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LITHIUM BATTERIES WITH VOLTAGE COMPATIBILITY WITH CONVENTIONAL SYSTEMS

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Summary

The possibility of using lead or lead–bismuth mixed oxides as positive materials in organic electrolyte lithium cells with a working voltage similar to those of conventional systems (1.5 V) has been considered. Performances and main characteristics of this new class of lithium batteries are described.

Introduction

Lithium organic electrolyte cells using metal oxides have recently recaptured attention as high energy power sources and as long life energy sources for memory maintenance and other low drain applications in the field of microelectronics [1, 2]. Most of these systems generally have a low working voltage (1.2 - 1.5 V) making them interchangeable with existing primary silver–zinc, mercury–zinc or zinc–manganese dioxide cells, allowing them to be used without the modification of existing equipment.

We have recently focused our attention on two lead compounds [3]: the red oxide, Pb_3O_4, and a mixed lead–bismuth oxide, $Bi_2Pb_2O_5$ [4], which have proven useful in miniature lithium cells for applications such as electric or electronic watches, pocket calculators and other portable electronic equipment. This paper summarizes recent research carried out on these systems.

Experimental

In order to establish the feasibility of the utility of the two selected compounds, Pb_3O_4 and $Bi_2Pb_2O_5$, as cathodic materials for lithium miniature cells, we chose the well-known "44" size cell (diameter 11.4 mm, height 5.4 mm) as a test device.

The materials used for the cathode were pure commercial product for Pb_3O_4, and a synthesized form for the mixed oxide $Bi_2Pb_2O_5$ was obtained

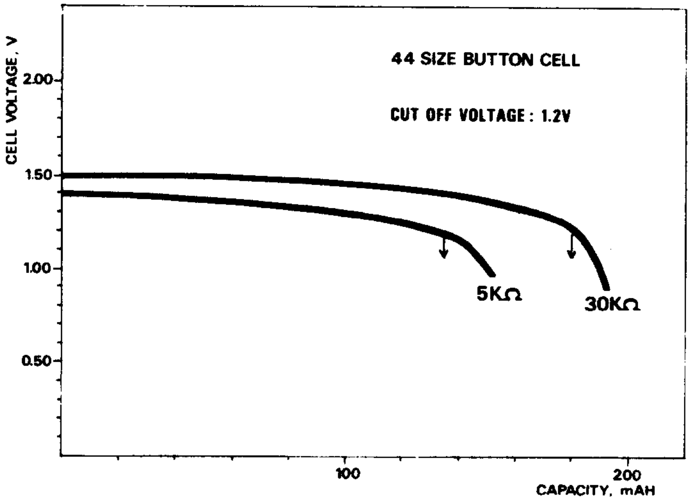

Fig. 1. Discharge curves of a 185 mA h Li–Pb_3O_4 cell.

at high temperature according to the binary diagram Bi_2O_3–PbO. To make the cathode, the selected compound was mixed with lead powder (which is used as an electronic conductor) and Teflon binder and then it was shaped into a pellet directly in the cell can by a cold pressing method. Button cells were built according to the detailed construction described in a previous paper [5].

The electrolyte contained 1,3-dioxolane and was 2M in $LiClO_4$. About 150 μl of electrolyte was found necessary for the cell size considered.

Results and discussion

Different loads were used for evaluation of the Li/Pb_3O_4 and Li/$Bi_2Pb_2O_5$ cell performance under conditions of continuous discharge at normal temperature. Typical discharge curves are shown in Figs. 1 and 2 for the 5 and 30 kΩ loads. A more complete comparison of the two systems under consideration was undertaken on the basis of total cell discharge characteristics. In Fig. 3 a semilog plot of cell capacity or average voltage to 1.2 V cut-off *versus* the corresponding average current obtained for cells discharged under various constant loads is shown. The cell capacity delivered by the cells was described in terms of performance parameters discussed by Selim and Bro [6] according to the following equation:

$$C = C_0 \frac{\tanh (i/i_0)^n}{(i/i_0)^n}$$

where C_0 = standard capacity (mA h), i = current drain (mA), i_0 = standard rate (mA), n = accomodation coefficient.

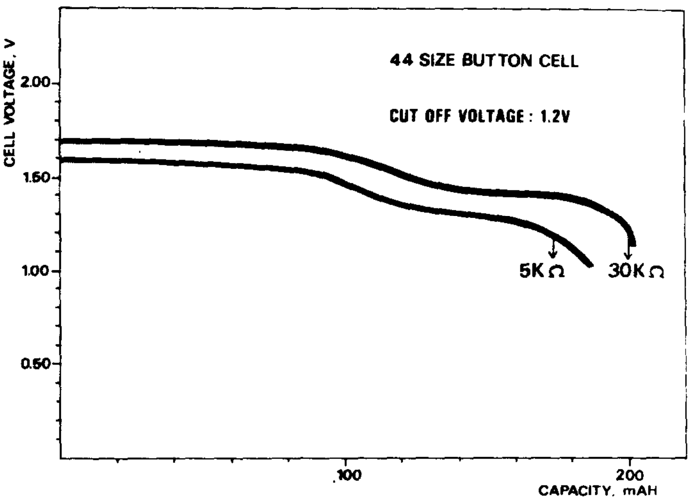

Fig. 2. Discharge curves of a 200 mA h Li–$Bi_2Pb_2O_5$ cell.

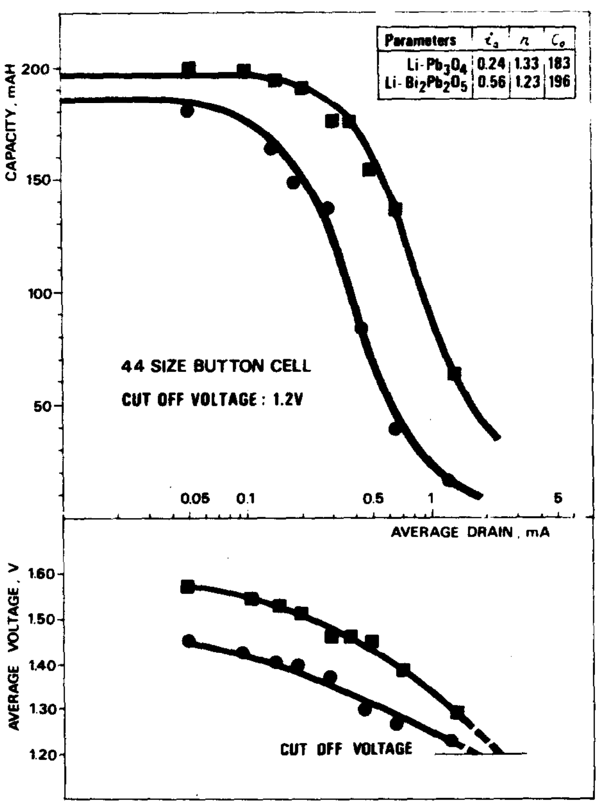

Fig. 3. General performances of Li–Pb_3O_4 and Li–$Bi_2Pb_2O_5$ cells. ●, Li–Pb_3O_4; ■, Li–$Bi_2Pb_2O_5$.

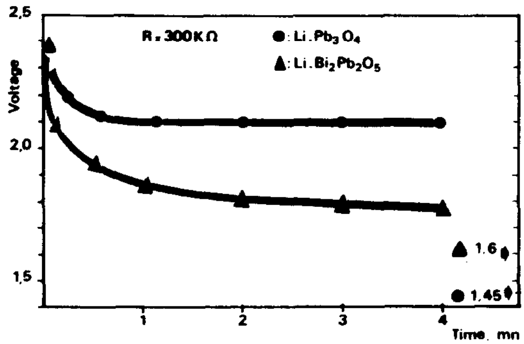

Fig. 4. Initial voltage–time profile for lithium–lead oxide button cells discharged at low drain, after 8 weeks storage at normal temperature. Average voltage for a complete discharge: ▲, $Bi_2Pb_2O_5$; ●, Pb_3O_4.

The standard capacity, C_0, represents the maximum capacity that can be delivered by the cell. At the standard rate ($i = i_0$) the capacity obtained is still 76% of the standard capacity. For $Li/Bi_2Pb_2O_5$ the standard rate is twice that of Li/Pb_3O_4; in addition, the standard capacity is slightly higher (196 mA h for $Li/Bi_2Pb_2O_5$ and 183 mA h for Li/Pb_3O_4). With silver–zinc cells of the same size, optimum capacity reaches comparable values at low drain (185 mA h under 30 kΩ load).

Some tests performed at very low drain (300 kΩ load) have shown initial voltage profiles as represented in Fig. 4, indicating that a voltage of 1.8 V is obtained after two minutes of operation when $Li/Bi_2Pb_2O_5$ is used instead of Li/Pb_3O_4. This finding is particularly important for applications needing a high voltage stability, especially at low drain, where most of the other lithium/oxide systems show initial voltage spikes or sloping plateaux in excess of 2 V.

Several storage tests have been undertaken at 60 °C for extended periods of time ranging from one to three months. For the two systems under consideration, a maximum loss of capacity of 5 - 6% was found after 3 months at 60 °C for cells discharged under 30 kΩ load, indicating a good storage ability for these systems.

Conclusions

The possibility of using lead or lead–bismuth mixed oxides as positive material in organic electrolyte–lithium cells with a working voltage similar to that of silver–zinc cells has been demonstrated. The properties of these non-silver systems, and more especially the $Li/Bi_2Pb_2O_5$ couple, make them more attractive taking in account the characteristics described.

Thus it is expected that these batteries will rapidly find useful applications in the near future.

References

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