

PRIMARY 1.5 V LITHIUM CELLS WITH BiVO_4 CATHODES

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Summary

Fergusonite, a monoclinic variety of bismuth orthovanadate, has been tested as a cathode in lithium cells. The reduction process, leading to the formation of Bi and Li_3VO_4 , corresponds to a potential of 1.6 V at 100 μA . Button cells, based on the Li/ BiVO_4 couple, have been built mainly in the IEC R 42 size (100 mA h) and have provided a volumetric energy density of 432 W h/l at 100 μA . This new material also features good capacity retention at low temperatures, under 500 μA pulses, and after storage.

Introduction

Oxides containing Bi^{3+} ions, such as Bi_2O_3 , $\text{Bi}_2\text{Pb}_2\text{O}_5$ and Bi_2CuO_4 , form couples with Li giving fairly high volumetric capacities at potentials near 1.5 V [1 - 5]. Commercial button cells based on the first two oxides have been produced by Varta [6] and SAFT [3], respectively.

1.5 V Li cells can replace analogous aqueous batteries, such as Zn-Ag₂O or Zn-HgO, with well-known advantages: longer shelf life, better low temperature performance, reduced environmental impact and, in some cases, better high current drain performance. While these advantages are shared by many 3 V and 1.5 V lithium systems, the latter allow a one-to-one replacement of aqueous cells without modifying the battery compartment; often a difficult task, especially in miniaturized devices.

This paper describes the evaluation of another Bi oxide, BiVO_4 , as a material for primary 1.5 V Li cells. To this end, after preliminary tests in laboratory cells, practical button cells were built and tested as reported for Li/ Bi_2O_3 cells [1].

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Experimental

Most of the cells used in this investigation had a capacity of 100 mA h (11.6×3.6 mm, R 42 IEC designation). Some 50 mA h and 180 mA h cells (11.6×2.0 mm and 11.6×5.4 mm, respectively) were also submitted to preliminary tests but these are not reported here.

A thin layer of graphite was pressed onto the bottom of the stainless steel case to improve the contact with the cathode pellet, which was directly shaped in the case at a pressure of 2 tons/cm². A few layers of glass wool separators, soaked with 150 μ l of a LiClO₄-PC/DME solution, were interposed between the cathode and the Li anode. The latter was made with a 1.5 mm thick disk pressed on a Ni net attached to the cell top. The overall cell weight was 1.08 g.

BiVO₄, fergusonite-type, was prepared by reacting stoichiometric amounts of Bi₂O₃ and V₂O₅ at 895 °C in the air, for 16 h. The V₂O₅ was obtained by heating NH₄VO₃ at 500 °C which gives rise to V₂O₅ with a higher surface area. The X-ray pattern of BiVO₄ so obtained matched the one reported for fergusonite [7].

A precipitation technique was also used for synthesizing BiVO₄ from mixed solutions of Na₃VO₄ and BiNO₃. The solid obtained was then washed and dried (at 110 °C). This material proved essentially amorphous under X-ray analysis, with a broad band around $2\theta = 28^\circ$. According to published information, a zircon-type variety of BiVO₄ should be formed in these conditions [7]. This form is converted into the fergusonite-type by heating at 500 °C [7] and, indeed, we observed the formation of fergusonite when heating the sample prepared by the precipitation technique.

The amorphous form of BiVO₄ did not show appreciable differences with respect to fergusonite when tested in Li cells. Therefore, as it also has a higher density (7.0 g/cm³) [7] the latter was used in this investigation.

Fergusonite-type BiVO₄ has a specific resistance of 3.9×10^7 ohm cm but button cells without conductive additives in the cathode were built. Metallic Bi formed during discharge (see 'Discussion') helped to maintain the resistance at sufficiently low levels.

Freshly prepared Li/BiVO₄ cells have a potential of 3 V. A short pre-discharge at the mA regime, however, reduced the voltage to 1.8 - 1.7 V without significantly affecting the overall capacity.

Results and discussion

In Fig. 1a the voltage-time curve at 100 μ A of a 100 mA h Li/BiVO₄ cell is shown. The curve profile bears a remarkable resemblance to that of analogous Li/Bi₂O₃ cells [1], thus hinting at a similar discharge mechanism, *i.e.* the formation of metallic Bi. A reduction reaction of the type



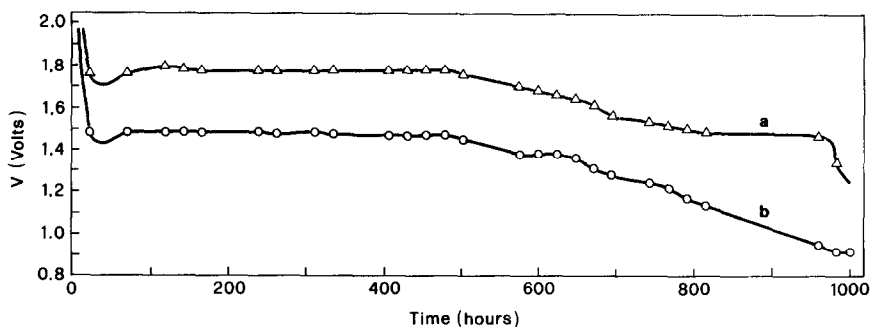


Fig. 1. Discharge at $100 \mu\text{A}$ (a); minimum voltage values measured when superimposing a $500 \mu\text{A}$ pulse of 100 ms (one per day) to the background current of $100 \mu\text{A}$ (b).

would correspond to a theoretical capacity of 0.25 A h per gram of active cathode material. This is, indeed, the recoverable capacity in cells discharged to a 1.2 V cut-off at low drains (or at medium drains when acetylene black is added to the cathode).

To further substantiate the above reaction scheme, X-ray analyses were carried out (Fig. 2). Whilst at intermediate discharge levels (*i.e.* $1.5 \text{ Li}^+/\text{mol}$ of BiVO_4) no appreciable change could be detected in the pattern of fergusonite (Fig. 2b), a 100% discharged cathode showed the onset of new peaks (Fig. 2c). This is more evident in the X-ray pattern of a cathode submitted to a few 'cycles' (Fig. 2d): the original peaks had almost entirely disappeared and the new peaks matched fairly well the most intense ones of metallic Bi.

On the basis of reaction (1), reversibility from Li/BiVO_4 cells is not expected. Li_3VO_4 formed during discharge has no stoichiometric range [8] and, therefore, cannot insert Li^+ . Discharged cells only showed a marginal rechargeability with a rapidly fading capacity. A similar behaviour was shown by $\text{Li}/\text{Bi}_2\text{O}_3$ cells [9].

The average potential at the $100 \mu\text{A}$ rate was 1.65 V , from which a volumetric energy density of 432 W h/l could be calculated for a 100 mA h cell. This value compares well with those of analogous Li cells of commercial interest (Table 1). Only Bi_2O_3 seems to show a better performance by virtue of its lower equivalent weight. The capability of sustaining current pulses superimposed on a drain of $100 \mu\text{A}$, was tested by submitting a cell to pulses of $500 \mu\text{A}$ for 100 ms (one per day). As shown in Fig. 1b, 80% of the capacity is still delivered under this regime before the potential drops to 1.2 V during a pulse. Preliminary measurements of the internal cell resistances by high frequency impedance tests gave values of $1.1 \times 10^2 \Omega$ and $1.3 \times 10^3 \Omega$ for fresh and fully discharged cells, respectively. Similar values have been reported for $\text{Li}/\text{Bi}_2\text{O}_3$ cells [6].

The capability of sustaining continuous high current drains is less satisfactory. At $160 \mu\text{A}$, 84% of the $100 \mu\text{A}$ capacity is obtained, and at $300 \mu\text{A}$ the value decreases to 55%. A better high current drain performance

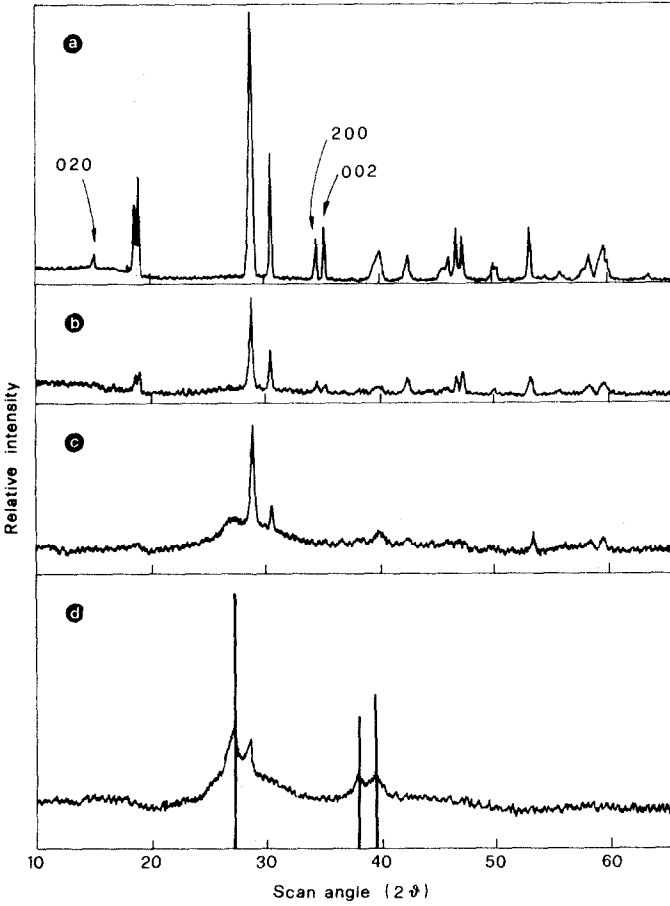


Fig. 2. X-ray diffractograms of BiVO_4 : (a) undischarged; (b) 50% discharged; (c) 100% discharged; (d) 'cycled'. In (d), the 3 main lines of Bi are also shown. In (c) the sensitivity was 3 times higher, and in (d) 6 times higher with respect to (a) and (b).

TABLE 1

Volumetric energy densities of some 100 mA h cells (at the 100 μA rate)^a

Cathode	Dimensions (mm)	Energy density (W h/l)
$\text{Bi}_2\text{Pb}_2\text{O}_5$	11.6 × 3.6	431
Bi_2O_3	11.6 × 3.4	454
FeS_2	11.6 × 4.2	325
FeS	11.6 × 3.6	350
CuO^b	11.6 × 4.2	390
BiVO_4	11.6 × 3.6	432

^aBased on the external cell dimensions assuming a perfectly cylindrical profile.

^b200 μA .

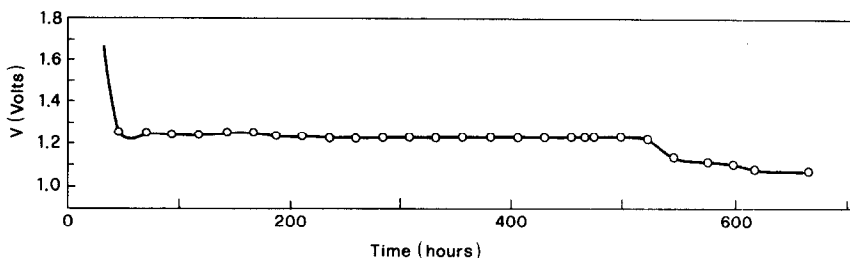


Fig. 3. Discharge profile at -10°C .

was shown by Bi_2O_3 [1] and $\text{Bi}_2\text{Pb}_2\text{O}_5$ [3]. The low-temperature behaviour was tested in an experiment at -10°C on a $15\text{ K}\Omega$ load (Fig. 3). To a 1.1 V cut-off, a capacity of 56 mA h was obtained with an average potential of 1.25 V. This performance is far superior to that of analogous $\text{Zn}/\text{Ag}_2\text{O}$ or Zn/HgO cells (showing capacities below 15 mA h) and approaches that provided by $\text{Li}/\text{Bi}_2\text{O}_3$ cells (64% of the room temperature capacity) [1].

Finally, an initial indication of the storage capability of these cells, was obtained after 6 months storage at room temperature. At the $100\ \mu\text{A}$ rate, a capacity loss of $\sim 1\%$ was measured.

Conclusion

The behaviour of fergusonite-type BiVO_4 as a cathode in Li cells confirms that pure or mixed Bi^{3+} -containing oxides can be of practical interest for 1.5 V primary batteries. Li/BiVO_4 button cells have been satisfactorily tested in analog watches and pocket calculators with a performance comparable to that of $\text{Li}/\text{Bi}_2\text{O}_3$ cells.

With respect to the latter oxide, BiVO_4 does not show advantages in terms of volumetric capacity or energy. It does, however, provide a more constant potential, especially when the cell is required to operate at current drains above $100\ \mu\text{A}$, at low temperature, and under current pulses. In particular the initial voltage delay (see Fig. 1) is shallower and shorter for Li/BiVO_4 cells. For selected applications, especially in the field of microelectronics, a steady potential may be an important pre-requisite.

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