THE MOLICEL® RECHARGEABLE LITHIUM SYSTEM: MULTICELL ASPECTS

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Summary

MOLICEL®* rechargeable lithium cells have been cycled in batteries using series, parallel, and series/parallel connections. The individual cell voltages and branch currents were measured to understand the cell interactions. The observations have been interpreted in terms of the inherent characteristics of the Li/MoS_2 system and in terms of a singular cell failure mode. The results confirm that correctly configured multicell batteries using MOLICELs have performance characteristics comparable with those of single cells.

Introduction

The MOLICEL is based on the rechargeable couple lithium/molybdenum disulfide. It is characterized as having high rate capability, high energy density, and good cycle life. The battery requirements for a large number of applications can be met using arrays of small cells with capacities from 0.6 to 2.5 A h. Such applications include lap computers, portable communications, consumer electronics, and cameras.

The technology is by no means confined to these examples. Larger cells of 45 A h capacity have been built by scaling up the basic MOLICEL design. Table 1 gives some specifications for a number of MOLICELs.

As will be seen, there are design trade-offs in the technology. For example, capacity can be increased during manufacture at the expense of cycle life. Furthermore, the user has many choices in matching performance characteristics with demand requirements. Most of the applications mentioned have cycle life requirements of 100 - 400 cycles. However, derating the capacity by using shallow discharges can extend the cycle life to 3000 cycles.

The work reported here was undertaken to find out how MOLICELs performed in series-connected and in series/parallel-connected battery packs. In this regard, the MOLICEL system has a number of characteristics which

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TABLE 1

Cell characteristics

Size	AA		A	BC
Model	06A600	06B800	51B1050	40A45000
Weight (g)	22	24	30	1250
Operating voltage (V)		2.4 - 1.3		
Nominal capacity (A h)	0.6	0.80	1.05	45
Cycle life (to 80% cap)	300+	100	100	300+
Operating temp (°C)		−30 to +55		
Charge retention		90% after 1 year at 21 °C		
Charge rate		$C/10$		

distinguish it from nickel–cadmium and lead–acid systems. Cell interactions within batteries of MOLICELs are significantly influenced by the following inherent characteristics of the Li/MoS_2 system:

- sloping voltage
- near 100% current efficiency
- large "reserve" capacity
- near perfect capacity balance.

The sloping voltage arises from the fact that the chemical potential of the cathode material varies with its state of charge. This does not occur with conventional cells which use displacement reactions. When MOLICELs are connected in parallel, the change of chemical potential with state of charge introduces a negative feedback phenomenon which tends to cancel any system imbalance. This effect works on both charge and discharge. Obviously, with series-connected cells, balance cannot be maintained by such a feedback mechanism.

The MOLICEL has no charge-limiting mechanism comparable with the water electrolysis of a lead–acid cell or the oxygen recombination reaction of nickel–cadmium cells. For this reason, the MOLICEL has 100% current efficiency and low heat output. There is, however, no mechanism for rebalancing cells within a battery pack.

A large reserve of capacity exists in MOLICELs and only a fraction of the total energy in the active materials is utilized during the standard cycling. The bulk of the normally non-utilized energy is only available below 1 volt. This ensures that a low capacity cell cycling in a series-connected battery will not be driven immediately into voltage reversal on discharge.

Finally, the capacity balance of fresh MOLICELs is extremely good. This is achieved by an electrical preconditioning step at the factory which fixes the amount of active cathode material based entirely on the highly controllable parameters of current and time. As an example, in a typical sample production run, the initial capacities were found to be 0.805 A h with a standard deviation of 0.017 A h. After 100 cycles ($C/10$ charge, $C/5$ discharge, 2.4 - 1.1 V) the capacities were 0.639 A h ± 0.010 A h.

From the foregoing, it would be expected that the cycling behaviour of MOLICEL multicell batteries would show certain unique characteristics. The initial capacity balance is expected to be excellent. The maintenance of this balance depends on individual cell capacity fade rates. The effect of the inevitable imbalance on the battery performance is somewhat difficult to predict. A series of experiments was therefore undertaken to investigate the situation.

Experimental

Three types of experiments were carried out:
- single cell simulation of battery pack effects (fixed capacity cycling)
- cycle testing of standard, balanced battery packs
- cycle testing of deliberately imbalanced packs.

Batteries were assembled as simply as possible using shrinkable adhesive tape and spot welded nickel tabs. Cycling was carried out at constant current in convection ovens. A multichannel data acquisition system recorded cell voltages and currents.

Two classes of AA size (0.6 A h) cells were used for these tests. The first were standard MOLICELs having passed all quality control checks. The second were rejects which had failed quality control as a result of having low capacity or exhibiting self-discharge. The test conditions for the latter were a maximum open circuit voltage loss of 0.062% per day over 42 days. The capacity criteria are defined earlier.

Fixed capacity cycling

This provides a convenient method of studying cell behaviour under conditions closely approximating those of a series-connected battery pack (all applications currently envisioned will have series-connected cells). Charge and discharge cut-off points in series arrays are determined by the overall voltage. Individual cells will cycle over ideal limits only if the pack remains perfectly balanced. A cell with lower capacity than the others will cycle over voltage limits which are less than ideal.

Such a 'bad' cell will simply cycle over a capacity which will be determined by the operating capacity of the 'good' cells. Thus, cycling of a single cell under fixed capacity conditions can be used to simulate the battery environment. Tests were done at 21 °C and 55 °C with $C/10$ charge and $C/3$ discharge. Even reject cells could achieve more than 100 cycles when the nominal 0.6 A h capacity was used. However, at 0.9 A h cycling, failure occurred after less than 30 cycles. In all cases the failure mode was the same. As can be seen from Fig. 1 (for a low capacity cell) and Fig. 2 (for a self-discharging cell) the voltage range over which the cells cycled increased until, at the point of failure, the lower limit reached zero volts. At this point the cells developed a permanent internal short circuit. This
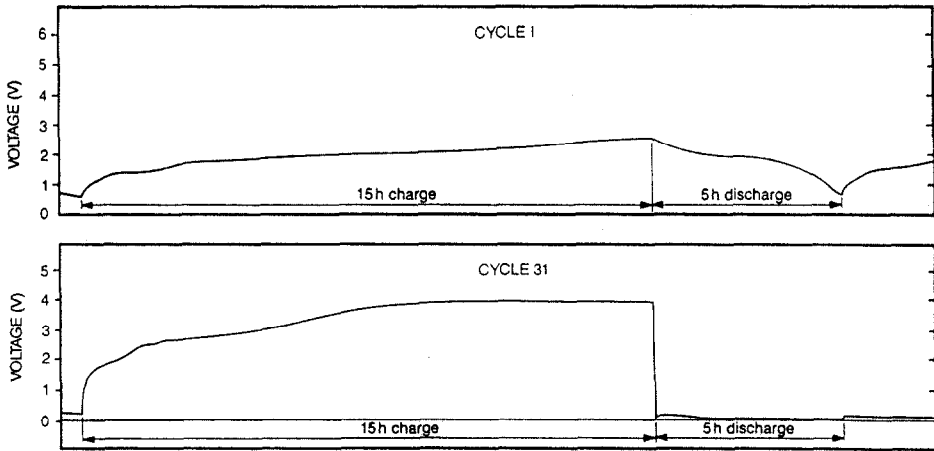
Fig. 1. Fixed capacity cycling at 21 °C of a MOLICEL AA cell (Q.C. reject because of low capacity). Charge current 60 mA, discharge current 180 mA, fixed capacity = 0.9 A h (150% of nominal).
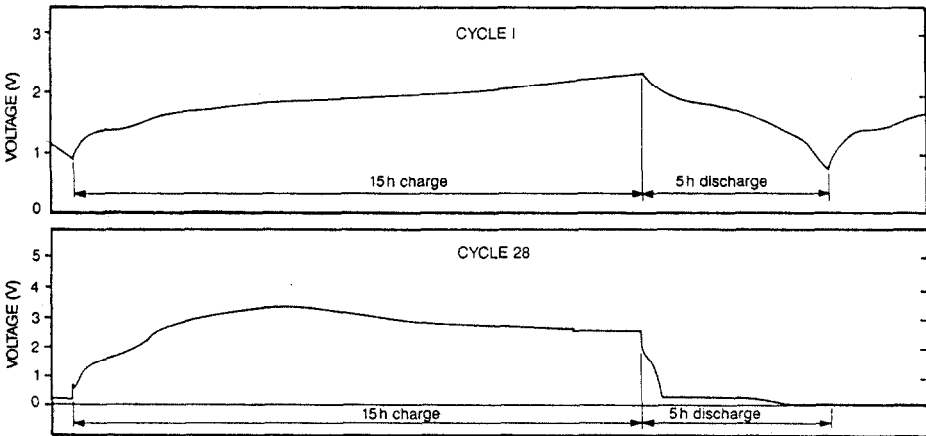

Fig. 2. Fixed capacity cycling at 55 °C of a MOLICEL AA cell (Q.C. reject because of self-discharge). Charge current 60 mA, discharge current 180 mA, fixed capacity = 0.9 A h (150% of nominal).

failure mode is totally benign and has obvious advantages insofar as the performance of series connected cells is concerned.

Cycling of standard balanced batteries

Batteries were cycled using groups of 8, 12 and 16 cells drawn from standard production runs after qualification procedures. The batteries were configured as shown in Fig. 3. Results are presented in Table 2. The data confirm the excellent performance of MOLICELs in multicell batteries. The
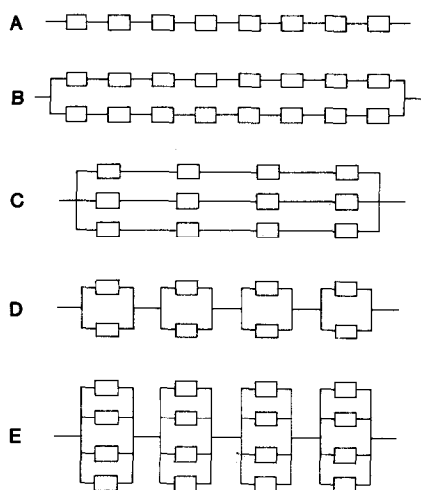
Fig. 3. Battery configuration of 8, 12 and 16 cells.

TABLE 2

Cycling of standard balanced packs

Configuration	Cycling conditions per cell				No. of cycles	Capacity remaining (% of nominal)	Imbalance* (%)
	Voltage range	Charge/disch. (mA)		Temp. (°C)			
A	2.4/1.3	80	240	21	400	40	5.3
	2.4/1.3	80	240	21	400	50	3.0
B	2.4/1.3	80	240	21	175	85	3.0
	2.4/1.3	80	240	21	225	80	3.5
C	2.4/1.3	60	180	21	299	88	2.9
	2.4/1.3	60	180	21	293	71	3.3
D	2.4/1.1	60	180	21	175	86	3.3
	2.4/1.1	60	180	21	175	89	0.5
E	2.4/1.1	60	180	60	171	60	10
	2.4/1.1	60	180	60	138	62	20

*Expressed as standard deviation as % of mean voltage measured at termination of cycling.

capacities and cycle lives of batteries up to 16 cells are very similar to those of individual cells under similar test conditions. This is true even at 60 °C, which is above the recommended operating limit of 55 °C. The capacity imbalance is initially less than 2%. After the battery cycling at 21 °C, the imbalance generally rose to about 3%. At 60 °C an imbalance up to 20% was found after more than 100 cycles.

Cycling of imbalanced batteries

Current quality control procedures at Moli Energy reject all low capacity cells. There is, however, a small but finite possibility that a self-discharging cell might not be detected and would, in fact, reach the customer. The imbalanced batteries were therefore tested using one deliberately planted cell which was a self-discharging, Q.C. reject.

Batteries of 4 and 8 cells were configured as shown in Fig. 4.
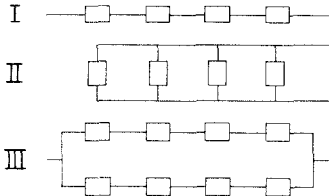
Cycling was conducted at 55 °C to accelerate the degradation process.

Fig. 4. Battery configurations of 4 and 8 cells.

Type I

The individual cell voltages at the start of cycling are shown in Fig. 5. The battery was initially well balanced except for the planted cell (cell 4) which cycled at lower voltage than the others. The cycle life performance of this battery was greatly degraded by the presence of the self-discharging cell. The capacity declined by 50% after only 80 cycles whereas a standard battery under similar test conditions would achieve 150 cycles. Figure 6 shows that the capacity decline is associated not only with the planted cell, but also with another cell. The planted cell subsequently cycled at ever lower voltage and, in fact, was below 0.1 V at end of discharge when the test was terminated because of almost zero pack capacity. It can be seen in Fig. 6 that the second cell was also failing to recharge completely. It also cycled over a low voltage range. It is coincidental that a second cell in the pack behaved in this way although the observation does reinforce earlier statements made about the singular failure mode of MOLICELs.

Type II

Figure 7 shows a typical early cycle for this battery. It can be seen that the planted cell (cell 4) carried high currents at the end of recharge and correspondingly bore a disproportionate share of the current at the end of discharge. An internal dendrite short would be expected to produce such behaviour. At cycle 39 the battery was placed on open circuit standby. Figure 8 shows the loop current which ran for about 10 h until the voltage had equilibrated at about 1.75 V. This is to be expected for an imbalanced, parallel-connected battery. All the cells are, of course, at the same voltage during charge. They are not, however, at the same equilibrium voltage due to differing impedances and, hence, differing overvoltages.
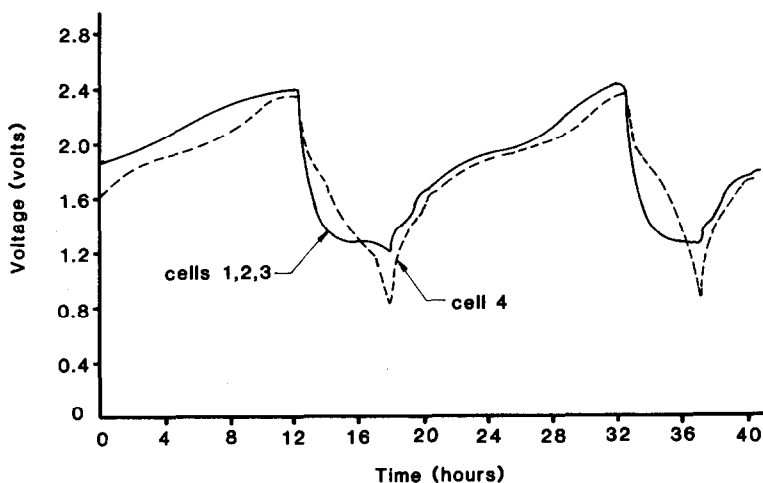
Fig. 5. Individual cell voltage profiles for an imbalanced 4 cell series-connected battery cycling at 55 °C. Charge current 60 mA, discharge current 180 mA, limits 9.6/4.4 V. Cycles 1 and 2 shown.
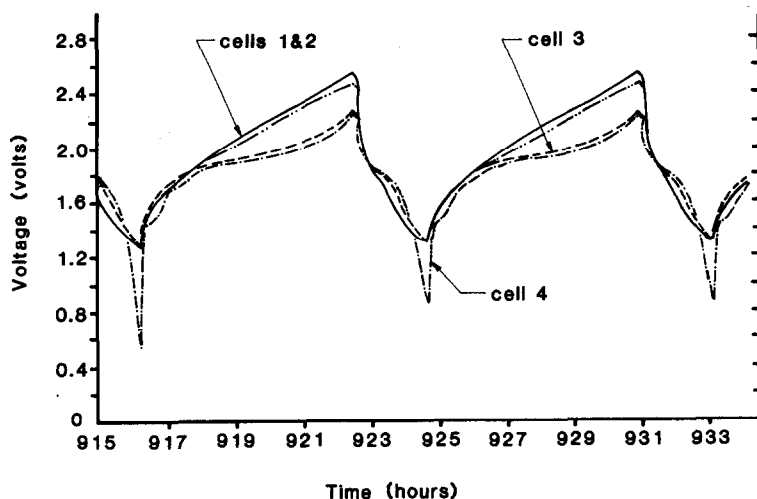

Fig. 6. Individual cell voltage profiles for an imbalanced 4 cell series-connected battery cycling at 55 °C. Charge current 60 mA, discharge current 180 mA, limits 9.6/4.4 V. Cycles 39 and 40 shown.

The ultimate demise of this pack is shown in Fig. 9. About half-way through the recharge, the planted cell took the full 240 mA charge current. After going onto open circuit the battery equilibrated to 1.7 V showing that the cell did not have a "hard short". No safety hazards were associated with this failure mode.
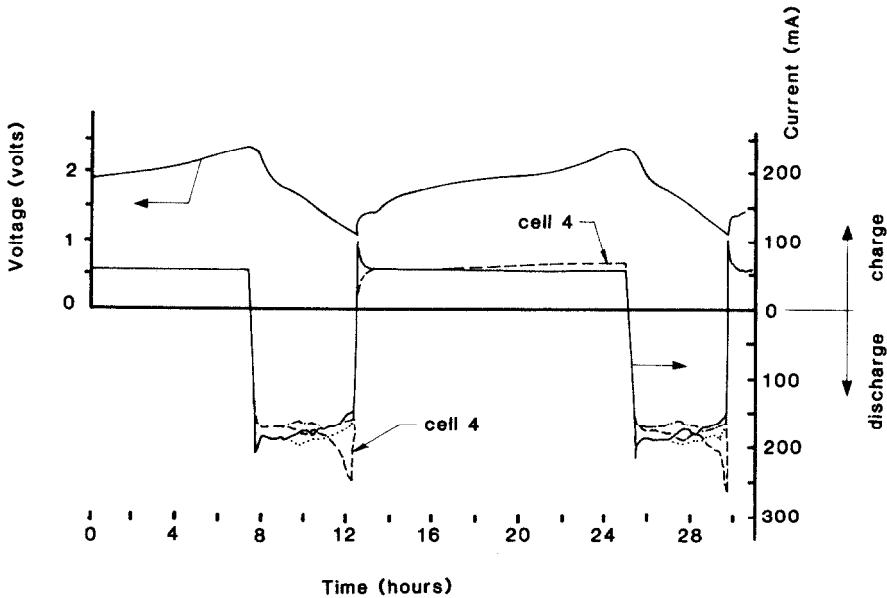
Fig. 7. Individual cell current profiles and battery voltage for a 4 cell, imbalanced, parallel-connected battery cycling at 55 °C. 240 mA charge to 2.4 V, 720 mA discharge to 1.1 V. Cycles 1 to 2 shown.
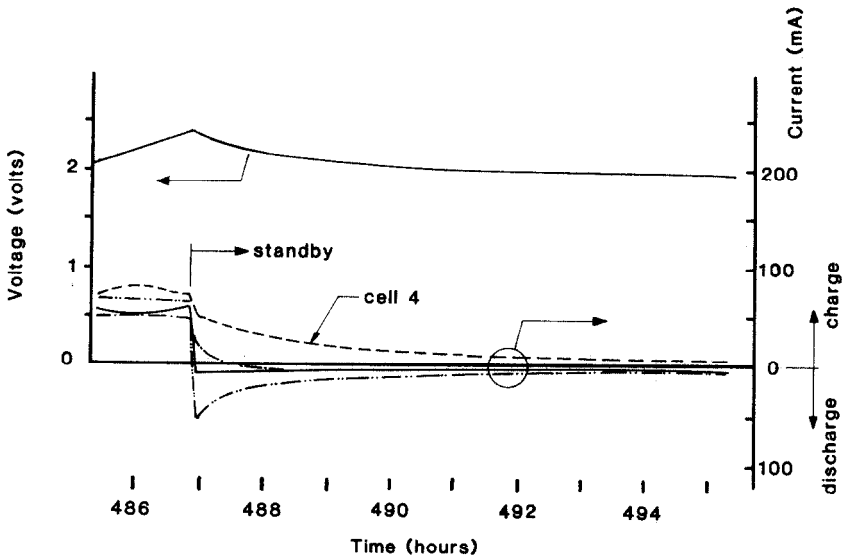

Fig. 8. Individual cell current profiles and battery voltage for a 4 cell, imbalanced, parallel-connected battery cycling at 55 °C. 240 mA charge to 2.4 V, 720 mA discharge to 1.1 V. Cycle 39 and subsequent open circuit standby shown.
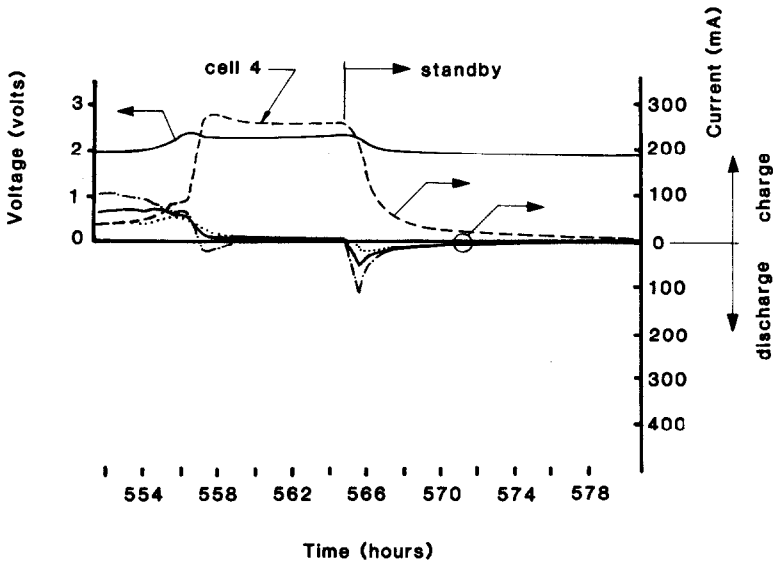
Fig. 9. Individual cell current profiles and battery voltage for a 4 cell, imbalanced, parallel-connected battery cycling at 55 °C. 240 mA charge to 2.4 V, 720 mA discharge to 1.1 V. Cycle 45 and subsequent open circuit standby shown.
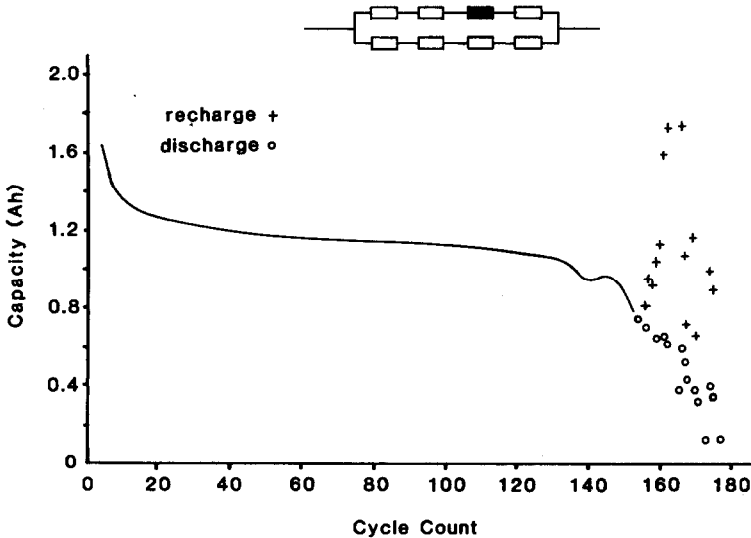

Fig. 10. Cycle-life plot of an imbalanced 8 cell series/parallel battery cycling at 55 °C. Configuration as illustrated (self-discharging cell shown shaded). Charge current 120 mA, discharge current 360 mA, limits 9.6/4.4 V.

Type III

This battery exhibited good cycle life, as shown in Fig. 10. The originally balanced limb remained virtually unchanged. Currents were higher
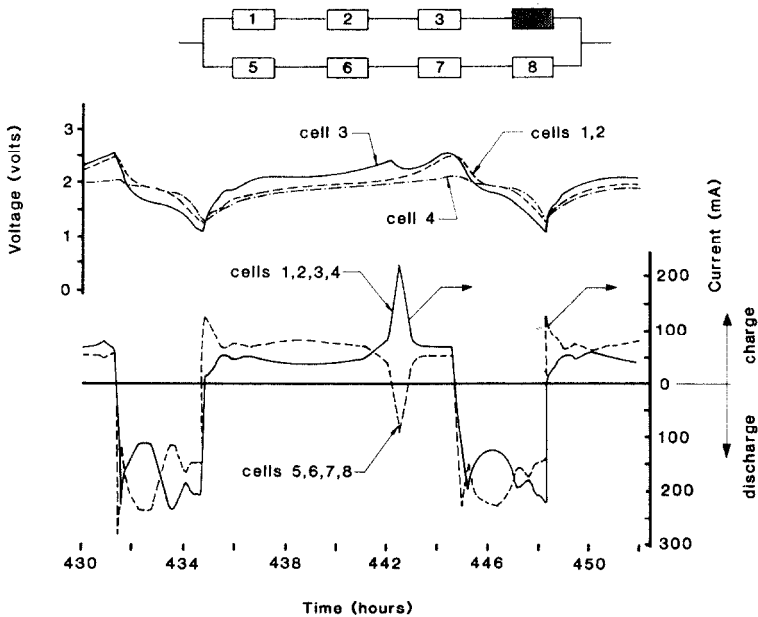
Fig. 11. Individual cell voltage profiles and current branching profiles for an 8 cell series/prallel imbalanced battery cycling at 55 °C. Configuration as illustrated. (Self-discharging cell shown shaded). Voltages in imbalanced string shown. 120 mA charge to 9.6 V, 360 mA discharge to 4.4. V. Cycles 26 and 27 shown.

in this limb at the start of discharge and higher in the imbalanced limb at the end of recharge. This is consistent with all previous observations and can be seen in Fig. 11 where the currents are plotted for both limbs but, for simplicity, only the voltages for the imbalanced limb are shown. Sporadic soft shorting occurred in one cell (cell 3) but the event was transient and the user would be unaware of this either from the standpoint of battery performance or cycle life.

Conclusions

The operation of MOLICEL rechargeable lithium cells in batteries has been found to be very satisfactory in spite of the absence of charge limiting mechanisms. The initial very good capacity balance was retained over many cycles, with the result that battery performance was indistinguishable from single-cell performance under similar conditions. The only exception to this was associated with the rare and singular failure mode of MOLICELs which leads to a low impedance or "soft short". This resulted in a performance penalty but no safety hazard.

The presence of a low impedance failure mode is consistent with the major findings of this study which are:

(i) best results will be obtained using series connections;

(ii) reliability will be increased by matching cell size to capacity requirements and avoiding parallel cell connections;

(iii) multicell arrays will perform best if series strings are made to meet voltage needs and then parallel connection of the strings are made to meet capacity needs. Avoidance of the latter parallel connections by choice of cell size will give performance and cost advantages.

Acknowledgement