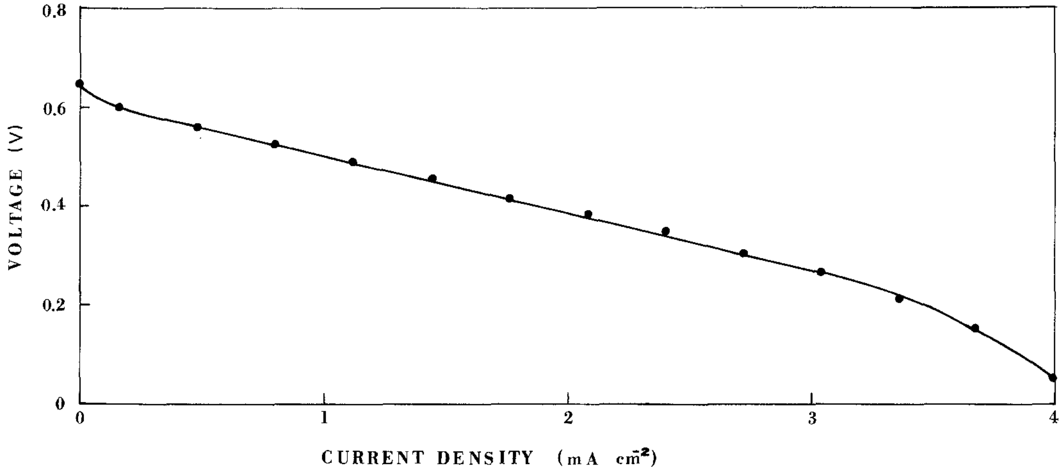

Fig. 6. Polarization curve of cell (V) at 25° C (electrolyte thickness 0·1 cm).

resistance data a value of $(0{\cdot}017 \pm 0{\cdot}002)\,\Omega^{-1}\,cm^{-1}$ for the total specific conductivity of the electrolyte is derived at 25° C.

The electronic contribution was determined by Wagner's [6] analysis to be less than $10^{-7}(\Omega\,cm)^{-1}$, thus indicating that the electrolyte, which may be indicated as $4{\cdot}25AgI–0{\cdot}75Ag_2Cr_2O_7$, is essentially an ionic conductor. To determine the nature of the ionic carriers, Tubandt's method [7] was used. The results, obtained on a series of samples under various conditions (see Table 2) show that the ionic conductivity through the electrolyte is solely due to silver ion movements, since the silver transport number is one within the experimental error.

The decomposition potential of the electrolyte was determined from the current-voltage curve shown in Fig. 5, obtained on a cell similar to (II), with the graphite electrode maintained positive. The result is reported in Table 3, where the properties of the electrolyte are summarized.

To test the applicability of the electrolyte for the development of solid-state power sources, the cell

$$Ag/4{\cdot}25AgI–0{\cdot}75Ag_2Cr_2O_7/I_2,\,C \qquad (III)$$

was assembled. It exhibited an e.m.f. of 0·686 V at 22° C. This value, which was stable and reproducible, is in very good agreement with the thermodynamic one (0·687 V) related to the process

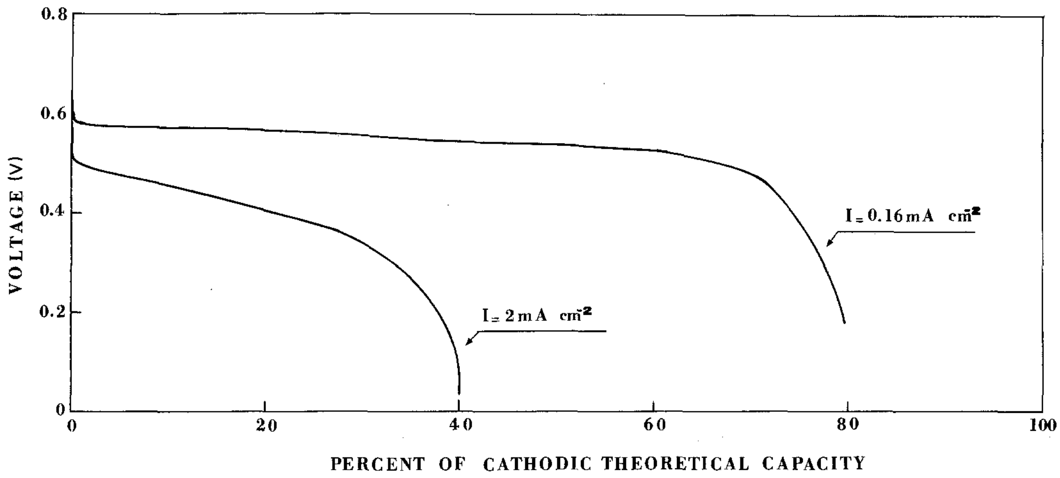

Fig. 7. Typical discharge curves of cell (V) at various current densities and at 25° C (electrolyte thickness 0·1 cm).

$$Ag + 1/2\, I_2 = AgI. \qquad (IV)$$

This in turn is a further indication that the conductivity of the electrolyte is predominantly ionic and due to silver movements only.

For practical applications, however, it is desirable to use as a cathode a material in which the iodine activity is somewhat reduced (to minimize tarnishing effects by free iodine) and which is an electronic conductor (to avoid addition of graphite). Such a material could very well be the iodine–perylene charge transfer complex which shows an excellent behaviour as cathode in silver-iodine solid cells, as previously evidenced [8]. The cell

$$Ag/4{\cdot}25AgI\text{–}0{\cdot}75Ag_2Cr_2O_7/I_2\text{–}P \qquad (V)$$

was therefore assembled in which, to reduce contact polarization, the electrolyte was added in a 2/1 weight proportion to silver in the anodic pellet.

The polarization curve, shown in Fig. 6, indicates that cell (V) may sustain discharge current densities of the order of several mA cm^{-2} without serious polarization. The possible application of the electrolyte in solid-state power sources is finally confirmed by the typical discharge curves of cell (V), reported in Fig. 7.

4. Conclusions

The results reported in this work show that the new phase $4{\cdot}25AgI\text{–}0{\cdot}75Ag_2Cr_2O_7$ is a solid electrolyte with a predominantly ionic conductivity, due to silver ion movements only. The electrolyte undergoes a water-catalyzed decomposition reaction but, if kept in dry conditions, may be effectively used at room temperature for the development of solid-state power sources. The silver iodide–silver dichromate electrolyte is of interest both on account of its electrochemical properties and also its particular structure. The first point has been discussed in this paper, while the second has stimulated a comprehensive examination of the entire class of these silver iodide–silver oxyacid salt conductors, in which the properties of the various components are correlated in terms of structure and stability. This study is in progress in our laboratory and will be reported in following papers.

Acknowledgement

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