

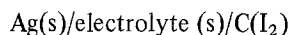
# $\beta$ -AgVO<sub>3</sub>·4AgI and AgNbO<sub>3</sub>·4AgI: two new solid silver electrolytes at room temperature

B. B. SCHOLTENS, A. BROUWER, G. H. J. BROERS

*Inorganic Chemistry Department, State University Utrecht, Croesestraat 77A, Utrecht, The Netherlands*

Received 27 June 1977

The specific conductivity of compounds in the  $\beta$ -AgVO<sub>3</sub>-AgI system above 50 mol% AgI has been measured. A maximum value of the conductivity was observed at 80 mol% AgI. The temperature dependence of the specific conductivity of both the compounds  $\beta$ -AgVO<sub>3</sub>·4AgI and AgNbO<sub>3</sub>·4AgI was also measured. Activation energies are 3·7 kcal mol<sup>-1</sup> and 3·8 kcal mol<sup>-1</sup> respectively. The specific conductivity of the  $\beta$ -AgVO<sub>3</sub> based compound is much higher than that of the AgNbO<sub>3</sub> analogue. The silver transport number in both compounds has been determined by Tubandt's method. In both cases a value of  $1\cdot00 \pm 0\cdot02$  was found. Galvanic cells of the type



were constructed. Electrochemical measurements on these cells indicate a better performance of those cells with a  $\beta$ -AgVO<sub>3</sub>·4AgI electrolyte with respect to the ones with an AgNbO<sub>3</sub>·4AgI electrolyte.

## 1. Introduction

In the past ten years several materials have been investigated for their possible applicability as solid ionic conductors in 'all-solid-state' cells. The most promising compounds up to now have been dominantly silver ionic conductors, based on silver iodide [1].

In silver iodide a solid state transition occurs at 145°C above which it has an extremely high silver ionic conductivity. Several investigators reported that substances used as additives to silver iodide resulted in a successful lowering of this transition point below room temperature.

The first additive (Ag<sub>2</sub>S) was introduced in 1966 by Takahashi *et al.* [2]. The results initially published of the formed compound Ag<sub>3</sub>SI seemed very promising. A more extensive study, however, showed that in Ag<sub>3</sub>SI some electronic conduction is present, prohibiting its use in galvanic cells. The magnitude of this electronic conduction is greatly influenced by the preparation procedure of the Ag<sub>3</sub>SI material [1].

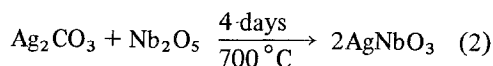
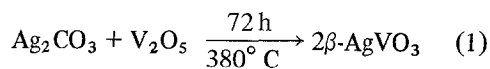
More promising results were obtained with the compounds MAg<sub>4</sub>I<sub>5</sub> (in which M = K, Rb, NH<sub>4</sub>). After the introduction of these compounds in 1966/1967 [3, 4, 5], more compounds were re-

ported, especially by an Italian group of investigators. A summary of the materials used as additives to AgI is given in Table 1, together with the mol% of AgI and the specific conductivity ( $\sigma$ ) of the formed compound at room temperature [6]. In almost all cases an optimal conduction has been achieved at 80 mol% AgI. In this article the compounds  $\beta$ -AgVO<sub>3</sub> and AgNbO<sub>3</sub> will be presented in relation to their ability to stabilize the good conducting high temperature  $\alpha$ -AgI phase below room temperature.

## 2. Experimental

### 2.1. Preparation of materials

$\beta$ -AgVO<sub>3</sub> and AgNbO<sub>3</sub> were prepared in air according to the following reaction schemes



The silver carbonate, niobium pentoxide and vanadium pentoxide were all of analytical grade.

Table 1. Ionic conductivities of various compounds based on silver iodide [6] at room temperature

Substitution compound	AgI (mol%)	$\sigma_{RT}^*$ ( $\Omega^{-1} \text{ cm}^{-1}$ )	Reference(s)
RbI	80	0.21	[7]
NH <sub>4</sub> I	80	0.19	[7]
KI	80	0.21	[7]
KCN	80	0.14	[8]
RbCN	80	0.18	[8]
KAg(CN) <sub>2</sub>	80	0.12	[8]
Me <sub>4</sub> Ni <sup>†</sup>	87	0.041	[7]
Me <sub>2</sub> Et <sub>2</sub> Ni <sup>†</sup>	87	0.064	[7]
Et <sub>4</sub> Ni <sup>‡</sup>	88	0.022	[7]
Ag <sub>3</sub> PO <sub>4</sub>	80	0.019	[9]
Ag <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	93	0.09	[9]
Ag <sub>2</sub> WO <sub>4</sub>	80	0.047	[10, 11]
Ag <sub>2</sub> CrO <sub>4</sub>	80	0.015	[11]
Ag <sub>2</sub> MoO <sub>4</sub>	80	0.006	[11]
Ag <sub>3</sub> AsO <sub>4</sub>	80	0.004	[12, 13, 14]
Ag <sub>3</sub> VO <sub>4</sub>	80	0.007	[12]
Ag <sub>2</sub> SeO <sub>4</sub>	75	0.012	[13]
Ag <sub>2</sub> TeO <sub>4</sub>	75	0.009	[13]
Ag <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	80	0.019	[13, 14, 15]
Ag <sub>2</sub> Mo <sub>2</sub> O <sub>7</sub>	75	0.008	[14]

\* Value given by first reference.

<sup>†</sup> Me = methyl-

<sup>‡</sup> Et = ethyl-

The several compounds in the system AgVO<sub>3</sub>-AgI and AgNbO<sub>3</sub>-AgI were prepared by melting the components in appropriate proportions in vacuum ampoules. These mixtures were melted, after which the ampoules were quenched to liquid nitrogen temperature. This quenching procedure was applied because it is well known that in this way an optimal ionic conduction is achieved [14].

X-ray patterns, taken with a Debye-Scherrer camera, show a very intense background radiation and an extremely large peak broadening, so that interpretation of these patterns was not possible. These problems were reported earlier for similar silver iodide based electrolytes [12, 14, 15].

The iodine-graphite material, which is used as the cathode material in the galvanic cell, was prepared by dissolving iodine in ether. After thorough mixing of graphite with this solution, the ether was evaporated. The weight ratio graphite:iodine was about 3:1. Silver, the anode material in the galvanic cells, was prepared according to a method published earlier [16].

## 2.2. Electrical measurements

The electrical conductivity of pressed pellets of the various materials was measured by a Wayne-Kerr bridge at an a.c. frequency of 1592 Hz.

The silver transport number was determined by Tubandt's method [17]. A pile of three electrolyte pellets was electrolysed between silver electrodes. After the electrolysis the weight changes of the various parts of the pellet arrangement were determined. By knowing the total amount of charge passed through the pellets it is possible to calculate the ionic transport number. In general the total amount of charge was about 4-6 C. A galvanostat was used to keep the current of about 0.1 mA constant during the electrolysis.

The pellets were obtained by using a pressure of about 3500 kg cm<sup>-2</sup>. Several galvanic cells were made in order to investigate the properties of the electrolytes. These cells were constructed by slowly pressing all the components together, one after another. The total arrangement was then pressed at a total pressure of 3500 kg cm<sup>-2</sup>. A small strip of nickel screen, serving as a current collector, was pressed in the graphite anode. The thickness of the electrolyte pellet was about 0.2 cm. Two current leads were then welded to both the silver and nickel current collectors of the cell. The cell was isolated from the environment by embedding it in a cold-curing resin on a methyl methacrylate basis (Technovit 4071-d).

The current density-potential plots were made dynamically using different loads, after which both current and cell potential were measured every minute. The potential was measured with a high impedance electrometer ( $R_i \approx 10^{14} \Omega$ ).

## 3. Results

### 3.1. Electrical transport measurements

The electrical conductivity at room temperature of various mixtures of AgI and AgVO<sub>3</sub> (from 50-90 mol% AgI) was measured. The results of these measurements are given in Fig. 1.

A maximal value of the specific conductivity occurs at a mole ratio AgI/AgVO<sub>3</sub> of 4. This corresponds with earlier observations for other solid silver electrolytes based on silver iodide (Table 1, [6]).

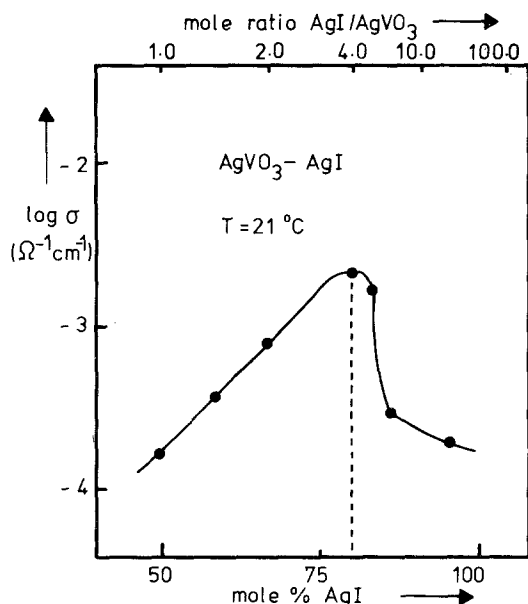


Fig. 1. Specific conductivities at 21° C of various mixtures in the AgI-AgVO<sub>3</sub> system.

The specific conductivity was measured as a function of temperature for both the compounds  $\beta$ -AgVO<sub>3</sub> · 4AgI and AgNbO<sub>3</sub> · 4AgI. The results obtained are given in Fig. 2 and from the observed lines an activation energy  $E_a$  for the ionic conduction is calculated: for  $\beta$ -AgVO<sub>3</sub> · 4AgI,  $E_a = 3.7$  kcal mol<sup>-1</sup>; and for the AgNbO<sub>3</sub> · 4AgI compound,  $E_a = 3.8$  kcal mol<sup>-1</sup>. These values are in accordance with those obtained for similar silver electrolytes (e.g. Ag<sub>3</sub>AsO<sub>4</sub> · 4AgI, 4.0 kcal mol<sup>-1</sup> [14]; Ag<sub>2</sub>WO<sub>4</sub> · 4AgI, 3.6 kcal mol<sup>-1</sup> [10]). The specific conductivity for the  $\beta$ -AgVO<sub>3</sub> based compound is about 10 × higher than that of the AgNbO<sub>3</sub> analogue. No decrease of the conductivity was observed for AgVO<sub>3</sub> · 4AgI when exposed to air, in contrast with the electrolyte AgNbO<sub>3</sub> · 4AgI. The conductivity of the latter compound decreases slowly with time. This is often observed for similar AgI-based electrolytes and is probably due to the catalytic effect of water from the air on the decomposition reaction of the electrolyte material [13, 14].

Tubandt experiments [17] were carried out on both  $\beta$ -AgVO<sub>3</sub> · 4AgI and AgNbO<sub>3</sub> · 4AgI with the following arrangement

Ag/Sample 1/Sample 2/Sample 3/Ag

The three pellets of the sample could be separated from each other very easily. In most cases the silver cathode could not be separated from the

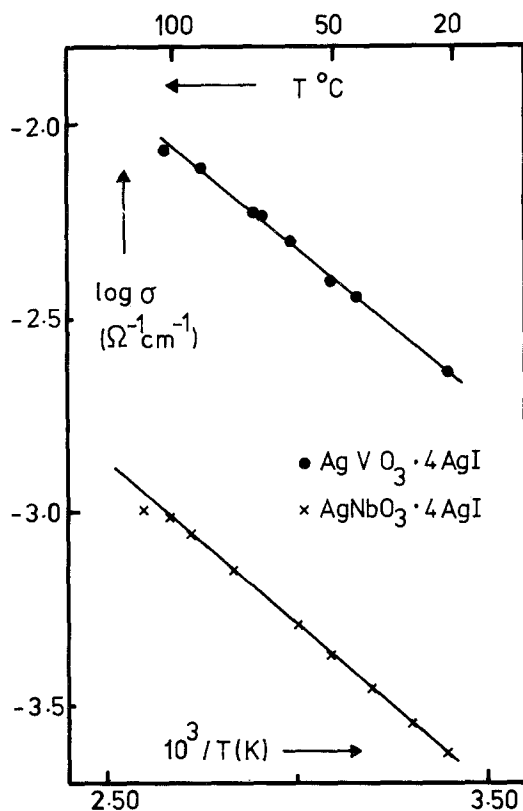


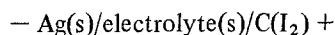
Fig. 2. Temperature dependence of the specific conductivity of the compounds  $\beta$ -AgVO<sub>3</sub> · 4AgI and AgNbO<sub>3</sub> · 4AgI.

adjacent sample pellet. The pellet indicated by Sample 2 did not show any weight change after electrolysis.

For each compound five Tubandt experiments were done. The calculated results indicate a silver transport number of  $1.00 \pm 0.02$  for both  $\beta$ -AgVO<sub>3</sub> · 4AgI and AgNbO<sub>3</sub> · 4AgI.

### 3.2. Galvanic cell measurements

In order to investigate the properties of cells with the presented new electrolytes, several galvanic cells of the type



were constructed. Current density-potential characteristics of these cells were recorded. Some typical results for sealed cells are depicted in Fig. 3.

The cell with a  $\beta$ -AgVO<sub>3</sub> · 4AgI electrolyte has a better performance at 21° C than the cell with a AgNbO<sub>3</sub> · 4AgI electrolyte. No reaction was observed between the iodine electrode and the electrolytes under investigation.

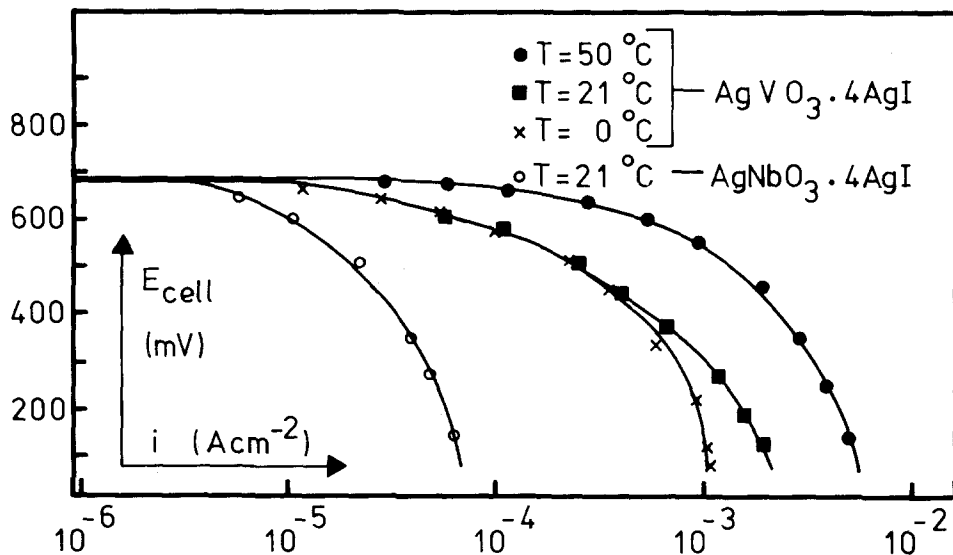


Fig. 3. Current density–terminal voltage plots of galvanic cells with the compounds  $\beta\text{-AgVO}_3 \cdot 4\text{AgI}$  and  $\text{AgNbO}_3 \cdot 4\text{AgI}$  as solid electrolytes.

The temperature dependence of the current density–potential characteristics for cells with a  $\beta\text{-AgVO}_3 \cdot 4\text{AgI}$  electrolyte is given in Fig. 3 as well. The performance of this cell is better at higher temperature.

The open cell voltage of 687 mV ( $T = 21^\circ\text{C}$ ) did not change with time during the measurements and its value is in accordance with the thermodynamic data for the AgI-forming reaction [2]. The polarization at the iodine cathode is dominant relative to that at the silver anode. This property was measured by inserting a silver probe in the electrolyte. This fact is often observed for these kind of cells [1]. The potentials were not corrected for an  $IR$ -drop, which is negligible up to about  $10^{-2}\text{ A cm}^{-2}$  for  $\text{AgVO}_3 \cdot 4\text{AgI}$ .

#### 4. Conclusions

Both the compounds  $\beta\text{-AgVO}_3 \cdot 4\text{AgI}$  and  $\text{AgNbO}_3 \cdot 4\text{AgI}$  are ionic conductors with a silver transport number of 1.00. The conductivity of the compound  $\beta\text{-AgVO}_3 \cdot 4\text{AgI}$  as well as its behaviour as an electrolyte in galvanic cells is much better than that of the  $\text{AgNbO}_3 \cdot 4\text{AgI}$  compound.

The measured properties of  $\beta\text{-AgVO}_3 \cdot 4\text{AgI}$  agree well with those of similar compounds from AgI with  $\text{Ag}_3\text{VO}_4$  [12],  $\text{Ag}_3\text{AsO}_4$  [12, 13, 14],  $\text{Ag}_2\text{Mo}_2\text{O}_7$  [14],  $\text{Ag}_2\text{MoO}_4$  [11].

#### References

- [1] C. C. Liang, 'Applied Solid State Science' (Ed. R. Wolfe), Vol. 4, Academic Press, New York (1974) p. 95.
- [2] T. Takahashi and O. Yamamoto, *Electrochim. Acta* **11** (1966) 779.
- [3] J. N. Bradley and P. D. Greene, *Trans. Faraday Soc.* **62** (1966) 2069.
- [4] *Idem, ibid* **63** (1967) 424.
- [5] B. B. Owens and G. R. Argue, *Science* **157** (1967) 308.
- [6] B. B. Scholtens and W. van Gool, 'Solid Electrolytes' (Ed. W. van Gool and P. Hagenmuller), Academic Press, New York (in press).
- [7] B. B. Owens, 'Advances in Electrochemistry and Electrochemical Engineering' **8** (Ed. P. Delahay and C. W. Tobias), Wiley Interscience, New York (1971) p. 2.
- [8] G. W. Mellors and D. V. Louzos, *J. Electrochem. Soc.* **118** (1971) 846.
- [9] T. Takahashi, E. Ikeda and O. Yamamoto, *ibid* **119** (1972) 447.
- [10] T. Takahashi and O. Yamamoto, *ibid* **120** (1973) 647.
- [11] G. Chiodelli, A. Magistris and A. Schiraldi, *Electrochim. Acta* **19** (1974) 655.
- [12] B. Scrosati, F. Papaleo, G. Pistoia and M. Lazzari, *J. Electrochem. Soc.* **122** (1975) 339.
- [13] A. Schiraldi, G. Chiodelli and A. Magistris, *J. Appl. Electrochem.* **6** (1976) 251.
- [14] M. Lazzari, B. Scrosati and C. A. Vincent, *Electrochim. Acta* **22** (1977) 51.
- [15] B. Scrosati, A. Ricci and M. Lazzari, *J. Appl. Electrochem.* **6** (1976) 237.
- [16] B. B. Scholtens, *Mat. Res. Bull.* **11** (1976) 1533.
- [17] C. Tubandt, 'Handbuch der Experimental Physik' **121** (1932) 383.