

A NEW RECHARGEABLE LITHIUM BATTERY

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Summary

A new, secondary lithium cell employing an Mo_6S_8 cathode has been developed to the prototype stage in an "AA" format. These cells can deliver about 2 W h of energy and are capable of high rate discharge up to about the 2 C rate. Cycle life testing of these cells has shown promising life characteristics, but a considerable dependence of cycle life on both charge and discharge rate is noted. Some preliminary testing has been done in series-connected batteries, pointing to areas where improvements can be made.

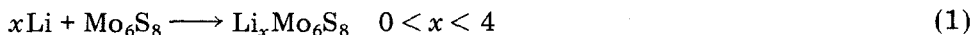
Introduction

Secondary "AA" size cells utilizing lithium molybdenum disulfide chemistry have been manufactured by Moli Energy Limited in pilot plant quantities since 1985 and in commercial quantity since September, 1987. These have a capacity of 0.6 A h and a sloping discharge curve with the cell voltage decreasing from 2.3 V for a fully charged cell to 1.3 V for a discharged cell, giving an average voltage of 1.8 V. While these cells have found ready application in certain markets, many large volume markets demand even greater energy density, higher voltage, and commensurately higher rate capability.

Moli Energy Limited has been investigating a variety of new electrochemical systems with a view towards the development of a cell that can provide a substantially increased energy density at discharge rates commensurate with most applications for secondary cells. One of the systems investigated employed a lithium anode, a Chevrel phase lithium molybdenum sulfide cathode, and a proprietary non-aqueous electrolyte. Prototype "AA" size cells with this chemistry showed a deliverable energy density twice that of the same size state-of-the-art nickel-cadmium cells at high discharge rates. The cells retained their high discharge rate capability for many cycles, with life cycle data on some early prototype cells showing that the deliverable capacity of the cells remained above 80% of the nominal capacity after 200 cycles. Preliminary data indicate that the charge retention capability of the cells is also very good, being comparable with that of other lithium cells.

Chemistry and construction

The Chevrel phase cathode material used in the cells has the formula $\text{Li}_x\text{Mo}_6\text{S}_8$. The cell reaction is according to eqn. (1).



The crystallography [1, 2] and electrochemistry [3 - 6] of $\text{Li}_x\text{Mo}_6\text{S}_8$ have been described by several workers. Lithium intercalates within a three dimensional network of channels within the lattice framework of Mo_6S_8 . For $0 < x < 1$, $\text{Li}_x\text{Mo}_6\text{S}_8$ exists as a single phase having a rhombohedral crystal structure. The lattice constant varies from 6.43 Å at $x = 0$ to 6.47 Å at $x = 1$. The rhombohedral distortion from the cubic structure increases with increasing x , with the lattice angle increasing from 91.3° at $x = 0$ to 92.3° at $x = 1$. For $1 < x < 3$, $\text{Li}_x\text{Mo}_6\text{S}_8$ exists as a two-phase mixture of $\text{Li}_1\text{Mo}_6\text{S}_8$ and $\text{Li}_3\text{Mo}_6\text{S}_8$.

The structure of $\text{Li}_3\text{Mo}_6\text{S}_8$ is also rhombohedral, but the lattice constant is 6.64 Å, larger than that for $\text{Li}_1\text{Mo}_6\text{S}_8$. The lattice angle is also increased at 94.5° . A single phase compound having the rhombohedral structure exists for $3 < x < 3.8$ with the lattice constant increasing to 6.66 Å at $x = 3.8$. For $3.8 < x < 4$, two single phase structures with lower symmetry exist. The phase existing at the lower end of this range of x has a rhombohedral structure similar to that for $3 < x < 3.8$, but with a lattice distortion incommensurate with the unit cell. The phase existing at the higher x range has a triclinic crystal structure with lattice constants $a = 6.645$ Å, $b = 6.665$ Å and $c = 6.67$ Å and lattice angles $\alpha = 95.3^\circ$, $\beta = 93.5^\circ$ and $\gamma = 95.7^\circ$.

The phases of $\text{Li}_x\text{Mo}_6\text{S}_8$ are metallic, thus providing good electrical conductivity for $0 < x < 4$. The relatively small unit cell volume changes over the entire range of x and the good electrical conductivity combines to facilitate the design of a high-rate, highly-reversible cathode. Tarascon *et al.* [7] have reported on the favourable properties of a related material, AgMo_6S_8 .

The prototype "AA" size cells we constructed employed a pure lithium anode and a microporous poly(propylene) separator. The cells were of a jelly roll construction with an electrode area of about 200 cm², hermetically sealed in a nickel-plated, mild steel casing with a glass-to-metal feed-through for the positive terminal. The electrolyte was a proprietary formulation of non-aqueous solvents containing LiAsF_6 .

Performance characteristics

The multiple phase behaviour of the $\text{Li}_x\text{Mo}_6\text{S}_8$ cathode material provides for a distinctive discharge profile. This is shown in Fig. 1. The open circuit voltage is about 2.4 V for the first 25% of the discharge, corresponding to $0 < x < 1$. The open circuit voltage drops abruptly after this to about 2.1 V where it remains until the discharge is 75% complete. This point

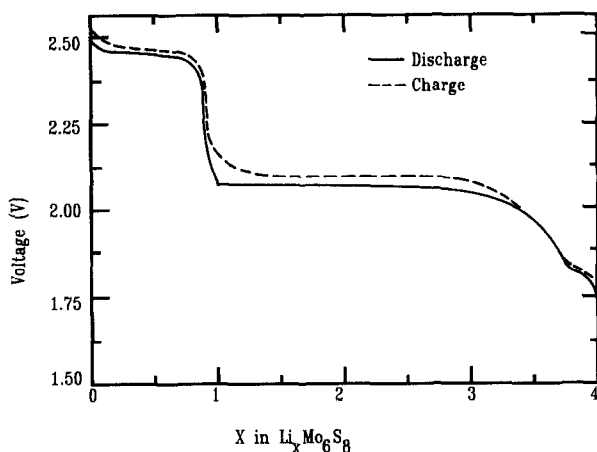


Fig. 1. Voltage of an $\text{Li}/\text{Mo}_6\text{S}_8$ cell as a function of x in $\text{Li}_x\text{Mo}_6\text{S}_8$.

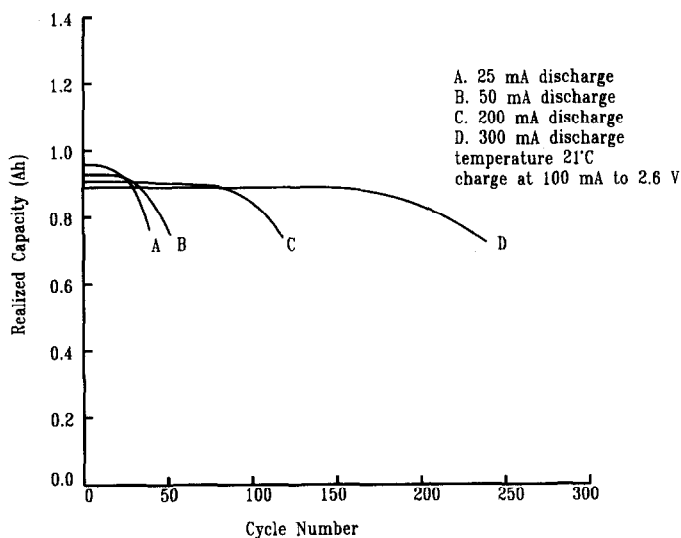


Fig. 2. Cycle life of "AA" size $\text{Li}/\text{Mo}_6\text{S}_8$ cells as a function of discharge rate.

corresponds to $x = 3$ in $\text{Li}_x\text{Mo}_6\text{S}_8$. For the final 25% of the discharge the open circuit voltage decreases gradually to about 1.75 V at full discharge.

Apart from the occasional random occurrence of shorts, the cycle life performance of the "AA" size $\text{Li}/\text{Mo}_6\text{S}_8$ cells of a fixed design under fixed test conditions was quite uniform. However, there is a considerable dependence of the cycle life on discharge and charge rates, as well as on depth of discharge and duty cycle. Generally, the cycle life was higher for higher constant current discharge rates, at least up to about 300 mA. In this discharge current range, at room temperature the cell capacity remained fairly constant until near end-of-life, where the capacity began to decline rapidly with increasing cycle number. This behaviour is shown in Fig. 2 for several

discharge rates and for charging at 100 mA to 2.6 V. Interestingly, there is an observed linear relationship between the discharge rate for constant current discharge and the realized cycle life over this range of discharge currents, as shown in Fig. 3. It is also observed, for pulsed discharges where short periods of high current discharge are interspersed with periods of open circuit stand, that the cycle life is higher than one would expect on the basis of the calculated average discharge current for this duty cycle. This deviation from the expected behaviour is also shown in Fig. 3. Figure 4 shows the dependence of cycling behaviour at room temperature on charge rate for a fixed 25 mA discharge. Although the data for the lower charge rate are incomplete, there is an apparent substantial increase in cycle life for a 25 mA charge as compared to a 100 mA charge.

The reasons for the observed trends in cycle life for different charge and discharge rates are not well understood at present, but may be related to decomposition of electrolyte at either the anode or the cathode. There is no evidence that the cathode material itself is unstable. The observed linear relationship between cycle life and constant current discharge rate can be tentatively explained by noting that the time available for electrolyte decomposition increases inversely with the discharge rate and by hypothesizing that failure occurs after a fixed quantity of electrolyte has decomposed. The observed failure may be due either to plugging of cathode pores with electrolyte decomposition products, resulting in loss of a continuous path for ions within the cathode pore network, as modeled by Dahn *et al.* [8], or to irreversible passivation and loss of electrical continuity of the anode due to its reaction with the electrolyte. The higher than expected cycle

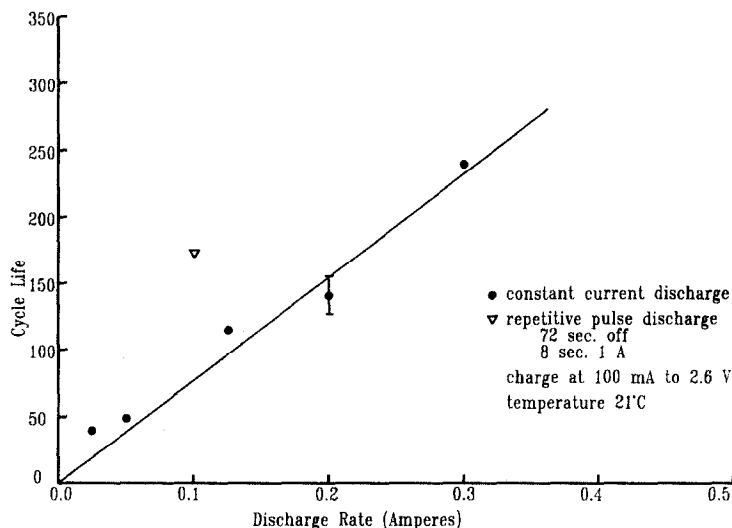


Fig. 3. Cycling behaviour of "AA" size $\text{Li}/\text{Mo}_6\text{S}_8$ cells at different discharge rates. Data for constant current discharges are shown by the closed circles, and data for pulsed discharge are shown by the triangle.

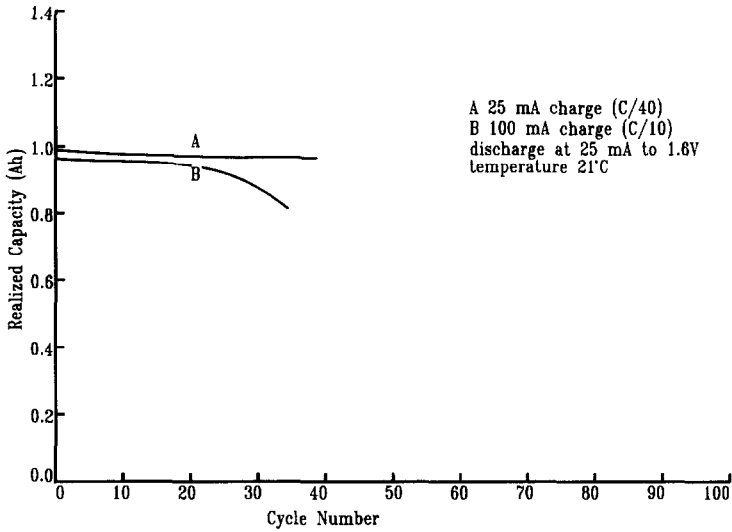


Fig. 4. Cycling behaviour of "AA" size $\text{Li}/\text{Mo}_6\text{S}_8$ cells at different charge rates.

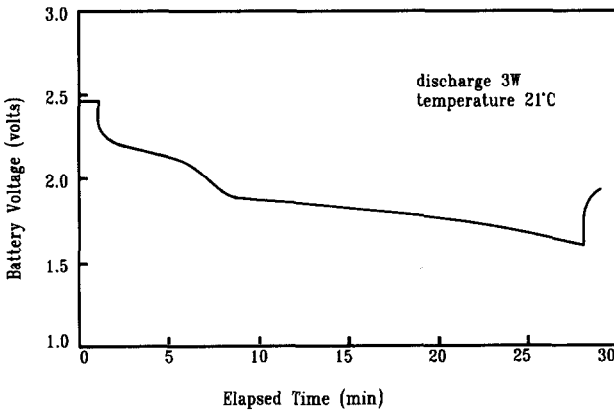


Fig. 5. Discharge curve for an "AA" size $\text{Li}/\text{Mo}_6\text{S}_8$ cell discharged at high constant power.

life for the pulsed discharge, and the lack of performance degradation with open circuit stand, suggest that the failure is associated with the anode and not with the cathode. The observed improvements with slower charging also suggest that the anode is the life-limiting component, as slower charging results in a lower surface area anode deposit. This type of failure mode is different from that observed for Li/MoS_2 cells where the failure is related to cathode deterioration [8].

At higher discharge rates a different failure mode is apparent. Figure 5 shows a discharge curve for a 3 W constant power discharge, and Fig. 6 shows the cycling behaviour of this cell at room temperature. The cell was

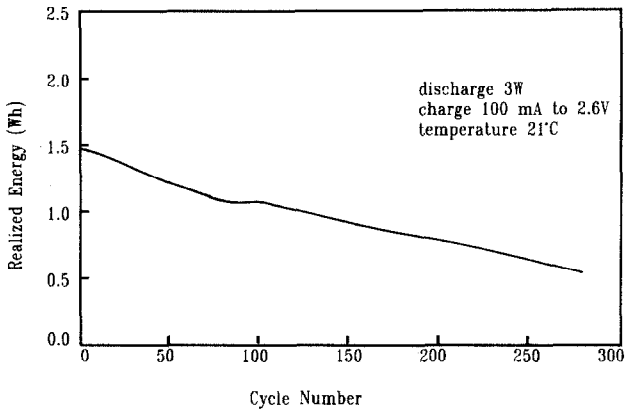


Fig. 6. Cycling behaviour of an "AA" size $\text{Li}/\text{Mo}_6\text{S}_8$ cell discharged at high constant power.

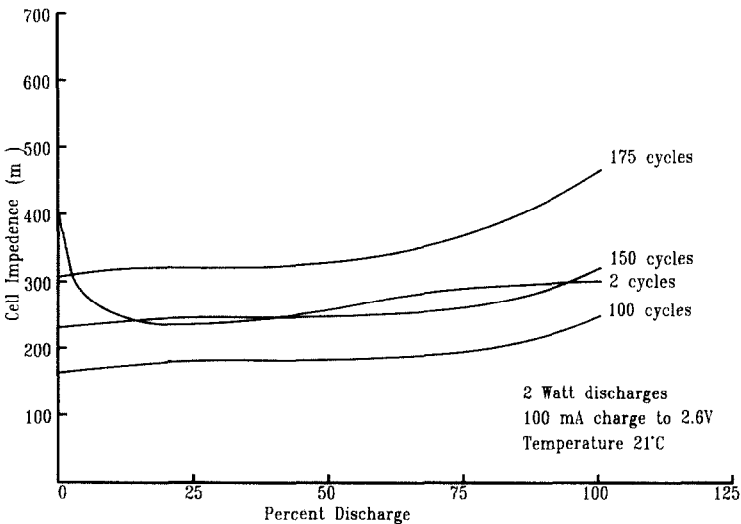


Fig. 7. D.C. impedance of an "AA" size $\text{Li}/\text{Mo}_6\text{S}_8$ cell as a function of depth of discharge at various cycle numbers.

charged at 100 mA to 2.6 V. The cell capacity in this case fades gradually with increasing cycle number as the cell impedance gradually increases.

The cell impedance as a function of depth of discharge at various numbers of cycles is shown in Fig. 7. As can be seen from the Figure, the cell impedance varies in an anomalous manner with depth of discharge during early cycles, but becomes almost independent of state-of-charge after a few cycles, with only a slight increase noted as 100% depth of discharge is approached. The initial anomalous behaviour is thought to be due to a gradual increase in the anode surface area during the first few cycles. During later cycles, the only observable change is a gradual impedance in-

crease that is independent of the state of charge. This impedance increase affects the realized capacity of the cells only at higher discharge rates, giving rise to the observed failure mode for high rate discharges.

The performance of $\text{Li}/\text{Mo}_6\text{S}_8$ cells has been evaluated for shallow cycling conditions. It has been found that for a given realized capacity a greater number of cycles can be obtained if cycling is restricted to the upper plateau on the discharge curve, rather than to the lower plateau. The reason for this is not known, but may be related to the greater total electrode volume, under these conditions, that would provide electrode compression and enhance the electrical continuity of the electrodes. Figure 8 shows the delivered energy as a function of cycle number for a cell cycled only over the upper discharge plateau, at room temperature, at a discharge rate of 200 mA. The cell was charged at 100 mA to 2.6 V. Approximately 1500 cycles were realized before appreciable loss of capacity occurred. The energy per cycle delivered in this test is equivalent to an energy density of 25 Wh kg^{-1} in the "AA" size cell. This energy density would increase to about 35 Wh kg^{-1} in large size cells based on scaling factors obtained from the development of "BC" size Li/MoS_2 cells [9], making $\text{Li}/\text{Mo}_6\text{S}_8$ batteries attractive candidates for aerospace applications.

The power delivery capability of the $\text{Li}/\text{Mo}_6\text{S}_8$ cells is quite respectable. Figure 9 shows the dependence of the volumetric energy density of "AA" size cells on the volumetric power density at room temperature. As can be seen from the Figure, nearly the full capacity can be realized for discharge rates of up to the C rate. Approximately 50% of the full nominal energy can be delivered at the $2C$ rate. The power delivery capability is reduced at low

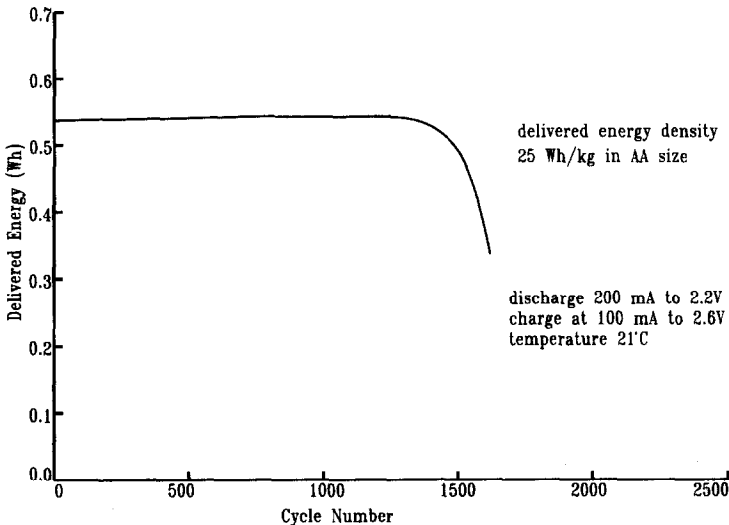


Fig. 8. Shallow cycling behaviour of an "AA" size $\text{Li}/\text{Mo}_6\text{S}_8$ cell.

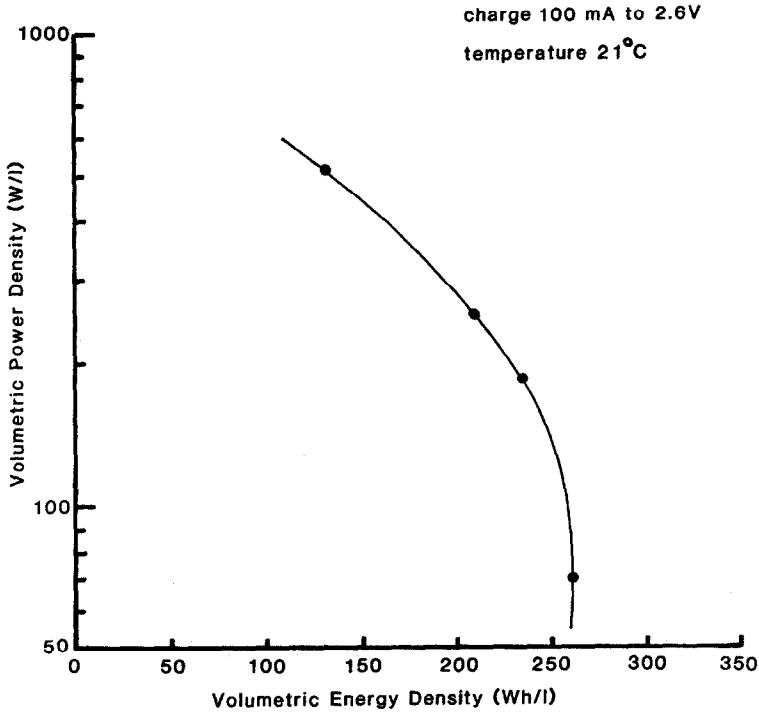


Fig. 9. Relationship between volumetric energy density and volumetric power density for Li/Mo₆S₈ cells.

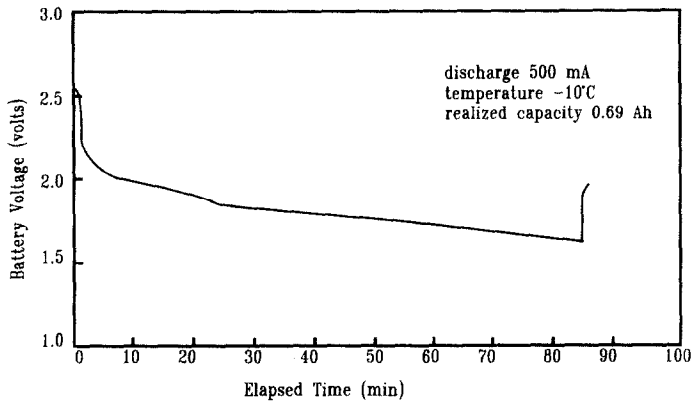


Fig. 10. Discharge curve for an "AA" size Li/Mo₆S₈ cell discharged at low temperature.

temperatures. Nevertheless, more than 70% of the nominal capacity can be obtained at a $C/2$ rate at -10°C as is shown in Fig. 10.

Some evaluation of the performance of "AA" size cells in series-connected batteries has been carried out. Figure 11 shows the cycling behaviour at room temperature of a 4-cell series-connected battery. For the

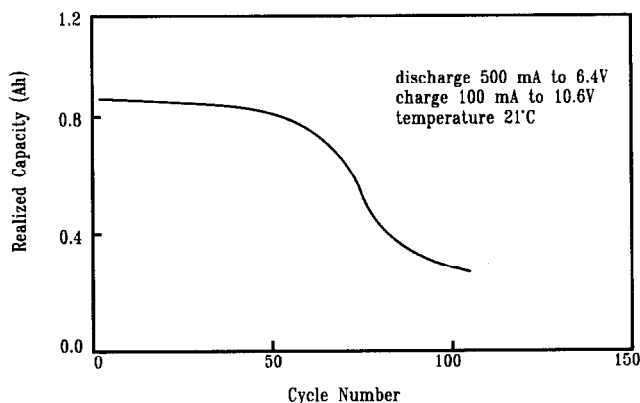


Fig. 11. Cycling behaviour of a battery containing 4 series-connected "AA" size Li/Mo₆S₈ cells.

first 50 cycles the realized capacity was equivalent to that deliverable by single cells tested with the same charge and discharge currents. Battery charging was terminated at 10.4 V (4 times 2.6 V) and discharge was terminated at 6.4 V (4 times 1.6 V). After 50 cycles, the realized capacity began to decline appreciably. This was due to a short which developed in one of the cells, causing it to discharge to a greater depth of discharge than the remaining cells. This caused the battery voltage to drop to the voltage for discharge termination too quickly and, hence, the measured battery capacity fell. After several more cycles, state of charge differences appeared between the remaining cells in the battery, causing a further drop in the battery voltage. Thus, it was observed that the cycle life of the battery was less than that of equivalent single cells tested independently. This behaviour is substantially different from that in the case of Li/MoS₂ cells, where the cycle life of series-connected batteries is equivalent to that of single cells [10]. The cause of the premature battery failure is not fully understood, but it is believed that it is associated with the abrupt step in the discharge curve. When the cells are charged across this step, large perturbations in the local current density can occur due to variations in the local impedance of the electrodes. This, in turn, can cause dendrites to bridge the gap between the two electrodes, causing a short. The problem was not observed when cells were not cycled across this step in the discharge curve.

Conclusions

The Li/Mo₆S₈ electrochemical system is an attractive candidate for rechargeable lithium cells. Prototype "AA" cells have been constructed that have a deliverable energy of about 2 W h. The power delivery capability of these cells is also quite good, with sustained discharge possible at greater than 2 C discharge rates. The cycle life of individual cells was found to be

quite reproducible, apart from the random incidence of shorts in cells that were cycled over the full depth of discharge. However, cycle life was found to decrease at lower rates of discharge, although cycle life at low rates of discharge could be improved by lowering the charge rate to a rate comparable with the discharge rate. Shallow cycling of the cells on the high voltage plateau out to 25% of the nominal capacity was impressive, with more than 1500 cycles achieved before appreciable loss of cell performance.

The incidence of shorts in cycled cells impacted negatively on the cycling performance of series-connected batteries, as the shorts caused imbalance in the state of charge of the cells in the battery. This is an area in which additional effort needs to be devoted in order to eliminate or counteract the effects of the shorts. Various methods can be tried to effect this, including the fabrication of electrodes with greater resistivity uniformity to reduce the probability of shorts, the development of charge equalizing chemical shuttle mechanisms in individual cells (similar to that provided by the oxygen recombination mechanism in nickel-cadmium cells), or the development of shunt diodes to shunt current around fully charged cells and allow the remaining cells in a series-connected battery to become fully charged.

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