EFFECT OF DISCHARGE CURRENT ON CYCLE LIFE OF A RECHARGEABLE LITHIUM BATTERY

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Summary

The cycle life of a rechargeable cell depends on operating conditions such as the depth of discharge, specific voltage limits during charge and discharge, recharge and discharge current, and operating temperature. These conditions can affect cycle life through their influence on degradation mechanisms which limit life.

For a rechargeable Li/MoS$_2$ cell, a strong dependence of cycle life on discharge current was found. For discharge rates ranging from 0 5 to 20 h, a maximum in cycle life was found, for intermediate discharge rates, of about 3 h. Three different regions of the dependence of cycle life on discharge rates could be identified. Experimental evidence indicates that in each region a different mechanism controls cycle life. At high discharge rates, cycle life appears to be determined by cathode degradation, while at intermediate and low discharge rates, cycle life is determined by electrolyte degradation, leading, respectively, to cathode or anode failure.

Introduction and review of earlier work

Lithium rechargeable cells using molybdenum disulfide cathodes [1] have been manufactured by Moli Energy Limited in Vancouver, Canada, and marketed under the name MOLICEL*.

The operation of the cell is based on the reversible reaction

$$x\text{Li} + \text{MoS}_2 \rightleftharpoons \text{Li}_x\text{MoS}_2 \tag{1}$$

In eqn. (1), x represents the mole fraction of lithium ions intercalated in MoS$_2$.

During discharge, the lithium anode dissolves and lithium ions are transported through the organic electrolyte to the cathode, where they intercalate into the MoS$_2$ host. An electrochemically modified form of MoS$_2$ is used as cathode active material. This form has a different crystal

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structure from the naturally occurring MoS_2 and allows reversible intercalation of lithium ions over the range $0 < x \leqslant 1$ [2]

The potential of the Li_xMoS_2 cathode of the modified form *versus* a lithium metal anode varies with the amount of lithium intercalated. At x close to 0, the potential is about 2 8 V, and at $x = 1.0$ the potential is lowered to 1.1 V In order to maximize cycle life and deliverable capacity, it is generally not recommended to charge and discharge the cell outside the 2.4 - 1 3 V range This choice is based on the limited stabilities of the electrochemically modified or high capacity form of MoS_2 at high cathode potentials [3] (where it undergoes a transition to a lower capacity form which is structurally very similar to the naturally occurring MoS_2) and of the electrolyte at low cathode potentials [4]

The limited stabilities of the active components lead to a gradual decline in deliverable capacity, when the cell is subjected to consecutive charge and discharge cycles.

Figure 1 shows an example of such a capacity decline for a cell which is discharged at 180 mA and charged at 60 mA between 2 4 and 1 3 V. The curve shows a typical S-shape [5], with regions of high capacity fade at both the early and final stages of cycling. As will be discussed in more detail below, it can be shown that the region of early capacity fade is associated with changes occurring in the cathode, while the region of final capacity fade is associated, in this particular case, with electrolyte depletion.

The early capacity fade is affected by the cathode stability in the following way. the stability of the modified MoS_2 decreases as its potential rises above 2 0 V. This causes the formation of the low capacity form as the cathode is charged slowly above 2.0 V. Some of the high capacity form can be re-formed at low cathode potentials during the discharge at low to intermediate rates The net result, however, is a loss in deliverable capacity as the cell is repeatedly charged above 2.0 V

To illustrate the effect of a charging voltage above 2 0 V, the capacity fade curves of cells repeatedly charged at 60 mA to 2.0, 2 2, and 2 4 V and
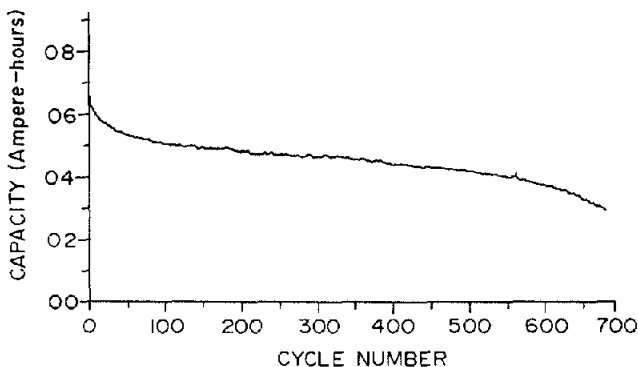

Fig 1 Cycle life curve for a cell cycled between 2 4 and 1 3 V at a discharge current of 180 mA and a recharge current of 60 mA
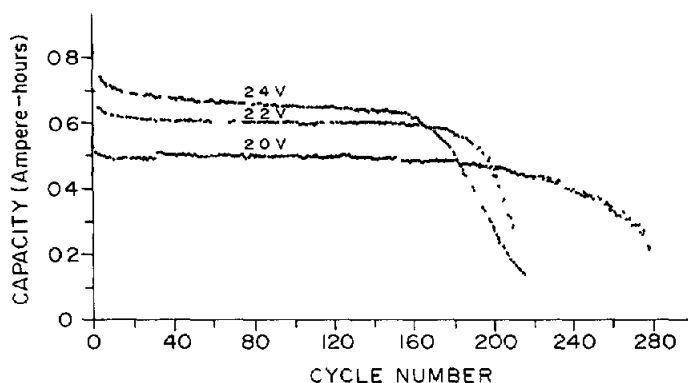
Fig 2 Capacity fade curves for cells repeatedly charged at 60 mA to 2 0, 2 2, and 2 4 V Cells are discharged to 1 1 V at 120 mA

discharged at 120 mA to 1 1 V are shown in Fig. 2. Figures 1 and 2 also show that the rate of capacity loss for a cell cycled to 2.4 V reduces eventually (after about 10 cycles) to nearly zero. X-ray diffraction studies have shown that this is the result of stabilization of the high capacity form of MoS_2 due to improvement in its crystallinity [6]. The crystallinity will improve with the number of times the cell is cycled in both directions through the phase transition. The ratio of the amount of high to low capacity form present in the stabilized material depends both on the voltage range and the currents used during cycling of the cell. This ratio is pushed towards the low capacity form when, during cycling, the average cell voltage is high and/or the ratio of discharge to recharge rate is high.

The final capacity fade is associated with the limited stability of the electrolyte in contact with the electrodes. Both the salt and the solvent component of the electrolyte will gradually decompose. The solvent breakdown leads to the formation of gaseous products (ethene and propene) as well as a solid product (lithium carbonate) [7]. The breakdown of the salt is less understood. However, it is believed that it leads mostly to film formation on the electrodes [8] The decomposition at the electrodes can either occur via an electrochemical or voltage dependent reaction, or via a chemical or voltage independent reaction. Because of the voltage dependency, the electrochemical reaction takes place only at the cathode/electrolyte interface, while the chemical reaction can occur at both electrode/electrolyte interfaces.

The decomposition leads to electrolyte depletion and therefore to a gradual increase in cell impedance. In addition to the depletion, the electrolyte decomposition also results in the accumulation of solid breakdown products within the cathode pores and/or the separator pores as well as on the anode surface. The accumulation of these products leads to a further increase in cell impedance. However, this process can give rise to a much more dramatic loss in deliverable capacity towards the end of cell life. A model to explain the high rate of capacity loss towards the end of cell life

based on percolation theory has been proposed by Dahn *et al* [9]. In this model the cathode powder is represented by a network of individual particles connected by electrolyte-filled channels The ionic conductivities of these channels are modelled as resistors As the electrolyte degradation proceeds, resistors are removed from the network leading to an accelerated increase in impedance and decline of deliverable capacity

It was found in earlier work [10] that, for shallow cycling, cells achieve a maximum in cycle life when they are cycled around the mid-state of charge. In this case it was also found that the integrated capacity delivered over the full life of the cell increases as the depth of discharge decreases Cycle life and integrated capacity for 100%, 60% and 30% D O D. are given in Table 1

TABLE 1

Cycle life and integrated capacity for various depths of discharge

Voltage range (V)	Capacity at cycle 10 (A h)	D O D (%)	Cycle life	Integrated capacity (A h)
2 4 - 1 3	0 58	100	650	300
2 0 - 1 5	0 36	60	1400	400
1 95 - 1 72	0 19	30	3000	500

Cycle life defined at 50% of 10th cycle capacity remaining
Cells were discharged at 180 mA and charged at 60 mA

Experimental

Cycle life tests were undertaken on "AA" size Li/MoS_2 cells. These cells have a nominal capacity of 0.6 A h The cells are constructed with an electrode stack consisting of a lithium anode, sandwiched between two cathodes, which is spirally wound around a central mandrel [11]. An electrolyte-filled porous polypropylene sheet acts as a separator and is placed between the electrodes. The area of the electrodes is about 250 cm^2 and the active mass of MoS_2 is about 8.0 g. The cell contains an excess of lithium (2.5 mole of Li per mole of MoS_2) and therefore the cell capacity is cathode limited. The electrolyte used in the cells is a 1 0 M solution of $LiAsF_6$ in a mixture of 50/50 percent by volume of propylene carbonate and ethylene carbonate.

The cell voltage provides a state of charge indication due to the chemical potential change of Li_xMoS_2 with x [12]. The voltage limits can therefore be used to define the degree of charge and depth of discharge.

Cells were charged and discharged between fixed voltage limits using constant current. The microprocessor-controlled cycling equipment was developed by Moli Energy Limited. The currents are set through hardware changes, while the voltage limits are set through software The current range

of the equipment is 1 mA - 1 A, with an accuracy of ±1% of the set value; the voltage range is 0 - 9 V with a resolution of 5 mV. The voltage–time data are recorded when the voltage change exceeds 50 mV or the time change exceeds 1 h. Data are recorded and evaluated with the help of a 9000 HP minicomputer All cells were cycled at a temperature of 21 ± 2 °C.

Results

Cycle life is often defined at the point where the battery has 50% or 80% of its initial capacity remaining For the MOLICEL battery, cycle life is defined at the point where the battery has 50% or 80% of its 10th cycle capacity remaining. The reason for this choice is associated with the characteristics of the cathode, as explained earlier. Definitions of cycle life with 50%, as well as with 80% of the 10th cycle capacity remaining at the end of life, are both being used here. This is done to distinguish between cells that lose deliverable capacity slowly towards the end of life and cells that fail with a rapid loss of capacity.

The useful life of the cell can also be expressed in terms of the integrated capacity delivered over the life of the cell, rather than the total number of discharges. The use of integrated capacity has the advantage that it takes into account the change in capacity delivered by the cell in a single discharge, where the depth of discharge varies either as a result of the conditions of use or as a result of changes to cell performance with increasing cycle number

"AA" size Li/MoS_2 cells were discharged at currents varying over nearly two orders of magnitude (30 mA - 1 A) while being charged at the standard current of 60 mA. The useful life of the battery was determined both in terms of cycle life and integrated capacity. The results are presented in Figs. 3 and 4, showing cycle life and integrated capacity, respectively, as a function of discharge current.

Both Figures show two characteristic features

(i) three distinct regions which can be associated with different mechanisms controlling the end of life of the battery,

(ii) a maximum in useful life of the battery at a discharge current of around 200 mA.

Discussion

High discharge rates

In the region of high discharge rates of three hours or less, the kinetic stability of the electrochemically modified high capacity form of MoS_2 plays an important role. As the discharge rate is increased for a cell charged to 2.4 V, two changes occur in the capacity fade curve. These changes are an increase in the rate of capacity fade during the early cycles and the absence
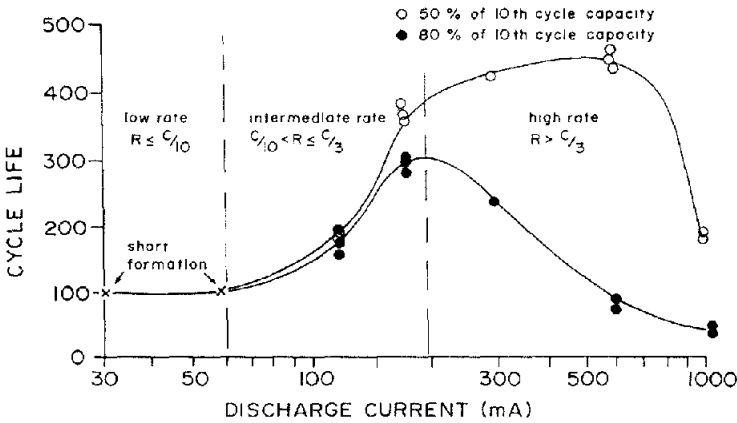
Fig 3 Cycle life as a function of discharge current Cycle life defined at 50% and 80% of 10th cycle capacity remaining Cells are cycled between 2 4 and 1 1 V, with a recharge current of 60 mA
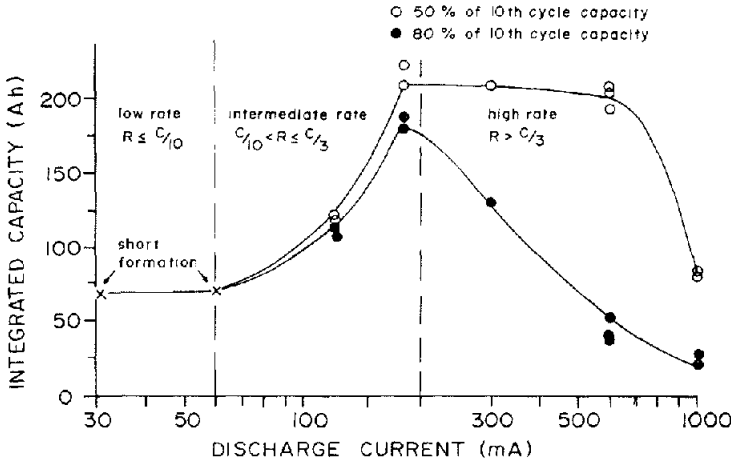

Fig 4 Integrated capacity over the life of the cell as a function of discharge current Life of the cell defined as number of cycles achieved until 50% or 80% of 10th cycle capacity remains Cells are cycled between 2 4 and 1 1 V, with a recharge current of 60 mA

of a drastic reduction in this rate of fade after about ten cycles, see Fig. 5. As was mentioned in the Introduction, the ratio of low to high capacity form increases with increasing discharge current This is associated with the slow kinetics of the phase transitions, which causes a build-up of the low capacity form during the slow recharge, with no depletion of this form taking place during the fast discharge and, in addition, no stabilization of the high capacity form.

The capacity loss occurring at high rate discharges is not irreversible The capacity can be regained through a low rate discharge. Figure 6 shows that the extra capacity at cycle #137, as the result of a discharge at 120 mA,
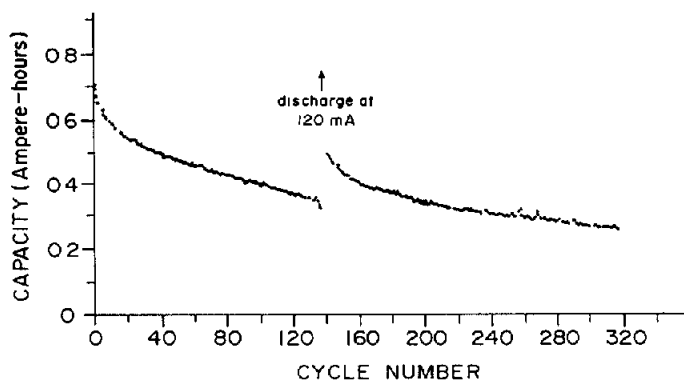
Fig 5 Capacity fade curve for a cell repeatedly discharged at 1 0 A from 2 4 to 1 1 V, charge current is 60 mA
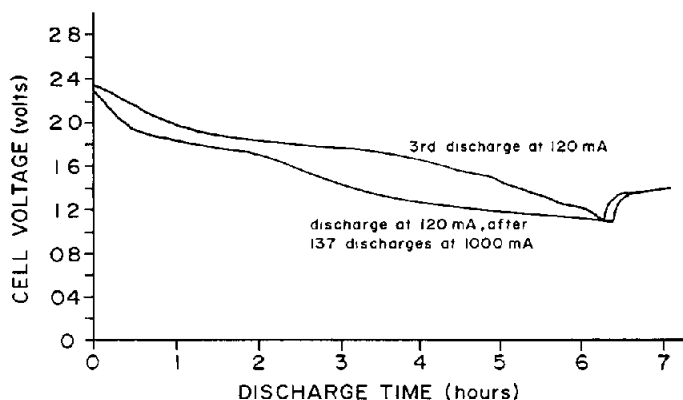

Fig 6 Voltage curves of cells discharged at 120 mA to 1 1 V One cell was previously discharged 136 times at 1 0 A to 1 1 V, and the other cell three times at 120 mA to 1 1 V

is delivered at a cathode potential where the low to high capacity phase conversion occurs [3].

It should be emphasized that the high rate of capacity fade for high rate discharges can be drastically reduced by restricting the charging voltage to 2.2 V. In other words, deliverable capacity can be traded for discharge rate capability.

Intermediate discharge rates

At discharge rates ranging from more than three hours to less than ten hours, cycle life is no longer determined by the stability of the cathode but, instead, by the stability of the electrolyte in contact with the electrodes. In this region of intermediate discharge currents cycle life becomes shorter as the discharge current decreases. This is predominantly thought to be a time effect, *i e*, at low discharge currents cells are being discharged for a longer period of time, resulting in more electrolyte decomposition per discharge
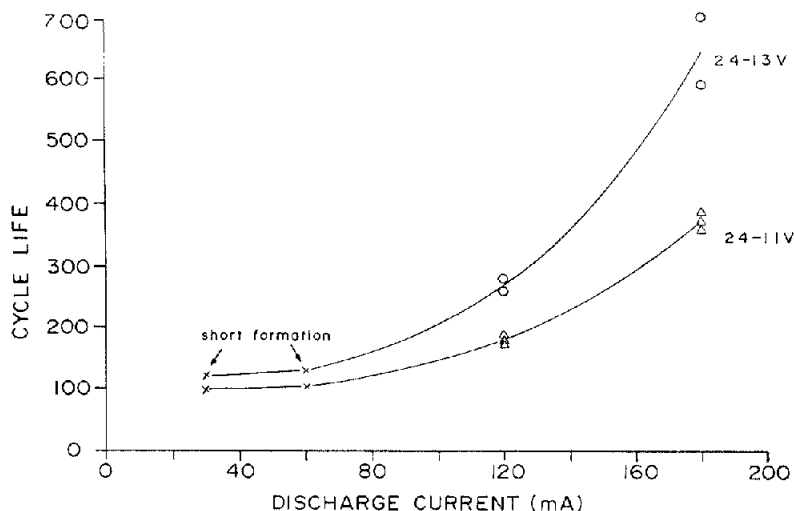
Fig 7 Cycle life as a function of discharge current in the region of intermediate discharge rates Cycle life defined at 50% of 10th cycle capacity remaining Cells are cycled between 2 4 and 1 3 V and between 2 4 and 1 1 V with a recharge current of 60 mA

and therefore a decrease in the number of discharge cycles This explanation assumes that a significant portion of the electrolyte decomposition occurs during discharge of the cell.

It should be noted here that the rate of electrolyte breakdown on open circuit stand is very small. Evidence for this comes from the fact that cycling tests with a 5 h open circuit stand inserted after each discharge, do not show a degradation in cycle life Furthermore, the cells have a good shelf life which far exceeds the length of the cycle life tests reported here. This difference in the rate of breakdown is most likely due to the formation of passivation layers on the electrodes

Measurements of charge imbalance [9] and gas evolution [13] have shown an increase in the rate of electrolyte breakdown with decreasing cell voltage In order to see whether the effect of discharge rate on cycle life is enhanced by discharging the cell below 1 3 V, parallel tests were conducted In these tests, cells were discharged at different rates between 2 4 and 1 3 V and 2 4 and 1 1 V, respectively The results presented in Fig 7 show that lowering the discharge cut-off voltage from 1 3 V to 1 1 V does decrease the cycle life more than would be expected from the increase in depth of discharge.

Low discharge rates

At very low discharge rates of ten hours or more, cycle life is still controlled by the stability of the electrolyte. In this region electrolyte decomposition leads eventually to a low impedance failure (or short formation) during charge and not a high impedance failure, as is the case for the higher discharge currents. This failure is most likely due to the non-

uniformity of the charge current density ι e , local areas of high current caused by the deposition of electrolyte breakdown products. It is known, in general, that high charge currents lead to the formation of lithium dendrites which, in this case, form locally in regions of high charge current densities. These dendrites lead to shorts before the cathode becomes completely inactivated as a result of the accumulation of solid breakdown products. The assumed role of poor lithium morphology in the cell failure at very low rate discharges is supported by the fact that the formation of shorts can be avoided when the charge rate is lowered from 60 mA to 30 mA. As is shown in Fig. 8, the incidence rate of shorts is increased by increasing the charge current density.

All cycle life data shown in Fig 8 (for a fixed discharge current of 120 mA) are for cells which failed due to the formation of shorts. The frequency of short formation decreases with decreasing charge current At a recharge current of 120 mA nearly 100% of the cells fail due to short formation, while at 60 mA, 50% fail due to short formation and 50% due to an increase in cell impedance (at about the same cycle number).

It should be emphasized that the problem of low cycle life at very low discharge rates can be avoided by reducing the charge rate simultaneously. As was stated earlier, in the latter case the cell fails via a gradual loss in deliverable capacity, due to an increase in cell impedance, at a much higher cycle number. An example of this is given with two tests in which cells are cycled between 2.4 and 1.3 V at a 60 mA discharge current, but with two different charge currents. The cell charged at 60 mA failed after 130 cycles due to short formation, while the cell charged at 30 mA failed with a high impedance after 280 cycles.
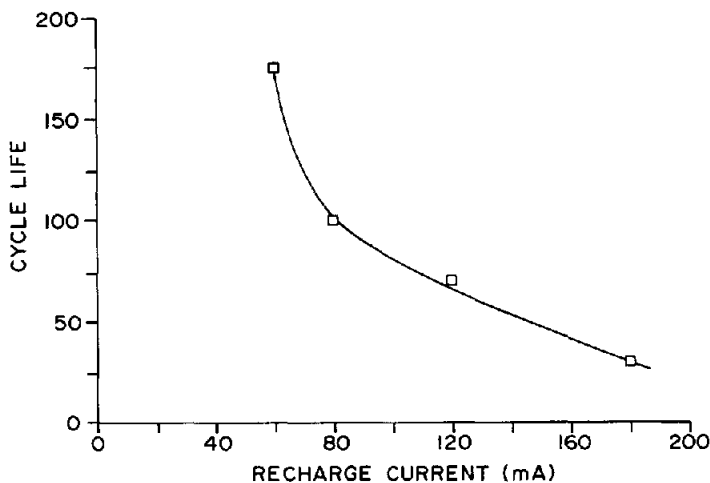

Fig 8 Cycle life as a function of recharge current at a fixed discharge current Cells are cycled between 2 4 and 1 1 V, with a discharge current of 120 mA Cycle life defined as the number of cycles achieved before a short occurs

In this region of very low discharge currents, cycle life limited by short formation is not much affected by the magnitude of the discharge current. This could be understood if it is assumed that for very low discharge currents the electrodes remain more or less undisturbed (i e , passivated) during discharge

Pulsed current discharges

For many practical applications, discharges are done in a pulsed mode, alternating high current pulses with low current standby periods. Examples of such applications are two-way radios, cellular phones, data transmitters. In this case cycle life predictions cannot be based on the response of the battery to the minimum or maximum discharge current, or to their average In general, the cycle life is significantly longer. Two examples given here are two-way radio and cellular phone applications

In the two-way radio test the battery (six cells series-connected) was discharged between voltage limits corresponding to 2 3 and 1 1 V/cell with currents of 1050 mA for 5 s, 140 mA for 5 s and 35 mA for 90 s. The battery delivered 0 52 A h at the 10th cycle, with a cycle life of about 500 and an integrated capacity of 215 A h (to 50% of the 10th cycle capacity)

In the cellular phone test, the battery (5 cells series-connected) was discharged between voltage limits corresponding to 2.4 and 1.2 V/cell, with currents of 700 mA for 3 min and 50 mA for 27 min. The battery delivered 0 56 A h at the 10th cycle with a cycle life of about 400 and an integrated capacity of 185 A h (to 50% of the 10th cycle capacity).

Conclusion

Most manufacturers of rechargeable batteries quote cycle life as a single-valued number This is an over-simplification since the cycle life performance depends greatly on a large number of operating conditions. This is shown to be true, in particular, for the discharge rate of a rechargeable lithium battery

At very high discharge rates, the deliverable capacity shows a continuous decline in capacity, as a function of cycle number, as a result of the accumulation of the low capacity or naturally-occurring form of MoS_2 The rate of this accumulation, i e , cathode degradation, increases with increasing rate of discharge, and therefore cycle life decreases as the discharge rate increases The rate of capacity loss, however, can be significantly reduced by restricting the charging voltage to 2 2 V

At intermediate discharge rates, decomposition of the electrolyte is the main degradation process, with the loss of electrolyte and the deposition of solid decomposition products on the electrodes and in the separator pores leading to eventual cell failure Even when the rate of electrolyte breakdown is independent of discharge current, the total amount of elec-

trolyte decomposition per discharge will increase with lower discharge current because of longer discharge times. Therefore in this region of discharge currents, cycle life decreases as the discharge current decreases

At very low discharge rates, decomposition of the electrolyte is still the main degradation process. However, rapid increase in current non-uniformity, giving rise to lithium dendrites on charge, leads to cell failure in advance of that due to the accumulation of breakdown products in the cathode. This low impedance failure can be avoided by reducing the charge current With the standard charge current of 60 mA, there is no observable effect of discharge current on cycle life in this region.

For discharges involving mixed currents, typical for many practical applications, the behaviour of the cell is not dictated by the maximum, minimum or average discharge current. Cycle life is generally significantly longer than would be predicted from these currents.

In none of these proposals does the lithium anode by itself limit the cycle life of the Li/MoS_2 cells This is consistent with the observation that all cells disassembled after cycling contained malleable anodes, showing electrochemically active lithium.

Acknowledgement

List of symbols

D.O D.	Depth of discharge
R	Discharge rate
C/n	Value of discharge rate corresponding to a full discharge in n hours

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