Journal of Power Sources, 25 (1989) 265 - 276

REPRODUCIBILITY AND RELIABILITY OF RECHARGEABLE LITHIUM/MOLYBDENUM DISULFIDE BATTERIES

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(Received December 21, 1988)

Summary

Groups of rechargeable lithium/molybdenum disulfide cells fabricated in Moli Energy Limited's pilot plant facilities have been subjected to cycle tests and charge retention tests to assess cell reproducibility and reliability. The results show excellent reproducibility as far as discharge capacity and charge retention are concerned. Cell failure occurs in two distinctive modes. The probability of early failures is low. Batteries assembled without attempts to match capacity and without means of charge equilibration of individual cells were subjected to similar tests. The results indicate that battery reproducibility and reliability are similar to those of single cells. The good performance of multicell batteries is attributable to the tightly controlled manufacturing process, sloping voltage characteristics, reserve capacity beyond the end points of charge and discharge, and near 100% coulombic efficiency of the single cell.

Introduction

Rechargeable "AA"-size lithium cells have been developed by Moli Energy Limited [1] and are now being manufactured and marketed under the trade name MOLICEL**. The cells, which are spirally wound, contain a lithium metal anode, a cathode based on a molybdenum disulfide intercalation compound, and an electrolyte composed of a lithium salt and a mixture of organic solvents.

In 1986 and 1987 Moli Energy Limited produced in its pilot plant facilities approximately 30 000 "AA" cells. The cells have a nominal capacity of 0.6 A h and an open circuit voltage varying between 2.4 and 1.3 V, depending on the state of charge, see Fig. 1. Cells essentially identical to the pilot plant product discussed here are now commercially available as MOLICEL Model 06A600.

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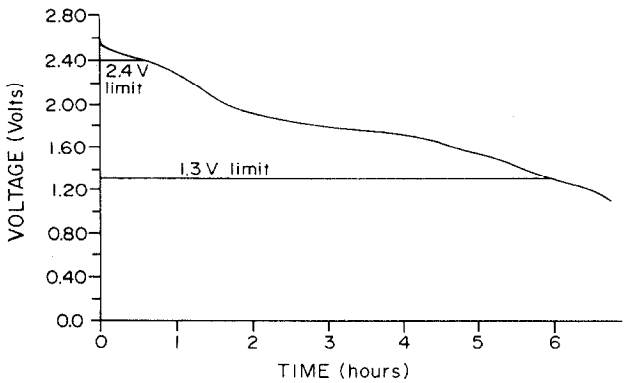

Fig. 1. Voltage profile for single "AA"-size cell. Charge at 60 mA to 2.6 V; discharge at 120 mA to 1.1 V.

From the cells produced in the pilot plant, random samples were subjected to various tests to evaluate their performance. These tests included cycle tests under various charge and discharge conditions and charge retention tests. During the evaluation period, a total of approximately 200 000 cell cycles were performed. Some cells were used to fabricate batteries ranging in size from 2 to 16 cells in series/parallel combinations, which were then subjected to similar performance tests. A total of approximately 15 000 battery cycles were performed.

A number of cells have been cycled to failure; only two failure modes were observed in these cycle life experiments. These modes are labelled high, and low, impedance failure. In the high impedance failure mode, cells lose deliverable capacity towards the end of life due to a gradual increase in cell impedance. In the low impedance failure, at first a temporary electrical short forms between the cell electrodes on charge. This short leads to a charge imbalance (charge capacity is higher than discharge capacity) and therefore to a loss in coulombic efficiency, which is normally close to 100% [2]. Eventually the short becomes permanent, resulting in failure to recharge. Both failure modes lead to a fairly gradual decline in cell performance and not to catastrophic failure.

Experimental

To determine discharge capacities, rate of loss of discharge capacity and cycle life, cells and batteries were cycled under a specific set of conditions of voltage range, and discharge and charge currents.

In all experiments, the cells and batteries were charged and discharged at constant current between fixed voltage limits. Charging in all cases was done at a charge current of 60 mA/cell and a charge voltage cut-off of 2.4 V/cell. The discharges were done to different depths and at different currents.

Because of the change in open circuit voltage with state-of-charge, the depth of discharge can be varied by choosing an appropriate lower voltage cut-off.

Charge retention tests were carried out as follows. Cells were first charged to their mid state-of-charge (1.85 V). This is done because at this potential the cathode is most stable, and loss in cell voltage is associated only with self-discharge of the cell and not with equilibration of the intercalation cathode. To increase cathode stability further, cells were kept for 21 days at the mid state-of-charge before changes in open circuit voltage with time were monitored, with a high resolution digital voltmeter, for the next 21 days. Because of the change in open circuit voltage with state-of-charge, the rate of open circuit voltage loss can be used to determine the rate of self-discharge. As with the cycling experiments, the charge retention tests were all carried out at room temperature.

Batteries were assembled from cells that were fabricated in the pilot plant and stored and shipped in the half-charged state. Batteries were cycle tested under conditions such that both the charge and discharge currents, and the voltage ranges per cell, were identical with those used in the single cell tests carried out for comparison.

Results

(i) Single cells

The reproducibility of the discharge capacities of single cells as a function of cycle number, was determined from a sample of 360 cells which were repeatedly discharged at a current of 120 mA to a lower voltage of 1.1 V, as part of the Quality Assurance program. These cells were fabricated over a period of about 12 months. Discharge capacities for cycle numbers 1, 10 and 100 are listed in Table 1. The reduction in sample size from 320 to 88 between cycle numbers 10 and 100, arises from a voluntary termination of most experiments between these cycle numbers.

The discharge capacity distribution is given in Fig. 2. This histogram shows that the distribution of capacities is very close to a normal distribution, with the mean of the capacity value slowly declining with increasing

TABLE 1

Capacity for single cells for different cycle numbers
Cycling conditions: voltage range per cell 2.4 V - 1.1 V; charge current 60 mA; discharge current 120 mA.

	1st cycle capacity	10th cycle capacity	100th cycle capacity
Sample size	320	320	88
Mean (mA h)	804	691	638
Std. deviation (mA h)	19	14	10
Range (mA h)	746 - 848	640 - 724	615 - 664

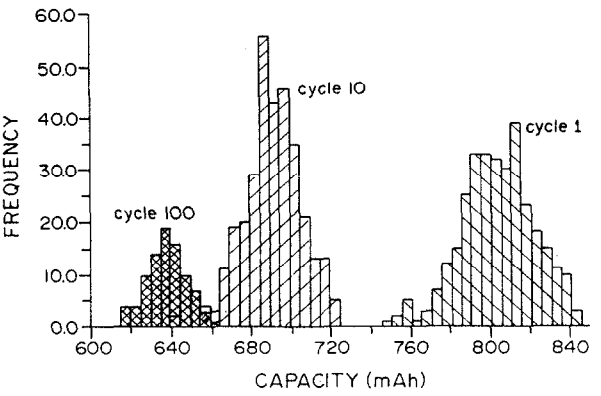

Fig. 2. Histograms of delivered capacity for cycles 1, 10, and 100. Voltage range 2.4 - 1.1 V; charge current 60 mA; discharge current 120 mA.

cycle number, and the width of the distribution decreasing with increasing cycle number. The standard deviation decreases from 19 mA h or 2.3% of the mean to 10 mA h or 1.6% of the mean from cycle number 1 to cycle number 100.

Some cells of this group were cycled to final failure to determine cycle life. Cycle life for a cell which fails through a high impedance is well defined as the number of cycles at which either 80% or 50% of the capacity delivered at the 10th cycle still remains. Cycle life for a cell which fails through a low impedance is less well defined. Final failure occurs at failure to recharge, but tests are often terminated when the charge imbalance reaches 50% - 100%.

In general, the less precise definition of cycle life for a low impedance failure does not impose a problem, since in this failure mode degradation in performance towards the end of life, in most cases, is much more rapid than for high impedance failures.

A so-called cycle life curve, showing deliverable capacity as a function of cycle number, for a cell which failed through a high impedance, is shown in Fig. 3, and a cycle life curve for a cell with a low impedance failure is shown in Fig. 4. In the latter cycle life curve, all charge capacities in which the charge capacity exceeded the discharge capacity by 1% are also plotted. Percentages of cell failures in either mode, as a function of cycle number, are shown in Fig. 5.

The data in Fig. 5 show a very low incidence of early cell failures, with only 0.5% cells failing within the first 20 cycles. All early failures are low impedance failures. In these cycle tests, the mean number of cycles to failure is 155.

A second group of cells was cycle tested under different conditions, with repeated discharges to 1.3 V at 180 mA. The cycle test results are presented in the form of the percentage of cells failed as a function of cycle number, Fig. 6. A comparison of Figs. 5 and 6 shows that the increase in discharge current from 120 mA to 180 mA, and the increase in lower voltage cut-off from 1.1 V to 1.3 V, causes an increase in the mean number of cycles

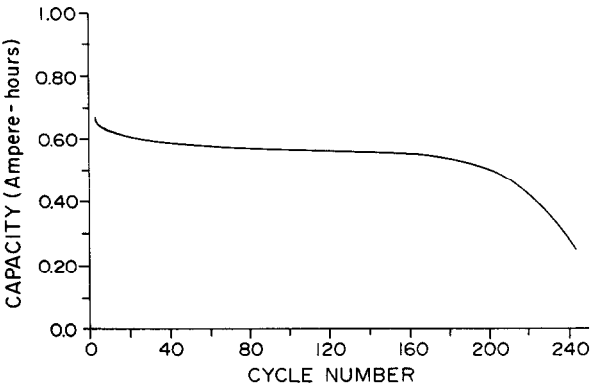

Fig. 3. Cycle life test result for single cell with a high impedance failure mode. Voltage range 2.4 - 1.3 V; charge current 60 mA; discharge current 120 mA.

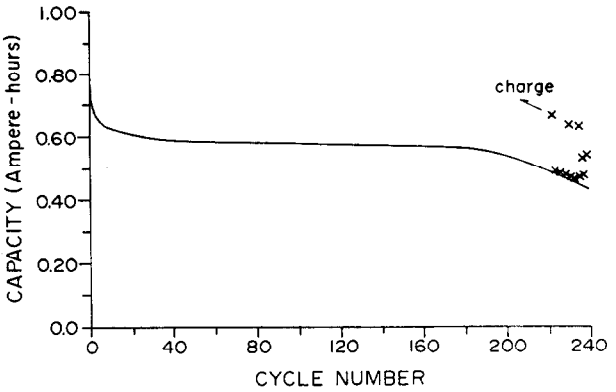

Fig. 4. Cycle life test result for single cell with a low impedance failure mode. Voltage range 2.4 - 1.3 V; charge current 60 mA; discharge current 120 mA.

to failure from 155 to 268. In addition, it causes a shift in the dominant failure mode towards high impedance failure and completely eliminates the early failures.

The reason for this shift in failure rate and failure mode with change in discharge conditions is discussed in detail in an earlier publication [3].

Charge retention at room temperature was measured for a group of 300 cells. A histogram of the distribution of loss in open circuit voltage per year, shown in Fig. 7, indicates a rate of change of open circuit voltage of 21 mV per year. Using a value of 0.7 V $(A\ h)^{-1}$ for the voltage slope of an "AA"-size cell at an open circuit voltage of 1.85 V, this corresponds to a loss of 20 mA h of capacity per year, or a self-discharge rate of 5% per year. The distribution of the capacity losses on storage deviate from normal, since there is a very small number of cells with a rate of self-discharge substantially higher than average. Excluding these cells, the width of the distribution of capacity losses on storage is quite narrow. The largest self-discharge rate observed in this experiment is about 32% per year.

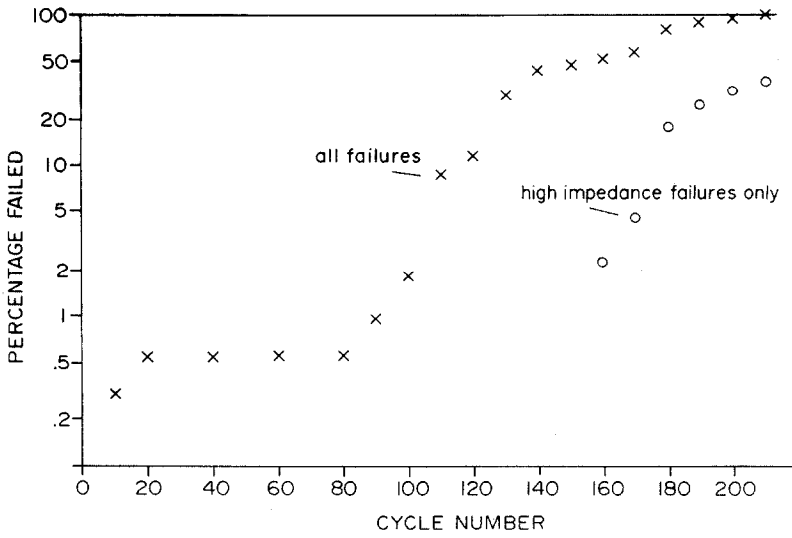

Fig. 5. Percentage of cells failed during cycle life tests as a function of cycle number. End of life due to high impedance failure defined at 50% of 10th cycle capacity. Voltage range 2.4 - 1.1 V; charge current 60 mA; discharge current 120 mA.

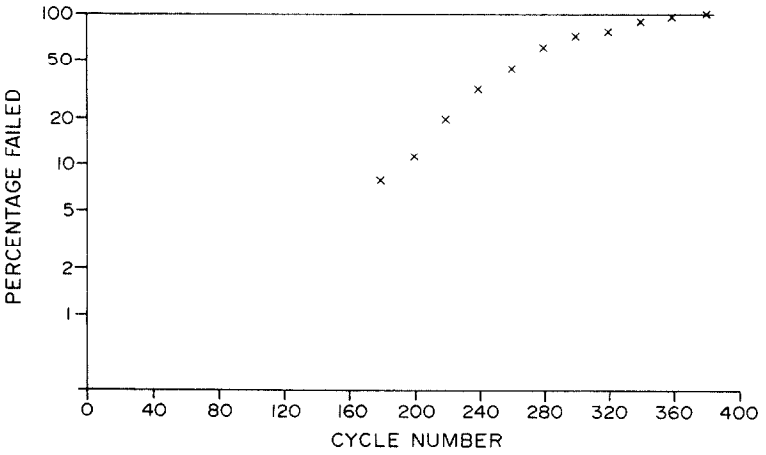

Fig. 6. Percentage of cells failed during cycle life tests as a function of cycle number. End of life defined at 80% of 10th cycle capacity. Voltage range 2.4 - 1.3 V; charge current 60 mA; discharge current 180 mA.

(ii) Batteries versus single cells

In one comparison, one hundred cells were taken from one day's production. Twenty cells were randomly selected and subjected to cycle life tests. The remaining eighty cells were used to build twenty, 4-cell (series-connected) battery packs, which were also subjected to cycle life tests. The single cells were cycled between 2.4 and 1.3 V with a discharge current of

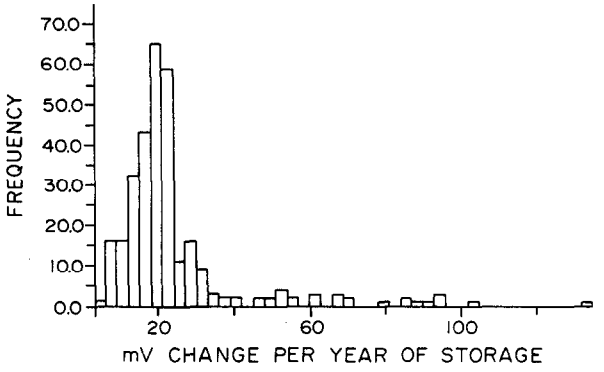

Fig. 7. Histogram for loss of cell open circuit voltage during room temperature storage.

TABLE 2

Comparison of capacity (in mA h) and capacity distribution delivered by single cells, and batteries consisting of 4 cells in series
Cycling conditions: voltage range per cell 2.4 V - 1.3 V; charge current 60 mA; discharge current 120 mA.

	Sample size	1st cycle capacity			10th cycle capacity		
		Mean	Width	Range	Mean	Width	Range
Single cell	20	680	28.5	605 - 719	626.0	20.9	647 - 587
4-cell battery	20	680	14.2	645 - 705	626.8	7.5	639 - 610
		50th cycle capacity			100th cycle capacity*		
Single cell	20	581.2	11.4	607 - 569	565.7	16.4	514 - 592
4-cell battery	20	584.1	6.4	593 - 572	566.6	8.9	537 - 576

*Sample size for single cell was 19, as one cell was accidentally abused due to hardware malfunction.

120 mA, while the batteries were cycled between 9.6 and 5.2 V with a discharge current of 120 mA. The distribution of discharge capacities at different cycle numbers for the single cells and 4-cell batteries is given in Table 2, and their respective histograms in Fig. 8.

The distribution of cycle life values of the single cells and single cell batteries is given in Table 3. Comparing the data of the single cells and the batteries shows the following:

(i) The mean of the capacities of the single cells and the batteries is well within one standard deviation.

(ii) The width of the distribution of discharge capacities of the batteries is smaller than that of single cells by about a factor of two for all cycle numbers.

(iii) Both single cells and batteries show a reduction in the width of the distribution of discharge capacities as a result of cycling.

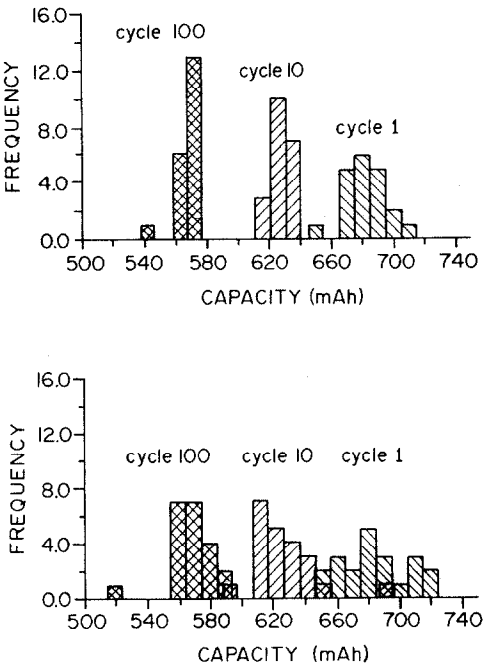

Fig. 8. Histograms of delivered capacity of cycles 1, 10, and 100, for single cells (lower histogram) and 4-cell series-connected batteries (upper histogram). Voltage range: single cells, 2.4 - 1.3 V; batteries, 9.6 - 5.2 V; charge current 60 mA; discharge current 120 mA.

TABLE 3

Comparison of capacity in mA h per cell, and cycle life to 50% of the 10th cycle capacity, for single cells and 4-cell series-connected batteries
Cycling conditions: voltage range per cell 2.4 - 1.3 V; charge current per cell 60 mA; discharge current per cell 120 mA.

	Sample size	10th cycle capacity			Cycle life		
		Mean	Width	Range	Mean	Width	Range
Single cell	19	626	20.9	587 - 647	233	18.5	187 - 263
4-cell battery	20	626.8	7.5	639 - 610	219	11.8	205 - 253

(iv) The mean cycle life value for batteries is only slightly lower than that for single cells, with no increase in the range of cycle life values.

In a second experiment, four 8-cell batteries (consisting of a parallel/series combination with 4 series-connected cells) were compared with four single cells. Single cells and batteries were cycle life tested with the same per-cell conditions of voltage range (2.4 - 1.3 V), discharge current (180 mA), and charge current (60 mA). The results from these tests are summarized in Table 4. They show the same trend for the cycle life values. However, with

TABLE 4

Comparison of capacity (in mA h) per cell, and cycle life to 80% of the 10th cycle capacity, for single cells and 8-cell batteries
8-cell batteries consist of a parallel/series combination with 4 cells in series. Cycling conditions: voltage range per cell 2.4 V - 1.1 V; charge current per cell 60 mA; discharge current per cell 180 mA.

	Sample size	10th cycle capacity		Cycle life	
		Mean	Range	Mean	Range
Single cell	4	673	652 - 683	309	265 - 336
8-cell battery	4	663	646 - 690	293	255 - 350

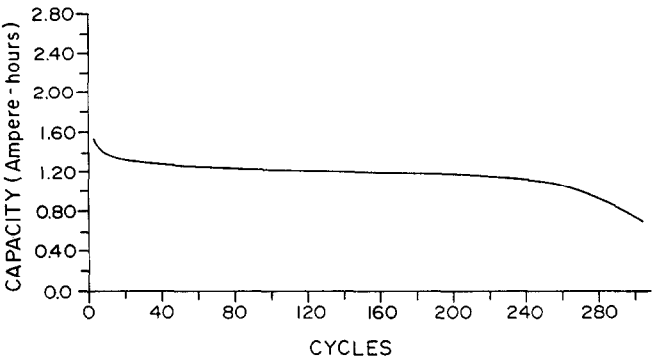

Fig. 9. Cycle life test results for 8-cell battery with a high impedance failure mode. Battery configuration parallel/series combination with 4 cells in series. Voltage range 9.6 - 4.4 V; charge current 120 mA; discharge current 360 mA.

the two parallel strings, the reduction in distribution width of cell capacities is not apparent. The range in cycle life values in this case increases.

Finally, a cycle life curve of discharge capacity *versus* cycle number for one of the batteries tested, is shown in Fig. 9. This particular battery failed in the high impedance mode. The shape of the curve is very similar to that for a single cell, shown in Fig. 3.

Discussion

The width of the distribution of single cell discharge capacities, is very narrow, and agrees with the distribution of the weight of active cathode material, indicating that this is the result of tightness of the control of cell manufacturing process parameters. When the cell is subjected to charge and discharge cycling, the width of the capacity distribution is further reduced. The exact reason for this is not known. However, it points towards non-uniformities which exist between cells immediately after manufacture that are removed through cycling.

As was mentioned earlier, the distribution of self-discharge rates deviates from normal because of the presence of a very small number of cells with relatively high self-discharge rates. These high rates of self-discharge are likely caused by cell assembly faults such as pinholes in the separator.

Cells show a high degree of reliability through the absence of early failures, the absence of sudden catastrophic failures, and the relatively narrow cycle life distribution. The absence of early failures can be explained by the fact that each cell is discharged and charged once as part of the manufacturing process [1]. During this process cell performance is monitored.

By comparing the results obtained with single cells and with batteries during cycle life tests, we can analyze them in terms of deliverable capacity and response to cycling.

The average capacity of batteries is the same as the average of cell capacities. However, the width of the distribution of discharge capacities of batteries is smaller than that for single cells. If cells only had deliverable capacity between the voltage limits which are acceptable for cycling, then the capacity of a multi-cell battery would be limited by the individual cell with the lowest capacity. This is the typical behaviour of systems such as nickel–cadmium. The lithium/molybdenum sulfide system used here has a voltage slope and delivers capacity beyond the voltage cut-off points (Fig. 1), allowing cells within the battery to be cycled over a voltage range exceeding these limits. This has an averaging effect on the discharge capacity of each cell in the battery. Simple statistical arguments show that the width of the distribution in discharge capacities for a 4-cell battery is reduced by a factor of 2, as compared with single cells. This is exactly what is observed in the 4-cell/single cell comparison, Table 3. This argument is only applicable to batteries with series-connected cells.

Another important result presented in the previous section, is that multi-cell batteries consisting of series-connected cells behave almost identically to single cells during their useful life when subjected to cycling under the same per-cell conditions. In general, it is expected that multi-cell batteries have a shorter life than single cells. The main reason for this expectation is that both the charge cut-off voltage and the depth of discharge are not controlled for each cell individually, but collectively for the whole battery. This means that due to small differences per cell (in capacity and impedance), cycling conditions for each cell will be somewhat different. This can lead to a different rate of degradation of the cells, causing a rapid increase in cell "imbalance" through a positive feedback. Additional problems for battery life are expected for systems such as the MOLICEL which do not have an electrochemical shuttle mechanism which is operational at the end of the charging process. This shuttle would allow the state of charge in each cell to equilibrate at the end of each battery charge, and thus would compensate for differences in the self-discharge rate between cells, as well as protect individual cells from overcharging. Without the shuttle, battery life could be severely shortened by uneven self-discharge of cells and by over-

charging of individual cells. These problems could be reduced by preselecting cells, for assembly into one battery, on the basis of discharge capacity and self-discharge rates. In addition, careful equilibration of the state-of-charge of individual cells prior to battery assembly would be required. These procedures are labour-intensive and therefore would significantly increase the cost of the battery manufacturing process. The data collected on MOLICEL batteries, however, show that this preselection and charge equilibration of cells is not necessary. The results presented in Tables 3 and 4 indicate that multi-cell batteries and single cells perform very similarly in terms of deliverable capacity and cycle life. There are three main reasons for this excellent performance of MOLICEL batteries with respect to single cell characteristics.

(i) The discharge capacity distribution of cells coming from the production line is very narrow as a result of tight control of the manufacturing process. Upon repeated discharge and charge, the width of this distribution is reduced even further.

(ii) The cell voltage slope and the reserve capacity outside the operational voltage limits of the cell reduce the rate of the degradation processes when cells are cycled with capacities which drive the cell voltage outside the specified limits. In addition, the Li/MoS_2 cells have a reserve capacity of more than twice the nominal capacity, at about 0.6 V/cell. Using this reserve capacity will degrade battery performance to some extent, but it will also protect the battery from catastrophic failure.

(iii) A very narrow distribution in coulombic efficiency, which is close to 100% for Li/MoS_2 cells, and the very low probability of single cells having an abnormally high rate of self-discharge.

In a battery built from a series/parallel combination of cells, the arguments presented above apply to the series-connected cells. For the parallel-connected strings, the voltage limits for each string are always the same and only the current through each string will show an imbalance. Significantly different branch currents could cause early failure, as the cycle life of individual cells depends both on charge and discharge currents [3]. However, the voltage slope of the MOLICEL provides a negative feedback for branch currents [4], and therefore allows reliable operation of batteries with cells connected in parallel. Differences in the range of cycle life values, shown in Tables 3 and 4, cannot be explained easily, since the rate of capacity fade near the end of the defined cycle life depends on the conditions of cycling and the definition used for cycle life. Both parameters are different for the data given in Tables 3 and 4.

In an earlier publication [4], the effect of the failure of a single cell in either the high or low impedance mode has been studied in some detail. It was shown that failure of a single cell leads to a reduction in battery performance but not to a catastrophic failure of the whole battery. This again can be attributed to the characteristics of sloping voltage, reserve capacity, and the near 100% coulombic efficiency of the Li/MoS_2 cell.

Conclusions

Rechargeable lithium cells manufactured by Moli Energy Limited exhibit a very narrow distribution in discharge capacities and self-discharge rates. The high reproducibility of discharge capacities of the cells is a direct consequence of the manufacturing process. Upon cycling, the width of the capacity distribution will further decrease. This high reliability of the single cell contributes to the good performance of MOLICEL batteries.

Multi-cell batteries have a discharge capacity distribution which is narrower than that of single cells, and which is consistent with an averaging effect of the discharge capacities of the number of series-connected cells. This averaging effect is associated with the sloping voltage characteristics of the Li/MoS_2 cell.

Concern over cycling multi-cell batteries with cells not having an intrinsic overcharge protection are unfounded for MOLICEL batteries. The performance of multi-cell batteries is as good as that of single cells in terms of the rate of capacity loss per cycle and cycle life, even without matching cells based on their capacities and self-discharge rates, and without equilibrating the states of charge of the cells prior to battery assembly. Furthermore, failure of a single cell, either in the high or low impedance mode in a multi-cell battery, does not lead to a catastrophic failure of the battery.

This high reliability of MOLICEL batteries is attributable to a number of characteristics of the Li/MoS_2 cell, specifically: accurate control of discharge capacity through the manufacturing process, sloping voltage, reserve capacity beyond the specified voltage limits, and the near 100% coulombic efficiency.

Significant improvements in the reliability of cells and batteries could be achieved by reducing the probability of early failures in the low impedance mode. In Moli Energy Limited's manufacturing plant, this is being attempted by a higher level of process control and improved quality assurance procedures.

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