

LITHIUM CELLS BASED ON SILVER SALTS AS CATHODES

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Summary

The performances of button-type lithium cells based on Ag_2CrO_4 , Ag_3PO_4 and AgIO_3 as cathodes have been evaluated in different electrolytes. It was found that each silver salt is influenced in a different way by the change of the electrolyte. When using solutions containing LiAlCl_4 , a silver complex is formed which affects the discharge behaviour and the storage life. Indications of the discharge processes have been obtained by determining the coefficients of utilization at low discharge rates and by X-ray analysis.

Introduction

Silver chromate has recently received growing attention as a cathode for non-aqueous cells [1 - 4]. Indeed, this salt can sustain relatively high current densities without excessive polarization, shows a very low solubility in an organic electrolyte based on LiClO_4 and has a long storage life in this electrolyte, especially at high temperature [1]. By virtue of these features, lithium cells based on Ag_2CrO_4 have recently reached the stage of commercial development. They seem particularly useful in the field of microelectronics, with particular reference to devices such as electronic watches and cardiac pacemakers [1]. However, little information is available at the moment on the discharge process of this salt and on the effect of different electrolytes on its cathodic efficiency and specific energy. Of the references cited, the first does not mention the solvent used, the second refers only to results obtained in LiClO_4 -PC, whereas in the third a cell based on Ag_2CrO_4 in LiAsF_6 -methyl formate is briefly mentioned. More substantial work is reported in the fourth reference, which, however, is mainly devoted to compatibility tests of lithium and Ag_3PO_4 , Ag_2CrO_4 and $(\text{CF}_x)_n$ cathodes in low viscosity solvents such as methyl formate and tetrahydrofuran. Furthermore, in the latter reference, the cells were discharged at the particular régime required by military transceivers (170 mA and 50 mA for 30 min, alternatively) so that a comparison with cells discharged at constant rates is made difficult.

Margalit [3] has compared the performances of cells based on Ag_3PO_4 with those of cells containing Ag_2CrO_4 . According to him the former salt is far superior in terms of energy density and rate capability, although a severe increase in the cell volume was noticed during discharge.

In our laboratory, where the possibility of using other silver oxysalts is now being investigated, the performances of Ag_2CrO_4 and Ag_3PO_4 were again examined mainly with the aim of ascertaining the nature of the discharge processes and the influence of the electrolytes. Among the new silver salts examined, AgIO_3 has proven to be the more promising one [5] and in this paper its performance will be compared with those of Ag_2CrO_4 and Ag_3PO_4 .

Experimental

Materials

Ag_2CrO_4 and AgIO_3 were reagent grade products. Ag_3PO_4 was prepared by a double exchange reaction between aqueous solutions of Na_2HPO_4 and NaIO_3 . The silver salts were dried in an oven in a nitrogen atmosphere. All the solvents were purified by fractional distillation (butyrolactone (BL) and propylene carbonate (PC) under vacuum). Methyl formate (MF) only was distilled over a 4 Å molecular sieve. LiAlCl_4 was prepared from LiCl and AlCl_3 according to the method described by Rao [6]. "Anhydrous" commercial LiClO_4 was freed from residual water by melting it at 250 °C under vacuum [7]. Commercial LiAsF_6 was used without any further purification. A lithium ribbon was used for the negative electrode.

All the manipulations were done in a dry box, the only exception being the preparation of the positive electrodes.

In preliminary tests, cells based on AgBrO_3 , AgIO_4 and Ag_5IO_6 were also examined; their performances were not sufficiently satisfactory to encourage further research.

Apparatus and procedure

The silver salts were mixed with 10% graphite in order to ensure electronic conductivity. Graphite-free cathodes were also tested and their performances in LiAlCl_4 -BL were surprisingly better than those of graphite-containing cathodes. The dry cathode materials were pressed at 1200 kg/cm² onto a silver powder pellet support and subsequently set in stainless-steel cells of the button type having an internal diameter of 1.26 cm. The electrolyte was supported on a triple layer of glass fibre separator (type 934 AH Whatman, described by Boden [8]). Microporous plastic separators proved to be unsatisfactory, owing to their high resistance.

The small electrochemical activity of the graphite was determined at 0.25 and 0.5 mA/cm² by using cathodes containing graphite only; its contribution to the overall capacity was very small.

Polarization measurements were made on fresh cells similar to those submitted to discharge. At each current value, the voltage was observed for five seconds.

TABLE 1

Performances of Ag_2CrO_4 , Ag_3PO_4 and AgIO_3 cathodes in lithium cells containing 1.0 M LiAlCl_4 -BL as electrolyte

Cathode	Specific capacity ^a (Ah/g)		Specific energy (Wh/g)		Utilization ^b (%)	
	with C	without C	with C	without C	with C	without C
AgIO_3	0.104	0.263	0.198	0.470	20	58
Ag_2CrO_4	0.027	0.061	0.067	0.125	6	16
Ag_3PO_4	0.048	0.124	0.095	0.290	30	72

^aDischarge at 0.5 mA/cm² to 1.0 V cut-off.

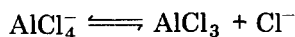
^bUtilization to 0.0 V based on 6, 5 and 3 electrons for the reduction processes of AgIO_3 , Ag_2CrO_4 and Ag_3PO_4 , respectively.

X-ray powder patterns were obtained on Ag_3PO_4 , Ag_2CrO_4 and AgIO_3 after discharge at 0.25 mA/cm² and after washing the cathodes with acetone to remove the electrolyte. The samples were analyzed under vacuum for 10 h by the Debye-Scherrer method, using Mo K α radiation filtered by Zr.

Results and Discussion

In a preliminary paper [5], the three silver salts have been examined in lithium cells containing LiAlCl_4 -BL as electrolyte. In terms of specific capacities and energy densities (both on a weight and on a volume basis) AgIO_3 behaves better than Ag_3PO_4 , which, in turn, shows a better performance than Ag_2CrO_4 . Surprisingly enough, cathodes not containing graphite could not only work in LiAlCl_4 -BL, in spite of a resistance of 10⁶ ohms, but their performances are even better than those of cathodes containing graphite, as shown in Table 1. Ag_2CrO_4 in LiAsF_6 -MF has also been reported [4] to work in the absence of conductive additives. The possibility of using electrodes not containing graphite may be welcomed in that it leads to an increased specific energy and avoids complications connected with the formation of graphite intercalation compounds.

In LiAlCl_4 -BL the silver ions of the oxysalts may give rise to the formation of complexes with the Cl^- ions contained in the electrolyte. Indeed, the equilibrium:



is shifted to the right in solvents such as BL and PC owing to the fact that the Lewis acid AlCl_3 is strongly coordinated by the negative dipole of the solvent [9].

The electrolyte, coming into contact with the cathode materials, could generate reactions of the type:

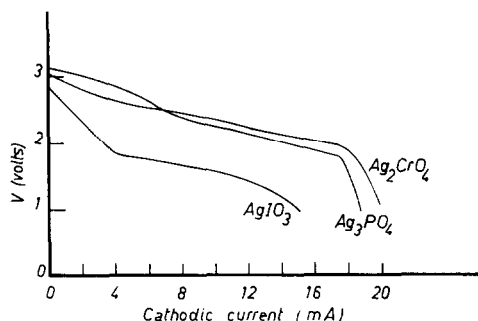
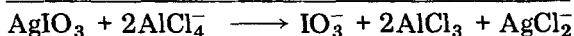
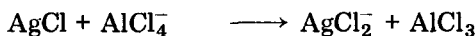
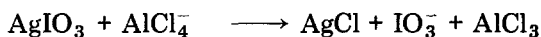


Fig. 1. Polarization curves of cells based on Ag_3PO_4 , Ag_2CrO_4 and AgIO_3 cathodes. Electrode area, 1.25 cm^2 .



Polarographic analysis was made after leaving AgIO_3 powder in contact with LiAlCl_4 -BL solutions for some days. Indeed, the reduction wave of a complex silver ion was recorded at -0.25 V (vs. S.C.E.), whereas blank experiments with LiAlCl_4 -BL solution did not give any wave near that potential value. No further attempt was made to characterize the silver complex more precisely, but probably it may be written as AgCl_2^- , as is also suggested from examination of the literature [10].

The poor performance of graphite-containing cells may possibly be related to a more porous structure of the cathodes so that complex formation is enhanced to the point where the dissolution becomes too fast. As expected, the shelf life of these cells (see below) is shortened by the formation of the silver complex.

In this electrolyte AgIO_3 does not exhibit a significant discharge of the silver ion, its capacity being given only by the reduction of IO_3^- (occurring at $2.1 - 2.2 \text{ V}$). This is quite surprising when considering that both Ag_2CrO_4 and Ag_3PO_4 show the discharge of Ag^+ (above 2.5 V). With or without graphite, the behaviour of Ag_2CrO_4 in this electrolyte is particularly disappointing both on the basis of coulombic utilization and of specific energy and capacity.

On the basis of these results, it seemed necessary to investigate other electrolytes. 1.5 M LiAsF_6 -BL and 1.0 M LiClO_4 -PC were considered for the three salts; in addition, 2.0 M LiClO_4 -MF, 1.0 M LiClO_4 -70% tetrahydrofuran (THF)/30% dimethoxypropane (DMP) and 2.0 M LiAsF_6 90%MF/10%BL were considered for AgIO_3 only.

Cell polarization curves were made in LiAsF_6 -BL (Fig. 1) and show that Ag_2CrO_4 and Ag_3PO_4 tend to polarize less extensively than AgIO_3 in the current range $0 - 4 \text{ mA}$. This may be explained by considering that in the latter, as previously stated, the silver ion is not reduced. For currents higher

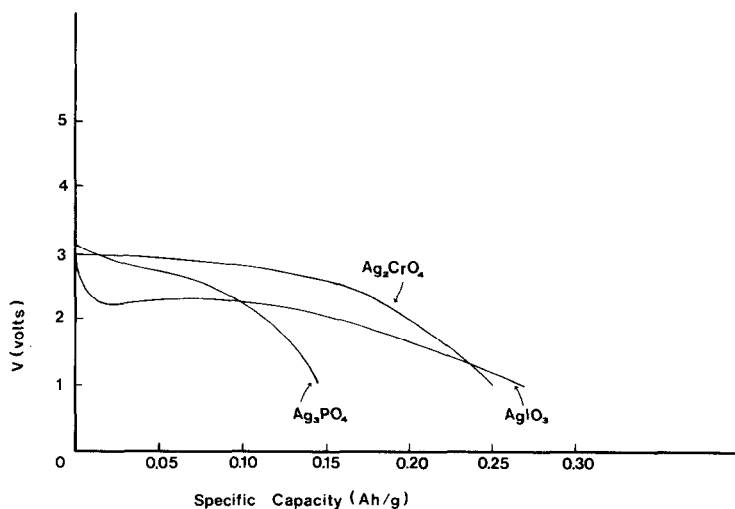


Fig. 2. Discharge curves at 0.5 mA/cm^2 in $\text{LiAsF}_6\text{-BL}$.

TABLE 2

Influence of the electrolyte on the performances of AgIO_3 , Ag_2CrO_4 and Ag_3PO_4

Cathode	Specific capacity ^a		Mean discharge voltage (V)	Specific energy		Utilization ^b (%)
	Ah/g	Ah/cm ³		Wh/g	Wh/cm ³	
$\text{LiAlCl}_4\text{-BL}$ (1.0 M), without graphite						
Ag_2CrO_4	0.061	0.343	2.05	0.125	0.700	16
Ag_3PO_4	0.124	0.790	2.34	0.290	1.85	65
AgIO_3	0.263	1.46	1.78	0.470	2.60	46
$\text{LiAsF}_6\text{-BL}$ (1.5 M), with graphite						
Ag_2CrO_4	0.252	1.41	2.30	0.580	3.26	62
Ag_3PO_4	0.148	0.943	2.50	0.372	2.09	77
AgIO_3	0.270	1.49	1.90	0.513	2.83	47
$\text{LiClO}_4\text{-PC}$ (1.0 M), with graphite						
Ag_2CrO_4	0.331	1.86	2.34	0.774	4.35	82
Ag_3PO_4	0.154	0.980	2.30	0.358	2.27	80
AgIO_3	0.144	0.800	1.94	0.280	1.55	25

^a Discharge at 0.5 mA/cm^2 to 1.0 V cut-off.

^b To 1.0 V cut-off based on 6, 5 and 3 electrons for AgIO_3 , Ag_2CrO_4 and Ag_3PO_4 , respectively.

than 4 mA, the three curves have comparable slopes, *i.e.* the polarization for the three discharge processes is similar. The discharge curves in $\text{LiAsF}_6\text{-BL}$ at 0.5 mA/cm^2 are shown in Fig. 2. AgIO_3 has the higher specific capacity in this solution and, again, does not show any discharge of the silver ion.

In Table 2 the performances of AgIO_3 , Ag_2CrO_4 and Ag_3PO_4 in $\text{LiAlCl}_4\text{-BL}$, $\text{LiAsF}_6\text{-BL}$ and $\text{LiClO}_4\text{-PC}$ are reported. In the last two elec-

TABLE 3

Behaviour of AgIO_3 cathodes in various electrolytes. Discharge at 0.5 mA/cm^2 to 1.0 V cut-off

Electrolyte	Specific capacity (Ah/g)	Mean discharge voltage (V)	Specific energy (Wh/g)	Utilization (%)	$\chi \times 10^3$ ($\text{ohm}^{-1} \text{ cm}^{-1}$)
$\text{LiAlCl}_4\text{-BL}$	0.263	1.78	0.470	46	10
$\text{LiAsF}_6\text{-BL}$	0.271	1.90	0.513	47	9
$\text{LiAsF}_6\text{-MF/BL}$ (90%:10%)	0.261	1.81	0.472	46	35
$\text{LiClO}_4\text{-MF}$	0.195	2.02	0.395	33	24
$\text{LiClO}_4\text{-THF/DMP}$ (70%:30%)	0.223	2.10	0.468	40	3
$\text{LiClO}_4\text{-PC}$	0.144	1.94	0.280	25	6

trolytes the results for cells based on cathodes containing graphite are reported, owing to the less satisfactory performances of cathodes without graphite. From the results shown in this Table it may be seen how largely the performance of Ag_2CrO_4 depends on the electrolyte used. On the contrary, Ag_3PO_4 is quite insensitive to such a factor. As for AgIO_3 , it behaves in a similar way in the electrolytes containing AlCl_4^- and AsF_6^- , whereas in electrolytes containing ClO_4^- (see also Table 3) its performance is somewhat less satisfactory.

The possibility of a complexing activity of AsF_6^- , similar to that of AlCl_4^- , was checked by a polarographic experiment with AgIO_3 in $\text{LiAsF}_6\text{-BL}$. No reduction wave around -0.25 V was found, the only wave recorded being that of the reduction of IO_3^- occurring at -1.26 V , a value which is similar to that found in aqueous solutions (-1.16 V) [11].

The values of specific conductivity reported in Table 3 do not correlate with the performances of the cells. In fact, in spite of the very low χ values, the behaviour of cells containing LiClO_4 in THF/DMP compares well with that of cells made with more conducting electrolytes. This indicates that mass transport is not the most important factor for these cells. The structure of each electrolyte-cathode interface seems to play a more important role.

In Table 4 the data related to the discharge of the three salts at different current densities are reported. For Ag_2CrO_4 and Ag_3PO_4 the performances are similar at the three currents examined, whereas for AgIO_3 some decrease is observed at the highest rate. From the Table it may be seen that, in terms of specific energy (Wh/g), Ag_2CrO_4 is still superior to both AgIO_3 and Ag_3PO_4 .

Throughout this paper it has been assumed, when determining the cathodic utilization, that the discharge processes involve 5, 3 and 6 electrons for Ag_2CrO_4 , Ag_3PO_4 and AgIO_3 , respectively. This assumption was based on the following considerations.

The discharge of Ag_2CrO_4 in an organic electrolyte was reported by Gabano [1] and Marincic [12] to involve the simple reduction of silver ions:

TABLE 4

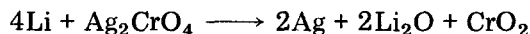
Behaviour of Ag_2CrO_4 and Ag_3PO_4 in LiClO_4 -PC and of AgIO_3 in LiAsF_6 -BL at different current densities (to 1.0 V cut-off)

Cathode	Current density (mA/cm ²)	Specific capacity (Ah/g)	Mean discharge voltage (V)	Specific energy (Wh/g)	Utilization ^a (%)
LiClO_4 -PC					
Ag_2CrO_4	0.25	0.315	2.38	0.749	78
Ag_2CrO_4	0.50	0.331	2.34	0.774	82
Ag_2CrO_4	1.00	0.330	2.40	0.790	81
Ag_3PO_4	0.25	0.170	2.30	0.390	89
Ag_3PO_4	0.50	0.154	2.30	0.358	80
Ag_3PO_4	1.00	0.168	2.41	0.405	89
LiAsF_6 -BL					
AgIO_3	0.25	0.237	2.01	0.478	42
AgIO_3	0.50	0.270	1.90	0.513	47
AgIO_3	1.00	0.192	1.92	0.368	33

^aBased on 6, 5 and 3 electrons for AgIO_3 , Ag_2CrO_4 and Ag_3PO_4 , respectively.

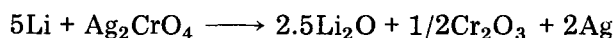


It has to be noted that Gabano limits the cell discharge to ~ 2.5 V. According to Dey [2], the chromate reduction has also to be taken into account for cell voltages below 2.5 V and would involve 4 electrons:



This author detected the presence of both Ag and Li_2O in the discharged cathode (by chemical tests); no information is given referring to CrO_2 . Margalit [3] has observed a distinct discharge plateau in LiAsF_6 -MF due to the reduction of the chromate ion, but no further information is available in the abstract of this communication.

We have found that both two- and four-electron processes would lead to cathodic utilizations higher than 100% for discharges to 0.0 V cut-off. Furthermore, in neutral solutions the more probable discharge product of hexavalent chromium is the trivalent ion [13]. Therefore, the following overall reaction, based on a five-electron process, seems more probable:



Utilizations of $\sim 90\%$ in LiClO_4 -PC were obtained according to this reaction.

X-ray analysis, made on a cathode discharged at low rate, has shown the presence of Li_2O , Ag and of several lines which seem attributable to different chromium oxides. The discharge curve of Ag_2CrO_4 at 0.5 mA/cm² does not show a distinct second plateau. However, in the curves made at 1.0 and 1.6 mA/cm² (Fig. 3) the discharge of CrO_4^{2-} is more evident and does

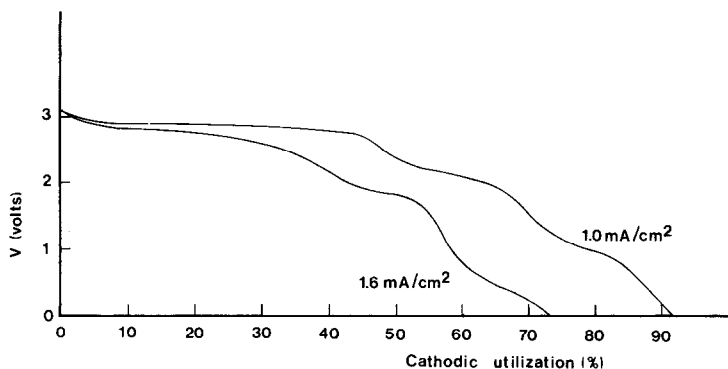
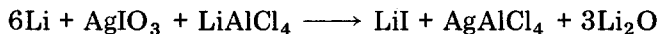


Fig. 3. Discharge curves of cells based on Ag_2CrO_4 in LiClO_4 -PC.

not seem to be a single-step process, this being in agreement with the X-ray analysis, *i.e.* more than one chromium oxide is formed during discharge.

The discharge of Ag_3PO_4 can only be based on a three-electron process involving the silver ions, which leads to utilizations of 90 - 100% in both LiClO_4 -PC and LiAsF_6 -BL. X-ray analysis confirms this assumption, showing the presence of Ag and Li_3PO_4 only.

The discharge of AgIO_3 , as noted above, does not show a significant reduction plateau for Ag^+ in any of the electrolytes examined (Fig. 2). The reduction of IO_3^- goes down to I^- , as evidenced by X-ray analysis and by precipitation of the iodide ion with AgNO_3 , after dissolution of the discharged cathode. Iodine was not detected and, furthermore, the polarogram showed only one wave which confirms the single step nature of the reduction. On the basis of these observations, the discharge process of AgIO_3 may occur according to a reaction of the type:



Both LiI and Li_2O were detected by X-ray analysis, whereas neither Ag nor Ag_2O were found. On the basis of this scheme a maximum cathodic utilization of ~60% was obtained (to 0.0 V in LiAsF_6 -BL). This value is low when compared with the very high efficiency found for both Ag_2CrO_4 and Ag_3PO_4 and may be possibly an inherent characteristic of a single step six-electron process.

From the data reported in Tables 2, 3 and 4 it may be seen that interesting values of specific energies may be obtained with these cathodes. This is particularly true for Ag_2CrO_4 in LiClO_4 -PC and for AgIO_3 in LiAsF_6 -BL. Considering the weight and the volume of the active cell components (anode, cathode, separators and solution), specific energies in excess of 800 Wh/dm³ and 250 Wh/kg may be obtained with the chromate. For the iodate, these figures are 600 Wh/dm³ and 170 Wh/kg, respectively. These data refer to cells having a capacity of 50 mAh when discharged at 0.5 mA/cm².

Very preliminary shelf life tests were made for AgIO_3 in cells containing LiAlCl_4 -BL and LiAsF_6 -BL. After two weeks storage the cell containing the

first electrolyte showed some loss of capacity, whereas this was not noticed with the latter electrolyte. This confirms that a soluble complex is formed when AgIO_3 is put in contact with AlCl_4^- , thus lowering the capacity of the cathodes. On the other hand, the shelf life for Ag_2CrO_4 in an electrolyte based on LiClO_4 has been reported to be very good [1]. On the basis of these observations, it may be stated that silver oxysalts may be used as cathodes for long life cells only when coupled with an electrolyte which does not contain complexing anions.

Conclusions

Button cells based on silver oxysalts as cathodes may be discharged with good coefficients of cathodic utilization and with high values of specific energies in terms of both weight and volume. With these salts, electrolytes containing LiAlCl_4 may be recommended only for reserve-type batteries owing to the formation of a soluble complex of silver. Of the several cathode-electrolyte couples examined, Ag_2CrO_4 in LiClO_4 -PC is the one giving the best results in terms of utilization, specific energy and capacity.

Acknowledgements

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