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ELECTROCHEMICAL POWER SOURCES WITH $RbAg_4I_5$

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ABSTRACT. A variety of battery power implantable devices are routinely implanted into patients to treat ailments ranging from irregular heartbeat to pain and epilepsy. Solid state batteries are used for the safety of patients, which have a number of very desirable features. The batteries with $RbAg_4I_5$ solid electrolyte are part of these galvanic cells.The solid electrolyte $RbAg_4I_5$ belongs to the compounds-group with general formula MAg_4I_5 (where $M^+ = Rb^+, K^+, NH_4^+$) having an exceptionally high ionic conductivity (about 10^{-1} S/cm) at room temperature.

In this paper we present our method for obtaining of $RbAg_4I_5$ solid electrolyte and the main characteristics of $Ag/RbAg_4I_5/AgI_3$ cell. The electrochemical behavior of the batteries with $RbAg_4I_5$ solid electrolyte was studied through performance curves in two discharge regimes.

INTRODUCTION

The advances in battery technology, electronics and medical knowledge have produced a wide variety of sophisticated implantable devices to treat ailments ranging from irregular heartbeat to pain and epilepsy. Also a great diversity of battery powered external devices are used to administer drugs, treat ailments and monitor bodily functions. Solid state batteriese used for the safety of patients, which have a number of very desirable features such as absence of any possible liquid leakage or gassing and the possibility of operation over a wide temperature range. The batteries with $RbAg_4I_5$ solid electrolyte are part of these galvanic cells.

The solid electrolyte $RbAg_4I_5$ belongs to the compounds-group with the general formula MAg_4I_5 (where $M^+ = Rb^+, K^+, NH_4^+$) having an exceptionally high ionic conductivity (about 10^{-1} S/cm) at room temperature. The structures of these solid electrolytes are not close-packed, but contain two- or three networks of passageways intercalated in crystalline structures.

According to the literature data [1 – 4], 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 the decreasing order of their transformation temperature. The α form has a cubic crystal 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 lower P 321 (D_3^2) symmetry. 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. For these materials the silver ion is the mobile specie and its transport into the lattice takes place by a defect mechanism.

EXPERIMENTAL DATA

The solid electrolyte $RbAg_4I_5$ was prepared through an original method. $RbAg_4I_5$ samples were obtained by isothermal crystallization (at 55^0C) from an acetone solution containing a mixture of RbI and AgI in the molar ratio 1:2. $RbAg_4I_5$ was obtained but impurified with Rb_2AgI_3 which favours the decomposition of the desired substance. To prevent that, AgI was added to the acetone solution in small portions until saturation. Through gravimmetric and chemical analyses, it was established that the prepared powder is $RbAg_4I_5$ having a 98.894% purity. The structural characterization of the prepared $RbAg_4I_5$ was performed by X-ray diffraction X-ray diffractograms were obtained with a DRON 3 powder diffractometer, with a Cu-cathode, using k_α radiation (λ =1.57051Å).

Two types (I- and II-type) of $Ag/RbAg_4I_5/RbI_3$ button cells with 8 mm diameter were realized with the prepared $RbAg_4I_5$ solid electrolyte. The cathodes for both types of batteries were performed from a mixture of RbI_3 (87.30%), graphite (6.75%) and $RbAg_4I_5$ (5.95%), which was pressed. The anode for the I-type cell was an amalgamated silver disk of 0.02 mm thickness and for II-type cell a mixture of Ag powder (88.00%), graphite (8.00%) and $RbAg_4I_5$ (12.00%), which was pressed. The cells were assembled by pressing their components (anode, solid electrolyte and cathode) at 1700 kgf/cm^2 for 20 minutes [5-8].

RESULTS AND DISCUSSION

X-ray diffraction pattern of the obtained powder shows that only specific diffraction lines of α -$RbAg_4I_5$ solid electrolyte are present (Fig.1).

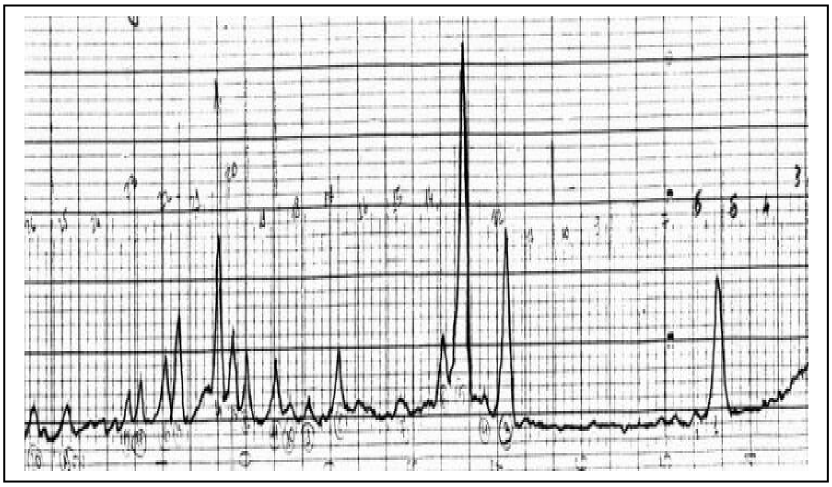

Fig.1. X-ray diffraction pattern of α - $RbAg_4I_5$

The values of e.m.f. for I-type cells were situated in the range 590-600 mV and for II-type were 650-660 mV. The electrochemical behavior of $RbAg_4I_5$ solid state cells was investigated through performance curves under constant load and galvanostatic regime.

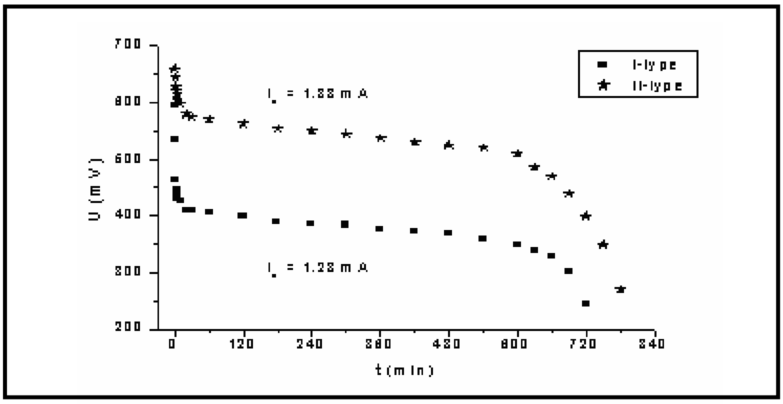

Fig.2. Discharge curves of I-type and II-type cells under R=100Ω

From Fig.2, where the discharge curves of I-type and II-type cells under constant resistance (R=100Ω) are shown, it can be seen that the II-type cell has higher characteristics than the I-type battery. Thus the discharge plateau of II-type was situated in the domain 525-575 mV, whereas for I-type in range 350-400 mV. The average discharge intensity was of 1.33mA for II-type and 1.28mA for I-type cell.

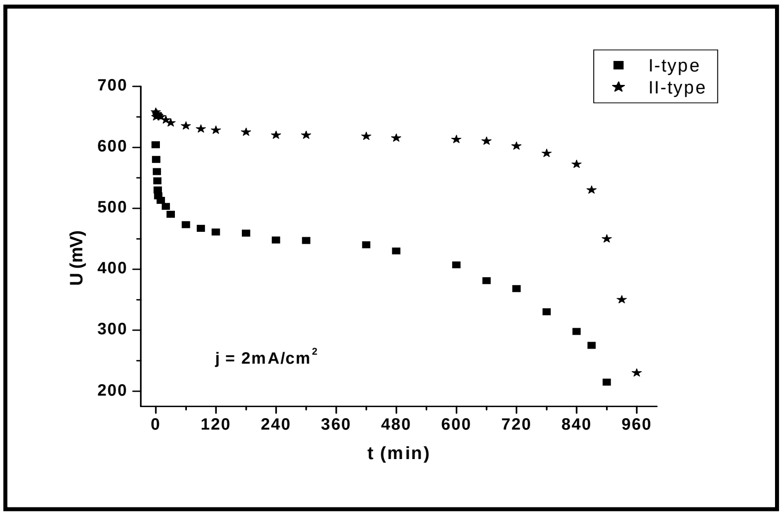

Fig.3. Discharge curves of cells at i=2mA/cm^2

The batteries were discharged at two current densities: i=2mA/cm^2 (Fig.3) and i=0.2mA/cm^2 (Fig.4) in galvanostatic regime. From the discharge curves it can bee ascertained that, at lower current density (0.2mA/cm^2), the discharge plateaus have higher values for I-type cell, close to those of II-type cell. At the current density of 0.2mA/cm^2, the total yielded energy was of 10.20mWh for I-type cell and 11.89mWh for II-type cell.

The electrochemical characteristics of Ag/$RbAg_4I_5$/RbI_3 cells are presented in Table 1. The mass capacities (C_g), the energy densities (W_g), and the utilization coefficients (u) of active material (silver) were calculated from the experimental data.

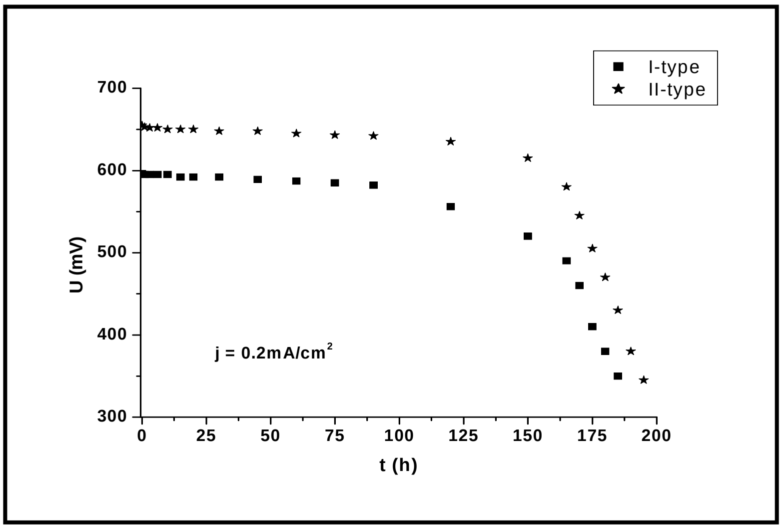

Fig.4. Discharge curves of cells at i = 0.2mA/cm^2

Table 1.

The electrochemical characteristics of batteries with $RbAg_4I_5$ solid electrolyte

Type cell	Mass [g]	Discharge regime	i [mA/cm^2]	C_g [Ah/kg]	W_g [Wh/kg]	u [%]
I	1.096	Load R=100 Ω	2.52	13.80	5.92	55.2
II	1.037		2.63	16.49	9.79	66.0
I	0.995	galvanostatic	2	15.07	6.22	62.8
II	1.053			15.20	9.00	63.3
I	0.915	galvanostatic	0.2	20.22	11.15	84.3
II	0.954			20.44	12.46	85.2

As it can be seen from Table 1, all calculated parameters are better for II-type cells than for I-type cells. The mass capacities and energy densities depend on the discharge regime. They are higher under galvanostatic regime at lower current densities (0.2mA/cm^2).

CONCLUSIONS

On the basis of the experimental data it can be conclude that the method proposed by authors is simple and allows the obtaining of $RbAg_4I_5$ solid electrolyte in a pure state. The α-$RbAg_4I_5$ form is the most stable crystallographic modification and presents a high ionic conductivity.

From the obtained results it can be establish that Ag/$RbAg_4I_5$/RbI_3 batteries present good electrochemical characteristics for usage in medical devices such as cardiac pacemaker.

REFERENCES

1. J.N. Bradley, P.D. Greene, *Trans. Faraday Soc*., **1967**, 63, 424-429.
2. K. Funke, *Ber. Bunsenges. Phys. Chem.* **1989,** 93, 1197-1201.
3. C.F. Holmes, *The Electrochemical Society-Interface*, **1999,** 8, 32-34.
4. C.A. Vincent, F. Bonino, M. Lazzari, B. Scrosati, “Modern Batteries”, Chap.7, edited by Edward Arnold (Publishers) Ltd., London, 1984.
5. Cs.C. Bolla, Georgeta Tarălungă, A.Borbely-Keri, L.D. Bobos, Silvia Avram, L.Oniciu*,* „Batteries for Portable and Electric Vehicle Applications”, A. Landgrebe Ed., The Electrochemical Society Inc. Pennington, N.J. USA, 1997, 518-523.
6. Cs. Bolla, Ildiko Szekely, A. Borbely-Keri, L. Oniciu, Georgeta Tarălungă, *Producerea, Transportul si Utilizarea Energiei, vol. XIV*, **1995**, 101-105.
7. Cs. C Bolla, Ph. D. Thesis *Electroliți solizi şi aprotici pentru pile galvanice neconvenționale,* “Babeş-Bolyai” University, Cluj-Napoca, 2001.
8. Georgeta Taralunga, Eleonora Maria Rus, *Romanian J. Biophys.,* **2002**, 12, (3-4), 97-101.