

STRUCTURAL AND ELECTROCHEMICAL CHARACTERISTICS OF RbAg_4I_5 SOLID ELECTROLYTE

GEORGETA ȚARĂLUNGĂ*, ELEONORA MARIA RUS**

*University of Agricultural Sciences and Veterinary Medicine, 3–5 Mănăștur Street, Cluj-Napoca, Romania

**Faculty of Chemistry and Chemical Engineering, “Babeș-Bolyai” University, 11 Arany János Street, Cluj-Napoca, Romania

Abstract. RbAg_4I_5 solid electrolyte is a superionic conductor with the highest ionic conductivity (0.3 S/cm) at room temperature, having many applications in medical devices. In this paper we present our method for obtaining RbAg_4I_5 and its structural and electrochemical properties.

Key words: RbAg_4I_5 solid electrolyte, superionic conductor, silver-iodine battery and biomedical devices.

INTRODUCTION

The solid electrolytes are materials with a high ionic conductivity and negligible electronic mobility. These materials are used in solid state batteries with applications in implantable electronic instrumentation such as cardiac pacemakers, physiological monitoring/telemetry package, etc.

The solid electrolyte RbAg_4I_5 belongs to the compounds-group of general formula $\text{M}^+\text{Ag}_4\text{I}_5$ (where $\text{M}^+ = \text{Rb}^+, \text{K}^+, \text{NH}_4^+$) having an exceptionally high ionic conductivity (about 10^{-1} S/cm) at room temperature. For a time these were referred to, rather inappropriately, as “superionic conductors”. These compounds were discovered by Bradley and independently by Owens.

Generally, the structures of solid electrolytes are not close-packed, but contain two- or three networks of passageways intercalated in crystalline structures. For these materials the silver ion is a mobile species and its transport into lattice takes place by a defect mechanism [3–5].

The crystallographic structure of RbAg_4I_5 was determined by X-ray diffraction. There are three crystalline modifications of RbAg_4I_5 , labeled as the α , β and γ phases in order of decreasing temperature. The α form has a cubic crystal

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lattice of $P4_1 32 (O^7)$ or $P4_3 32 (O^6)$ symmetry, β form has a rhombohedral crystal lattice of $R 32 (D_3^7)$ symmetry and γ modification has a hexagonal structure of loss $P 321 (D_3^2)$ symmetry.

There are four units of $RbAg_4I_5$ in a cubic unit cell with $a = 11.24 \text{ \AA}$, the refinement structure, by least squares, belongs to space group $P4_1 32(O^7)$. The number of sites available for mobile ions is much larger than the number of mobile ions themselves. For example, in $RbAg_4I_5$ the 6 silver ions in each unit cell are distributed over 56 available sites. The high conductivity is due to a combination of a high concentration of mobile ions and a low activation energy for ionic motions from site to site.

MATERIALS AND METHOD

The solid electrolyte $RbAg_4I_5$ was prepared by an original method [1, 2]. In order to obtain the electrolyte samples we prepared silver iodide from diluted solution (8–10%) of $AgNO_3$ and HI . The obtained precipitate AgI was washed until $pH=6$ and dried into vacuum box some days at room temperature and moreover 6 hours at $32\text{--}40 \text{ }^\circ\text{C}$ into the vacuum drying stove. This substance was structurally characterized by X-ray diffraction (Fig. 1).

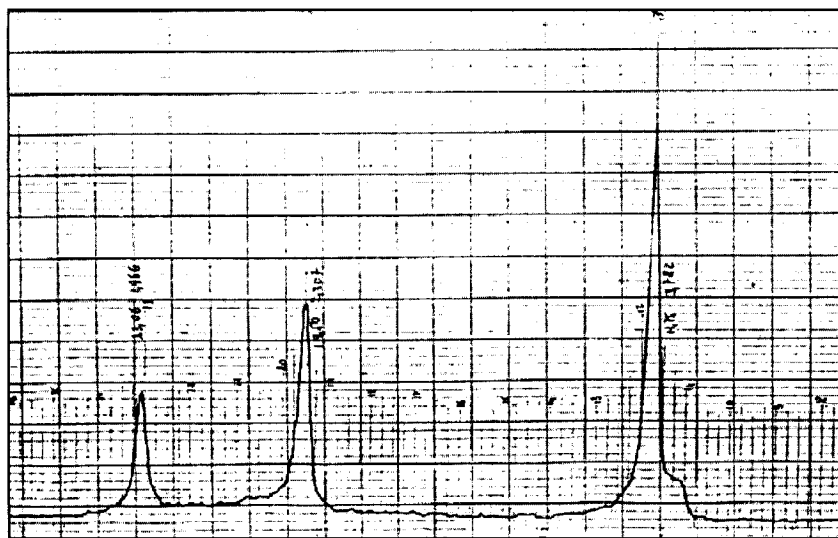


Fig. 1. – X-ray diffraction pattern of α -AgI.

$RbAg_4I_5$ samples were obtained by isothermal crystallization from acetone solution containing a mixture of RbI and AgI in a molar ratio 1:2. We obtained $RbAg_4I_5$, but impurified with Rb_2AgI_3 which favours the decomposition of wished substance. To prevent that, we added in acetone solution, in small portions,

AgI until saturation. The samples were crystallized at 20°. The structural characterization of the prepared was performed by X-ray diffraction. To determine the electrochemical properties, the RbAg₄I₅ powder was pressed at 2500 kgf/cm² into a stencil with 8 mm diameter. The contact electrodes were achieved by pressing a mixture of silver powder and solid electrolyte in a weight ratio 1:1.

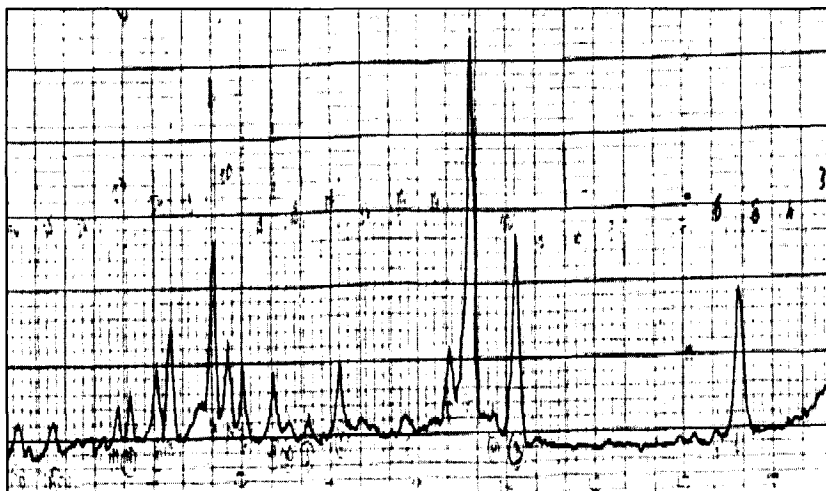


Fig. 2. – X-ray diffraction pattern of α -RbAg₄I₅.

The ionic conductivity was determined by means of Radelkis conductometer at a frequency of 1 kHz.

RESULTS AND DISCUSSION

From X-ray diffraction pattern of obtained powder (Fig. 1) it comes out that only specific diffraction lines of α -AgI form are present. In the X-ray spectrum, shown in Figure 2, are found the characteristic diffraction lines of α -RbAg₄I₅ solid electrolyte. Also, the gravimetric analysis demonstrated that the prepared substance corresponds to stoichiometric formula.

Because RbAg₄I₅ is the most stable of its compounds-group, the ionic conductivity of the sample was performed from liquid nitrogen temperature until room temperature. Experimental data are shown in Figure 3 and represent the mean values.

It is noticed that at two values of temperature (122 K and 209 K) modifications of the shape slope take place. From 120 K to 125 K ionic conductivity was grown suddenly from $5.12 \cdot 10^{-8}$ S/cm at $1.33 \cdot 10^{-5}$ S/cm. Precisely at 122 K γ - β phase transformation takes place, therefore the passing from the tidy phase to the untidy phase, when it appears the possibility of one fast diffusion of silver ions into the solid electrolyte. At 209 K it can be seen a modification of the shape of Arrhenius line, which corresponds to β - α phase transformation.

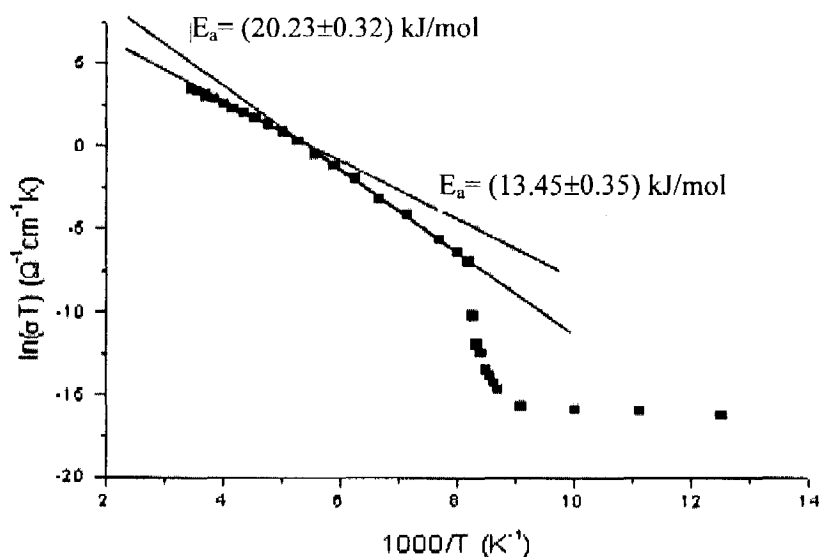


Fig. 3. – Dependence of RbAg_4I_5 conductivity on temperature.

Between the three crystallographic modifications $\alpha\text{-RbAg}_4\text{I}_5$ is the most suitable form for high ionic mobility. The specific conductivity value of $\alpha\text{-RbAg}_4\text{I}_5$ determined for our sample is 0.106 S/cm at 20 °C. From the slope of Arrhenius lines the active energies of silver ions diffusion were calculated, thus the found values are 13.45 kJ/mol for α form and 20.23 kJ/mol for β phase. These values of active energy are in accord to the literature data.

CONCLUSIONS

On the basis of the experimental data we can conclude that the method proposed by the authors is simple and allows the obtaining of RbAg_4I_5 solid electrolyte in pure state.

The $\alpha\text{-RbAg}_4\text{I}_5$ form is the most stable crystallographic modification and presents a high ionic conductivity.

This electrolyte can be used in solid state batteries of common applications in medical devices.

REFERENCES

1. BOLLA, Cs.C., GEORGETA ȚARĂLUNGĂ, A. BORBELY-KERI, L.D. BOBOS, SILVIA AVRAM, L. ONICIU, Batteries with RbAg_4I_5 solid electrolyte, in: *Batteries for Portable and Electric Vehicle Applications*, A. Landgrebe ed., the Electrochemical Society Inc. Pennington, N.J. USA, 1997, **18**, 518–523.

2. BOLLA, Cs., ILDIKO SZEKELY, A. BORBELY-KERI, L. ONICIU, GEORGETA ȚARĂLUNGĂ, Pile galvanice miniaturizate, in: *Producerea, Transportul și Utilizarea Energiei*, vol. XIV, pp. 101-105, Cluj-Napoca, 1995.
3. BRADLEY, J. N., P. D. GREENE., Solid with high ionic conductivity in group 1 halide systems, *Trans. Faraday Soc.*, 1967, **63**, 424-429.
4. FUNKE, K., Transport and relaxation in ionic crystal, *Ber. Bunsenges. Phys. Chem.* 1989, **93**, 1197-1201.
5. VINCENT, C.A., F. BONINO, M. LAZZARI, B. SCROSA'II, *Modern Batteries*, Chap.7, Edward Arnold (Publishers) Ltd., London, 1984.