

CONDUCTIVITY TENSOR FOR THE SOLID ELECTROLYTE $\text{Ag}_{26}\text{I}_{18}\text{W}_4\text{O}_{16}$

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1.1 SOLID ELECTROLYTES

In recent years a considerable amount of interest has been shown in the area of the solid electrolytes. This term has been used to describe a particular state of matter in which one subset of ions in a crystal has a substantial measure of translational freedom, and to this extent is fluid-like, while the remainder of the ions execute motion (rotation and/or vibration) about fixed centers.

The transition from a normal crystalline solid, in which all the ions are confined to fixed sites, to a solid electrolyte is in some ways analogous to a melting transition, and it is now common to refer to "sub-lattice melting" in this context /1/.

These new compounds, with high (more than $10^{-2} (\Omega\text{cm})^{-1}$) ionic and very low (less than $10^{-8} (\Omega\text{cm})^{-1}$) electronic conductivity are becoming important in technology: in solid state batteries, coulometers /2/, etc. A few more types of solids /3-5/ are known to exhibit high ionic conductivity but at relatively high temperatures. They are of use in devices operating at high temperatures, e.g. fuel cells /6/ etc. Materials with high ionic conductivities at room temperatures are mainly silver ion conductors based on silver iodide.

1.2 SYSTEM $\text{AgI} + \text{Ag}_8\text{W}_4\text{O}_{16}$

The solid state system $\text{AgI} + \text{Ag}_8\text{W}_4\text{O}_{16}$ has been under extensive study as a source of electrolytes for use in Ag/I_2 batteries. In 1973, Takahashi et al. reported /7/ a series of electrical conductivity and differential thermal analysis measure-

ments from which they constructed a phase diagram for the $\text{AgI} + \text{Ag}_8\text{W}_4\text{O}_{16}$ system. Several ordered structures result/7/ from different admixtures of AgI and $\text{Ag}_8\text{W}_4\text{O}_{16}$: $\text{Ag}_4\text{I}_2\text{WO}_4$, $\text{Ag}_5\text{I}(\text{WO}_4)_2$ and $\text{Ag}_6\text{I}_4\text{WO}_4$. All these materials are based on the prototype structure $\text{Ag}_8\text{W}_4\text{O}_{16}$ and have a characteristic $(\text{W}_4\text{O}_{16})^{-8}$ complex in which the tungsten ion is octahedrally coordinated /8/.

The best characteristics for an electrolyte material were found in $\text{Ag}_6\text{I}_4\text{WO}_4$. X-ray structure work by Geller and Chan /9/ proved that the correct formula is $\text{Ag}_{26}\text{I}_{18}\text{W}_4\text{O}_{16}$. This material has fewer silver ions per cubic centimeter than RbAg_4I_5 , the most studied solid electrolyte ($0.78 \times 10^{22} \text{ cm}^{-3}$ compared with $1.13 \times 10^{22} \text{ cm}^{-3}$), but it has many more silver sites (most of which are empty) in comparison with RbAg_4I_5 ($4.96 \times 10^{22} \text{ cm}^{-3}$ versus $3.94 \times 10^{22} \text{ cm}^{-3}$). The chemical stability of $\text{Ag}_{26}\text{I}_{18}\text{W}_4\text{O}_{16}$ is better than that of RbAg_4I_5 in the iodine containing environments present in Ag/I_2 type batteries. This stability is evidenced by the constant internal resistance in the cells of type $\text{Ag}/\text{Ag}_{26}\text{I}_{18}\text{W}_4\text{O}_{16}/\text{I}_2$ which has been maintained over a period of more than two years. This combination of excellent physical properties has resulted in the selection of $\text{Ag}_{26}\text{I}_{18}\text{W}_4\text{O}_{16}$ as the electrolyte by Sanyo in a silver battery consisting of $\text{Ag}/\text{Ag}_{26}\text{I}_{18}\text{W}_4\text{O}_{16}/\text{Ag}_2\text{Se} + \text{Ag}_3\text{PO}_4$. This battery is marketed under the trade name "Memoroide" and is used in timing, integrating and memory applications.

1.3 CONDUCTIVITY MEASUREMENTS AS A FUNCTION OF TEMPERATURE

Since the crystal belongs to the space group C_2^3 the conductivity tensor has four independent values, as will be shown in detail in Section 1.4. To obtain data sufficient to determine these elements, measurements along four directions in crystal have to be done. Measurements were done along $\vec{a}, \vec{b}, \vec{c}$ and \vec{c}^* directions in the crystal. First, the measurements from room temperature down to 173 K and up to room temperature were performed. After this cycle, high temperature measurements up to 473 K were performed. The frequency of the square wave voltage applied in the measurement was chosen on the basis of the complex plane technique. The plot of conductivity measurement in the direction of \vec{a} -axis is shown in Fig. 1.

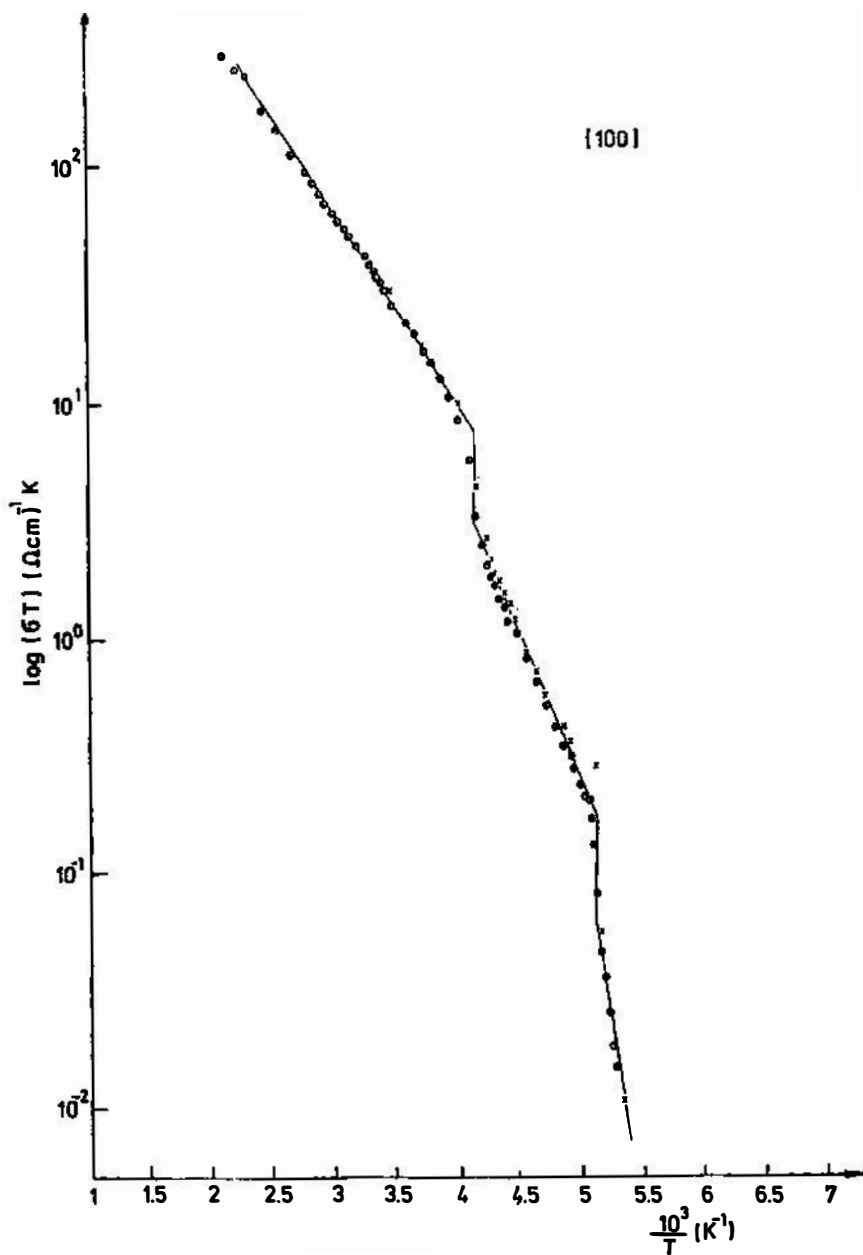


Fig 1. Plot of \log_{10} of the conductivity in the direction of \vec{a} -axis multiplied by temperature vs. reciprocal temperature for $\text{Ag}_{26}\text{I}_{18}\text{W}_4\text{O}_{16}$. The points X are used for denoting measurements on cooling down from room temperature to 173 K. The points \odot are used to denote measurements on heating up from 173 K to 373 K.

1.4 CONDUCTIVITY TENSOR FOR $Ag_{26}I_{18}W_4O_{16}$

At room temperature our crystal belongs to the space group C_2^3 . For this class (monoclinic with one twofold axis) the conductivity tensor referred to axes $\vec{x}_1, \vec{x}_2, \vec{x}_3$ in conventional orientation /10/ looks like:

$$\begin{bmatrix} S_{11} & 0 & S_{31} \\ 0 & S_{22} & 0 \\ S_{31} & 0 & S_{33} \end{bmatrix} \quad (1.4.1) \quad S_{ij} = \sigma_{ij}$$

A general quadratic form with C_2 symmetry has one axis - x_2 parallel to the diad axis. We are going to choose our axis as: $\vec{a} // \vec{x}_1, \vec{b} // \vec{x}_2, \vec{c} // \vec{x}_3$. Structural parameters are: $a=16.76, b=15.52, c=11.81 \text{ \AA}$, and $\beta=103.9^\circ$.

The expression for the conductivity in the general direction in the crystal is /10/: $\sigma = \sigma_{ij} l_i l_j$ (1.4.2)

So in our case, the magnitude, σ , of the conductivity in the direction x_1 , is:

$$\sigma_1 = \sigma_{11} l_1^2 + 2\sigma_{31} l_3 l_1 + \sigma_{22} l_2^2 + \sigma_{33} l_3^2 \quad (1.4.3)$$

To determine S_{31} in tensor, we are going to express the magnitude σ_c of the conductivity in the direction \vec{c} in system of chosen axes ($\vec{a}, \vec{b}, \vec{c}$). Direction cosines are: $l_1 = \cos\beta, l_2 = 0$ and $l_3 = \cos(\beta - 90^\circ) = \sin\beta$.

$$\begin{aligned} \sigma_c &= \sigma_{11} \cos^2\beta + 2\sigma_{31} \sin\beta \cos\beta + \sigma_{22} \cdot 0 + \sigma_{33} \sin^2\beta \\ \sigma_{11} &= \sigma_a, \quad \sigma_{33} = \sigma_{c^*} \end{aligned} \quad (1.4.4)$$

From that expression:

$$\sigma_{31} = \frac{\sigma_c}{2\cos\beta\sin\beta} - \frac{\sigma_a}{2\operatorname{tg}\beta} - \frac{\sigma_{c^*} \operatorname{tg}\beta}{2} = 0.0243 (\Omega\text{cm})^{-1} \quad (1.4.5)$$

Our measurements of conductivities in the directions of axes $\vec{a}, \vec{b}, \vec{c}$, and in direction of \vec{c}^* are:

$$\begin{aligned} \sigma_a &= 0.100 (\Omega\text{cm})^{-1} & \sigma_{c^*} &= 0.0852 (\Omega\text{cm})^{-1} \\ \sigma_b &= 0.0624 (\Omega\text{cm})^{-1} & \sigma_c &= 0.0747 (\Omega\text{cm})^{-1} \end{aligned}$$

The conductivity tensor is:

$$\sigma = \begin{bmatrix} 0.100 & 0 & 0.0243 \\ 0 & 0.0624 & 0 \\ 0.0243 & 0 & 0.0825 \end{bmatrix} (\Omega\text{cm})^{-1} \quad (1.4.6)$$

To calculate the average conductivity, using relation (1.4.3) and integrating over a sphere, we have:

$$\sigma_{\text{av}} = \frac{\sigma_a}{3} + \frac{\sigma_b}{3} + \frac{\sigma_{c^*}}{3} = 0.0825 (\Omega\text{cm})^{-1} \quad (1.4.7)$$

To express the conductivity tensor in the system of principal axes, we are using the Mohr circle construction. To get the new set of axes, the old system is rotated around the b-axes.

1.5. CONCLUSION

Directional measurements of conductivity were performed on $\text{Ag}_{26}\text{I}_{18}\text{W}_4\text{O}_{16}$ to explain Raman and conductivity data of Habbal et al./11/. As a conclusion about directional conductivity measurements on $\text{Ag}_{26}\text{I}_{18}\text{W}_4\text{O}_{16}$, we can say:

1. The average conductivity at room temperature, calculated from the conductivity tensor by integrating over a sphere is $0.0825 (\Omega\text{cm})^{-1}$ and in the direction of the highest conductivity is $0.130 (\Omega\text{cm})^{-1}$.
2. The average conductivity of a monocrystal specimen, $\sigma=0.0825 (\Omega\text{cm})^{-1}$ is higher than that of polycrystalline material, $\sigma=0.0590 (\Omega\text{cm})^{-1}$, as expected and contrary to the value obtained by Habbal et al. /11/, which was 100 times lower than that of polycrystalline material. The conclusion is that their electrolyte-electrode contacts were not satisfactory.

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