

SILVER SELENATE AND SILVER TELLURATE AS POSITIVE MATERIALS FOR LITHIUM PRIMARY POWER SOURCES

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Summary

The performances of button-type lithium cells based on Ag_2SeO_4 and Ag_2TeO_4 as cathodes have been determined in various organic electrolytes. These silver salts present relevant energetic properties and may be considered as interesting cathodic materials for application in primary lithium power sources.

Information on the discharge processes has also been obtained by determining the electrode utilization at low rates and by X-ray analyses of the discharge products.

Finally, Ag_2SO_4 has been examined also as a cathode material in lithium cells. However, its performance was rather poor, probably because of a slight solubility in the electrolyte media considered.

Introduction

Silver oxysalts have been recently studied [1 - 8] or proposed in patents [9 - 13] as cathode materials for lithium cells suitable for applications in the field of microelectronics. Some of these salts are characterized by low solubility and excellent electrochemical behaviour in most common organic electrolytes.

However, only lithium cells based on silver chromate [1] have so far reached the stage of commercial development and are currently used for powering cardiac pacemakers even though other systems based on silver tungstate [4, 9], phosphate [2, 6], iodate [3, 5], arsenate [7] appear to be as well suited for applications in lithium primary power sources.

Although a large amount of work has been carried out on the general electrode properties of silver salts when coupled with lithium in organic electrolytes, the field is still open for investigation, especially in the direction

of the characterization of new systems, the clarification of discharge processes and the study of the influence of different electrolytes on the performances of the positive materials.

In our laboratories the behaviour of various silver [4, 7, 8] and copper [14] oxysalts, as well as of oxides characterized by crystallographic shear [15] has been examined. Within this systematic research programme, silver sulphate, selenate and tellurate have also been considered with the investigation of their performances as cathodes in lithium cells using electrochemical and X-ray analyses. The relevant results are reported in this paper.

Experimental

Silver sulphate, a reagent grade product, was used without further purification. Silver selenate was prepared by precipitation, adding a solution of silver nitrate to one of selenic acid. The precipitate, after being washed, was dried under vacuum. The X-ray powder pattern of the final material was in agreement with that of Ag_2SeO_4 , as reported in the A.S.T.M. 14-94 card. Silver tellurate was prepared similarly, by adding a silver nitrate solution to one of potassium tellurate. The final salt was dark brown in colour and its composition was determined to be Ag_2TeO_4 by chemical analysis.

Lithium ribbon (Alfa Ventron) was used as received. Lithium aluminium tetrachloride, LiAlCl_4 , was prepared from LiCl and AlCl_3 , according to the method described by Rao [16]. Reagent grade lithium perchlorate, LiClO_4 , was dried by melting it at 250°C under vacuum [17]. Lithium hexafluoroarsenate, LiAsF_6 , an Alfa Ventron reagent grade product, was used as received. The organic solvents, γ -butyrolactone (BL) and propylene carbonate (PC), were purified by fractional distillation under reduced pressure. The electrolyte solutions, *i.e.* 1.0 M LiClO_4 -PC, 1.5 M LiAsF_6 -BL and 1.0 M LiAlCl_4 -BL, respectively, were prepared and kept in a dry box flushed with purified argon.

The cells, also assembled and kept in the dry box, were of the button type (1.2 cm internal diameter) and were formed by putting into contact a lithium disc, three glass fibre separators (GF/A Whatman) soaked with the electrolyte solution and a pellet of the cathodic material. The latter was obtained by pressing the material (pure or mixed with 10% by weight of graphite) at 2500 kg/cm^2 onto a support of silver powder. The cells, having an average volume of 0.3 cm^3 were housed in a Teflon container with stainless steel terminals.

The electrochemical measurements were performed and recorded using standard equipment. The polarization curves were obtained by submitting the cell to progressively increasing current pulses of 1 min duration and recording the potential attained. The single-electrode polarizations were carried out using three-electrode cells, similar in configuration to that described above, where the working and the reference electrodes were two parts, isolated from each other, of the same pellet. Therefore, in all cases isoelectrode references were used.

The X-ray powder patterns were obtained with a Jeol-8S diffractometer, using $\text{CuK}\alpha$ radiation. The samples to be analyzed, *i.e.* the cathodic material after low rate discharges, were mounted on the holder in dry box and protected from atmospheric contamination during the analysis by a thin layer of Parafilm.

Results and discussion

The applicability of silver selenate, tellurate and sulphate as electrodes in lithium cells, was first investigated by testing the solubility in the electrolytes considered.

The materials were equilibrated in the various different solutions for 48 hours. The supernatant liquid was then withdrawn, diluted 1:1 with distilled water and tested for Ag^+ with a NaCl solution (using a 10^{-4} M AgNO_3 solution as standard).

Relevant turbidity was observed with all the salts in LiAlCl_4 -BL, thus showing some solubility in this electrolyte solution. This phenomenon, already observed for other silver oxysalts [5, 7], might be attributed to complexing of silver by the chloride ions.

No turbidity was observed for Ag_2TeO_4 and Ag_2SeO_4 in LiAsF_6 -BL and LiClO_4 -PC, thus indicating that the salts may be considered as insoluble in these electrolytes.

The electrochemical properties of the three salts were investigated using cells of the following basic structure:



where X was in turn S, Se or Te and the electrolyte the LiAlCl_4 -BL, LiClO_4 -PC and LiAsF_6 -BL solution, respectively.

The mean open circuit voltages (OCV) for the three salts in LiAsF_6 -BL and in LiClO_4 -PC, respectively, were of the order of 3.5 V at room temperature, while in LiAlCl_4 -BL they were of the order of 3.0 V.

In Figs. 1(a), (b) and (c) typical discharge curves at room temperature of cells of type(I) are reported. The cathodic utilization was calculated to 1 V cut-off on the basis of a two electron reduction process, assuming the following:



to be the main discharge reaction.

The poor utilization of Ag_2SO_4 in all the solutions is shown in Fig. 1(a), while Figs. 1(b) and 1(c) indicate a much better behaviour for Ag_2SeO_4 and Ag_2TeO_4 in LiClO_4 -PC and in LiAsF_6 -BL, respectively. The poor performances observed for all the salts in LiAlCl_4 -BL are in line with the observed solubilities in this medium.

The three silver oxysalts have been tested either pure or mixed with graphite (10 w/o). In all cases graphite-free cathodes behaved satisfactorily at

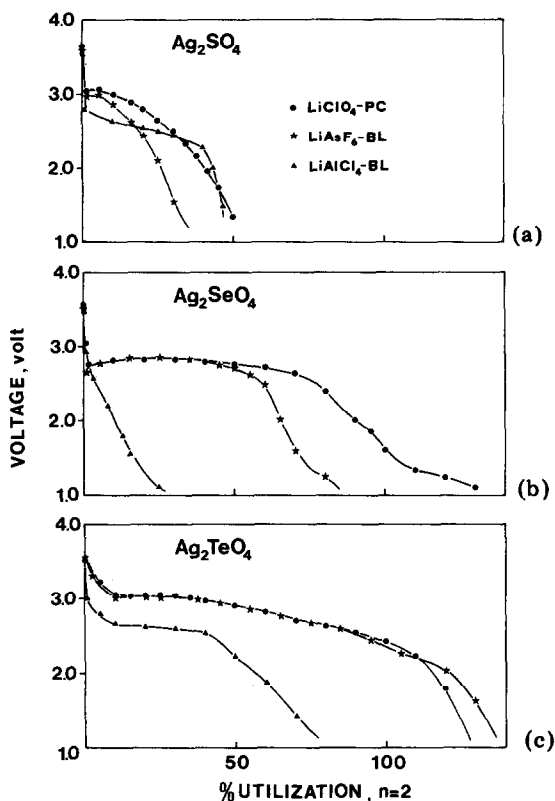


Fig. 1. Typical discharge curves at 0.5 mA/cm^2 and at room temperature of the $\text{Li/Ag}_2\text{XO}_4$ ($\text{X} = \text{S}, \text{Se}, \text{Te}$) couples in various organic solvent electrolytes.

low rates, in spite of the very low intrinsic electronic conductivity. This is a rather general phenomenon in the case of silver oxysalts [5, 7, 8, 18, 19] and though in the present work a systematic study has not been performed, it seems possible to relate it to a high porosity of the cathodic materials, which allows a good permeation by the electrolyte, and to an electrochemical process which assures the necessary electronic conductivity via the formation of metallic silver.

Typical polarization curves of cells of type(I) are shown in Fig. 2 for the most promising systems. While the poor behaviour of Ag_2SO_4 is again shown here by the severe polarizations even under low current densities, the satisfactory performances of Ag_2SeO_4 and, especially, of Ag_2TeO_4 are clearly indicated by the related curves. This is also confirmed by the single electrode polarization studies. Typical results, presented in Fig. 3, are evidence in fact of the excellent behaviour of the Ag_2TeO_4 electrode whose polarization values in $\text{LiAsF}_6\text{-BL}$ approach those of the lithium electrode, showing very low overvoltages under high current densities. Even if poorer, the performances of the Ag_2SeO_4 electrode in $\text{LiClO}_4\text{-PC}$ are also to be considered satisfactory, especially under low current drains.

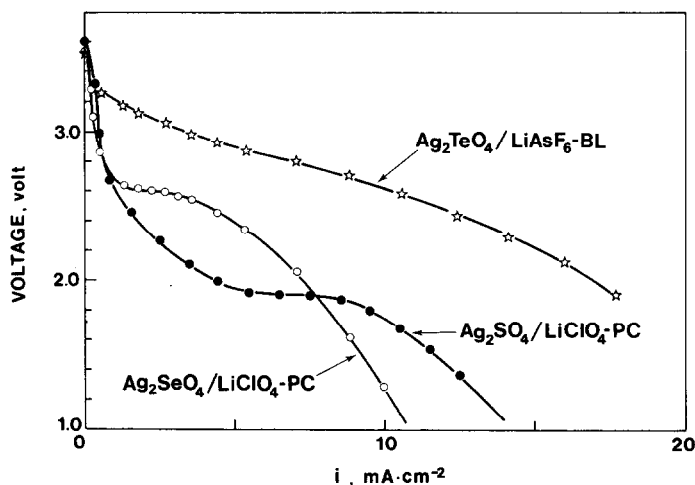


Fig. 2. Polarization curves (1 min current pulses) of the Li/ Ag_2XO_4 ($\text{X} = \text{S}, \text{Se}, \text{Te}$) couples at room temperature in organic solvent electrolytes.

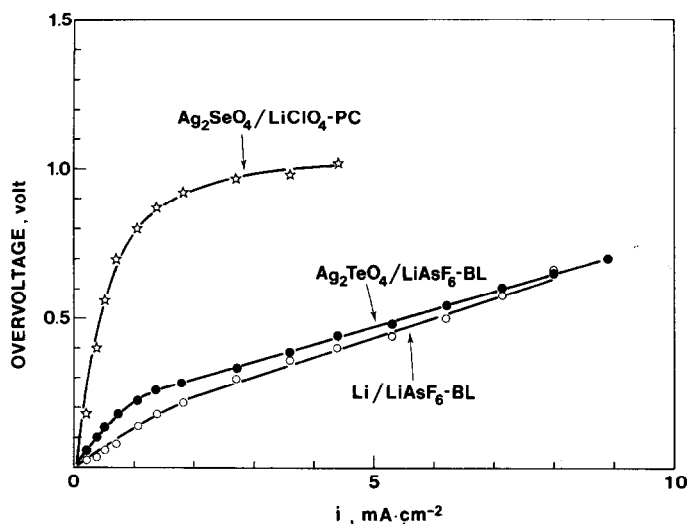


Fig. 3. Polarization curves of Ag_2SeO_4 , Ag_2TeO_4 and Li electrodes (*vs.* reference electrodes of the same nature), in various organic solvent electrolytes.

The characteristics of the two cathodic materials are evidenced in Figs. 4(a) and 4(b), where discharge curves under various constant current densities are reported. While the voltage of cells using Ag_2TeO_4 remains high and reasonably constant over the entire range, cells based on Ag_2SeO_4 show failures under high drains, this being in agreement with the polarization behaviours described above.

Finally, the stability and the shelf life of the Li/ Ag_2SeO_4 and Li/ Ag_2TeO_4 systems have been determined by discharge tests after storage.

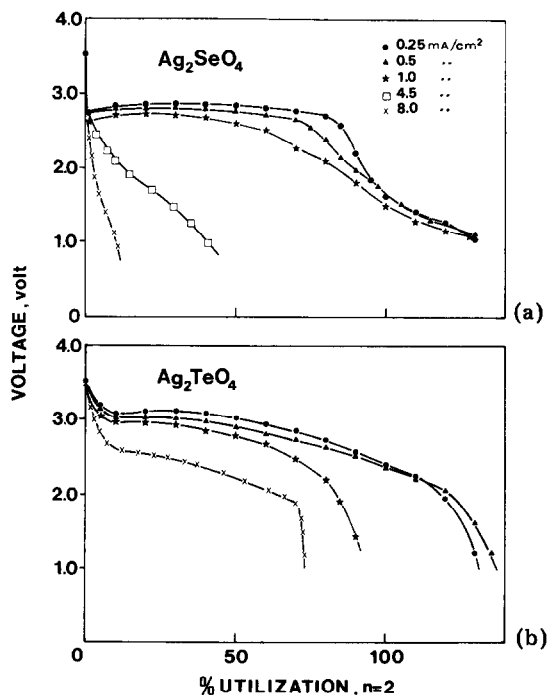


Fig. 4. Discharge curves at various current densities of the couples $\text{Li}/\text{Ag}_2\text{SeO}_4$ in $\text{LiClO}_4\text{-PC}$ and $\text{Li}/\text{Ag}_2\text{TeO}_4$ in $\text{LiAsF}_6\text{-BL}$ at room temperature.

Typical results reported in Fig. 5 show that no significant loss in capacity takes place in cells stored for 36 days at room temperature. In Fig. 5 are also shown discharge curves at 37°C which indicate the good behaviour of the cells at this temperature.

The mean discharge voltages and the cathodic utilization coefficients shown in Figs. 4 and 5 seem to indicate that reaction(II) is indeed the main discharge process. X-ray analyses on the discharged cathodic materials do not conclusively confirm this. In fact only silver was clearly detected in the spectrum. However, it is reasonable to expect that lithium selenate and tellurate could be soluble in the electrolyte solutions. Furthermore no data for the powder diffractions of these salts were found in the literature and so the attribution of some unknown reflections of the discharged products was not possible.

One should add that for both Ag_2SeO_4 and Ag_2TeO_4 , in addition to the reduction of silver, a partial reduction of the anions may also take place. In this respect, it is interesting to report that Messina *et al.* [20] recently demonstrated by careful electrochemical measurements that Ag_2CrO_4 in $\text{LiClO}_4\text{-PC}$ can be reduced in a lithium cell through different routes according to the current density values. At low current densities the reaction pattern is mainly the reduction of silver, while at high current

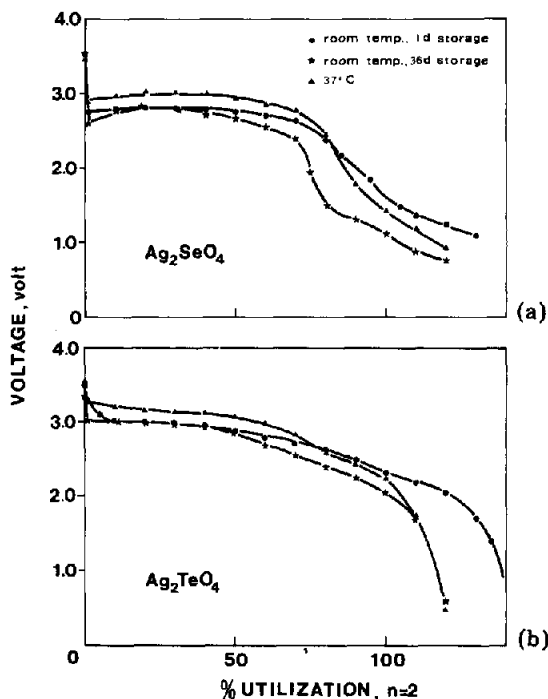


Fig. 5. Discharge curves at 0.5 mA/cm^2 of the couples $\text{Li}/\text{Ag}_2\text{SeO}_4$ in $\text{LiClO}_4\text{-PC}$ and $\text{Li}/\text{Ag}_2\text{TeO}_4$ in $\text{LiAsF}_6\text{-BL}$ at room temperature, after 1 and 36 days storage at this temperature, and at 37°C , respectively.

densities the primary formation of a metastable non-stoichiometric phase, $\text{Li}_x\text{Ag}_2\text{CrO}_4$, was postulated. This phase then decomposes to silver metal, lithium chromate and silver chromate which are the final products. A similar mechanism cannot be excluded in the present case.

In conclusion, the results reported above and summarized in Tables 1 and 2, indicate that lithium button cells based on silver selenate and silver tellurate as positive active materials are characterized by high values of specific capacity and energy and could therefore be suitable for practical applications. Particularly interesting in this respect is the system based on the tellurate in $\text{LiAsF}_6\text{-BL}$ which can sustain high discharge currents but still retain a high energy density.

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TABLE 1

Performances of Ag_2SeO_4 -10% graphite positives in lithium cells

Electrolyte	Current density (mA/cm^2)	Specific capacity (Ah/g)	Mean discharge voltage (V)	Specific energy (Wh/g)	Utilization (%) ^a (1.0 V cutoff)
1.0 M LiClO_4 -PC	0.25	0.195	2.39	0.464	130
1.0 M LiClO_4 -PC	0.50	0.196	2.29	0.449	130
1.0 M LiClO_4 -PC	1.00	0.204	2.09	0.426	130
1.0 M LiClO_4 -PC	4.50	0.062	1.77	0.110	40
1.0 M LiClO_4 -PC	8.00	0.015	1.64	0.024	10
1.0 M LiClO_4 -PC	0.50	0.155 ^b	2.29 ^b	0.355 ^b	100
1.0 M LiClO_4 -PC	0.50	0.173 ^c	2.51 ^c	0.433 ^c	120
1.5 M LiAsF_6 -BL	0.50	0.133	2.37	0.316	90
1.5 M LiAsF_6 -BL	0.50	0.097 ^d	2.27 ^d	0.220 ^d	65
1.0 M LiAlCl_4 -BL	0.50	0.047	1.64	0.077	30

^aBased on a two-electron reduction process.^bAfter 36 days storage.^cAt 37 °C.^dWithout graphite.

TABLE 2

Performances of Ag_2TeO_4 -10% graphite positives in lithium cells

Electrolyte	Current density (mA/cm^2)	Specific capacity (Ah/g)	Mean discharge voltage (V)	Specific energy (Wh/g)	Utilization (%) ^a (1.0 V cutoff)
1.5 M LiAsF_6 -BL	0.25	0.173	2.69	0.466	135
1.5 M LiAsF_6 -BL	0.50	0.182	2.58	0.469	140
1.5 M LiAsF_6 -BL	1.00	0.116	2.69	0.313	90
1.5 M LiAsF_6 -BL	8.00	0.099	2.29	0.226	75
1.0 M LiClO_4 -PC	0.50	0.166	2.68	0.447	125
1.5 M LiAsF_6 -BL	0.50	0.155 ^b	2.67 ^b	0.415 ^b	120
1.5 M LiAsF_6 -BL	0.50	0.155 ^c	2.56 ^c	0.398 ^c	120
1.5 M LiAsF_6 -BL	0.50	0.152 ^d	2.77 ^d	0.422 ^d	115
1.0 M LiAlCl_4 -BL	0.50	0.109	2.21	0.241	80

^aBased on a two-electron reduction process.^bWithout graphite.^cAfter 36 days storage.^dAt 37 °C.

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