TESTING METHODS FOR LITHIUM MOLYBDENUM DISULFIDE INTERCALATION BATTERIES

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1. Introduction

Moli Energy Limited has, during the past seven years, developed rechargeable lithium molybdenum disulfide batteries which have a number of superior performance characteristics, including a high energy density relative to other rechargeable batteries, a high power density, and a long charge retention time. These characteristics have been demonstrated in "A" size (IEC nomenclature: R-6) and "C" size (R-14) configurations as well as in a developmental "BC" size (R-40) format.

The fundamental chemistry of this system is the intercalation of lithium into molybdenum disulfide according to the following equation:

$$x\mathrm{Li} + \mathrm{MoS_2} \longleftrightarrow \mathrm{Li}_x\mathrm{MoS_2} \quad 0 < x < 1 \tag{1}$$

This reaction is reversible for an MoS_2 host lattice which has a different crystal structure from naturally occurring MoS_2, molybdenite [1]. This battery system uses a non-aqueous electrolyte and achieves a coulombic efficiency of the charge/discharge reaction of 100%. A special feature of the intercalation system is that the chemical potential of the compound Li_xMoS_2 depends on the state-of-charge of the cell. The cell voltage can therefore be used as a state-of-charge indicator.

These unique features of a lithium intercalation battery require specialized testing methods. In this paper, methods to evaluate cycle life, energy, and power densities will be discussed. These methods have been used over the years to evaluate the progress of the development of this battery system. They can be used to test single cells of different sizes as well as batteries.

2. Test methods

2.1. Charging of cells and batteries

For a standard test, single cells are recharged at a constant current which is determined by dividing the nominal capacity, C, of the cell by 10 hours, *i.e.*, a $C/10$ rate. The endpoint of charge is controlled using the voltage at the cell terminals. A fully charged cell is charged to a cutoff voltage of

2.4 V. A cell charged to a cutoff voltage of 2.6 V is called supercharged. The latter procedure is occasionally used to increase the usable capacity of the cell.

Similarly, a battery is charged at a $C/10$ rate with C the nominal battery capacity. The endpoint of charge is determined by the voltage at the battery terminals. A fully charged battery containing N cells in series is charged to a cutoff voltage of $N \times 2.4$ V. Charging is always performed at a temperature of 21 °C for this type of testing.

2.2. Cycle life and delivered energy

A standard cycle life test consists of a series of constant current charge and discharge half cycles which follow each other immediately. The depth-of-discharge (D.O.D.) is determined by the voltage cutoff. A fully discharged cell is discharged to 1.1 V (100% D.O.D.). The standard discharge rate is $C/5$.

Accelerated cycle life tests use standard charge conditions, but use an increased discharge rate of $C/3.33$ and a reduced D.O.D. of 90% which corresponds to a cutoff voltage of 1.3 V. Both tests are performed at 21 °C. Cycle life testing of batteries is performed in a similar manner by using the voltage at the battery terminals to determine the endpoint of discharge. A fully discharged battery containing N cells in series is discharged to a cutoff voltage of $N \times 1.1$ V.

The results of these tests are displayed by plotting the realized discharge capacity as a function of cycle number. The energy delivered is determined by integrating the product of the terminal voltage and the discharge current over the duration of a discharge.

2.3. Rate capability and delivered power

The rate capability of a cell or battery is determined by discharging the fully charged cell at a given discharge rate to 100% D.O.D. Each measurement at a different rate requires a fully charged cell. From the voltage profile, both the realized capacity for various D.O.Ds and the delivered power can be determined.

A technique which is less time consuming in determining the realized capacity as a function of the discharge rate is the signature curve technique. A fully charged cell or battery is first discharged at the highest current of the experiment to 100% D.O.D. The battery is then rested on open circuit for a period of 30 min. During this time, the battery equilibrates and the battery voltage recovers. The battery is then further discharged, at the next lowest current, to the same D.O.D. The delivered capacity at this lower rate is taken to be the sum of the discharge capacity of the two discharges. This process is repeated until the discharge rate has been reduced successively to the lowest rate to be measured. A plot of the realized capacity *versus* the discharge current is called a signature curve [2].

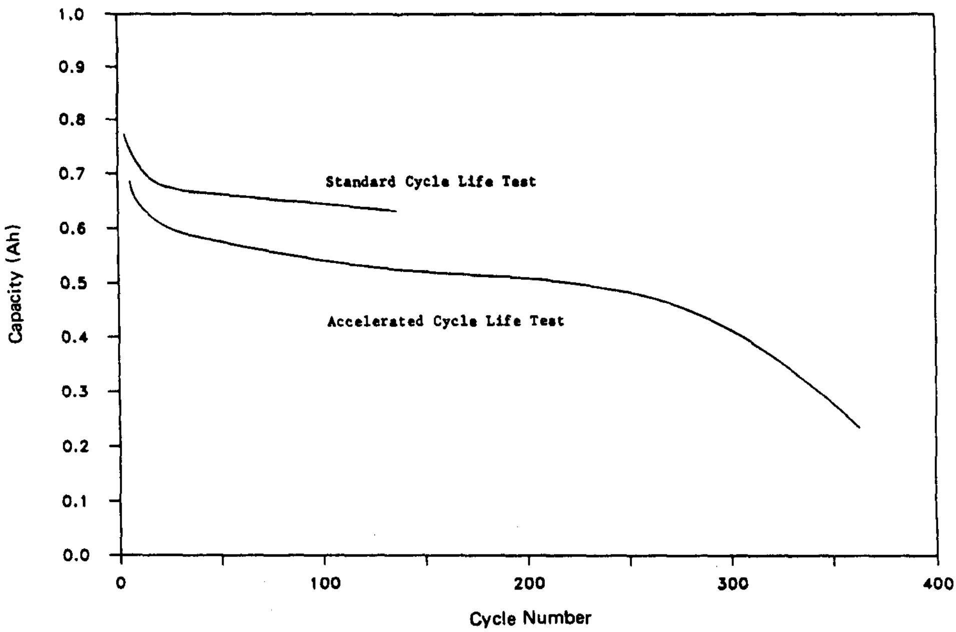

Fig. 1. Realized capacity of "AA" size cells *vs.* cycle number for standard and accelerated cycle life tests. Charge rate $C/10$; cutoff 2.4 V; discharge rate for standard test $C/5$ cutoff 1.1 V; discharge rate for accelerated test $C/3.33$, cutoff 1.3 V. Temperature 21 °C.

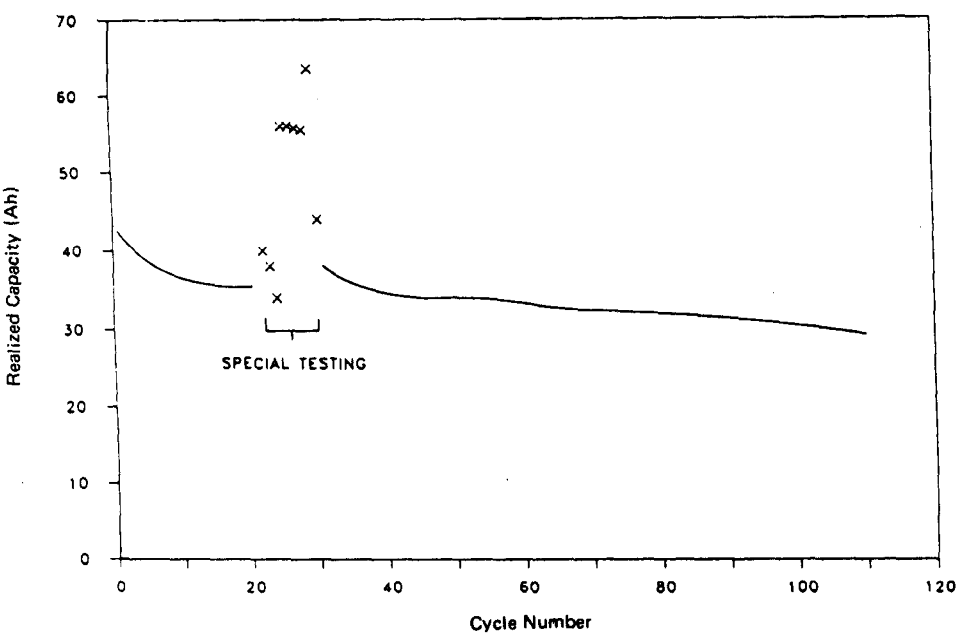

Fig. 2. Accelerated cycle life test for battery consisting of 6 "BC" size cells in series.

3. Test results

3.1. Cycle life and delivered energy

Figure 1 shows the results of standard and accelerated cycle life tests of "AA" size cells with a nominal capacity of 0.6 A h. The accelerated cycle life test was terminated when the cell reached a realized capacity of 0.3 A h after 340 cycles The standard cycle life test is still continuing. The delivered energy on the 10th cycle of the standard test is 1.26 W h.

Figure 2 shows the results of an accelerated cycle life test of a "BC" cell battery pack consisting of 6 cells in series. The battery pack has a nominal capacity of 50 A h. The voltage of the fully charged battery is 14.4 V. Between cycles 21 and 30, some special testing was performed which included a supercharge followed by a discharge to 100% D.O.D. The realized capacity for this cycle was 63 A h and the delivered energy was 680 W h. With a battery weight of 7.23 kg, this corresponds to an energy density of 94 W h kg^{-1}.

3.2. Rate capability and delivered power

Figure 3 shows the voltage profiles for an "AA" size cell discharged at *C*/5, *C*, and 2.5 *C* rates at 21 °C. The shape of the voltage profile is due to the properties of the intercalation compound and is not affected by the rate. The discharge curves for various rates are simply offset by a constant voltage relative to each other. The delivered power changes with the state-of-charge. It is about 3 W for a fully charged cell at a 2.5 *C* rate.

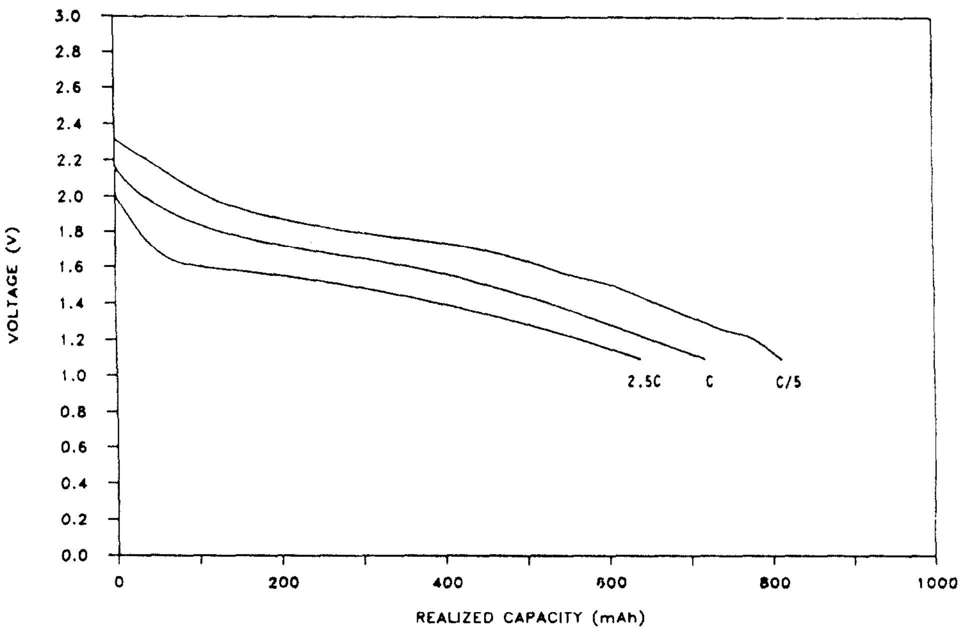

Fig. 3. Voltage profile for "AA" cell discharged at various rates.

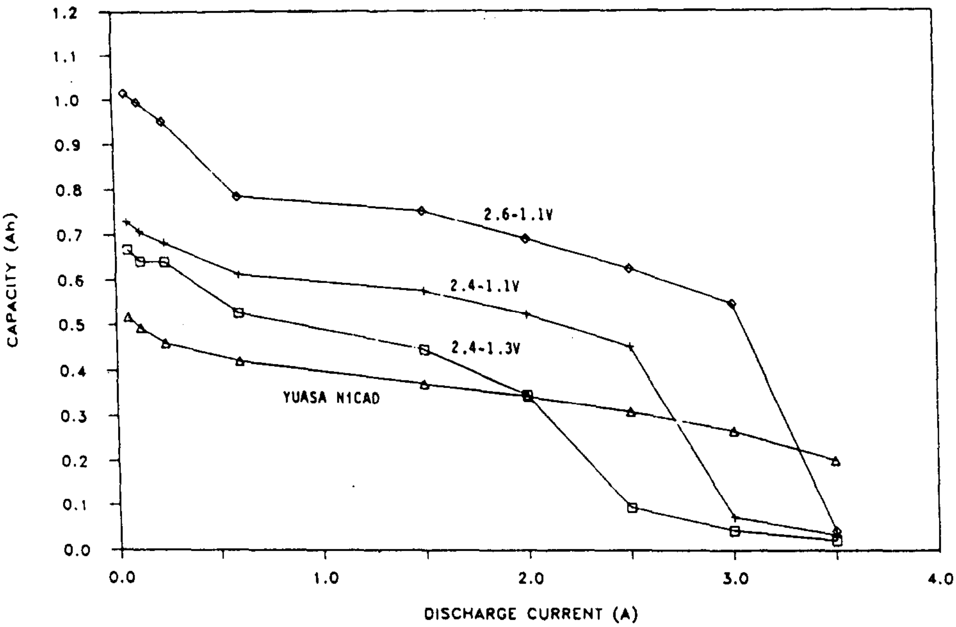

Fig. 4. Signature curves for a supercharged "AA" cell to 100% D.O.D. (2.6 - 1.1 V); a fully charged "AA" cell to 100% D.O.D. (2.4 - 1.1 V); a fully charged "AA" cell to 90% D.O.D. (2.4 - 1.3 V). The signature curve for an "AA" size Ni–Cd cell is shown for comparison.

Figure 4 gives signature curves for a supercharged "AA" cell to 100% D.O.D. and for fully charged "AA" cells to 100% and 90% D.O.D. The curves have an "S" shape and show than an "AA" cell can provide a continuous current output of 3 A which corresponds to a 5 *C* rate at a temperature of 21 °C.

Figure 5 gives a signature curve for the "BC" cell battery pack. The battery pack has been supercharged and the signature curve has been determined for 100% D.O.D. with a maximum current of 50 A which corresponds to a *C* rate discharge. This measurement was performed after 21 standard cycles.

4. Discussion

The scaling of the MOLICEL™ technology from "AA" to "BC" size cells was achieved by increasing the electrode area without changing the electrode thickness. The nominal capacity was determined by the average electrode area for the cell size in question. Using the nominal capacity as a basis for determining test currents assured similar current densities for different cell sizes. This was the main reason for the similarity of the test results for "AA" and "BC" size cells, both in the cycle life tests and the rate capability test.

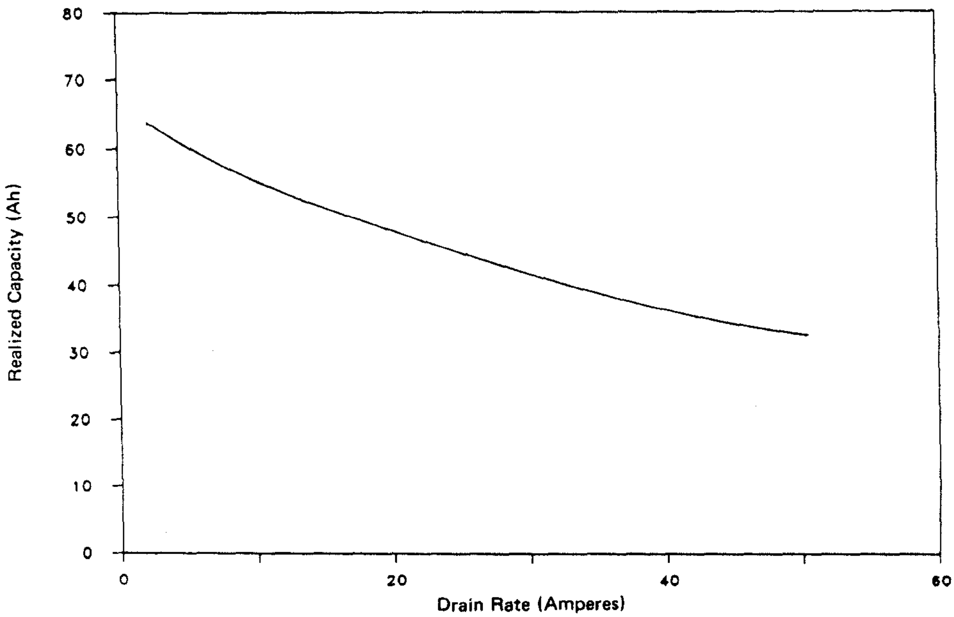

Fig. 5. Signature curve for supercharged 6 cell "BC" battery to 100% D.O.D.

A comparison of the realized capacities during the accelerated cycle life test of the two test objects (Figs. 1 and 2) shows a realized capacity of 106% of nominal capacity for the "AA" cell and 84% for the "BC" battery. This difference reflects the different stages of development for the two cell sizes, with the "AA" cell being a fully engineered product and the "BC" battery being a prototype in the early stages of development. At a *C* rate, the supercharged "AA" cell achieves about 146% of nominal capacity on its 1st cycle, the "BC" battery 68% on its 22nd cycle (Figs. 4 and 5). The difference in fractional capacity is due also, in part, to the different stages of cycle life at which the tests were performed.

The discharge voltage profiles in Fig. 3 demonstrate the dependence of the cell voltage on the state-of-charge. At the low discharge rate of $C/5$, the voltage under load is close to the cell open circuit voltage. For higher rates, the voltage under load is lowered by a nearly constant offset voltage which is due to the small cell impedance which does not change significantly with the depth-of-discharge. This results in a reduction of the realized cell impedance from 0.810 A h at a $C/5$ rate (120 mA discharge current) to 0.630 A h at a 2.5 *C* rate (1.5 A). The signature curve technique gives somewhat lower realized capacities of 0.59 A h and 0.71 A h, respectively. This discrepancy is probably due to the fact that the rest period of 30 min between the discharges of the signature curve technique is of insufficient length to ensure complete equilibration of the cell between successive discharges.

5. Conclusion

Special testing methods for determining the cycle life, energy, and power capabilities of lithium molybdenum disulfide batteries have been developed by taking advantage of the properties of a battery system based on an intercalation reaction. These methods allow a direct comparison of the performance of different cell and battery sizes.

References

1 R. R. Haering, J. A. R. Stiles and K. Brandt, *U.S. Pat. 4,224,390*, September 23, 1980.
2 H. H. Harowitz and K. Strohmaier, *Proc. 29th Power Sources Conf., Atlantic City, NJ, 1980*, pp. 205 - 208.