

# *AgI - Ag oxysalt electrolytes for solid state cells*

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Among the family of solid electrolytes obtained from AgI and Ag oxysalts, new materials exhibiting high electric conductivity have been identified. The investigation is extended to the study of their behaviour at temperatures higher than 25°C.

The product with the composition of 80 mol % AgI in the system AgI-Ag<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> performs well at 25°C; the product with the composition of 75 mol % AgI in the system AgI-Ag<sub>2</sub>TeO<sub>4</sub> is the most promising at 60°C.

Solid state electrolytic cells containing such materials have been discharged against various external loads.

## 1. Introduction

High ionic conductivity electrolytes were recently obtained from AgI and Ag oxysalts [1-5]. Table 1 reports a list of such products together with their specific conductivities,  $\sigma$ , at 25°C.

These electrolytes showed, at 25°C, conductivity values lower than the ones so far obtained for other silver ion conductors (RbAg<sub>4</sub>I<sub>5</sub>  $\sigma = 2.1 \times 10^{-1} \Omega^{-1} \text{cm}^{-1}$ ; KAg<sub>4</sub>I<sub>5</sub>  $\sigma = 2.1 \times 10^{-1} \Omega^{-1} \text{cm}^{-1}$ ; NH<sub>4</sub>Ag<sub>4</sub>I<sub>5</sub>  $\sigma = 1.9 \times 10^{-1} \Omega^{-1} \text{cm}^{-1}$ ; etc. [6]); however they appeared more inert with respect to moisture and iodine vapours [4, 5].

Moreover, as remarked in previous works [4, 5], solid state cells containing such materials gave larger emf's and longer life times when compared to analogous devices containing RbAg<sub>4</sub>I<sub>5</sub> and supporting the same external loads.

In the present work the investigation was extended to the systems AgI-Ag<sub>n</sub>XO<sub>4</sub> (X = Se, Te, V, As) and AgI-Ag<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> which could be compared to those previously studied [1-5]. Moreover conductivity measurements concerning the whole family of these materials were carried out under isothermal conditions, at various temperatures, in order to test the possibility of obtaining good electrochemical performances also at higher temperatures.

Finally, the discharge behaviour of electrolytic cells containing the most promising materials was observed.

## 2. Experimental

The electrolytes investigated in the present work were obtained by quenching the molten mixtures of the systems AgI-Ag<sub>n</sub>XO<sub>4</sub> and AgI-Ag<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in liquid nitrogen.

The cells for the conductivity measurements as well as for the discharge tests had a pellet shape with a diameter of 0.8 cm and an average thickness of 0.5 cm. Other details concerning the arrangement of the specimens and the instrumental apparatus for the conductivity determinations were reported in previous papers [5].

Eight conductivity cells were mounted between large teflon discs and electrically insulated from one another: by means of a time switch they could be connected in turn to the measuring bridge, so that measurements of  $\sigma$  versus time under isothermal conditions, at various temperatures, could be carried out simultaneously for several systems.

For the systems AgI-Ag<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and AgI-Ag<sub>2</sub>TeO<sub>4</sub>, which appeared to be the most suitable for further determinations, solid state electrolytic cells were set up by employing mixed electrodes whose compositions were:

Anode: 50 mg of 4AgI:Ag<sub>2</sub>WO<sub>4</sub> + 20 mg Ag powder (200 mesh)

Cathode: 55 mg of 4AgI:Ag<sub>2</sub>WO<sub>4</sub> + 50 mg I<sub>2</sub> + 7 mg of graphite.

Such electrodes, as is well known, reduce

Table 1. Electrical conductivity at 25°C of AgI:Ag oxysalts products

| System   | Composition             | $\sigma_{25^\circ\text{C}} (\Omega^{-1} \text{cm}^{-1}) \times 10^{-2}$ |
|--|-------------------------|---|
| AgI:Ag <sub>2</sub> SO <sub>4</sub>                | X <sub>AgI</sub> = 0.80 | 5.0 (a)<br>2.0  |
| AgI:Ag <sub>2</sub> CrO <sub>4</sub>               | X <sub>AgI</sub> = 0.80 | 1.5   |
| AgI:Ag <sub>2</sub> MoO <sub>4</sub>               | X <sub>AgI</sub> = 0.80 | 0.6   |
| AgI:Ag <sub>2</sub> WO <sub>4</sub>                | X <sub>AgI</sub> = 0.80 | 4.7 (a)<br>2.3  |
| AgI:Ag <sub>2</sub> SeO <sub>4</sub>               | X <sub>AgI</sub> = 0.75 | 3.0 (b)<br>1.2  |
| AgI:Ag <sub>2</sub> TeO <sub>4</sub>               | X <sub>AgI</sub> = 0.75 | 0.9   |
| AgI:Ag <sub>3</sub> PO <sub>4</sub>                | X <sub>AgI</sub> = 0.80 | 1.9 (a)<br>1.4  |
| AgI:Ag <sub>3</sub> VO <sub>4</sub>                | X <sub>AgI</sub> = 0.80 | 0.3 (c)<br>0.4  |
| AgI:Ag <sub>3</sub> AsO <sub>4</sub>               | X <sub>AgI</sub> = 0.80 | 0.2 (c)<br>0.8  |
| AgI:Ag <sub>4</sub> P <sub>2</sub> O <sub>7</sub>  | X <sub>AgI</sub> = 0.94 | 9.0 (a)   |
| AgI:Ag <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> | X <sub>AgI</sub> = 0.80 | 1.9   |

Values not labelled refer to the present work and to [5]. (a) T. Takahashi *et al.* [1, 2, 4]; (b) D. Kunze [3]; (c) B. Scrosati, F. Papaleo, G. Pistoia and M. Lazzari [7].

Discrepancies among our and other Authors' results might be due to differences in cooling procedures and in contact resistances.

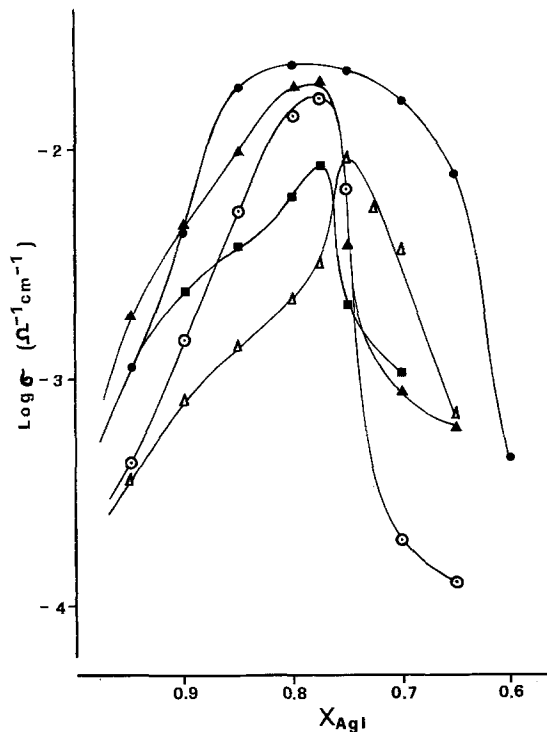


Fig. 1. Maximum of  $\sigma_{25^\circ\text{C}}$  for the systems AgI-Ag<sub>2</sub>WO<sub>4</sub> ●; AgI-Ag<sub>2</sub>CrO<sub>4</sub> ○; AgI-Ag<sub>2</sub>MoO<sub>4</sub> ■; AgI-Ag<sub>2</sub>TeO<sub>4</sub> △; AgI-Ag<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> ▲.

contact resistances and polarization effects during the discharge process.

### 3. Results

Measurements of  $\sigma$  at 25°C for various compositions of the systems AgI-Ag<sub>n</sub>XO<sub>4</sub> (X = Se, Te, V, As) and AgI-Ag<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> allowed one to identify in every case a critical composition range, 75–80 mol % AgI, where a conductivity maximum was observed. Analogous results were obtained in previous investigations concerning the other systems of the family [1–5].

As an example Fig. 1 reports some of these determinations.

Due to the glass-like nature of the investigated materials [8], the determined values of electrical conductivity were more or less stable with time according to the temperature and to the system; e.g.  $\sigma_{25^\circ\text{C}}$  decreased quite rapidly (2–3 days) for 4AgI:Ag<sub>2</sub>SO<sub>4</sub> [1], whilst it remained unchanged after three months storage in open air for the other investigated materials.

At higher temperatures quite different behaviours were observed. As an example, Fig. 2 reports the variations of  $\sigma_{60^\circ\text{C}}$  over a large time interval. A peculiar time stability in the case of

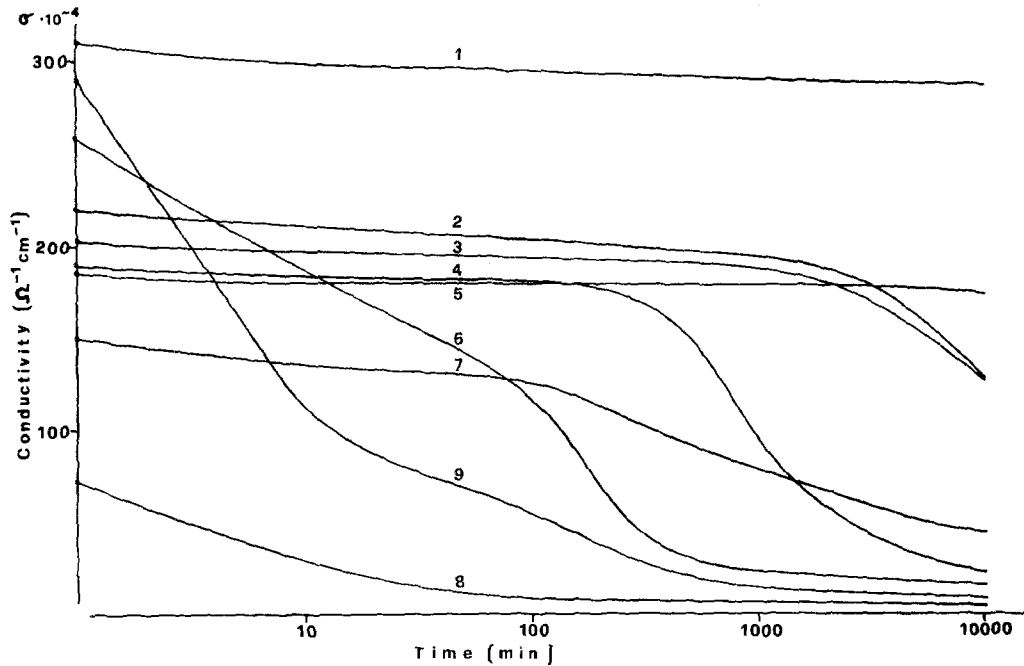


Fig. 2. Isothermal variation of  $\sigma_{60^\circ\text{C}}$  for critical composition products obtained by a quenching procedure from molten mixtures of the systems  $\text{AgI-Ag}_n\text{XO}_4$ ;  $\text{X} = \text{W}$  (1);  $\text{P}$  (2);  $\text{Te}$  (3);  $\text{Se}$  (4);  $\text{As}$  (5);  $\text{Cr}$  (6);  $\text{Mo}$  (7);  $\text{V}$  (8); and of the system  $\text{AgI-Ag}_2\text{Cr}_2\text{O}_7$  (9).

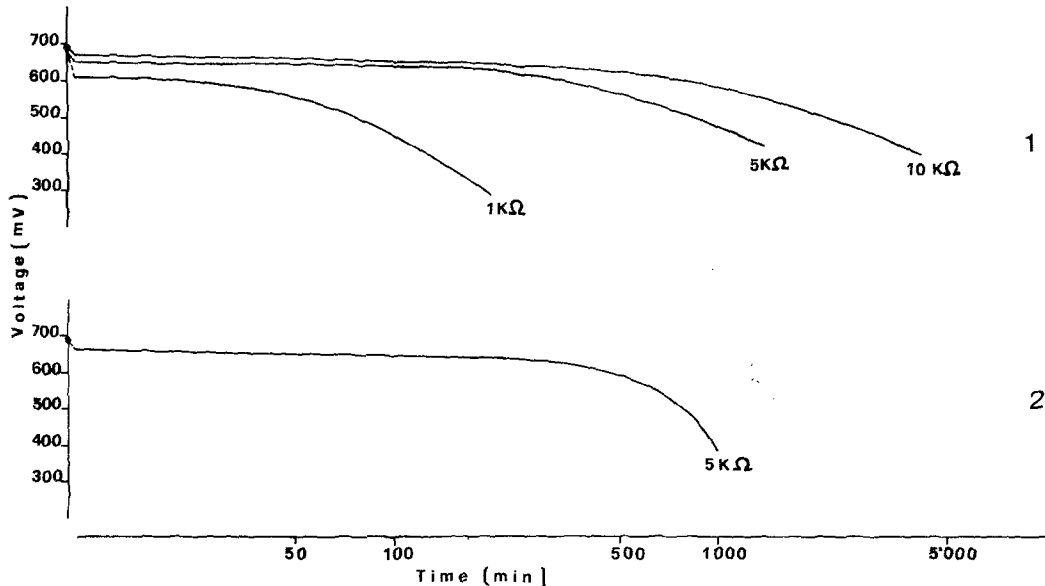


Fig. 3. Discharge behaviour against different external loads of the cells. (1)  $\text{Ag}(4\text{AgI}:\text{Ag}_2\text{WO}_4)/4\text{AgI}:\text{Ag}_2\text{Cr}_2\text{O}_7/1_2(4\text{AgI}:\text{Ag}_2\text{WO}_4)(\text{C})$  at  $25^\circ\text{C}$ ; (2)  $\text{Ag}(4\text{AgI}:\text{Ag}_2\text{WO}_4)/3\text{AgI}:\text{Ag}_2\text{TeO}_4/1_2(4\text{AgI}:\text{Ag}_2\text{WO}_4)(\text{C})$  at  $60^\circ\text{C}$ .

|          | Initial current density<br>(mA cm <sup>-2</sup> ) | Ext. load |
|----------|---|-----------|
| Cell (1) | 0.13  | 10 kΩ     |
|          | 0.26  | 5 kΩ      |
|          | 1.25  | 1 kΩ      |
| Cell (2) | 0.13  | 5 kΩ      |

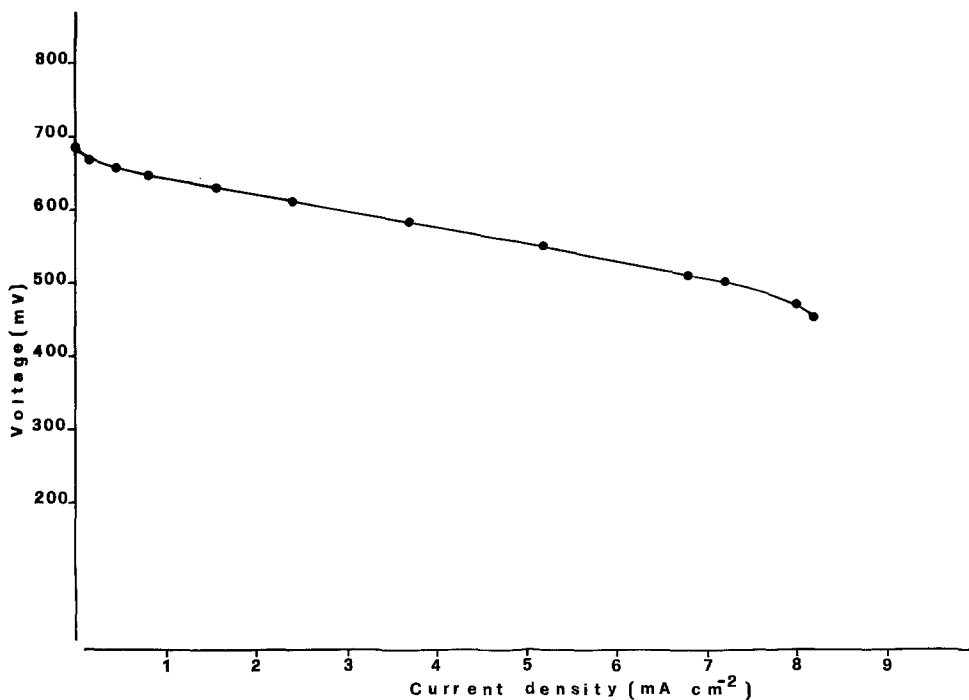


Fig. 4. Current voltage curve for the cell  $\text{Ag}(4\text{AgI}:\text{Ag}_2\text{WO}_4)/4\text{AgI}:\text{Ag}_2\text{Cr}_2\text{O}_7/\text{I}_2(4\text{AgI}:\text{Ag}_2\text{WO}_4)(\text{C})$  at  $25^\circ\text{C}$ : initial behaviour.

$4\text{AgI}:\text{Ag}_2\text{WO}_4$  was observed also at higher temperatures, even near to the melting point,  $T_m = 293^\circ\text{C}$ , reported in the phase diagram [4, 8] of the system  $\text{AgI}-\text{Ag}_2\text{WO}_4$ , where at the composition 80 mol %  $\text{AgI}$  an actual compound is predicted.

Conversely, for the other investigated materials, the decrease of  $\sigma$ , which was already detectable for some of them at  $60^\circ\text{C}$ , became more rapid at higher  $T$ 's: at  $90^\circ\text{C}$  for all of these products  $\sigma$  fell to less than  $10^{-3}\ \Omega^{-1}\text{cm}^{-1}$  in a few minutes. Such a behaviour is probably due to the formation of crystalline thermodynamically stable phases exhibiting low  $\sigma$ . This phenomenon, which was in effect observed and investigated [8] in the systems  $\text{AgI}-\text{Ag}_n\text{XO}_4$  ( $X = \text{Cr}, \text{Mo}, \text{W}$ ), required anyway a long annealing time to be definitely accomplished.

Among the materials investigated in the present work, the products obtained from the system  $\text{AgI}-\text{Ag}_2\text{Cr}_2\text{O}_7$  at the composition 80 mol %  $\text{AgI}$  and from the system  $\text{AgI}-\text{Ag}_2\text{TeO}_4$  at the composition 75 mol %  $\text{AgI}$  gave the best performances at 25 and  $60^\circ\text{C}$ , respectively. Therefore they were further studied (at  $25^\circ\text{C}$  the former, at  $60^\circ\text{C}$  the latter).

For both of them the electronic conductivity

was determined according to a previously suggested procedure [9] and was found to be less than  $10^{-6}\ \Omega^{-1}\text{cm}^{-1}$ ; from ionic transport number determinations according to Tubandt's method  $t_{\text{Ag}^+} = 1$  was obtained in both cases.

The OCV of the Cell  $\text{Ag}/4\text{AgI}:\text{Ag}_2\text{Cr}_2\text{O}_7/\text{I}_2(\text{C})$  was 687 mV at  $25^\circ\text{C}$ ; the cell  $\text{Ag}/3\text{AgI}:\text{Ag}_2\text{TeO}_4/\text{I}_2(\text{C})$  showed an OCV = 685 mV at  $60^\circ\text{C}$ .

Finally, solid state cells containing these products were discharged against different external loads (see Fig. 3) and showed a behaviour as satisfactory as analogous devices containing other electrolytes of the same family [5]. The initial current densities of the discharge processes are given in the caption of Fig. 3.

Fig. 4 reports the current voltage curve for the cell containing  $4\text{AgI}:\text{Ag}_2\text{Cr}_2\text{O}_7$ .

The discharge efficiency of such cells as well as of the devices reported in [5] could be improved by adjusting the composition of the electrodes (e.g. with depolarizing products such as  $\text{RbI}_3$ , perilene- $\text{I}_2$  mixtures etc.) and by increasing the contact surface (which in the present case was only  $0.5\text{cm}^2$ ); however such aspects were out of the scope of this work which was principally devoted to the study of the electrolytic phase.

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**References**

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