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Short communication

Development of high energy density small flat spiral cells and battery pack based on lithium/carbon monofluoride (Li/CF_x)

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Abstract

Small spiral-wound lithium–carbon monofluoride (Li/CF_x) cells, which were discharged at the C/40 rate, had a nominal capacity of 300 mAh and a gravimetric energy density of about 464 Wh kg^{-1}. These cells delivered pulse current loads (>22 mA) with good capacity (>200 mAh) if they were subjected to a pre-discharge step. A 17 V, 2.2 kW battery based on Li/CF_x flat cell technology has also been fabricated and tested. The battery had gravimetric and volumetric energy densities of 360 Wh kg^{-1} and 700 Wh dm^{-3}, respectively. This compares with a value of 330 Wh kg^{-1} and 522 Wh dm^{-3} for an equivalent battery based on $Li/SOCl_2$.

Keywords: Lithium; Carbon monofluoride; Battery; Spiral-wound cells

1. Introduction

Li/CF_x primary cells are known to have the highest energy density of all lithium primary cells, with a theoretical energy density of 2180 Wh kg^{-1}, cf. 1470 Wh kg^{-1} for lithium/thionyl chloride or 1005 Wh kg^{-1} for lithium/manganese dioxide [1–3].

Li/CF_x primary cells are commercially available, e.g. in button cells [4–6], but are largely used for low rate applications, such as pagers, cameras, computer clock and memory back-up [5], gas meters [7], electronic and communications equipment.

QinetiQ has recently demonstrated [2,3] very high practical energy densities (up to 650 Wh kg^{-1}) with Li/CF_x chemistry when lightweight plastic packaging is used. Because of their high energy density, Li/CF_x cells have the potential to replace a number of in-service military batteries based on lithium thionyl chloride and lithium sulphur dioxide. Other applications that could potentially benefit from the superior performance of Li/CF_x packet cell technology include man-pack radios and communication devices, GPS and thermal imaging sights, which currently use primary batteries based upon other chemistries. The aim of the work described in this paper was to improve performance by combining a higher capacity with lightweight and/or small volume package. QinetiQ previously presented [1–3] test results for large flat Li/CF_x packet cells in sizes ranging from 4 to 50 Ah. This paper will describe the development and evaluation of small cells, large cell modules and a battery pack. In order to maximise capacity in small cells, a flat spiral-wound configuration was adopted. This invariably introduced a number of practical difficulties in adequately sealing the cells, which resulted in gassing and bulging and consequently a high cell resistance and poor performance. Once these difficulties had been overcome, the cells were tested for the effect of the following parameters on performance:

- capacity;
- rate;
- storage time and temperature;
- temperature.

The development of the large (>2 kWh) battery prototypes involved scaling from individual cells up to modules and the full battery pack in a number of steps, ensuring that the quality of the final product was maintained in the process. The battery pack prototype contained 42 cells, each with a nominal

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capacity of 25 Ah and connected in the 7P 6S configuration, i.e. six parallel strings (each string consisting of seven cells in parallel) connected in series. At an on-load voltage of 2.5 V per cell, the battery was expected to have a rated capacity of 2.5 kWh at a nominal voltage of 18 V.

The cells used for this battery were optimised for safety, which reduced the gravimetric energy density because of the use of excess electrolyte and inclusion of a copper gauze current collector.

2. Experimental

2.1. Design and construction

Two cell designs were adopted for this work namely, the flat spiral-wound and flat pack prismatic.

2.1.1. 25 Ah cells and boxed battery

The design and construction of single flat pack cells has been described in a previous publication [1–3]. The electrical assembly of the large battery pack occurred in two stages. Firstly, seven 25 Ah cells were connected in parallel to produce a single module or with a nominal capacity of 175 Ah and an open circuit voltage (OCV) of 3 V. The photograph of a module is shown in Fig. 1. A total of 42 cells were used in six modules. Each module weighed 770 g. Secondly the modules were positioned in the box and connected in series as shown in Fig. 2. The photograph of the complete battery pack, including the lid, is shown in Fig. 3. The OCV of the partially assembled pack was monitored during each stage of assembly and the complete battery had an OCV of ca. 18 V. Thermocouple wires were placed at strategic points in the battery to monitor temperature changes during discharge.

Fig. 2. Photograph showing module connection and configuration.

Fig. 1. Photograph of a 7-cell parallel string 175 Ah, 2.5 V module.

2.1.2. 300 mAh flat spiral-wound cells

The electrode layer configuration, arrangement and electrolyte used were as described previously [1–3]. However, instead of folding the electrode layers as in the flat pack design, they were wound in a jelly roll format. Wound electrode layers were then inserted in lightweight Surlyn laminate packaging, electrolyte was injected and the cells sealed under vacuum. A sealed cell is shown in Fig. 4. After overcoming the initial sealing difficulties these cells could be reproduced with a high level of confidence. The average weight, length, width and thickness of these cells were 1.55 g, 45 mm, 10 mm, and 5 mm, respectively. Electrical tests showed that the practical capacity of these cells varied from 200 to 300 mAh.

2.2. Cell and battery testing

2.2.1. Large battery

The battery was pulse-discharged according to a standard battery test specification. This involved applying a continuous background current of 2.5 A with a pulse of 5 A for a duration of 15 s every 6 h to a cut-off voltage of 10.4 V at 20 °C. The average discharge rate according to this pulse regime was 70 h (C/70).

Fig. 3. Battery pack complete with lid.

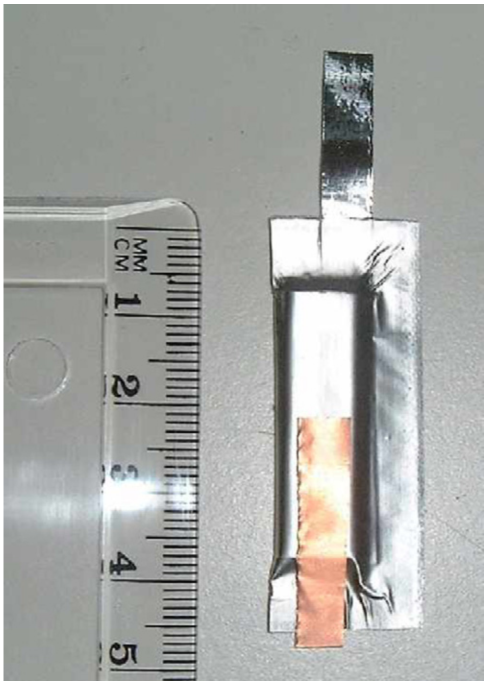

Fig. 4. Photograph showing the appearance and dimensions of a spiral-wound cell.

2.2.2. Small spiral-wound cells

The cells were discharged at constant current at the C/40 rate and according to the following continuous pulse regime:

- background current $i_b = 0.8$ mA,
- pulse current, $i_p = 22$ mA,
- pulse current duration = 1 s,
- background current duration = 1 s.

At a nominal capacity of 300 mAh per cell, this corresponds to an average discharge rate of C/26.3. CF_x is intrinsically a poor electronic conductor and as a result, Li/CF_x batteries are more suited to low rate discharge (<C/40) rather than pulse load applications. However, as a Li/CF_x cell is discharged the electronic conductivity of the CF_x cathode increases due to the formation of a conductive carbon matrix. This results in an increase in the rate capability of the CF_x cathode. Hence, it was possible to achieve the pulse load conditions specified above as long as the cells were pre-discharged. The pre-discharge step reduces the practical/useable capacity of the cells and it was conducted for as short a time as possible and the effect of pre-discharge currents and capacities on the rate performance and residual capacity of the cells was investigated. Other effects including storage time and temperature, discharge temperature, and different cathode current collectors on nominal capacity were also investigated.

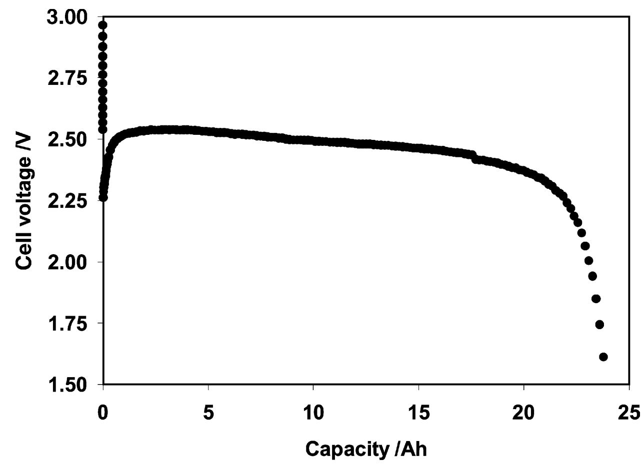

Fig. 5. Voltage–capacity plot for a 25 Ah cell discharged at the C/100 rate.

3. Results and discussions

3.1. Large battery tests

The battery was tested in three stages: single cells were tested followed by modules and finally the complete battery pack.

3.1.1. Single cell

Fig. 5 shows the voltage plot for the constant current discharge of a 25 Ah cell at the C/100 rate. The electrode utilisation for this cell was close to 95% thus giving a nominal capacity of 24 Ah. Table 1 shows the gravimetric and volumetric energy densities of this cell compared with those for a commercial DD cell based on lithium/thionyl chloride.

The gravimetric energy density for QinetiQ's packet cell (which was not fully optimised for specific energy) is nearly 16% higher than that for the DD lithium/thionyl chloride cells. These results are summarised in the table below.

3.1.2. Module

Fig. 6 shows the voltage plot for a 175 Ah module discharged at a constant current of 1.75 A (C/100) to a cut-off voltage of 1.0 V. The utilisation of the module was 94% giving a practical/useable capacity of 165 Ah. Based upon the weight of the module, this corresponds to a gravimetric energy density of 496 Wh kg^{-1}.

Table 1
Comparison of electrical parameters of Li/CF_x packet cells and boxed battery with commercial thionyl chloride ($SOCl_2$) systems

Cell chemistry/configuration	Nominal capacity (Ah)	Specific energy (Wh kg^{-1})	Energy density (Wh dm^{-3})	Energy density battery pack (Wh dm^{-3})	Cell packing efficiency (%)
Li/CF_x packet	24	545	817	700	94
$Li/SOCl_2$ cylinder	28	470	900	522	58

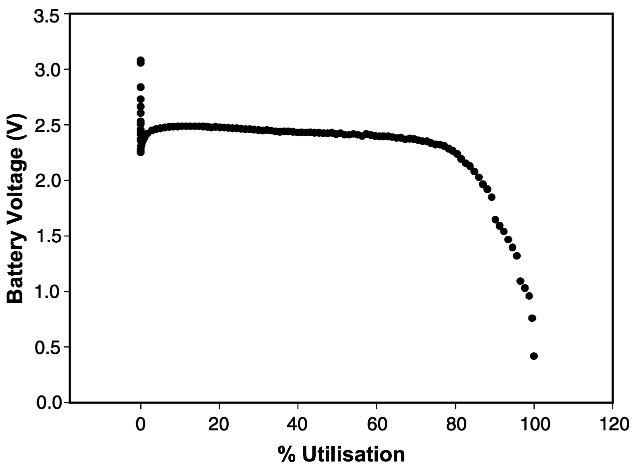

Fig. 6. Constant current discharge of a 7-cell, 2.5 V parallel string module at the C/100 rate.

3.1.3. Battery pack

The discharge plot for the battery pack is given in Fig. 7. The spikes on the discharge curve correspond to IR drop due to the current pulse. The rated capacity of the battery was 2.5 kWh but a practical value of 2.2 kWh was achieved. This corresponds to a utilisation of 88% and equates to a gravimetric energy density of 450 Wh kg^{-1} based on the cells and 360 Wh kg^{-1} based on the overall weight of the battery. This compares with a value of 330 Wh kg^{-1} for a similar battery based on 36 DD thionyl chloride cells. In addition, the much higher packing efficiency of QinetiQ's flat pack cells makes the volumetric energy density of the battery pack 36% higher than a similar battery containing DD thionyl chloride cells (Table 1).

The important points to note relating to the performance of the battery are:

- the flat discharge profile (an average voltage of 14.7 V);
- all cells were closely matched in terms of capacity;
- the discharge characteristics of the battery pack and single cells were similar;
- the cells were stored for up to 3 months prior to discharge without any significant capacity loss;
- no degradation, or bulging of cells was evident during discharge;
- the quick recovery of the battery after the pulse load;
- the temperature of the battery increased during discharge.

3.2. Flat spiral-wound cell tests

The spiral cells were subjected to two modes of discharge namely low rate constant current discharge and continuous pulse discharge.

3.2.1. Low rate discharge

Fig. 8 shows the discharge plot for a cell discharged to 1.5 V at the C/40 rate. The cell discharged at an average voltage of 2.4 V and the electrode utilisation was close to 100% thus giving a capacity of 300 mAh and a gravimetric energy density of 464 Wh kg^{-1}.

3.2.2. Pulse discharge

Fig. 9 shows the voltage profile for a cell pre-discharged at 14.1 mA for 1 h (inset) before being subjected to the pulse regime specified above. The pre-discharge capacity is 14.1 mAh thus resulting in a nominal capacity of 285.9 mAh for the cell. The discharge curve is diffuse but can be deconvoluted into two traces separated by the IR drop due to the pulse current load.

The higher voltage plot is due to the background current while the lower one is due to pulse current. The average IR drop during discharge is 50 mV but increases to over 100 mV towards the end of discharge. The total discharge duration is 63 519 s to 2.1 V. This corresponds to a useable capacity of 201 mAh (194 + 7 mAh) at an average voltage of 2.4 V to achieve a gravimetric energy density of 311 Wh kg^{-1}.

Fig. 10 shows the voltage profile for a cell subjected to the same pulse discharge conditions as above but following pre-

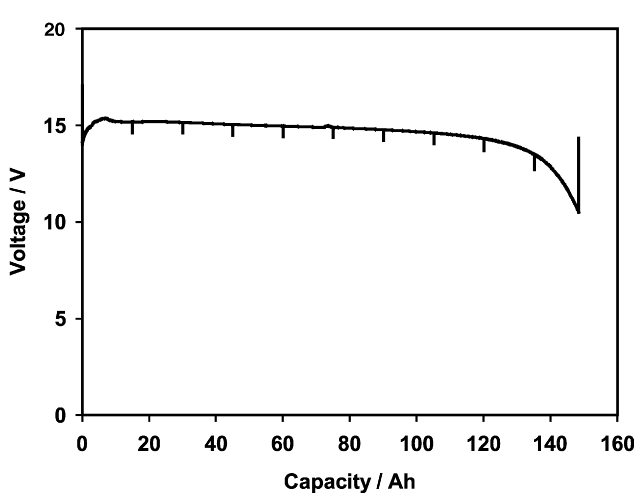

Fig. 7. Discharge curve for battery pack under pulse load conditions.

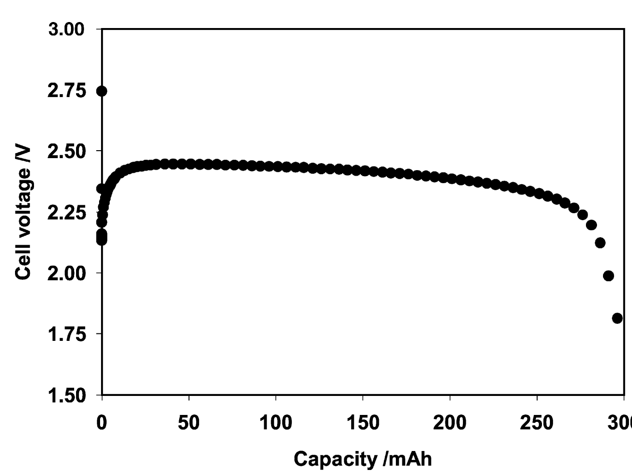

Fig. 8. Voltage–capacity plot for a small spiral-wound cell discharged at constant current at the C/40 rate.

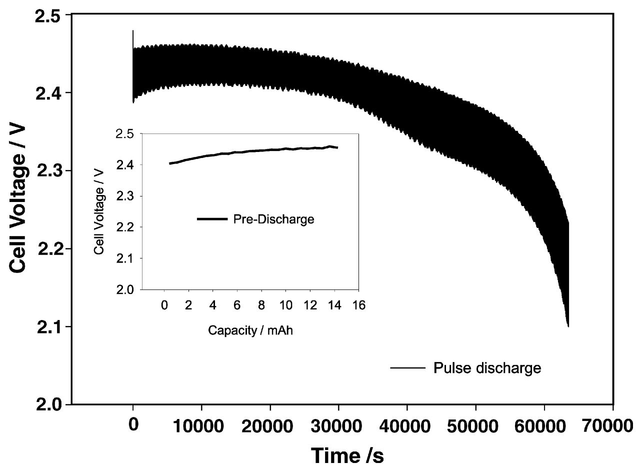

Fig. 9. Voltage–time profile for a spiral-wound cell subjected to pulse load conditions following pre-discharge by 14 mAh.

discharge for the longer duration of 2 h (inset). The features of the discharge curve are similar but in this case a capacity of 178 mAh was obtained. This suggests that pre-discharging the cell for longer durations has no beneficial effects on the performance of the cells.

3.2.3. *Effect of substrate*

In common with the battery industry, the standard cathode substrate used was aluminium foil. However, the foil is physically weak and it is not possible to spot-weld or solder to aluminium. Other substrates, notably nickel and titanium were investigated. Coherent cathode layers on titanium were successfully achieved, though it is not possible to solder to titanium so it is not the ideal substrate. Attempts to form coherent cathode coatings on nickel were unsuccessful, though further work should resolve this. A comparison between the two substrates, titanium and aluminium is shown in Fig. 11.

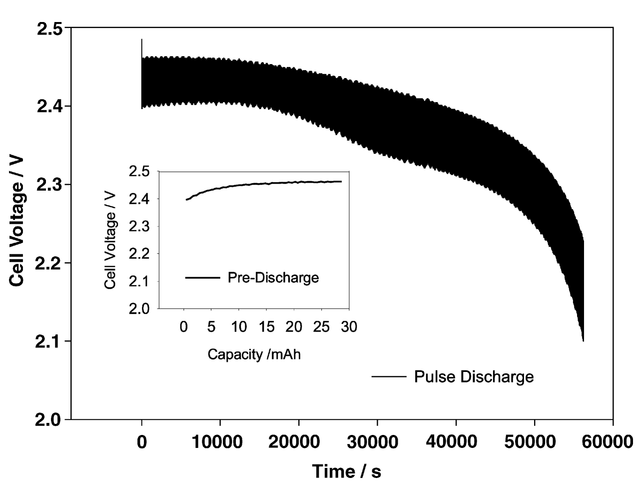

Fig. 10. Voltage–time profile for a spiral-wound cell subjected to pulse load conditions following pre-discharge by 28 mAh.

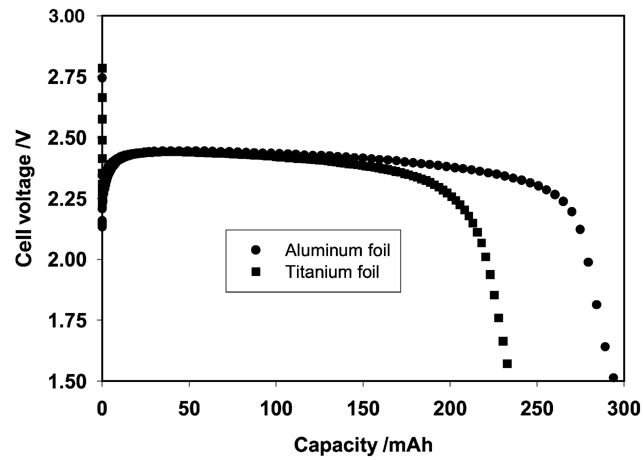

Fig. 11. Effect of cathode substrate/current collector on the performance of spiral-wound cells discharged at the C/40 rate.

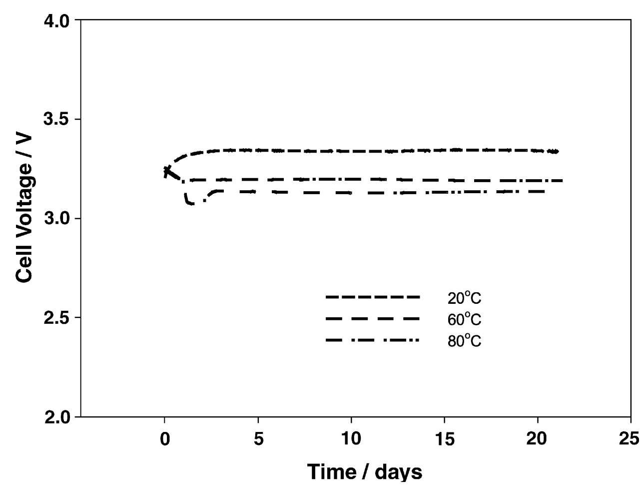

Fig. 12. Effect of time and temperature on OCV.

3.2.4. *Effect of storage temperature*

It is likely that the cells will be required to survive temperatures in excess of 50 °C. Therefore cells were stored at temperatures up to 80 °C and then discharged at room temperature to determine the effect of storage at these temperatures on capacity. The recorded OCVs against time are shown in Fig. 12 and the final discharge capacities are given in Table 2. The cells showed no visible signs of deterioration, and although the cell capacity is reduced at higher temperatures, it does not seem to cause a problem on subsequent discharge.

Table 2
Effect of storage temperature on capacity

Storage temperature (°C)	Discharge capacity (mAh)
80	152
60	171
25	198

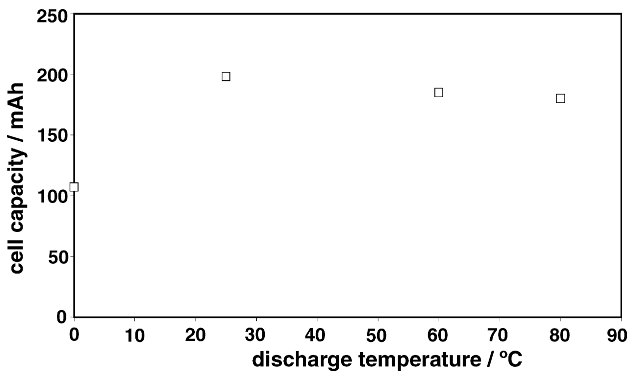

Fig. 13. Effect of temperature on discharge capacity.

3.2.5. Effect of discharge temperature

The cells were discharged at 0, 20, 60 and 80 °C. The effect of these temperatures on discharge capacity was determined, and is shown in Fig. 13. The cells lose 50% of their room temperature capacity at 0 °C. There are a number of steps, which can be taken to improve low temperature performance, such as increased quantities of carbon in the cathode substrate or changing electrolytes.

4. Conclusions

QinetiQ has demonstrated the feasibility of making large (>2 kWh) batteries from Li/CF_x packet cells and cell modules connected in the appropriate configuration. A 2.2 kW, 15 V battery, which consisted of 42, 25 Ah cells has been successfully built and tested and was found to have a gravimetric energy density of 360 Wh kg^{-1}. This compares with 330 Wh kg^{-1} for a battery of a similar size based on 36 DD thionyl chloride cells. On a volumetric basis, the energy density was 700 Wh dm^{-3}, which is 36% higher than the equivalent thionyl chloride system. QinetiQ has also developed small flat spiral/cylindrical cells (<300 mAh) with a high gravimetric energy density (>310 Wh kg^{-1}) and capable of medium rate performance following a pre-discharge step. There was no significant deterioration in cell performance between 0 and 80 °C or following storage at these temperatures for periods of up to 1 month. The prototype batteries and cells described in this paper are still not optimised, so further improvements in energy density of up to 20–30% are projected.

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