

BUTTON CELLS BASED ON THE Li/Bi₂O₃ COUPLE

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Summary

Lithium button cells (1.5 V) with thermally treated Bi₂O₃ cathodes (additive free), mainly of 11.4 × 3.4 mm standard size (100 mA h), have been constructed. They are characterized by high volumetric energy densities even at high discharge rates. The cell behaviour is also satisfactory after 1 year's storage, at low temperature (-10 °C), and under 500 μA pulses. Comparison with analogous Li cells (Li/FeS₂ and Li/Pb₂Bi₂O₅) or aqueous cells (Zn/HgO and Zn/Ag₂O) confirms the usefulness of this system as a power source for microelectronic devices. This was also substantiated by field tests.

Introduction

A number of lithium primary batteries have entered the consumer market in the last 15 years, showing excellent performance as power sources for electronic devices. A newcomer to this company is represented by the Li/Bi₂O₃ system recently developed by Varta [1] in the form of 35 and 45 mA h cells to be used mainly in quartz analogue watches. This system had received some attention as early as 1968 [2]. After that, however, neither patents nor reports appeared for some time. Perhaps, the 1.5 V of this couple were not judged sufficiently attractive by comparison with the 3 V offered by several other materials. In the middle 70s, however, the importance of power sources as alternatives to Zn/HgO and Zn/Ag₂O button cells was recognized and a research program on Li/Bi₂O₃ cells commenced in our laboratory at the beginning of 1976 [3]. In October 1976 a German patent

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was issued by Varta [4] on the same system. Japanese workers have also shown an interest in $B_{12}O_3$, either alone [5] or admixed with other materials [6, 7], as a cathode for L_1 cells.

The $L_1/B_{12}O_3$ couple has attractive features for use in button cells. The oxide can be reduced to the metal in the potential range $\sim 1.7 - \sim 1.2$ V, corresponding to gravimetric and volumetric capacities of 0.34 A h g^{-1} and 3.1 A h cm^{-3} , respectively. The latter value is of particular significance in primary cells and also stems from a very high density, 9.32 g cm^{-3} [8]. At the rates currently used in button cells for microelectronics, i.e., in the μA range, most of this theoretical capacity is delivered. This makes such cells potentially interchangeable with the 1.5 V aqueous button cells quoted above.

In our laboratory, some attention has been devoted to practical $L_1/B_{12}O_3$ cells of 50 - 200 mA h capacity. We have attempted further to improve the exploitation of the volumetric capacity of the oxide through a thermal treatment. Some results are reported in this paper.

Experimental

Most of this investigation was carried out on 100 mA h cells (diameter 11.4 mm, height 3.4 mm) corresponding to the R 42 IEC size designation. In Fig. 1 a "cutaway" cell shows the construction details. The can and the cell top were formed in a drawing die from a 0.25 mm stainless steel ribbon. A thin layer of graphite was pressed onto the can bottom to improve the contact with the cathode powder. The latter was either directly pressed in the can or shaped in a die. Some layers of separators (preferably of the glass wool type) were soaked with about $150 \mu l$ of an L_1ClO_4 -PC/DME solution. A 1.5 mm-thick L_1 disk was attached to the cell top through a stainless steel net. The total cell weight was 1.05 g.

Some 50 mA h, 11.4×2.0 mm cells (IEC designation: R 55) were also constructed on the same basis as the 100 mA h cells.

According to Varta [4], a proper cathode formulation can be achieved by mixing $B_{12}O_3$ with small amounts of Sb_2O_3 and graphite. Sb_2O_3 should lower the initial potential, but Bi powder may be used to the same end.

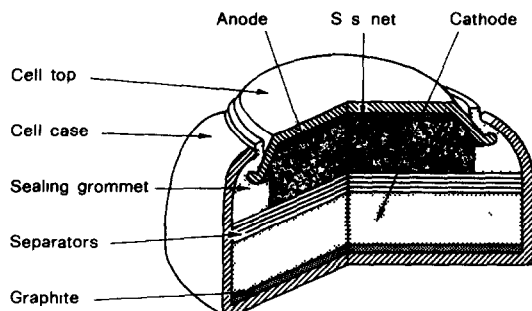


Fig 1 Cutaway view of a 100 mA h cell

In our previous investigation on $\text{Li}/\text{Bi}_2\text{O}_3$ [3], it was noticed that Bi produced during discharge provided the cathode with a satisfactory electronic conductivity, at least for loads below about $500 \mu\text{A cm}^{-2}$, *i.e.*, for many applications the cathode does not need initial additions of conductive diluents. This raises the possibility of heating Bi_2O_3 at 750°C to increase its powder density. Following an overnight stand at this temperature, the oxide showed a volume contraction of $\sim 15\%$, *i.e.*, the apparent density had increased from 6.4 to 7.4 g cm^{-3} . In some cases the treated powder was pelletized and the pellet sintered at the same temperature. Such pellets were thinner, and allowed more weight to be concentrated in the same volume, by comparison with pellets obtained from powder heated only once.

A few tests were also carried out following the addition of small amounts (1 - 3% by weight) of graphite and Teflon powder to thermally treated Bi_2O_3 .

The high initial voltage (above 2 V) does not constitute a problem because a short, high rate pre-discharge reduces it to $\sim 1.8 \text{ V}$.

During discharge, the cells expanded somewhat reaching 3.5 - 3.6 mm, the latter figure being the maximum height allowed for standard 100 mA h cells of this type.

Results and discussion

The cells described in this work are intended for operations at loads of 2 - 20 μA (the first figure typically pertains to analogue watches and the second to pocket calculators) with possible pulses of some hundreds of microamperes [1]. It became immediately apparent that $\text{Li}/\text{LiClO}_4\text{-PC} + \text{DME}/\text{Bi}_2\text{O}_3$ batteries could sustain continuous loads well above 100 μA throughout their operating life, as shown in Fig. 2 for 100 mA h cells. These cells still deliver 98 mA h at 500 μA .

The rationale for this behaviour may be found in the formation of Bi , which raises the electronic conductivity to a sufficient level. Similar rate capabilities have been reported for the $\text{Li}/\text{Pb}_2\text{Bi}_2\text{O}_5$ system developed by SAFT [9 - 11].

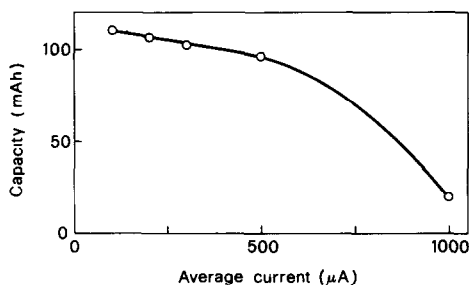


Fig 2 Capacity vs average current drain

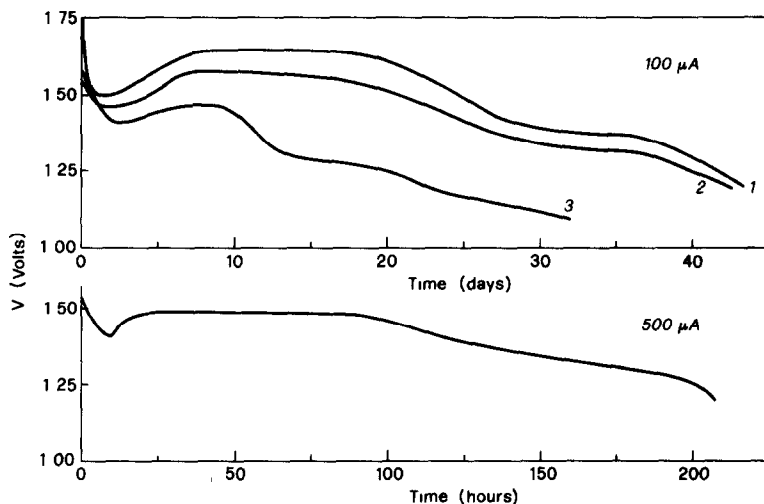


Fig 3 Discharge profiles of 100 mA h cells in various conditions 1, Fresh cell at room temperature, 2, after 1 year storage, 3, at -10°C

A direct comparison of the performances of these two batteries was made through literature data and the direct testing of some cells in our laboratory*. There is a close similarity in terms of capacity and load voltage between the two systems, as also found at SAFT for LP 1154 (11.6×5.4 mm) cells [12]. The $\text{Li}/\text{Bi}_2\text{O}_3$ cells of the present investigation, however, have a slightly smaller volume (0.347 versus 0.380 cm^3 for the 100 mA h cells); this enables them to reach somewhat higher energy densities. Taking as reference the discharges on loads of 3 and 15 $\text{k}\Omega$, one obtains the following energy outputs: 356 and 431 W h l^{-1} for the SAFT LP 1136 cell, and 398 and 454 W h l^{-1} for our equivalent cell.

If Li/FeS_2 cells (mainly developed by Union Carbide and Sanyo) are also compared, it is remarkable that a capacity of 100 mA h is obtained with larger cells (11.6×4.2 mm) [11, 13]. This corresponds to an energy of 325 W h l^{-1} on a 15 $\text{k}\Omega$ load [13]

A typical discharge curve for $\text{Li}/\text{Bi}_2\text{O}_3$ with a 3 $\text{k}\Omega$ load is shown in Fig. 3. The initial voltage delay is due to the higher cell resistance which exists before a sufficient amount of Bi is formed inside the cathode. In no case did this effect reduce the potential to below 1.4 V.

The rate capability of these cells was also compared with that of analogous aqueous systems, *i.e.*, a $\text{Zn}/\text{Ag}_2\text{O}$ cell (SR 42) and a Zn/HgO cell (MR 42). At 500 μA , 44 and 67 mA h, respectively, were obtained with these cells, as compared with 98 mA h for $\text{Li}/\text{Bi}_2\text{O}_3$.

*The $\text{Li}/\text{Pb}_2\text{Bi}_2\text{O}_5$ battery has now been withdrawn from the market for commercial reasons (source SAFT representatives in Italy)

At -10°C the performance is still acceptable, as shown in Fig. 3. At the cut-off of 1.1 V, 67 mA h were obtained (64% of the capacity at room temperature). The $\text{Li}/\text{Pb}_2\text{Bi}_2\text{O}_5$ system has a better performance than that of similar aqueous and nonaqueous button cells, *i.e.*, 80 mA h on a $5\text{ k}\Omega$ load and 1.2 V cut-off [11]. This seems to be connected with the higher potentials obtained by the use of additives in the cathode. Tests are now in progress with cathodes containing some graphite, we expect to see an improved capacity at low temperature as well as a better pulse capability at the end of discharge. Preliminary tests have supported this expectation.

Li/FeS_2 cells [13] at -10°C on $15\text{ k}\Omega$ discharge with potentials which are below 1.2 V for 80% of the discharge time. Such low potentials may be unsuitable for many applications. As for the aqueous cells, the two cited above were tested and gave, as expected, poor capacities (below 15 mA h).

The shelf life of $\text{Li}/\text{Bi}_2\text{O}_3$ cells is also satisfactory. As shown in Fig. 3, a 1 year storage (at room temperature) resulted in only a minor capacity loss.

The pulsing ability was evaluated in a cell discharged on $15\text{ k}\Omega$ and submitted every day to a single 30 s period of $500\text{ }\mu\text{A}$ (Fig. 4). The difference in potential between the curves decreases initially due to the formation of bismuth, and then increases again due to the higher total cell impedance associated with films of electrolyte decomposition products depositing on the electrodes and to changes in the cell geometry. In spite of the severe regime, potentials higher than 1.1 V were recorded for most of the battery life. However, the addition of conductive diluents has to be considered for heavier pulses.

The use of sintered Bi_2O_3 pellets must also be mentioned. The shrinkage produced by sintering (22% with respect to untreated Bi_2O_3) allows the use of more material and this, in turn, results in higher capacities: 120 - 130 mA h may be obtained with nominal 100 mA h cells. These pellets have a reduced porosity and were normally used after a 24 h stand in solution. Their initial rate capability, however, was not comparable with that afforded by a single heating of Bi_2O_3 , and currents greater than $\sim 200\text{ }\mu\text{A}$ produced too high a voltage drop. This effect tended to fade with discharge time and

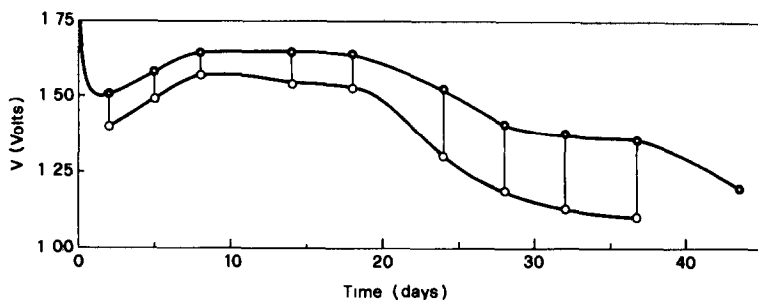


Fig. 4 Effect of current pulses on voltage. Background load $15\text{ k}\Omega$. Current pulse $\cdot 500\text{ }\mu\text{A}$ for 30 s (one per day)

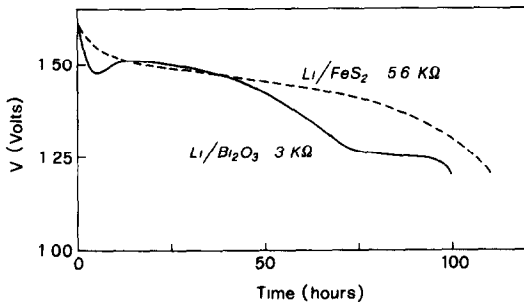


Fig 5 Comparison of 50 mA h cells Li/FeS_2 from ref 14

the 500 μA drain was again applicable. Overall, these cathodes appear to be useful at low, continuous currents, but not with heavy pulses.

Finally, some high rate tests were undertaken on 50 mA h cells. The discharge characteristics of similar Li/FeS_2 and $\text{Li}/\text{Bi}_2\text{O}_3$ cells are compared in Fig. 5. The first cell [14] delivered 28 mA h at $\sim 255 \mu\text{A}$ (200 W h l^{-1}), while 46.5 mA h were obtained from the second at $465 \mu\text{A}$ (320 W h l^{-1}). The last figure compares well with the 370 W h l^{-1} obtained at Varta with the 45 mA h battery (DR 926) at $270 \mu\text{A}$ [1].

Conclusions

$\text{Li}/\text{Bi}_2\text{O}_3$ button cells can advantageously replace aqueous cells as power sources for such electronic devices as analogue quartz watches and pocket calculators. The batteries referred to in this paper have been tested for these applications.

Long term storage tests, evaluation of the operating temperature range, and safety tests were not included in this initial programme. The evidence collected at Varta with smaller $\text{Li}/\text{Bi}_2\text{O}_3$ cells [1], however, is positive in this respect and may be extended to the 100 mA h cells reported here.

Work is now in progress to improve further the cell behaviour at low temperatures and at high continuous or pulse currents. This may be achieved by adding small amounts of additives (such as graphite, acetylene black or Bi powder) to the cathode and slightly modifying the cell geometry

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