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SHORT COMMUNICATION

Silver arsenate as the cathodic material in lithium batteries

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1. Introduction

A systematic research on new cathodic materials to couple with lithium in organic electrolyte batteries has been carried out in our laboratories during recent years. In the course of this research we have found that certain silver [1] and copper [2] oxysalts behave quite well in terms of stability, discharge performance and energetic characteristics. We have therefore extended the study to the properties of silver arsenate as a possible cathodic material in lithium power sources.

The possibility of applying this material in lithium batteries has been already mentioned by Dey *et al.* [3]. However, the reported discharge curve at 1 mA cm^{-2} appeared rather poor, showing a progressively decreasing voltage [3]. This behaviour could possibly be related to a certain solubility of the cathodic material in the electrolyte used. In fact we have found that silver arsenate is quite soluble in electrolytes containing chloride ions. It therefore seemed of interest to reconsider the investigation of the Li/Ag_3AsO_4 couple in electrolytes where the silver salt is insoluble. In this respect, the 1·5 M solution of $LiAsF_6$ in γ-butyrolactone (BL) turned out to be the most suitable medium.

2. Experimental

Silver arsenate was prepared by precipitation, mixing an aqueous solution of $Na_2HAsO_4 . 7H_2O$ with a solution of $AgNO_3$. The precipitate was washed with distilled water and acetone and dried under nitrogen at 70° C. The X-ray diffraction patterns of the material so obtained agreed with those of Ag_3AsO_4, as reported in the literature [4].

Lithium ribbon (Foote Mineral Co.) and lithium hexafluoroarsenate (Alfa Ventron) were used as received. High purity butyrolactone (MERCK) was further purified by distillation under reduced pressure. The electrolyte solutions were prepared in a dry-box with a procedure previously described [1].

The testing cells were of the 'button' type and assembled in a dry-box by contacting a lithium disc, three glass wool separator discs soaked with the electrolyte and a pellet of the cathodic material supported on an inert metal substrate. Both graphite–silver salt (10 wt% graphite) mixtures and graphite-free cathodes were used. The final cells, of 1·25 cm^2 surface, were housed in a Teflon container with stainless steel terminals and kept in the dry-box for the electrochemical measurements.

The solubility of Ag_3AsO_4 in various electrolytes was qualitatively tested by adding sodium chloride solutions to the system examined. The solubility in the selected medium, i.e. 1·5 M $LiAsF_6$–BL, was finally controlled by three-electrode polarography, using dropping mercury as the working electrode and silver/silver perchlorate as the reference electrode.

3. Results and discussion

While quite insoluble in pure solvents (e.g. γ-butyrolactone or propylene carbonate), Ag_3AsO_4 appears to dissolve in large amounts in electrolyte

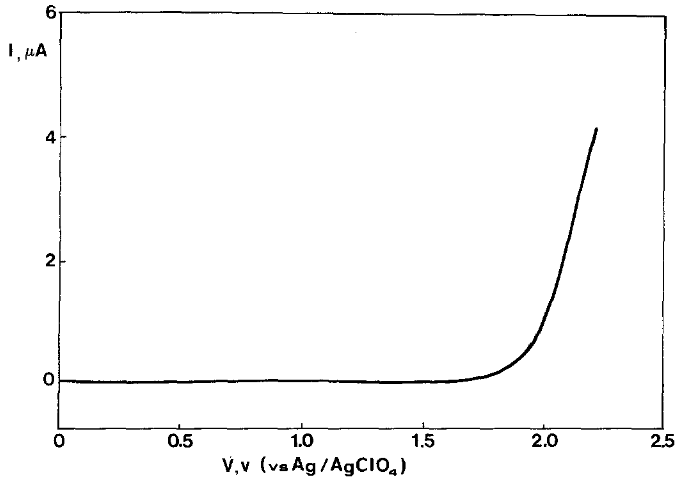

Fig. 1. Polarogram of the $LiAsF_6$–BL solution above Ag_3AsO_4 at room temperature (sweep rate: 80 mV min^{-1}).

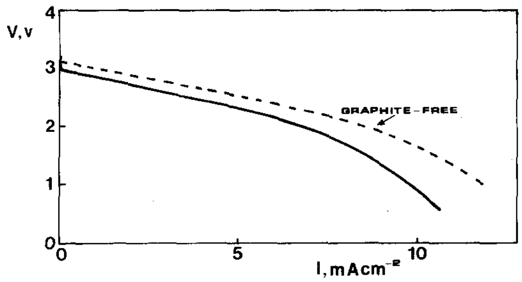

Fig. 2. Typical polarization curve of Cell I at room temperature (60 s current pulses).

systems containing chloride ions, as for instance is the case of $LiAlCl_4$ in BL. As suggested by Conte *et al.* [5] and by Lee [6], this high solubility could be related to the complexing of the silver ion by the chloride ions of the electrolyte.

No such effect was noticed in the $LiAsF_6$–BL system: solutions left in contact with powdered silver arsenate for long periods of time showed no precipitate after sodium chloride additions. These solutions were then finally examined by polarographic analysis. A typical polarogram, schematically reported in Fig. 1, showed no detectable waves up to the reduction of the supporting electrolyte.

The $LiAsF_6$–BL system was then selected for the investigation of the properties of Ag_3AsO_4 as the cathode in cells of the type

$$Li/LiAsF_6\text{–}BL/Ag_3AsO_4\ (C)\,. \qquad (I)$$

Cell I had an open circuit voltage (OCV) of 3·2 V at room temperature and displayed the typical polarization curves shown in Fig. 2, where the dotted line refers to graphite-free cathodes. The latter shows better performances, the reason for which is difficult to explain. A similar phenomenon has already been noticed for other oxysalt cathodes [5] and such graphite-free cathodes may be considered advantageous in terms of overall specific energy density.

Fig. 2, which illustrates the initial behaviour of the cell, gives a preliminary indication of the good performance of the system which is able to sustain relatively high current densities without under-

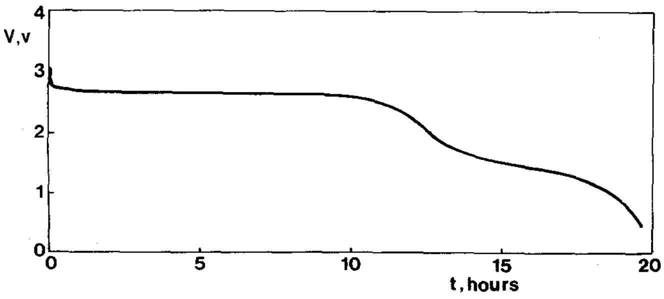

Fig. 3. Typical discharge curve at 0·5 mA cm^{-2} and at room temperature of Cell I (average cathodic weight: 80 mg).

Table 1. Performance and energetic characteristics of the cathodic material of Cell I at room temperature and at 0·5 mA cm^{-2} discharge rate. Data related to Ag_2WO_4* [1] are also reported for comparison purposes*

Salt	*Mean discharge voltage* (V)	*Specific capacity* (Ah g^{-1})	*Specific energy* (Wh g^{-1})	*Efficiency* (%)
Ag_3AsO_4	2·7	0·10	0·27	100
Ag_2WO_4	3·2	0·11	0·35	98
Ag_2MoO_4	2·8	0·14	0·39	98

* First plateau only

going serious polarization. This is further confirmed by the long-term discharge characteristics, such as those shown in Fig. 3, in which a typical discharge curve at 0·5 mA cm^{-2} is reported. In contrast with the results of Dey [3], in this case the discharge voltage remains reasonably constant and the shape of the curve indicates a discharge process characterized by two distinct plateaus.

In order to determine the number of electrons involved in this process, a coulometric analysis was carried out. Cells containing a known amount of cathodic material (typically around 50 mg) and lithium in excess, were galvanostatically discharged at low rates (typically around 0·25 mA cm^{-2}) and from the coulombs delivered the number of electrons was derived. This number, as an average of various determinations, was found to be two (per mole of Ag_3AsO_4) at the end of the first plateau and three (per mole of Ag_3AsO_4) at the end of the discharge.

In an attempt to further investigate the discharge process, a low rate discharge of a cell of type I was interrupted both at the end of the first plateau and at the end of the discharge, and the related cathodic masses were submitted to X-ray analyses. The results indicated the presence of silver and of silver arsenate at the end of the first plateau and of silver only at the end of the discharge.

On the basis of the above results, one may tentatively indicate the following

$$3Li + Ag_3AsO_4 \rightarrow 2/3\ Li_3AsO_4$$

$$+ 1/3\ Ag_3AsO_4 + 2Ag \rightarrow Li_3AsO_4 + 3Ag$$

as the most probable electrochemical reaction of Cell I, which involves the replacement of silver by lithium in two successive steps. Some uncertainties in the exact nature of this reaction, however, still remain since Li_3AsO_4 has not been detected in the X-ray analysis.

Finally, the energetic characteristics of Ag_3AsO_4 are summarized in Table 1, where also data related to silver oxysalts previously investigated [1] are shown. The comparison indicates that Ag_3AsO_4, if used in a suitable electrolyte, may also be regarded as an interesting material for the development of lithium power sources.

Acknowledgements

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