

Scale-up of lithium rechargeable batteries

A.G. Ritchie ^{a,*}, C.O. Giwa ^a, J.C. Lee ^a, P. Bowles ^a, A. Gilmour ^b, J. Allan ^b

^a DERA, Haslar, Gosport, Hants PO12 2AG, UK

^b Lexcel Technology, Henley-on-Thames, Oxon. RG9 1LU, UK

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Abstract

Small-size lithium rechargeable cells in an envelope format were reported at the 20th International Power Sources Symposium [1,2]. This design offers the possibility of making cells using much lighter packing than cells with metal cans. The prismatic format allows good packing in rectangular boxes. Hence they offer the potential for high gravimetric and volumetric energy densities. The cells have now been developed to a size sufficient to form components of a large battery, built to power Army man-portable equipment. Lithium-ion cells have been manufactured using lithium cobalt oxide cathodes and other cathode materials are under investigation. Individual cells up to the 3 A h size have been successfully cycled, with further development possible. A 24 V battery has been constructed and its performance and prospects are described. Crown Copyright © 1999 Published by Elsevier Science S.A. All rights reserved.

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1. Introduction

Lithium-ion cells are widely available, particularly from Japanese suppliers, in small cell sizes (e.g., 18650). These cells were developed for the more critical civil applications, such as portable telephones or computers. For military use, larger sizes of cells are needed to make into batteries, for, e.g., man-portable equipment such as the 24 V, 5 A h size, presently available as a nickel/cadmium rechargeable, which weighs over 3 kg. For optimum packing, prismatic cells are needed. In order to minimise weight, a plastic packaging has been used, instead of the heavy metal cans used for most commercially available cells. Previous work [1,2] described the development of envelope cells. These were small cells of typically are 45 mm square, single-folded, with capacities around 150 mA h. This work describes the scale-up to cells of 1200 cm² with capacities around 3 A h. A 24 V battery has also been built. The earlier work described cells using lithium metal anodes. These are still used for materials testing, but the actual cells used for making a battery contain lithium-ion anodes, in line with most of the battery industry.

A preliminary presentation of this work was given at the 6th Ulm electrochemical conference (6UECT) and an abstract of this has been published [3].

2. Experimental

The electrochemical system used in the cells described here was lithium-ion/lithium cobalt oxide. The carbon anodes were made from graphite (KS44/SFG44 from Timcal, formerly Lonza), mixed with some carbon black (Super P, MMM). The carbon and graphite were mixed into a slurry with a solution of polyvinylidene fluoride binder (PVDF, Elf Atochem) in *N*-methyl pyrrolidinone (NMP). This anode mix was coated on to a copper backing foil using a home-made doctor blade coater. Sheets over a metre in length can be coated. The cathode active material was lithium cobalt oxide. This was used in preference to the lithium manganese oxide used earlier because of higher capacity and better cycling performance. Different cathode materials will continue to be investigated and possible materials are described in another paper [4,5]. Cells have been made using lithium cobalt oxide from various commercial sources.

Cathode sheets were coated in a similar way using LiCoO₂/carbon mixtures in a slurry of PVDF dissolved in

* Corresponding author

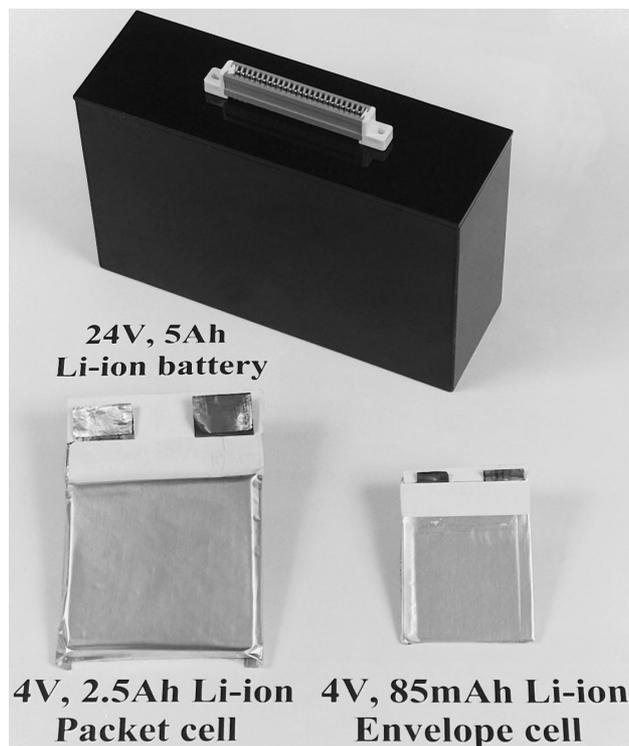


Fig. 1. An envelope and a packet cell, also a 24 V, 5 A h battery.

NMP. The electrolyte was ethylene carbonate (EC)/diethyl carbonate (DEC)/lithium hexafluorophosphate (LiPF_6 -Merck LP40).

Cells were made by coating the anode and cathode sheets, folding them with a Celgard separator between, packing the folded anode–separator–cathode package into an inner bag of polyester/Surllyn material (DuPont), adding the electrolyte, evacuating excess electrolyte and air, heat

sealing the inner bag, putting this into the outer polyester/aluminium/Surllyn bag and heat sealing. The evacuation process caused the packet cell to be flat (see Fig. 1). It was found that atmospheric pressure was sufficient to maintain contact between the electrodes and no external pressure was needed, as was the case for cells with metallic lithium anodes [1,2].

Cells with up to 20 folds have been made (1200 cm^2 active area). These 20-fold cells will be referred to as ‘packet’ cells, to distinguish them from the single fold ‘envelope’ cells described earlier.

Packet cells were charged and discharged using a commercial cycling unit (Bitrode). A two-step charging process was used in which constant current charging, usually at 0.5 A for a 20-fold packet cell, up to a voltage limit of 4.2 V, was followed by charging at constant voltage (4.2 V) until the current fell to a low level. Cells were discharged at 0.5 A to 2.5 V.

3. Results from the cycling of individual cells

Results from the cycling of 20-fold packet cells have been compared with cycling of materials in laboratory cells, as described earlier [1,2]. When normalised for the different cell areas, the results showed very similar performances (see Fig. 5. in Ref. [6]) so that scale-up has been successfully achieved and the cells cycle without the high pressure applied in laboratory cells.

Cells have been cycled at room temperature for over 250 cycles and are still on test. In agreement with the well-known characteristics of lithium-ion cells with cobalt cathodes, the capacity stability (cycle life) and the charge balance (charge in vs. charge out) are very good (see Fig.

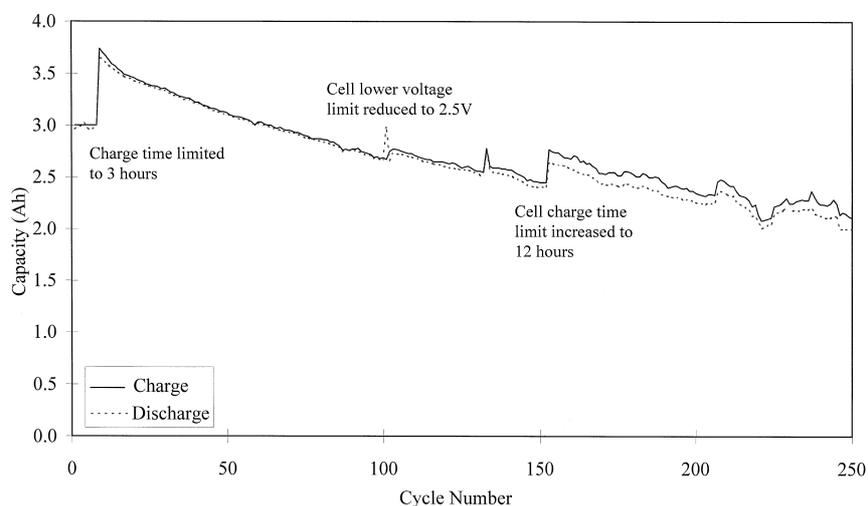


Fig. 2. Packet cell cycling performance at 0.5 A.

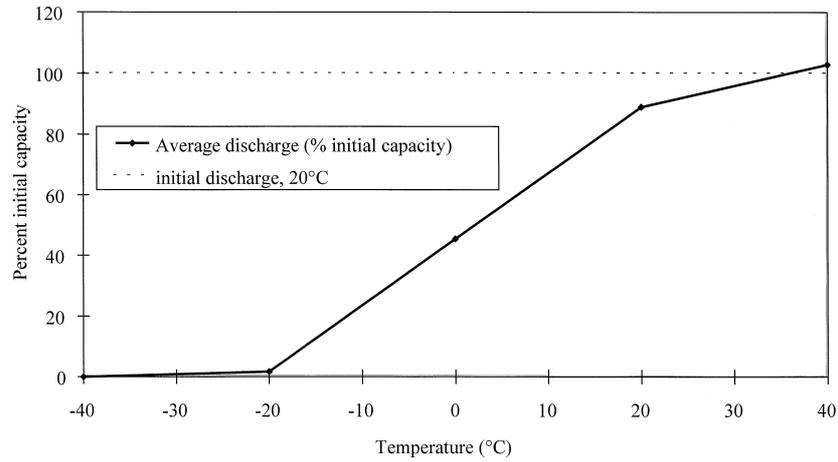


Fig. 3. Effect of temperature on the discharge of packet cells.

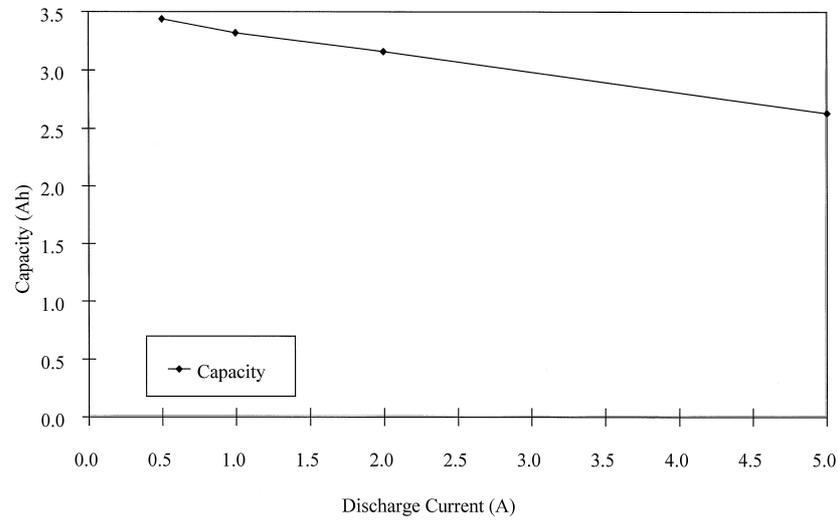


Fig. 4. Effect of discharge current on capacity at 20°C.

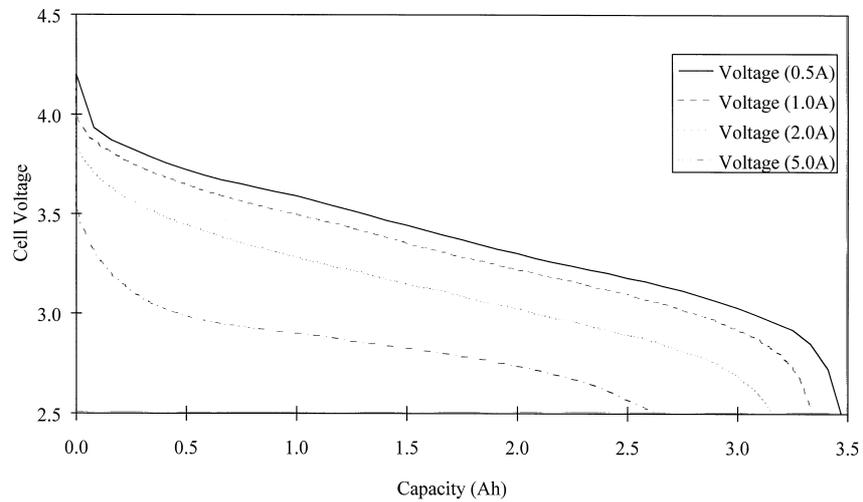


Fig. 5. Discharge voltages of packet cell at various rates.

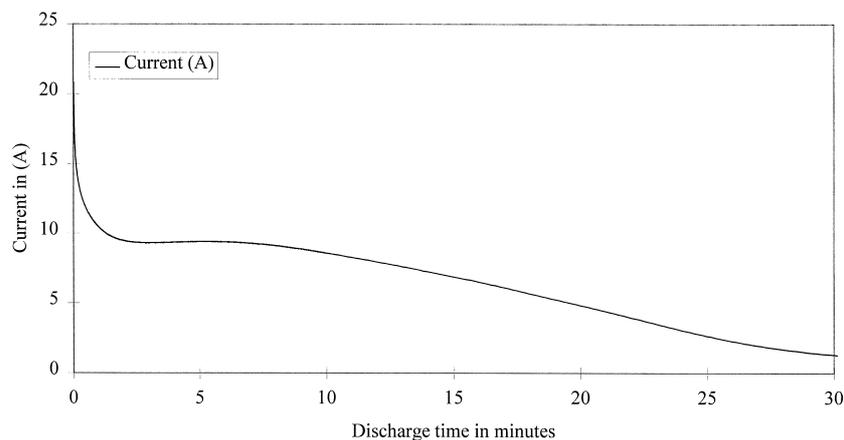


Fig. 6. Discharge of a packet cell giving maximum power output.

2). This indicates that the packet cell construction can achieve similar performances to those from spirally wound cylindrical cells.

The effect of temperature on cycling has been studied. A packet cell was cycled at -40 , -20 , 0 , 20 and 40°C . The discharge capacities are compared with the initial discharge capacity at 20°C in Fig. 3. It can be seen that the capacities at 20 and 40°C were similar, but only about half the capacity was obtained at 0°C with very little capacity being obtained at -40 or -20°C . This is probably due to the freezing of the EC/DEC/LiPF₆ electrolyte. An alternative electrolyte, EC/EMC (ethyl methyl carbonate)/LiPF₆, has been recommended for low temperature operation [7].

The packet cells showed good high-current performance (see Figs. 4 and 5), with good discharges at 5 A (4.17 mA cm^{-2}) which is relatively high for a lithium battery. The maximum power capability was measured by a constant

voltage discharge at 2.1 V , half of the open-circuit voltage at full-charge.

Fig. 6 shows this discharge, with an initial current of nearly 21 A (over 17 mA cm^{-2}), with a continuous discharge at 10 A or over for about 10 min . Hence, very high pulse currents are possible and give the cells a continuous high-power capability. The overall capacity was 3.2 A h , similar to that at constant current discharges, showing that the high-power discharge did not reduce the capacity.

The capacity loss on storage was measured. Two individual cells lost 17 and 23% capacity in over two months, i.e., about 10% per month, a value typical for lithium-ion cells. So, the packet cell construction does not show any increased capacity loss on storage in comparison with cylindrical cells.

A packet cell was stored at 85°C for 5 h in an air oven. No signs of leakage were seen. The open-circuit voltage

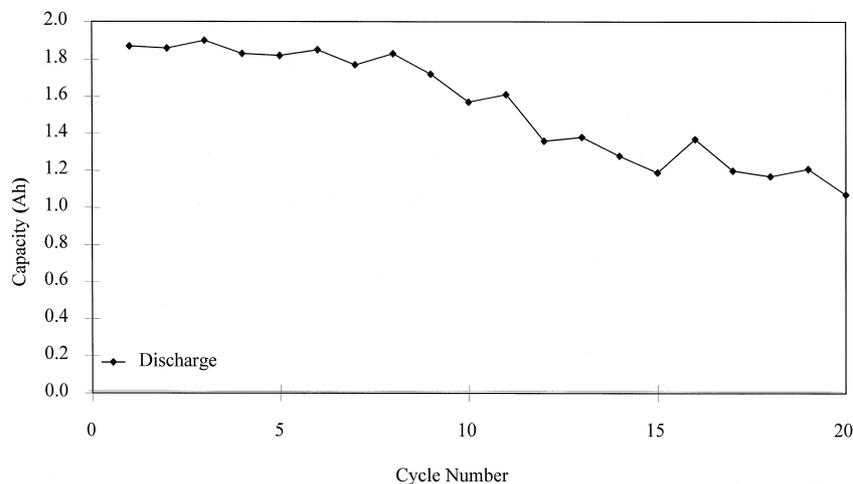


Fig. 7. Charge/discharge cycling (tapered charges to 4.2 V/cell , discharges at 0.5 A) of a 24-V , 2.5-A h , six-cell battery.

showed small and reproducible voltage changes, presumably according to the Nernst equation.

4. Results from cycling multi-cell batteries

Fig. 1 shows an individual 4 V, 2.5-A h packet cell, the configuration of a 24 V, 5 A h battery containing two parallel strings each with six of these packet cells and, for comparison, a 4 V, 85 mA h envelope cell. Following some preliminary charge/discharge cycling of the individual cells, a prototype 24 V, 2.5 A h battery, containing a single string of six packet cells, was treated as a complete unit using Bitrode cycling equipment which gave individual cell control. The battery had no internal electronic control of the voltages of the individual cells, so these were controlled through the Bitrode unit. The series string was charged at progressively lower currents from 0.5 down to 0.05 A with the charging voltage for each cell being limited to 4.2. When any one cell reached 4.2 V, the current was stepped down. This process was repeated until all cells had reached 4.2 V and the charging current was 0.05 A. The battery was discharged at 0.5 A until one cell fell to 3.0 V. Hence at the end of discharge, some cells had voltages considerably above 3.0 V and these had unused capacity. The cycling performance of the complete battery is illustrated in Fig. 7. It can be seen that the capacity was initially just under 2 A h but fell below 1.5 A h after 20 cycles. Examination of the charge capacities of the individ-

ual cells (Table 1) showed that some cells (particularly cell number 3) tended to undercharge. This indicates that for a multi-cell battery, it is important for all the cells to be balanced and for the charging conditions to be such that all cells are fully charged.

5. Future development

The battery design described here clearly has potential for further development. Optimisation is needed to increase the energy density. Several individually straightforward steps are needed: reduction in thickness of anode and cathode current collectors to reduce dead weight of metal; reduction in electrolyte quantity, increase in electrode capacities and more accurate balancing of anode and cathode capacities. With these planned improvements, but without radical changes in chemistry, cell energy densities of 140 W h kg⁻¹ are predicted, or about 110 W h kg⁻¹ for a full battery.

Apart from performance improvements, design improvements are needed to ensure safety. These include electronic battery management to control and monitor individual cell voltages and to monitor state-of-charge and battery temperature. In addition, further safety devices, such as fuses and positive temperature coefficient devices need to be included. An assessment of the ability of the battery to meet known safety standards, which have been described and compared previously [8], is also needed.

Table 1
Cell capacities within battery

Cycle no.	Charge (A h)						Total battery discharge capacity ^a (A h)
	Cell 1	Cell 2	Cell 3	Cell 4	Cell 5	Cell 6	
1	2.13	1.97	1.75	1.92	1.92	2.05	1.87
2	1.97	1.85	1.82	1.85	1.85	1.86	1.86
3	2.00	1.89	1.86	1.88	1.88	1.90	1.90
4	1.96	1.84	1.84	1.85	1.84	1.84	1.83
5	1.95	1.82	1.80	1.81	1.81	1.82	1.82
6	1.98	1.86	1.86	1.87	1.87	1.86	1.85
7	1.94	1.78	1.79	1.79	1.79	1.78	1.77
8	1.82	1.82	1.78	1.80	1.83	1.82	1.83
9	1.72	1.73	1.72	1.73	1.73	1.73	1.72
10	1.57	1.57	1.54	1.56	1.57	1.57	1.57
11	1.62	1.61	1.54	1.59	1.59	1.60	1.61
12	1.35	1.36	1.38	1.35	1.36	1.36	1.36
13	1.38	1.38	1.34	1.34	1.35	1.38	1.38
14	1.25	1.29	1.27	1.28	1.28	1.29	1.28
15	1.22	1.20	1.23	1.21	1.22	1.19	1.19
16	1.37	1.37	1.31	1.34	1.34	1.37	1.37
17	1.21	1.21	1.21	1.22	1.22	1.21	1.20
18	1.16	1.23	0.92	1.15	1.12	1.15	1.17
19	1.19	1.19	1.19	1.21	1.21	1.20	1.21
20	1.07	1.07	1.06	1.07	1.06	1.08	1.07

^aTotal battery discharge capacity = discharge capacity for each cell.

6. Conclusions

Lithium-ion cells in light-weight plastic packaging have been successfully scaled up from small (40 cm²) envelope cells to packet cells (1200 cm²) of a useful capacity (3 A h) for constructing large batteries. The packet cells have good cycle life, good charge efficiency, high power capability and good cycling performance down to 0°C, although an improved electrolyte would be needed for lower temperature operation. A 24 V battery has been constructed and cycled, though further development is needed.

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