

ON THE POSSIBILITY OF USING SILVER SALTS OTHER THAN Ag_2CrO_4 IN ORGANIC LITHIUM CELLS

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Summary

Several silver salts, including compounds listed in the literature and new compounds, have been examined to ascertain if their performances as cathodes for lithium cells could exceed that of Ag_2CrO_4 . Discharges at various rates, polarization and cyclic voltammetry experiments were used to characterize their behaviour. Coulombic and X-ray analysis have enabled information to be obtained on the discharge reactions but the reductions of the anions still have uncertain features. Of the compounds examined, $\text{Ag}_4\text{P}_2\text{O}_7$ is the most promising one, especially by virtue of a higher load voltage. Ag_5IO_6 and AgIO_3 , at low rates, and AgIO_4 , at high rates, also approach the performance of Ag_2CrO_4 .

Introduction

Lithium cells based on Ag_2CrO_4 as a cathode material have created a new generation of power sources for electronic devices [1]. The successful use of Ag_2CrO_4 has encouraged more research on silver oxysalts, so that a number of patents and papers has been issued, some of which claim better performance than Ag_2CrO_4 .

Table 1 summarizes the silver compounds examined heretofore and gives a short account of the reported performances. In view of their possible application in practical cells, a reassessment of the characteristics of silver oxysalts appears to be appropriate. Therefore, the most interesting salts in Table 1 have been re-examined together with some new compounds in standard experimental conditions, so as to make the comparison reliable.

Twenty silver compounds have been evaluated, choosing as a first criterion for their selection their performance when discharged at 0.5 mA/cm² in cells containing LiClO_4 -PC as an electrolyte.

TABLE 1

Silver salts (other than Ag_2CrO_4) reported in the literature as cathode materials for Li cells

Salts	Reported performance	Authors
Ag_3PO_4	Higher energy density and rate capability than Ag_2CrO_4 . Volume variation	Margalit [2]
Ag_3AsO_4	Volumetric capacity higher than that of Ag_2CrO_4 [3]. Low polarization [4]	Dey [3], Scrosati [4]
$\text{Ag}_3\text{PO}_4\text{-Ag}_2\text{CrO}_4$	Limited cell change. Energy densities close to that of Ag_3PO_4	Margalit [5]
AgIO_3	High specific capacity due to IO_3^- discharge (8e)	Pistoia [6]
Ag_2MoO_4	High and constant load voltage. High rate capability	Di Pietro [7]
Ag_2WO_4	Same as above [7]. Higher voltage and volumetric capacity with respect to Ag_2CrO_4 [8]	Di Pietro [7], Japan Kokai [8]
Ag_2SnO_3	Voltage on load (100 K Ω) and volumetric capacity higher than that of Ag_2CrO_4	Japan Kokai [9]
Ag_2CO_3	High voltage and specific energy (700 Wh/L)	Ger. Offen [10]
$\text{Ag}_4\text{P}_2\text{O}_7$	Voltage on load (100 K Ω):3.53 V. With Ag_2CrO_4 :3.02 V	Japan Kokai [11]
Ag_3AsO_3	Behaves better than Ag_3AsO_4	Ger. Offen. [12]
Ag_2SiO_3		Ger. Offen. [13]
$\text{Ag}_4[\text{Fe}(\text{CN})_6]$	2.7 - 2.9 V at 0.1 mA/cm ²	Ger. Offen. [14]
Ag_2MoO_7	} Good specific capacity. Low polarization	Bonino [15]
$\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$		Bonino [15]
$\text{Ag}_2\text{W}_2\text{O}_7$		Bonino [15]
$\text{Ag}_2\text{W}_4\text{O}_{13}$		Bonino [15]
Ag_2SeO_4		Scrosati [16]
Ag_2TeO_4		Scrosati [16]
Ag_2SO_4	} Work in progress	Scrosati [16]
$\text{Ag}_2\text{Cr}_2\text{O}_7$		Scrosati [16]

Experimental

AgIO_3 , AgBrO_3 , AgO , Ag_2O , Ag_2SO_4 , Ag_2CO_3 and AgNO_2 were high purity commercial products used without any further purification.

Ag_3PO_4 , Ag_2CrO_4 , $\text{Ag}_4\text{P}_2\text{O}_7$, Ag_2SO_3 , $\text{Ag}_2\text{S}_2\text{O}_5$, Ag_2MoO_4 , AgAsO_2 , AgSCN and AgVO_3 were prepared by metathetic reactions between AgNO_3 and the corresponding sodium salts. The preparation of $\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$ has been reported by Kohlmuller and Faurie [17]. The instructions given in the literature for each particular preparation were followed to avoid the formation of unwanted impurities. The purity of the compounds so prepared was checked by X-ray analysis (Debye-Scherrer method, Cr $K\alpha$ radiation). For the salts not listed in the literature (such as $\text{Ag}_2\text{S}_2\text{O}_5$ and Ag_5IO_6) a gravimetric technique was used to check their composition through determination

of the Ag content [18]. All the salts were dried under vacuum at low temperature to avoid decomposition. After drying, weighed amounts of salts were analyzed by the above technique in order to check the absence of water of crystallization. Finally, the compounds were stored in desiccators in the dark.

Preparation and handling of the other materials have been described elsewhere [6], as well as the technique of cathode preparation, the button cell assembly and its discharge [19]. Cell polarization curves were obtained automatically by varying the current at the rate of 3.0 mA/min. Cyclic voltammetry experiments were done on planar microelectrodes obtained by pressing the test materials mixed with 2% graphite on an Ag net. An Ag net was used as a counter electrode and a Li rod as a reference electrode. The last was separated from the working electrode by a notched Luggin capillary which ensured a fixed position relative to the microelectrode. The sweep rates were in the range 20 - 50 mV/s and in order to further limit iR drops, LiAsF₆-methyl formate (MF) solutions with high conductivity were used [20].

The solubility of Ag₄P₂O₇, Ag₅IO₆, Ag₂CrO₄ and AgBrO₃ was checked by leaving these salts in LiClO₄-PC solutions for 10 - 15 days and then adding Cl⁻ ions to the filtered and H₂O-diluted solutions to precipitate Ag⁺. In no case was a precipitate obtained, thus indicating that the solubility of the above salts is below a detectable limit.

During this test, no visible reactions (discoloration and/or gassing) were observed between Ag salts and solution. This may be taken as a first compatibility test.

To ascertain the nature of the products formed on discharge, X-ray analyses were carried out on the cathodes having reducible anions.

Results and Discussion

Table 2 summarizes the theoretical capacities for the various Ag compounds. When the reduction of the anion occurred, the theoretical capacity was calculated from the more probable reduction reaction. Table 3 reports the performances obtained in Li/LiClO₄-PC/Ag salt, 10% C cells at 0.5 mA/cm². AgNO₂ and AgVO₃ display only very poor discharge curves with almost nil capacity. For the other salts the capacity at the first inflection point of the curves, if any, was also reported. In devices with invariable resistance, such as electronic watches or cardiac pacemakers, the first plateau only is of importance. In this case, a good voltage regulation with no steps is obviously required. Several compounds were eliminated on a specific energy and capacity basis. In general, those having capacities below 0.20 Ah/g (1.0 V cut-off) were not considered, with the exception of Ag₄P₂O₇, which shows a high and constant load voltage.

Polarization experiments were then made on 6 different cathodes, chosen from among the best of Table 3 (Fig. 1). Ag₃PO₄-based cells proved

TABLE 2

Theoretical specific capacities (Ah/g) for the silver salts examined

Salt	Capacity for $\text{Ag}^+ \rightarrow \text{Ag}^0$	Capacity for anion reduction	Total capacity
Ag_2CrO_4	0.162	0.242 (3e)	0.404
$\text{Ag}_4\text{P}_2\text{O}_7$	0.177		0.177
Ag_5IO_6	0.176	0.281 (8e)	0.457
AgIO_3	0.095	0.568 (6e)	0.663
AgBrO_3	0.114	0.682 (6e)	0.796
AgIO_4	0.090	0.717 (8e)	0.807
$\text{Ag}_2\text{S}_2\text{O}_5$	0.149	0.298 (4e)	0.447
Ag_3PO_4	0.191		0.191
Ag_2MoO_4	0.142	0.142 (2e)	0.284
AgO	0.430		0.430
Ag_2O	0.230		0.230
Ag_2SO_4	0.172		0.172
Ag_2CO_3	0.194		0.194
Ag_2SO_3	0.181		0.181
AgAsO_2	0.125		0.125
$\text{Ag}_2\text{C}_2\text{O}_4$	0.176		0.176
AgSCN	0.161		0.161
AgNO_2	0.174		0.174
AgVO_3	0.129		0.129
$\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$	0.075	0.251 (2e)	0.326

to be the last ones to fall down to 1.0 V, thus confirming the rate capability reported by Margalit [2]. However, the best performance in terms of voltage retention is shown by AgIO_4 .

Ag_3PO_4 was not further examined as this salt has been well characterized by Margalit, especially in mixtures with Ag_2CrO_4 [5], and its performance in LiClO_4 -PC solutions does not appear superior to that of Ag_2CrO_4 with the exception of lower polarization losses at high current drains.

Tables 4 and 5 report the performances obtained during discharges at 1.0 and 2.0 mA/cm², respectively. Cells based on AgIO_4 and $\text{Ag}_4\text{P}_2\text{O}_7$ approach the performance of those based on Ag_2CrO_4 . It is perhaps unexpected that AgIO_4 , in spite of the excellent polarization behaviour, is not superior to Ag_2CrO_4 . During long-lasting discharges, the nature of the products formed (especially their volume, solubility and conductivity) is of the utmost importance. On the other hand, rapid-sweep electrode polarizations depend to a limited extent on such factors, being more influenced by the rate of mass and charge transfer.

Table 6 reports the data obtained at a very low discharge rate (40 $\mu\text{A}/\text{cm}^2$). At this rate, information can be obtained on the possibility of using these compounds for powering cardiac pacemakers, although the actual rate in these devices is of the order of 3 $\mu\text{A}/\text{cm}^2$ [1]. In terms of capacity, Ag_5IO_6 and AgIO_3 approach the results obtained with Ag_2CrO_4 to a 1.4 V cut-off. In Fig. 2, the discharge curves of Li/AgIO_3 and $\text{Li}/\text{Ag}_2\text{CrO}_4$ cells are

TABLE 3

Performances of silver salts examined at 0.50 mA/cm^2 (referred to the weight of cathode material only)

Salt	To first inflection point			To 1.0 V cut-off		
	Spec. cap. (Ah/g)	Mean voltage (V)	Spec. en. (Wh/g)	Spec. cap. (Ah/g)	Mean voltage (V)	Spec en. (Wh/g)
Ag_2CrO_4	0.16	2.75	0.45	0.32	2.37	0.76
$\text{Ag}_4\text{P}_2\text{O}_7$	0.14	2.94	0.42	0.17	2.62	0.46
Ag_5IO_6	0.13	2.02	0.27	0.28	1.71	0.48
AgIO_3				0.20	1.78	0.35
AgBrO_3				0.31	1.72	0.53
AgIO_4	0.02	3.35	0.08	0.24	2.20	0.53
$\text{Ag}_2\text{S}_2\text{O}_5$	0.15	2.37	0.36	0.25	1.99	0.50
Ag_3PO_4				0.21	2.15	0.45
Ag_2MoO_4	0.13	2.39	0.31	0.19	2.06	0.39
AgO	0.11	2.30	0.25	0.23	2.00	0.46
Ag_2O	0.05	2.80	0.15	0.13	2.27	0.30
Ag_2SO_4				0.06	1.73	0.10
Ag_2CO_3				0.18	1.93	0.34
Ag_2SO_3	0.15	2.13	0.33	0.20	1.93	0.38
AgAsO_2				0.15	1.42	0.21
$\text{Ag}_2\text{C}_2\text{O}_4$				0.06	1.55	0.09
AgSCN	0.12	2.70	0.31	0.18	2.25	0.40
AgNO_2				~0	~0	~0
AgVO_3				~0	~0	~0
$\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$ *	0.087	2.40	0.21	0.28	2.05	0.58

*Data from ref. [15].

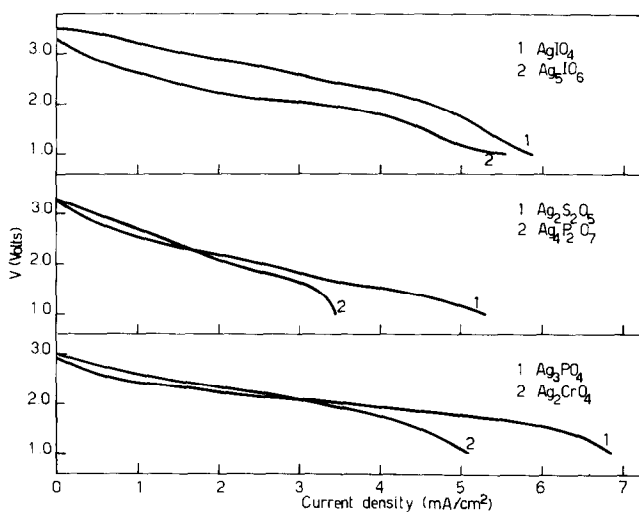


Fig. 1. Cell polarization curves for various Ag salts in $\text{LiClO}_4\text{-PC}$. Scanning rate, 3.0 mA/min .

TABLE 4

Performances of silver salts at 1.0 mA/cm²

Salt	To first inflection point			To 1.0 V cut-off		
	Spec. cap. (Ah/g)	Mean voltage (V)	Spec. en. (Wh/g)	Spec. cap. (Ah/g)	Mean voltage (V)	Spec. en. (Wh/g)
AgBrO ₃				0.11	1.36	0.14
Ag ₂ CrO ₄	0.17	2.60	0.44	0.27	2.31	0.63
Ag ₄ P ₂ O ₇	0.14	2.77	0.40	0.18	2.61	0.47
AgIO ₄	0.02	3.35	0.08	0.24	2.20	0.53
Ag ₂ S ₂ O ₅				0.14	2.08	0.30

TABLE 5

Performances of silver salts at 2.0 mA/cm²

Salt	To first inflection point			To 1.0 V cut-off		
	Spec. cap. (Ah/g)	Mean voltage (V)	Spec. en. (Wh/g)	Spec. cap. (Ah/g)	Mean voltage (V)	Spec. en. (Wh/g)
Ag ₄ P ₂ O ₇	0.11	2.52	0.28	0.16	2.27	0.37
Ag ₅ IO ₆				0.17	1.63	0.27
Ag ₂ CrO ₄				0.16	2.32	0.37
AgIO ₄				0.16	2.05	0.33
Ag ₆ Mo ₁₀ O ₃₃				0.14	1.69	0.24

TABLE 6

Performances of silver salts at 40 μA/cm²

Salt	To first inflection point			To 1.4 V cut-off		
	Spec. cap. (Ah/g)	Mean voltage (V)	Spec. en. (Wh/g)	Spec. cap. (Ah/g)	Mean voltage (V)	Spec. en. (Wh/g)
Ag ₅ IO ₆	0.17	2.40	0.40	0.47	2.00	0.94
Ag ₅ IO ₆ (without C)	0.14	3.00	0.42			
Ag ₄ P ₂ O ₇	0.15	3.21	0.48	0.17	3.04	0.52
Ag ₂ CrO ₄	0.17	2.90	0.49	0.42	2.46	1.05
AgBrO ₃				0.12	1.99	0.24
AgIO ₃				0.49	2.04	0.99
AgIO ₄	0.02	3.13	0.07	0.31	2.34	0.72
Ag ₂ S ₂ O ₅				0.32	2.38	0.76
Ag ₆ Mo ₁₀ O ₃₃	0.10	2.55	0.25	0.31	2.15	0.79

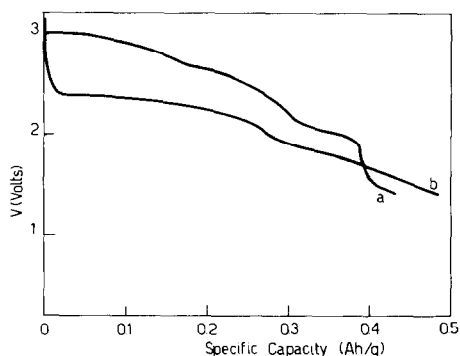


Fig. 2. Discharge curves of (a) $\text{Li}/\text{Ag}_2\text{CrO}_4$ and (b) Li/AgIO_3 cells at $40 \mu\text{A}/\text{cm}^2$.

compared. If the first inflection point is taken into account, $\text{Ag}_4\text{P}_2\text{O}_7$ can equal the capacity and energy output of Ag_2CrO_4 . Furthermore, the first salt shows a substantially higher voltage. Also the performance of Ag_5IO_6 cathodes without graphite is remarkable (their behaviour was observed only during the first step).

From the shape of the discharge curves and from coulometric and X-ray analysis, it was possible to obtain some information on the discharge processes of the salts examined. Some of them discharge Ag^+ only; variations of the oxidation state of the metal of the anion were also observed in other salts and, finally, AgBrO_3 and AgIO_3 do not show a significant discharge of Ag^+ . The first category includes most of the compounds examined, whereas the following salts: Ag_2CrO_4 , Ag_5IO_6 , AgIO_4 , $\text{Ag}_2\text{S}_2\text{O}_5$, Ag_2MoO_4 and $\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$ belong to the second.

However, the question of the anion reduction is not yet clearly understood. Our results of X-ray analysis on Ag_5IO_6 , AgIO_4 , AgIO_3 , AgBrO_3 and $\text{Ag}_2\text{S}_2\text{O}_5$ have still left many doubts on this matter. In particular, the halogen-containing compounds do not show a common pattern. Furthermore, the reduction of the anion does not always seem to proceed through a simple path, as was also indicated by the coulombic analysis at low rate. The results of Table 6 indicate that the capacities expected on the basis of Table 2 are approached or surpassed for $\text{Ag}_4\text{P}_2\text{O}_7$, Ag_5IO_6 , Ag_2CrO_4 and $\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$ in spite of the cut off at 1.4 V. Since electrolyte decomposition is very unlikely above this voltage (we notice decomposition around 0.8 V), this result would indicate the occurrence of anionic reactions different from the ones listed in Table 2. Non-stoichiometric phases are possibly formed through Li^+ insertion in the lattices which are being formed during discharge. Such reactions would be more important at low rates. Ag_3PO_4 and AgSCN have capacities a little higher than the theoretical ones even at $0.5 \text{ mA}/\text{cm}^2$, this being possibly attributable to a limited Li^+ insertion.

The absence of graphite in the cathodic mixture sometimes produces unexpected results. Table 7 reports the specific capacities obtained using cathodes with and without graphite. With the exception of AgO , which is a

TABLE 7

Capacities (Ah/g) of cathodes with and without graphite at 0.50 mA/cm² to 1.0 V cut-off

Salt	With 10% C	Without C (thin layer)	Without C (thick layer)
Ag ₄ P ₂ O ₇	0.18	0.17	0.10
AgBrO ₃	0.31	0.053	~0
Ag ₂ O	0.13	0.14	0.13
AgO	0.23	0.28	
Ag ₂ CrO ₄	0.25	0.19	
Ag ₃ PO ₄	0.21	0.18	
AgIO ₃	0.20	0.20	0.007
AgIO ₄	0.28	0.28	0.08
Ag ₅ IO ₆	0.28	0.27	0.06

semiconductor [21], all the silver compounds are insulators, so that one should not expect them to work in the absence of conductive additives. Indeed, resistances of the order of 10⁵ ohm were measured for thick cathodes (~1 mm of thickness), the performances of which are reported in the third column. Nevertheless, with the exception of AgBrO₃, all the compounds examined do not suffer markedly as a result of the absence of graphite (in thin layers) and some of them even behave slightly better. Figure 3 shows that a graphite-free AgIO₄ cathode has a higher potential than a AgIO₄/C cathode (whereas the specific capacity is the same).

The difference observed between thin and thick layer cathodes suggests a mechanistic model in which the reduction begins at the interface between cathode pellet and support. In this model, the electrolyte is supposed to have diffused through the porous cathode material towards the support. We have sought experimental confirmation to this interpretation with the use of a

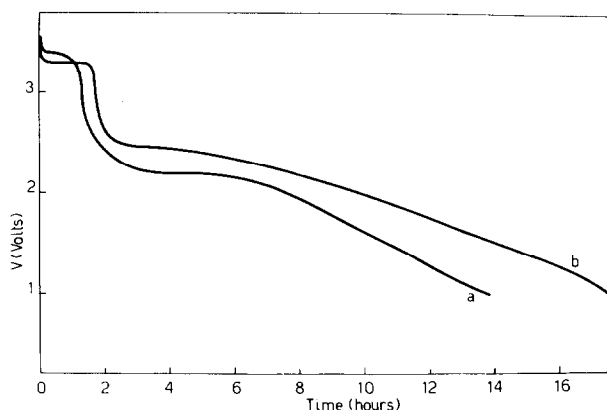


Fig. 3. Discharge curves of Li/AgIO₄ cells with (a) C and (b) without C at 0.50 mA/cm². Specific capacity, 0.28 Ah/g for both cells (1.0 V cut-off).

graphite-free AgIO_3 cathode. After a partial discharge, the white cathode appeared blackened at the support–electrode interface and mostly unchanged, with a few black spots, at the electrode–solution interface. Obviously, the thicker the layer the smaller the amount of electrolyte reaching the inner interface, so that the performances are less satisfactory. Formation of Ag during discharge improves the electronic conductivity and may explain the voltage increase sometimes observed during the early stages of discharge.

Even the voltages in the absence of graphite do not vary appreciably. Ag_5IO_6 represents a peculiar case, the load voltage being markedly higher in the absence of graphite. At $40 \mu\text{A}/\text{cm}^2$ this salt shows (see Table 6) the plateau of Ag^+ reduction at 3.0 V, thus enabling it to approach the performance of Ag_2CrO_4 . This phenomenon is obviously kinetic in nature but it is hard to explain why the absence of graphite should facilitate the reduction of Ag_5IO_6 to such an extent.

Cyclic voltammetry experiments were done on some of the salts, mainly with the aim of ascertaining the reversibility of the reduction of Ag^+ . The cathodic sweep for $\text{Ag}_4\text{P}_2\text{O}_7$ (Fig. 4) and Ag_2CrO_4 was purposely limited to the reduction of Ag^+ . The anodic portion of the curves do not show relevant oxidation phenomena, so that it may be assumed that Ag^+ reduction is not reversible, this confirming the results obtained with AgO and Ag_2O [22]. Messina *et al.* [23] found an anodic peak for the reduction of Ag_2CrO_4 in LiClO_4 -PC. It has to be noted that these authors found, during the cathodic sweep, a rapid increase of current after the first peak at 2.9 V *vs.* Li/Li^+ .

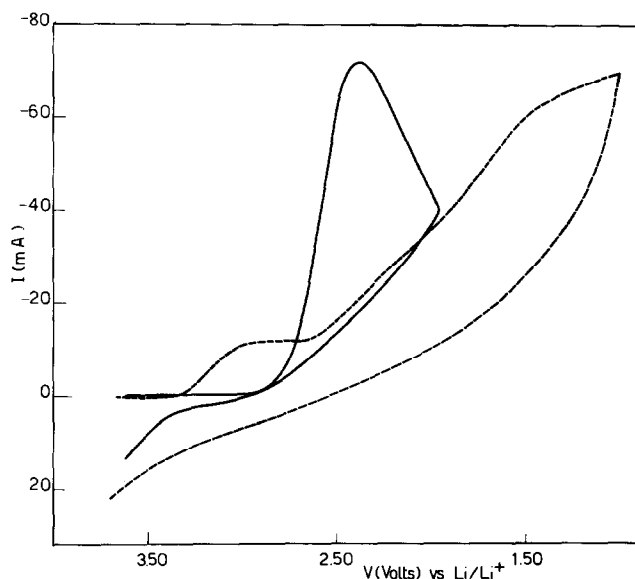


Fig. 4. Cyclic voltammetry on $\text{Ag}_4\text{P}_2\text{O}_7$ (continuous curve) and Ag_5IO_6 (-----) cathodes in LiAsF_6 -MF. Scanning rate, 20 mV/s.

Possibly, their anodic peak may be attributed to re-oxidation of a species other than Ag.

Ag_5IO_6 (Fig. 4) and AgIO_3 show significant anion reduction. For Ag_5IO_6 too, no appreciable anionic peak was observed even when the cathodic sweep was stopped before anion reduction.

Conclusion

The screening of several Ag salts has shown that a few of them may approach the performance of Ag_2CrO_4 . In particular, $\text{Ag}_4\text{P}_2\text{O}_7$ seems to have the possibility of challenging Ag_2CrO_4 when the discharge is limited to Ag^+ reduction. Indeed, at medium-low rates, $\text{Li}/\text{Ag}_4\text{P}_2\text{O}_7$ cells have potentials on load higher than those of $\text{Li}/\text{Ag}_2\text{CrO}_4$ cells. The voltage regulation of the former cells is as excellent as that of the latter and makes the system attractive for use in electronic equipment. Figure 5 reports three discharge curves at different rates for $\text{Li}/\text{Ag}_4\text{P}_2\text{O}_7$ cells.

At very low rates, Ag_5IO_6 (especially without graphite) and AgIO_3 also have interesting values of specific capacity and energy. At high rates, the performance of AgIO_4 is also relevant on the same basis.

All these salts are not significantly soluble in $\text{LiClO}_4\text{-PC}$ and are compatible with this electrolyte suggesting that the systems should have long shelf-lives. It has still to be ascertained if significant volume variations take place during their reduction, as observed with Ag_3PO_4 [2].

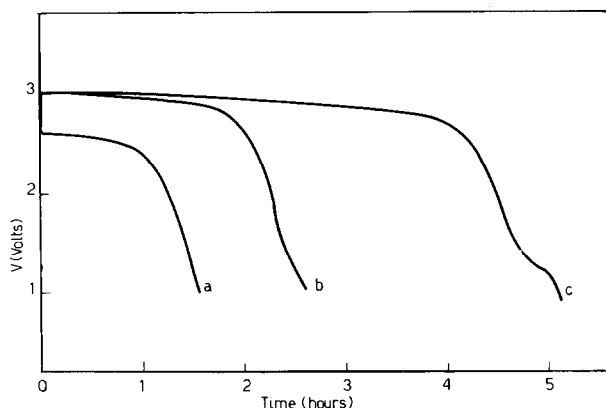


Fig. 5. Discharge curves at various rates of $\text{Li}/\text{Ag}_4\text{P}_2\text{O}_7$ cells; (a) 2.0 mA/cm^2 ; (b) 1.0 mA/cm^2 ; (c) 0.5 mA/cm^2 . Specific capacities in Tables 3, 4 and 5.

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