

## Short Communication

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### Use of silver iodate as a cathode for lithium cells

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(Received January 3, 1976)

New cathodes based on silver oxysalts have been recently proposed for lithium organic batteries.  $\text{Ag}_2\text{CrO}_4$  [1, 2] and  $\text{Ag}_3\text{PO}_4$  [3, 4] have been reported to be the most efficient systems, especially when used for low rate applications, such as power for microelectronics.

The  $\text{Li}/\text{Ag}_2\text{CrO}_4$  cell seems to be particularly suitable for cardiac pacemaker applications due to the high volumetric capacity and the long storage life [1]. According to Margalit [4], the  $\text{Li}/\text{Ag}_3\text{PO}_4$  system exhibits better performance in terms of energy density and rate capability. However, due to the increase of the cathode volume during discharge, a severe increase in the height of button cells was observed with this material.

As part of a program to test the possibility of using other oxysalts in lithium cells, we considered silver iodate as a cathode in button cell which also included a lithium anode and  $\text{LiAlCl}_4$  in butyrolactone (BL) as electrolyte. The performance of this cell is compared with those of analogous systems having  $\text{Ag}_2\text{CrO}_4$  and  $\text{Ag}_3\text{PO}_4$  as cathodes.

#### *Experimental*

$\text{Ag}_2\text{CrO}_4$  was a pure Merck product, while  $\text{Ag}_3\text{PO}_4$  and  $\text{AgIO}_3$  were prepared by reaction of  $\text{AgNO}_3$  with  $\text{Na}_2\text{HPO}_4$  and  $\text{NaIO}_3$  in solution.

The dry cathode materials were pressed at  $1200 \text{ kg/cm}^2$  onto a pellet of silver powder. The button cells were made by interposing between the lithium foil and the cathode three layers of a glass fiber separator wet with the electrolyte (1.0 M  $\text{LiAlCl}_4$ -BL).

The cells, having an internal diameter of 1.26 cm and an internal height of  $\sim 0.2$  cm, were assembled and discharged at constant current in a dry box.

#### *Results and discussion*

In Fig. 1 discharge curves are shown, at  $0.5 \text{ mA/cm}^2$ , of cells containing  $\text{Ag}_2\text{CrO}_4$ ,  $\text{Ag}_3\text{PO}_4$  and  $\text{AgIO}_3$  cathodes.  $\text{Ag}_3\text{PO}_4$  behaves better than  $\text{Ag}_2\text{CrO}_4$ , as expected on the basis of the results reported by Margalit [4].  $\text{AgIO}_3$ , however, shows a much higher capacity than either the chromate or the phosphate, although at a lower load voltage.

TABLE 1

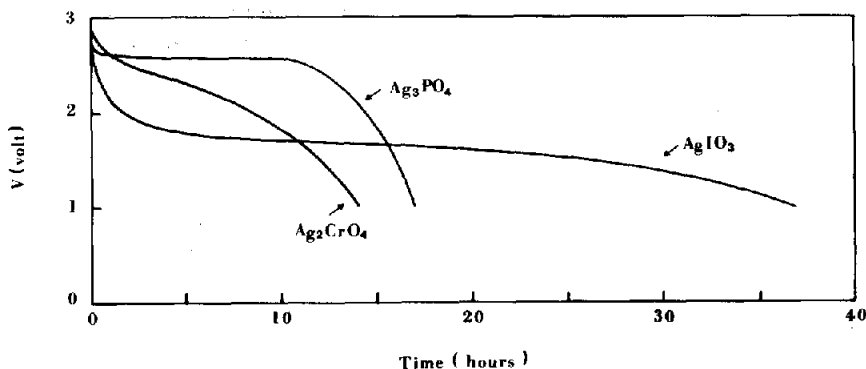
Performances of  $\text{Ag}_2\text{CrO}_4$ ,  $\text{Ag}_3\text{PO}_4$  and  $\text{AgIO}_3$  cathodes in lithium cells

Cathode	Open circuit voltage (V)	Specific capacity*		Mean discharge voltage (V)	Specific energy		Cost** (US\$)	Capacity efficiency† (%)
		(Ah/g)	Ah/cm <sup>3</sup>		(Wh/g)	(Wh/cm <sup>3</sup> )		
$\text{Ag}_2\text{CrO}_4$	2.82	0.061	0.343	2.05	0.125	0.700	0.67	40 (2e)
$\text{Ag}_3\text{PO}_4$	2.76	0.124	0.790	2.34	0.290	1.85	1.06	72 (3e)
$\text{AgIO}_3$	2.88	0.263	1.46	1.78	0.470	2.60	0.53	58 (6e)

\*Discharge at 0.5 mA/cm<sup>2</sup> to 1.0 V cut-off. Only the cathode weight was considered.

\*\*Referred to 10 g of very pure materials.

†Efficiency (to 0.0 V based on the more probable reduction process).

Fig. 1. Discharge curves at 0.5 mA/cm<sup>2</sup> of lithium cells based on different cathodes:  $\text{Ag}_2\text{CrO}_4$ , 0.148 g;  $\text{Ag}_3\text{PO}_4$ , 0.086 g;  $\text{AgIO}_3$ , 0.089 g.

The performances of the three silver oxysalt cathodes are also reported in Table 1, from which it can be seen that specific capacities and energies are higher for the iodate. This is unexpected if the reduction process for the salt were to involve a silver ion discharge mechanism similar to that of  $\text{Ag}_2\text{CrO}_4$  [1] and  $\text{Ag}_3\text{PO}_4$  [4]:



On the basis of cathode efficiency, the discharge process of  $\text{AgIO}_3$  involves at least four electrons. Three reactions are therefore theoretically possible:





The first reaction should lead to an unknown hypoiodite [5]; the second to  $\text{I}_2$ , which was not detected, and the third to  $\text{LiI}$ , which was indeed detected both by chemical and X-ray analysis. On the other hand, only the reduction of  $\text{IO}_3^-$  to  $\text{I}^-$  has been found by polarography in neutral solutions [6]. X-ray analysis showed also the presence of  $\text{Li}_2\text{O}$  but not that of  $\text{Ag}$ . This is in agreement with the shape of the discharge curve of  $\text{AgIO}_3$ , in which no appreciable reduction of silver ion (above 2 volts) is visible.

Therefore, the actual discharge reaction of  $\text{AgIO}_3$  only involves the single-step reduction of  $\text{IO}_3^-$  to  $\text{I}^-$ . The silver ion remains in its original oxidation state, possibly as a complex formed with the electrolyte. Indeed,  $\text{LiAlCl}_4$  is capable of releasing  $\text{Cl}^-$  anions which can form with silver complexes of the  $\text{AgCl}_2^-$  type. If this is ascertained for the system under investigation, some problems may be encountered in terms of storage life; in this case, more inert electrolytes, such as  $\text{LiClO}_4$  or  $\text{LiAsF}_6$ , will be used.

Work is now in progress on the  $\text{Li}/\text{AgIO}_3$  system to evaluate the influence on its performance of factors such as discharge rate, type of electrolyte and storage. Comparison will be made again with cells containing  $\text{Ag}_2\text{CrO}_4$  and  $\text{Ag}_3\text{PO}_4$ . If the initial promising results are confirmed, the  $\text{Li}/\text{AgIO}_3$  system may represent a worthwhile improvement over existing systems and become of commercial interest.

The authors wish to thank Dr. B. Scrosati for helpful discussions.

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