

## Li-AgBi(CrO<sub>4</sub>)<sub>2</sub>: A NEW HIGHLY RELIABLE LITHIUM BATTERY FOR LONG SERVICE LIFE APPLICATIONS

M. BROUSSELY, J. P. RIVAULT and J. P. GABANO

*Saft-Gipelec, rue Georges Leclanché, 86009 Poitiers (France)*

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### Summary

The Li/AgBi(CrO<sub>4</sub>)<sub>2</sub> battery system was patented in 1977. It has been studied for several years to obtain a better knowledge of the electrochemical reactions as well as of the discharge characteristics of a prototype cell.

An exceptionally low level of self discharge and the use of a very well-known stable electrolyte such as propylene carbonate 1M Li/ClO<sub>4</sub> satisfy the necessary requirements for long service life application: high efficiency was obtained on long time discharges even at high temperature, *e.g.*, 70 °C at the two years rate.

Performances over a wide range of current drains and temperatures are presented as well as projected results at a very low drain.

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### 1. Introduction

Research carried out at Saft in the field of lithium-metal chromate cells using an organic electrolyte [1, 2] have led us to introduce a new battery system based on silver bismuth chromate as the cathodic material.

This new system was discovered in 1977 [4] and since then a detailed study has been undertaken to obtain greater knowledge of the electrochemical mechanism as well as the discharge characteristics of prototype cells.

Although the lithium-silver bismuth chromate cell has an average working voltage slightly lower than the lithium-silver chromate cell, the former was found to satisfy the requirements of medical implantable device manufacturers and a variety of other electronic devices which require low to moderate power consumption.

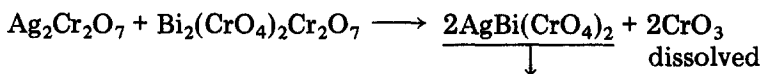
In addition, lithium-silver bismuth chromate was found to adapt well to long time operation at 70 °C, a temperature at which few if any other systems will operate reliably for an extended period.

### 2. Main characteristics and synthesis

The preparation of silver bismuth chromate, AgBi(CrO<sub>4</sub>)<sub>2</sub>, has been described in detail by Gerault and Lecerf [3]. The first step consists of

adding solid bismuth nitrate,  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  to an aqueous solution saturated with  $\text{CrO}_3$  at  $20^\circ\text{C}$  in order to synthesize an intermediate compound,  $\text{Bi}_2(\text{CrO}_4)_2\text{Cr}_2\text{O}_7$ .

In the second step,  $\text{Bi}_2(\text{CrO}_4)_2\text{Cr}_2\text{O}_7$  is allowed to react with silver bichromate in aqueous solution according to:



The resulting insoluble product  $\text{AgBi}(\text{CrO}_4)_2$  is then filtered, washed, and dried.

Debye-Scherrer X-ray examination showed a quadratic structure for this compound with the following lattice parameters:  $a = 5.095 \text{ \AA}$ ,  $C = 11.858 \text{ \AA}$ .

Comparison of the calculated and measured densities, 5.92 and 5.79, respectively leads us to propose two moles per unit lattice. This compound was found to be quite insoluble in 1M  $\text{LiClO}_4$ -propylene carbonate electrolyte even at temperatures as high as  $70^\circ\text{C}$ .

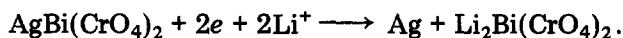
### 3. Electrochemical reduction of $\text{AgBi}(\text{CrO}_4)_2$ in 1M $\text{LiClO}_4$ -propylene carbonate electrolyte

Our electrochemical investigations were performed on so called "membrane electrodes" [2] of  $1 \text{ cm}^2$  surface area and about 0.1 mm in thickness containing only small quantities of active material ( $\approx 0.5 \text{ mg}$ ) mixed with 90 wt.% pure graphite.

The mixture containing the active material was pressed onto a stainless steel grid. Beaker cells with an excess of electrolyte (1M  $\text{LiClO}_4$  in propylene carbonate) were used for the electrochemical measurements. Pure lithium was used for both counter and reference electrodes.

Figure 1 shows a typical galvanostatic discharge obtained at a low rate ( $10 \mu\text{A}/\text{cm}^2$ ,  $60^\circ\text{C}$ ) for  $\text{AgBi}(\text{CrO}_4)_2$  membrane electrodes to a cut off voltage of 2 V. The overall discharge process involves 5 Faraday/mole under these conditions.

The discharge profile so defined exhibits two different regions: a first plateau at about 3.1 V and a slope between 3 and 2 V. Contrary to silver chromate, the first plateau does not correspond to the reduction of silver only, as demonstrated by the two Faraday/mole so obtained, indicating a simultaneous reduction of silver and chromium ions. This reaction can be written as follows:



X-ray analysis confirms that silver metal is effectively produced during this process.

Additional electrochemical studies, performed in the sloping region (charge/discharge galvanostatic cycles) indicated that the second process involves a topochemical reversible reaction according to:

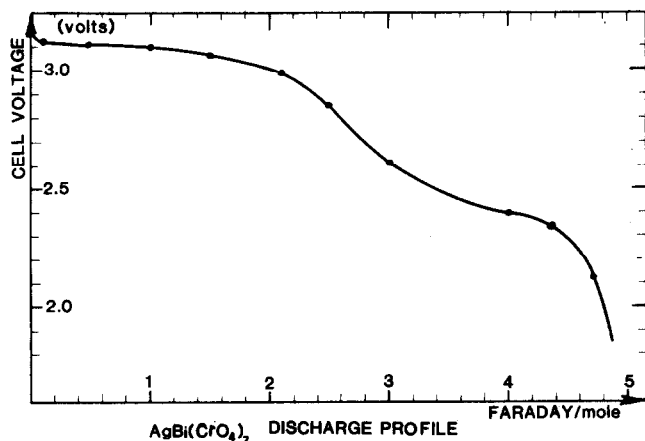
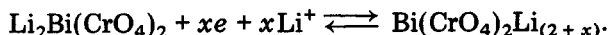


Fig. 1. Discharge characteristics of  $\text{Li}/\text{AgBi}(\text{CrO}_4)_2$  experimental test cells using membrane electrodes at  $60^\circ\text{C}$  and  $10\ \mu\text{A}/\text{cm}^2$ .



This mechanism explains the continuous decrease in cathode potential. Moreover, equilibrium potentials *vs.* depth of discharge, measured at zero current, were found to be quite close to potentials obtained at low discharge rates, consequently demonstrating the presence of such a process.

It was found that this mechanism was not completely reversible, suggesting that the insertion compound so formed decomposes slowly into the different oxides  $\text{Li}_2\text{O}$ ,  $\text{CrO}_2$  and  $\text{Bi}_2\text{O}_3$ . In any case,  $\text{Bi}^{3+}$  was not found to be electrochemically active (reduction of  $\text{Bi}^{3+}$  to bismuth metal) for the cathodic voltage range considered.

The theoretical specific capacity of the couple is  $0.836\ \text{A h}/\text{cm}^3$ , taking into account only the volumes of the anodic and cathodic materials. The theoretical energy density is  $2340\ \text{W h}/\text{dm}^3$ , the average voltage being about 2.8. By comparison the values for silver chromate are  $0.747\ \text{A h}/\text{cm}^3$  and  $2211\ \text{W h}/\text{dm}^3$ , with a second plateau balance of about 25% of the capacity.

#### 4. Cell technology

The cell technology is similar to that of the  $\text{Li}-\text{Ag}_2\text{CrO}_4$  system [1].

The first test vehicle was made in the Li 210 button cell configuration (21 mm dia., 9.6 mm high) using the crimped, sealed version. A mixture of pure  $\text{AgBi}(\text{CrO}_4)_2$  powder and an electronic conductor was pressed directly into the positive stainless steel can. The electrolyte (1M  $\text{LiClO}_4$  in propylene carbonate) is absorbed in a non-woven cellulosic separator material. The cell was sealed with a polypropylene grommet which also insulated the positive from the negative compartment.

The theoretical electrochemical capacity of this prototype was 0.85 A h.

Rectangular and D-shape cells using a glass to metal seal have also been designed in the same manner as the  $\text{Ag}_2\text{CrO}_4$  cells.

## 5. Cell discharge characteristics

### 5.1. Continuous discharges

Figures 2 and 3 show discharge curves of Li 210 button size cells for different rates and temperatures. From these Figures it can be seen that increasing temperature or decreasing discharge rate do not change the cell discharge profiles, indicating that the associated discharge mechanisms,

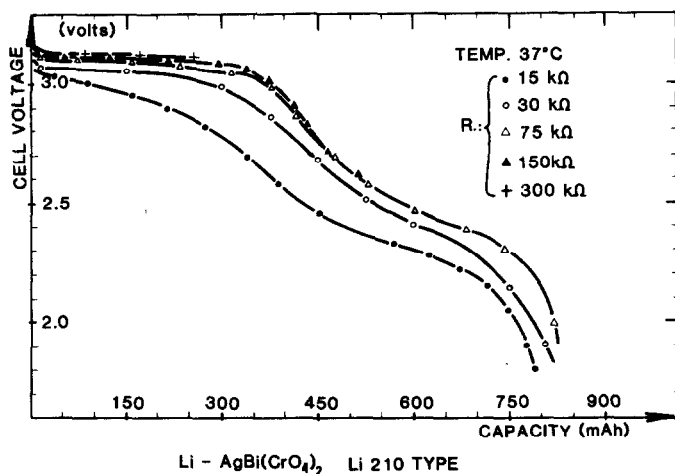


Fig. 2. Discharge characteristics for 210  $\text{Li}/\text{AgBi}(\text{CrO}_4)_2$  button cells at  $37^\circ\text{C}$  through different loads.

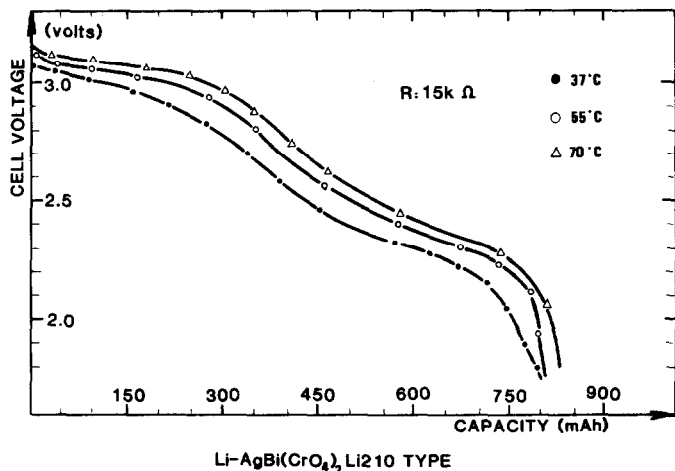


Fig. 3. Discharge characteristics for 210  $\text{Li}/\text{AgBi}(\text{CrO}_4)_2$  button cells on  $15\text{ k}\Omega$  load at different temperatures.

contrary to the  $\text{Li-Ag}_2\text{CrO}_4$  system, are the same over these wide ranges of conditions.

The curves plotted in Fig. 4 are particularly interesting: after 31 months discharge under a load of  $75\text{ k}\Omega$  the efficiency recovered is about 95% for temperatures ranging from  $37$  to  $70^\circ\text{C}$ . These exceptional results prove the total absence of self-discharge or parasitic reactions which are generally drastically enhanced by temperature rises.

### 5.2. "Switched" discharge

To anticipate the behaviour of this system at low drains, several cells were first discharged to different depths of current at a high drain ( $15\text{ k}\Omega$ ,

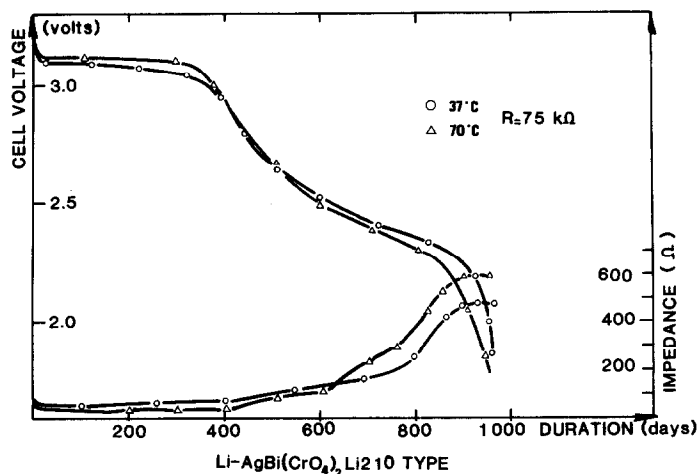


Fig. 4. Discharge characteristics for 210  $\text{Li/AgBi}(\text{CrO}_4)_2$  button cells on  $75\text{ k}\Omega$  load at different temperatures.

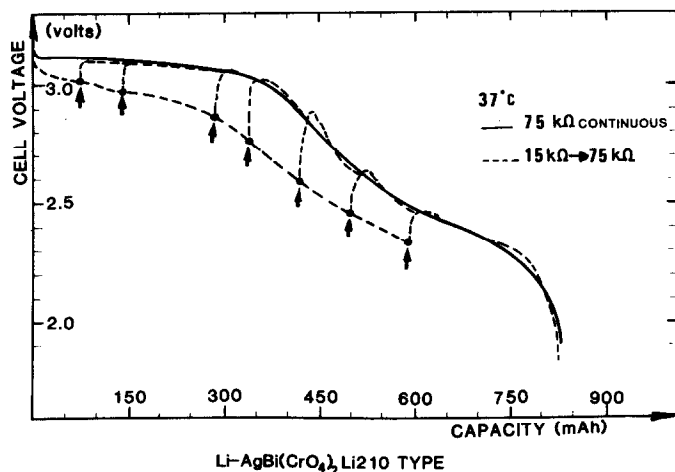


Fig. 5. "Switched" and continuous discharge tests performed on 210  $\text{Li/AgBi}(\text{CrO}_4)_2$  button cells. —, Continuous drain ( $75\text{ k}\Omega$ ); - - -, switched drain ( $15\text{ k}\Omega$  then  $75\text{ k}\Omega$ ).

$\approx 200 \mu\text{A}$ ) and then switched to lower drains ( $75 \text{ k}\Omega$ ,  $\approx 40 \mu\text{A}$ ) for the remainder of their lives. This type of experiment is only valid if self discharge is negligible and if the reactions we suppose to occur are not changed by the discharge rate, as shown earlier.

Figure 5 confirms this: it can be seen that the discharge curves obtained on  $75 \text{ k}\Omega$  continuous load, or on  $75 \text{ k}\Omega$  after the various predischarges on  $15 \text{ k}\Omega$ , are quite similar. Figure 6 reveals the same type of discharge but under a  $15/300 \text{ k}\Omega$  load. From this Figure the true discharge profile under a  $300 \text{ k}\Omega$  load can be projected with reasonably good accuracy. It will be noticed that the curve presently recorded after 3 years on  $300 \text{ k}\Omega$  continuous load exactly follows the values expected from the switched cells.

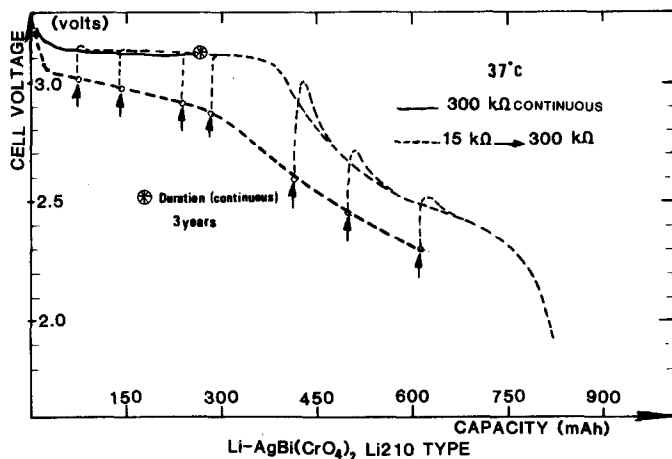


Fig. 6. "Switched" and continuous discharge tests performed on 210  $\text{Li}/\text{AgBi}(\text{CrO}_4)_2$  button cells. —, Continuous drain ( $300 \text{ k}\Omega$ ); - - -, switched drain ( $15 \text{ k}\Omega$  then  $300 \text{ k}\Omega$ ).

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