

Lithium-ion polymer cells for military applications

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Abstract

Defence R&D Canada (DRDC) is investigating lithium-ion polymer cells for possible future use in army communications and soldier systems, because of their high specific energy. Military operation requires good performance at -20°C but the standard commercial lithium-ion polymer cells yield only approximately 30% of their room temperature capacity at this temperature. The standard electrolyte is known to be poorly conducting at -20°C , so DRDC has been working with a Canadian company to produce a cell containing an electrolyte that gives good low temperature performance. Prototype cells have been built and cycled under various conditions. The performance of these cells and the standard cells is discussed.

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1. Introduction

Lithium-ion polymer cells are now in commercial production and their utilisation is likely to expand rapidly. Lithium-ion polymer batteries are a potential replacement for portable sealed nickel–cadmium batteries, which are in widespread use in communications equipment with the Canadian Forces (CF). Although sealed nickel–cadmium batteries are robust and reliable, their future production is in question because of the toxicity of cadmium. A Canadian company, ElectroVaya Inc. (previously known as Electrofuel Inc.) manufactures an 11 Ah (nominal) capacity lithium-ion polymer cell, which they market as lithium-ion SuperPolymer. The ElectroVaya cells are flat, with dimensions of $12.5\text{ cm} \times 9.5\text{ cm} \times 0.9\text{ cm}$ and they weigh 230 g. The electrode–electrolyte assembly is contained inside an aluminised plastic pouch. The cells are designed for use with laptop computers and are connected in series to make a flat, 16 V battery that fits underneath the computer. Only individual cells were used in the present work. The cells are rated for charging and discharging at 1.2 A, which is only about the $C/10$ rate. This low rate is mainly a consequence of the electrode materials being highly compacted and, therefore, not very porous. The solid polymer is gel type, with the electrolyte immobilised by pores in the polymer, so it is more conducting than a true solid-state

electrolyte. The production cells have a very high specific energy of around 210 Wh kg^{-1} and an energy density of 450 Wh dm^{-3} .

The cells use meso-carbon micro-beads as the negative electrode active material, on a copper foil substrate, plus lithium cobalt oxide for the positive electrode, on an aluminium substrate. Polyvinylidene fluoride is used as binder in the electrodes and the electrolyte gel is made using polyethylene oxide. The electrolyte is 1.0 M LiPF_6 in 1:1 ethylene carbonate (EC) + ethyl methyl carbonate (EMC), although older cells contained dimethyl carbonate (DMC) instead of EMC. EMC has a lower freezing point than DMC (-14°C cf. 3°C) and yields lower freezing point electrolytes. The electrolyte also contains 2% of a proprietary additive that is used to stabilise it. The recommended charging method is a constant current of 1.2 A to a limit of 4.2 V, followed by constant voltage charging until the current falls to 0.3 A. Discharging is recommended at 1.2 A to a cut-off voltage of 2.75 V. For cycle life studies, we define the life as the number of cycles until the capacity has fallen to 80% of the initial value. However, the cycling experiments carried out in this study were continued beyond 80% capacity in most cases, and the number of cycles to 60% capacity is reported for many of the cells. In practice, fresh cells were usually found to have capacities close to 12.0 Ah. The data presented in this report involve cells from several different batches, received over a 2-year period. The cell capacity data, plus the cycle lives, were variable between batches: this was because earlier samples of cells were

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hand-assembled in non-ideal conditions during a period when the company was in the process of building a new plant with automated assembly. The cells made at the new plant have proven to have higher capacity and longer cycle life, possibly because of lower moisture contamination.

2. Experimental

Cells that were received for studies were first weighed and their voltage and internal resistance measured. A milliohm-meter operating at 1 kHz was used for the latter. Cycling studies were carried out using an 8-channel Arbin BT2000 that has limits of ± 10 A and 40 V. Experiments at reduced temperatures were performed using a Thermotron S-8 environmental chamber. The majority of cell cycling was carried out at ambient room temperature, so any small perturbations to the capacity during cycling may be attributable to changes in the room temperature. Infrared spectra of gasses were measured in a 10 cm path length cell using a Perkin-Elmer 2000 spectrometer.

3. Cell cycling results

3.1. Standard production cells

3.1.1. Cycling limits

Cells were normally cycled using the manufacturer's recommended rate and limits (1.2 A discharging to 2.75 and 1.2 A charging to 4.2 V, then constant 4.2 V to 0.3 A). The older hand-assembled cells were found to have specific energies in the range of 190–200 Wh kg⁻¹, whilst the automated production cells (January 2002 onwards) have been in the range of 204–214 Wh kg⁻¹. The automated production cells have yielded cycle lives (to 80% of initial capacity) in the region of 250–350 cycles, for full discharges to 2.75 V. The capacity tended to fall away faster after 200–300 cycles as degradation increased. Fig. 1A shows the cycle life data of a typical cell from the automated production line, which was cycled only at room temperature, using the recommended parameters. Because there is the possibility that electrolyte degradation may proceed at a low level at 4.2 V, two cells were cycled using a charging limit of 4.1 V, instead

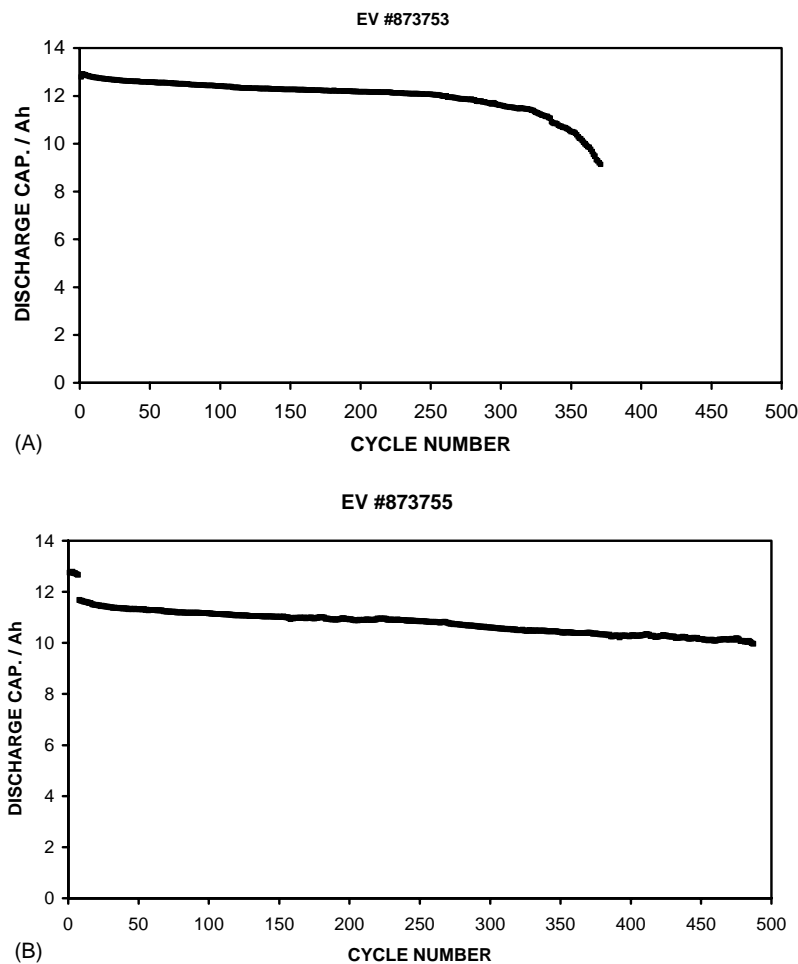


Fig. 1. Comparison of the cycle lives of standard cells cycled at room temperature using 1.2 A. (A) The charging limit was 4.2 V. (B) The charging limit was reduced to 4.1 V after the first seven cycles.

of 4.2 V. Fig. 1B shows the cycle life data for one of those cells. Note that the cell was charged to 4.2 V during the first seven cycles, in order to establish its capacity, before lowering the limit to 4.1 V. For these cells, the available capacity was 8% lower than at 4.2 V, but the cycle life was extended to over 500 cycles (the cells are still cycling) in terms of an end-of-life of 80% of the initial capacity obtained from charging to 4.1 V. In terms of the capacity obtained from charging to the 4.2 V limit, the cell in Fig. 1B yielded 438 cycles to 80% capacity, which translates to approximately 10% more total lifetime capacity than the cell in Fig. 1A that was charged to 4.2 V. Therefore, from the limited number of samples studied, it appears that the total number of ampere-hours that can be extracted from the cells during their lifetime is higher for cells charged to only 4.1 V.

Some other variations on the constant voltage portion of the charging were also investigated for charging at room temperature, such as charging at 4.2 V until the current fell to 0.1 A and also for 6 h at 4.2 V. There was no apparent change in the capacity fade rate from using such extended charging and, because the extra discharge capacity obtained was marginal, the company recommended cut-off of 4.2 V and 0.3 A was maintained.

3.1.2. Low temperature discharging

Most of the cells used in this work were not cycled continuously at room temperature but were subjected to occasional discharges at reduced temperatures, at higher currents, or using pulsed currents. Although the ElectroVaya cells are only recommended for discharging at 1.2 A, it was found that they could be discharged at 2.5 A at room temperature with only a 3% loss in capacity. Fig. 2 shows a cell that was nominally cycling at room temperature using 1.2 A, but was also subjected to discharging at higher currents and lower temperatures. Using a current of 2.5 A, the capacity dropped to 82% at -10°C and to 13% at -20°C (recharging was

carried out at room temperature). With 1.2 A, the capacity dropped to 34% at -20°C . Following these low temperature discharges the cell capacity recovered to close to the previous room temperature value, with a 2% irreversible loss of capacity. Similar behaviour was also seen with other cells, although the available capacity at -20°C and 1.2 A varied significantly, between 20 and 45%. Fig. 3 compares the voltage profiles of a cell discharged using 1.2 A at temperatures of 22, 0 and -20°C ; in this case there was a reduction in capacity compared with room temperature to 92% at 0°C and to 43% at -20°C . Therefore, the standard cells appear to be unsuitable for the low temperature applications that are commonplace in the Canadian military.

3.1.3. Pulsed discharging

Although the standard cells were not expected to be suitable for repeated discharging at continuous currents of 2.5 A and higher, the cells were tested for pulsed 2.5 A. High, pulsed currents are encountered in communications radio operation during transmission (TX). Much smaller currents are needed for reception (RX) and, for some radios, standby mode. Fig. 4 compares the discharge curves obtained at 22, -10 and -20°C using a duty cycle of 2.5 A for 10 s TX: 0.33 A for 200 s RX. There is very little difference between the voltage profiles at 22 and -10°C and the capacity remained the same, whilst there is a large difference between -10 and -20°C ; in particular a large increase in cell polarization during the 2.5 A pulses. Nevertheless, the fall in capacity between 22 and -20°C , to 65%, is smaller for pulse discharging than for constant current discharging (20–45%), showing that further capacity is available if the cells are given time to recover from the higher current pulses. The experiments were repeated using double the current values: 5 A TX and 0.66 A RX. This did not affect the capacity at 22°C , but lowered the capacity to 95% at -10°C and to only 10% at -20°C . Therefore, the cells are capable of pulses

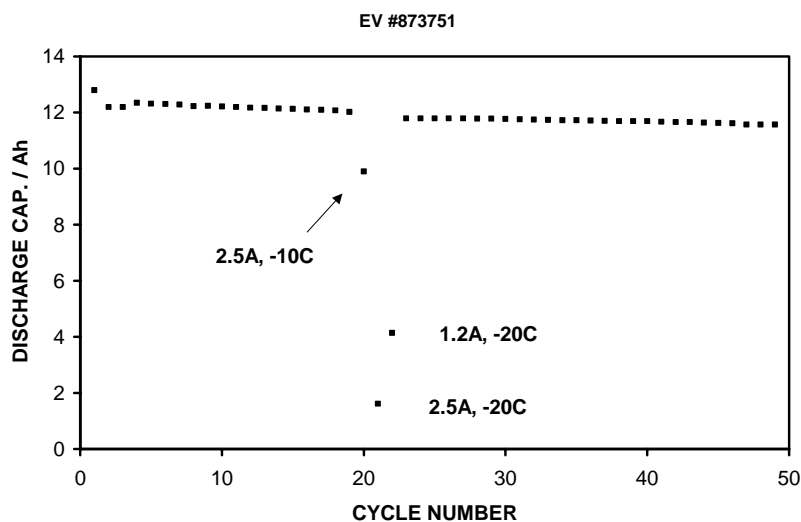


Fig. 2. Discharge capacity data for a standard cell being cycled nominally at room temperature using 1.2 A. The data show that the capacity is much reduced at -20°C , especially at 2.5 A (the recommended discharge current is 1.2 A).

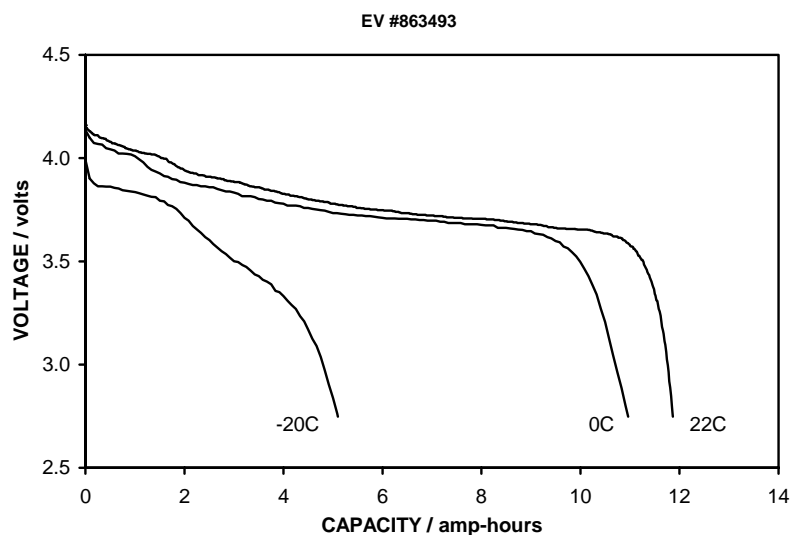


Fig. 3. A comparison of the discharge curves obtained from a standard cell at room temperature, 0 and -20°C , using 1.2 A.

at the $C/2.5$ rate (5 A) down to -10°C . The same cell was used for all of these pulse-discharge experiments and this cell still had a cycle life of 250 cycles to 80% of capacity; therefore, the small number of high current discharges that the cell was subjected to did not lead to an obvious drop in cycle life.

3.1.4. Higher rate discharging

Although there was no apparent immediate effect on these lithium-ion polymer cells from using a higher discharge current than the recommended value of 1.2 A, it was decided to discharge one cell at 2.4 V repeatedly, while still recharging at 1.2 A. The cell was first cycled at room temperature using 1.2 A, then switched to 2.4 A discharging after 60 cycles. The cell heated up by 5°C during discharging and there was a 1.5% drop in capacity, but the capacity fade rate remained the same. After 50 of these 2.4 A discharges, the fade rate began to increase and it was noticed that the plastic pouch had swelled due to the formation of gas inside the cell. A sample of the gas was extracted from the cell using a syringe and analysed by infrared spectroscopy (which only detects molecules that generate a change in dipole moment during a vibration, so will not detect homonuclear diatomics such as hydrogen). The dominant bands in the spectrum were identified as arising from EMC and CO_2 , plus there were weak bands from CH_4 and CO, see Fig. 5. The spectrum cannot be fully interpreted without a detailed quantitative study of the various components, which has not been done at this time. However, the presence of CO_2 , CO and CH_4 indicates that decomposition of EMC has taken place. Ethane should also be a decomposition product of EMC, but the infrared bands of this species would have been obscured by those of EMC, unlike those of methane, which have widely spaced rotational fine structure that stand out over the broader bands of EMC.

Such decomposition products have been reported by other workers [1] but from electrolyte decomposition that was a

consequence of cell overcharging and thermal runaway. In the present case, the formation of gas was apparently due to using a higher than recommended current during discharging. However, further discharge studies are required in this area before any definite conclusions can be reached.

3.2. Low temperature cells

3.2.1. First batch of cells

Because the standard cells manufactured by Electrovaya do not have an electrolyte that is optimised for low temperature operation, work was initiated to develop one. Several groups have reported on the use of various tertiary and quaternary mixtures of solvents in electrolytes for the low temperature operation of lithium-ion batteries. These mixtures usually employ LiPF_6 in different cyclic and aliphatic (symmetric and asymmetric) alkyl carbonates [2–5]. Ethyl methyl carbonate has been reported to be particularly useful because it can be used to make very low freezing point electrolytes (-55°C) that have good conductivity. Electrovaya consequently developed a low temperature electrolyte and delivered four 11 Ah (nominal capacity) cells to DRDC for study. These cells were hand-assembled in their old facility. The electrolyte used was 1.2 M LiPF_6 in 1:1:1 EC + EMC + diethyl carbonate (DEC), along with 2% of a proprietary additive to stabilise the electrolyte. All four cells were first cycled at room temperature using 1.2 A and yielded between 12.0 and 12.1 Ah. The second discharges were carried out at -20°C : two cells were discharged at 1.2 A and yielded 77 and 82% of their room temperature values. This was a big improvement over the 20–45% obtained from the standard cells. The other two cells were discharged at 2.5 A at -20°C and yielded 49 and 55% of the room temperature capacity. All of the cells had 2–3% less capacity on subsequent room temperature discharges. Two of the four cells were left to cycle to the 80% end-of-life at room temperature only (one each of the cells that had been discharged at

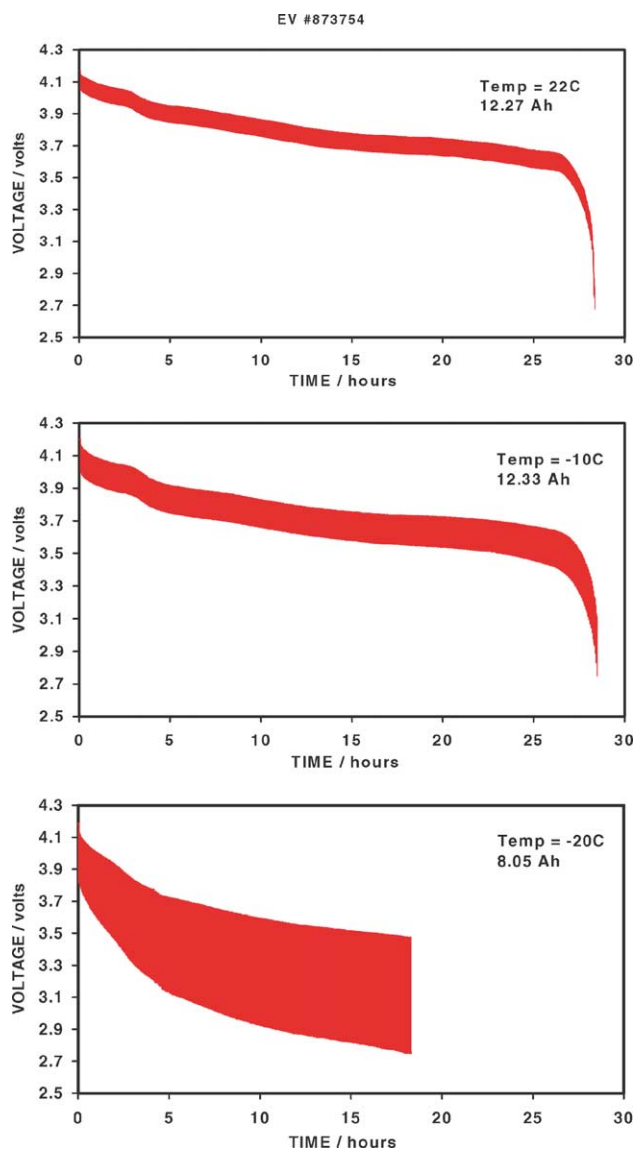


Fig. 4. A comparison of the pulse discharge data for a standard cell being discharged at room temperature, -0 and -20°C . The duty cycle was 2.5 A for 10 s (TX) and 0.33 A for 200 s (RX), to simulate a communications radio.

1.2 and 2.4 A at -20°C), while the other two were cycled at room temperature, with intermittent discharging and full cycles at lower temperatures.

The two cells that were left to cycle only at room temperature completed 204/240 cycles to 80% capacity and 405/460 cycles to 60% capacity. After the 80% end-of-life, the cells were discharged at $-20^{\circ}\text{C}/1.2$ A and yielded 53 and 60% of their capacity at room temperature; this compares with 77% achieved on the second cycle for one of the cells (the other was discharged at 2.4 A so it cannot be compared), so it would appear that the low temperature performance may be degrading at a faster rate than that at room temperature. This would be expected where degradation leads to higher resistance at the electrode–electrolyte interface and also between electroactive particles in the electrode. Two complete

cycles were also performed at -20°C and the cells yielded 36 and 43% capacity, so the cells were still amenable to low temperature cycling after 250 cycles. The cycle life of the cells is shown in Fig. 6, where it can be seen that the cells took two cycles at room temperature to recover from the low temperature cycling. It should be noted that the low temperature cycling did not lead to an increase in the capacity fade rate. The fade rate was the same for both cells over the first 175 cycles (0.07% per cycle) but then quadrupled for one of the cells for about 50 cycles, before slowing down again. The second cell had an accelerated fade rate only after 350 cycles. The origins of this increased fade rate have not yet been investigated.

The other two low temperature cells were subjected to much more extensive low temperature cycling. The first 40 cycles were performed mainly at room temperature using 1.2 A, with discharges intermittently carried out at -25°C (61 and 66% capacity), -30°C (34 and 37%) and -40°C (3 and 3%). Therefore, the cells still had significant capacity available at -30°C . Fig. 7 compares the discharge curves at five different temperatures and it can be seen that the running voltage is quite depressed at temperatures below -20°C . Fig. 8 shows the cycle life data of the two cells: four complete cycles were performed at -20°C beginning around cycle 40. In Fig. 8A, the first complete cycle at -20°C yielded 53% capacity but, on the two subsequent cycles, this value actually increased, first to 60% then to 66%. Similar behaviour was observed for the other cell and it is interesting that the capacity should rise in this manner. There was no decrease in the cell internal resistance during this period and the reasons for the increase in capacity are not understood. Following 10 more cycles at room temperature, the cells were then subjected to 15 further cycles at -20°C . One cell had 7.18 Ah on its first full cycle at -20°C , which declined to 6.52 Ah over the 15-cycle period (9% drop), while the other cell went from 7.61 to 5.74 Ah (a 25% drop). In spite of this variation between the two cells, it is considered that the low temperature cycling performance is good for a solid polymer cell. Upon returning to room temperature cycling, it was found that the cell in Fig. 8B had irreversibly lost 16% capacity (relative to its previous room temperature cycle) and its capacity fade rate was now much higher. The other cell had lost 7% of capacity and its fade rate was only slightly increased. Following 10 more cycles at room temperature, further cycling was carried out at -20°C , which resulted in the same trends in capacity fade for the two cells. The cell in Fig. 8A was relatively stable at -20°C for 14 cycles but then had an increased fade rate at room temperature. This cell delivered 108 cycles to 80% capacity and 176 cycles to 60%, so the prolonged low temperature cycling had apparently led to a reduction in cycle life (the two cells that were cycled only at room temperature yielded over 200 cycles to 80% capacity). The cell in Fig. 8B continued to lose capacity at a high rate and yielded approximately 65 cycles to 80% and approximately 90 cycles to 60% capacity. It appears that cycling at -20°C may

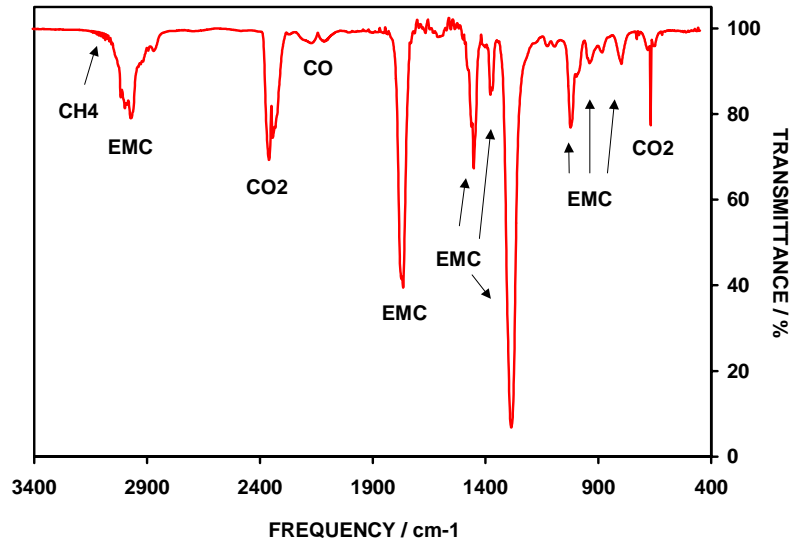


Fig. 5. Infrared spectrum of gas extracted from a cell that had been repeatedly discharged at 2.4 A.

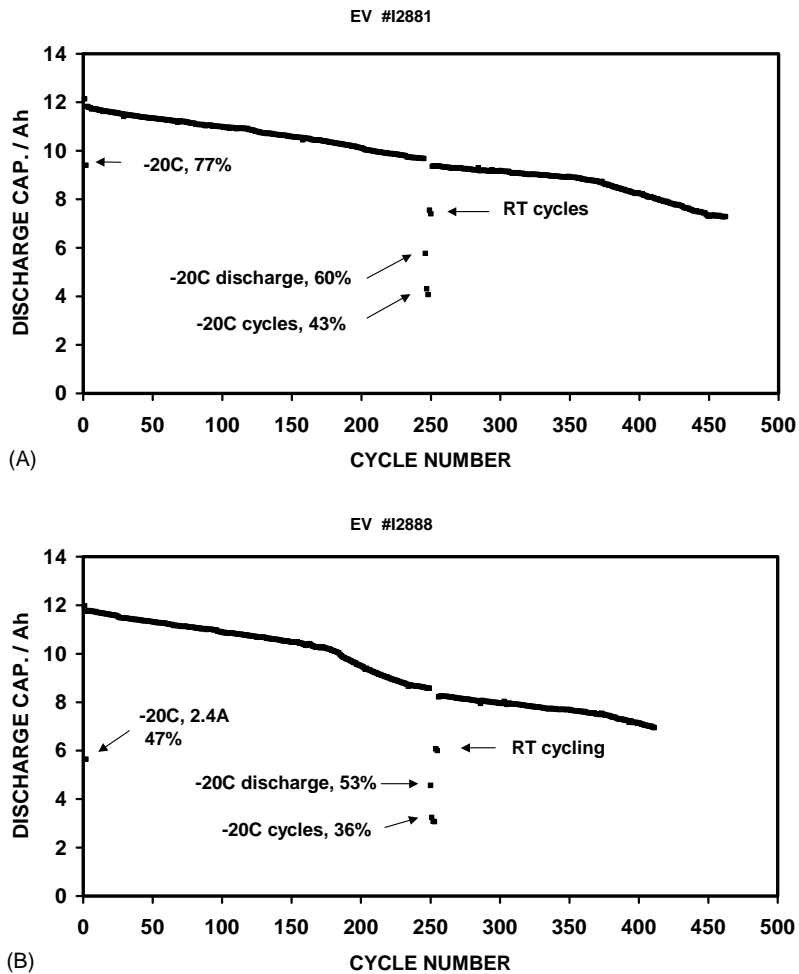


Fig. 6. Cycle life data from the first batch of low temperature cells (RT: room temperature). All discharges are at 1.2 A unless otherwise stated.

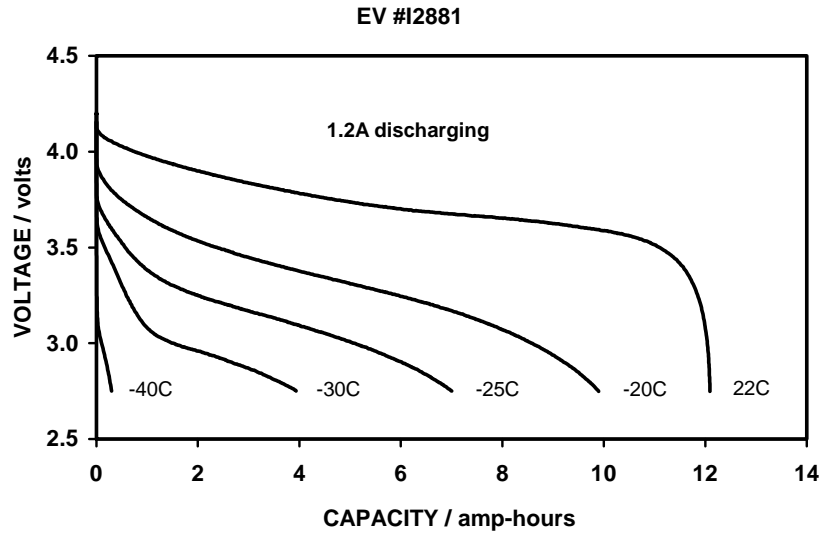
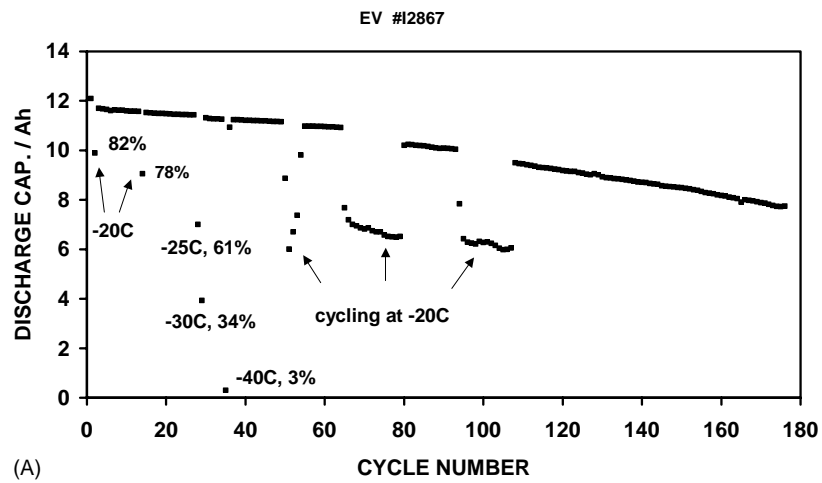
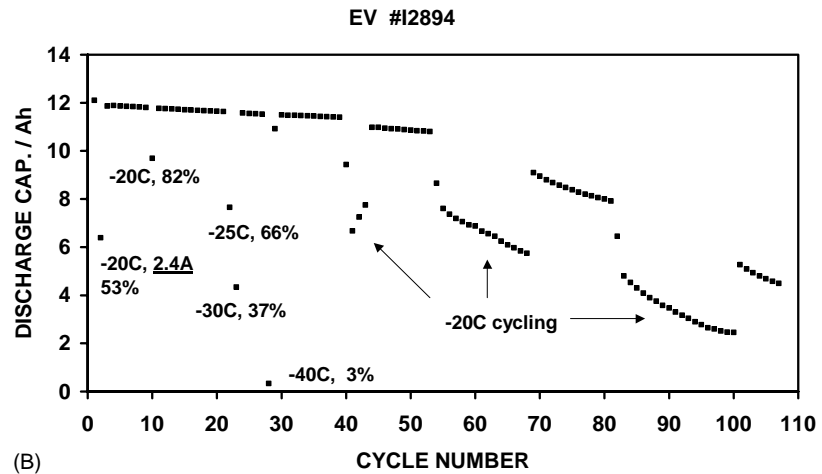


Fig. 7. A comparison of the discharge curves obtained, at different temperatures, from the first batch of low temperature cells.



(A)



(B)

Fig. 8. Cycle life data from the first batch of low temperature cells. Cells were cycled at room temperature and 1.2A unless otherwise stated.

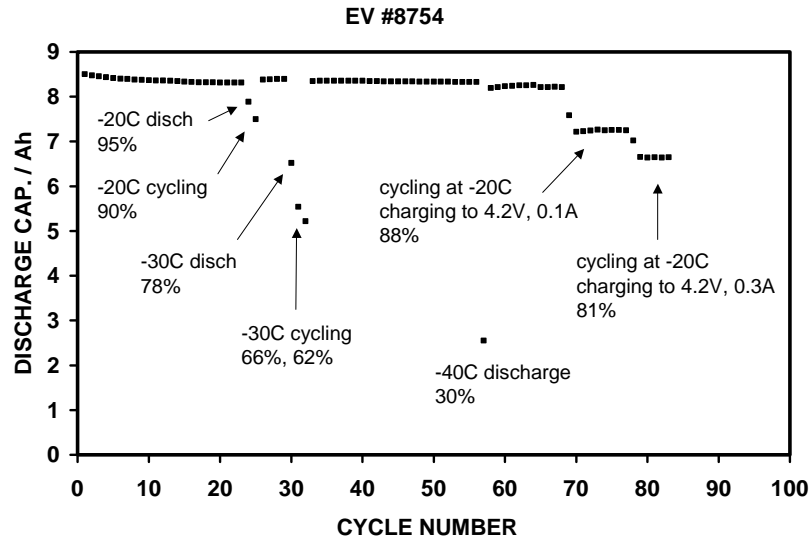


Fig. 9. Cycle life data from the second batch of low temperature cells.

have exacerbated small differences between the two cells. This could prove problematic for a multicell battery pack, but the present cells were hand-assembled and automated production cells should have more uniform behaviour. This aspect will be borne in mind in the future.

3.2.2. Second batch of cells

A second batch of four low temperature cells is now being investigated. These were assembled as a special small run using automated equipment and were expected to be higher quality than the first batch. These cells have the same chemical composition as the first batch, but are thinner and are rated at 8 Ah. Three out of four cells were found to have similar cycling properties to one another, whilst the fourth cell had a higher capacity fade rate. This cell weighed slightly less than the others and was probably defective during assembly, so it will not be discussed.

Fig. 9 shows cycle life data typical of the three good cells. Although these cells were lower capacity, they were still cycled using 1.2 A (now $C/6.6$ rate rather than $C/10$). During recharging at low temperatures, it was noticed that the current at 4.2 V did not decrease as fast as at room temperature. Therefore, the current cut-off for low temperature charging was extended from 0.3 to 0.1 A. This led to a 7% increase in discharge capacity, albeit increasing the charging time by 3 h. These cells yielded 95% of capacity with discharging at -20°C , whilst 90% was obtained following recharging at -20°C . This was a major improvement over the first batch of low temperature cells, which yielded 80% capacity for discharging only and approximately 60% for complete cycles at -20°C . After four more cycles at room temperature, the cells were subjected to three complete cycles at -30°C . The first discharge yielded between 72 and 78% of the room temperature capacity for the three cells, then the

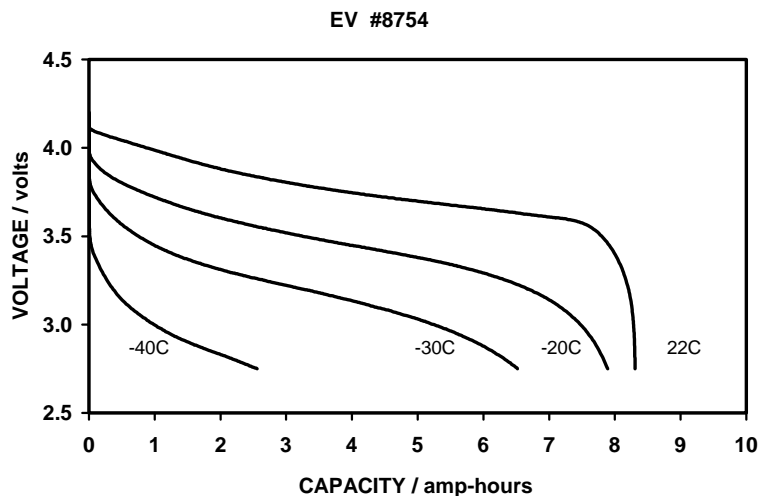


Fig. 10. A comparison of the discharge curves obtained from the second batch of low temperature cells, at different temperatures using 1.2 A.

two complete cycles at -30°C yielded 60–66 and 56–62% capacity. Again, this was a marked improvement over the previous cells (approximately 35% for discharge only). The capacity fully recovered on subsequent cycles at room temperature and, after a further 20 cycles, a discharge was made at -40°C : this yielded 24–34% capacity, which compares with 3% with the previous batch. After about 70 cycles, the cells were subjected to repeated cycling at -20°C . Fifteen cycles have been made so far and the cells have maintained a steady capacity (apart from when the cut-off current for charging was increased back to 0.3 A from 0.1 A, see Fig. 9). This contrasts with the first batch of low temperature cells in which the capacity steadily declined (see Fig. 8) under the same conditions.

Fig. 10 compares the discharge curves obtained from the second batch of cells at four different temperatures. The performance of the cells is seen to be substantially better than that of the first batch of cells (shown in Fig. 7). The data in Fig. 10 are similar to that reported in Ref. [2] for lithium-ion cells (non-polymer) in which the electrolyte used was 1.0 M LiPF_6 in 1:1:1 EC + EMC + DMC (in the present work DEC was used in place of DMC). The results obtained from this second batch of cells are very encouraging and cycling studies are continuing, including low temperature pulsed discharging. Following these studies, safety and abuse testing will be carried out, in particular to determine what measures are necessary to protect these plastic pouch cells from physical and mechanical abuse.

4. Conclusions

Lithium-ion polymer cells of the gel type were found to look promising for military application, provided that they contain an electrolyte that has good low temperature performance. The standard production cells produced by

Electrovaya Inc. were found to have a high specific energy of around 210 Wh kg^{-1} , plus an energy density of 450 Wh dm^3 . The standard cells were found to have a cycle life at room temperature in the region of 250–350 cycles, but the cells did not have good performance at -20°C . Substitution of the electrolyte with 1.2 M LiPF_6 in 1:1:1 EC + EMC + DEC led to a substantial increase in performance at low temperatures. At the C/10 rate, the low temperature cells have been demonstrated to yield 95% of their room temperature capacity at -20°C , 78% at -30°C , and 30% at -40°C . The low temperature cells have also proven to have comparable energy density and cycle life to those of the standard cells. These results are most encouraging and the development of a battery for military applications will continue to be pursued.

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