

TESTING AND EVALUATION OF LITHIUM-ION BATTERIES FOR LEO SPACE MISSIONS

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1. Introduction

In 1990, Sony corporation announced their intention to manufacture a rechargeable lithium ion battery, based on the highly reversible intercalation of lithium ions into the carbonaceous anode and metal oxide cathode. The cells were first introduced for portable telephone use in June, 1991¹. Since that time, other Japanese companies have indicated their plans to manufacture lithium-ion batteries. A copy of Sony's initial specifications are attached to this report in Appendix A, and are summarized below^{2,3}:

- 1) A 3.6V average cell voltage (4.1-2.75V range)
- 2) Excellent cycle life (1200 @ 100% DOD)
- 3) Good capacity retention (70% after 6 months)
- 4) Wide temperature range performance (-20°C to +60°C)
- 5) Excellent Discharge rate (82% capacity at 30 min. discharge rate).
- 6) Excellent Charge rate (100% Charge in <3 hrs).
- 5) High energy density (264 W•hr/l and 120 W•hr/kg for "D" size cell).

Later, specifications for the smaller, "US" series cells were released (see Appendix B). The energy density values for those cells were lower than the initial "D" cell values (e.g. "AA" size specific energy quoted as 78 W•hr/kg).

These specifications show significant promise for application of these batteries in low earth orbit (LEO) small satellites, particularly when compared to existing NiH₂ and NiCd technology. The very high energy density and specific energy will reduce power system volume and weight. The wide temperature range enables simpler

thermal design, particularly for new, small, high power satellites. These batteries also promise to be very low cost. Sony has sold early sample quantities of the sub-C cells for \$90 each and is rapidly increasing production for use in cellular phones and camcorders. The materials used in the lithium ion batteries are relatively inexpensive and benign, so that we expect costs to come down substantially in the future. The low cost will potentially enable inexpensive power systems for "cheapsats". The specified cycle life at 100% DOD is also 50% longer than most NiCds, so low DOD (depth of discharge) performance could be substantial.

This study was undertaken to: a) assess the feasibility for using lithium ion cells on small satellite LEO missions and b) verify the claims of the manufacturer. This was accomplished by performing various depth of discharge and rate tests on the cells. Of special interest was the cycle life performance of these cell at various depths of discharge (DOD's), to get an initial measure of the reduction in capacity fade with cycle conditions. Low DOD's are used to extend the life of all batteries used in a space application.

2. Cell Procurement and Subassembly Packaging

Sony lithium ion batteries were initially introduced into the commercial market in cellular telephones (Figure 1). In mid 1992 we purchased a number of the Sony cellular phone battery packs and removed two US 20500 sub-C cells from each for testing. The cells were labeled as rated at 0.9 A•hr. The two cells in series were disconnected from each other. A thermister connects the two cells, and acts as an external cell safety feature to ensure that a battery short circuit condition cannot be sustained. The positive and negative metal

foil leads that are spot welded to each cell were cut and soldered to the 4 wire lead assembly to the battery from the Maccor battery tester.

3. Rate Performance

Constant current charge/discharge curves for a new cell at a C/5 to 2C rate are shown on in Figure 2. The capacity ordinate is used to make the curves comparable on the same figure. Differences in the initial ohmic drop on discharge can be seen. The calculated cell resistance from the data is about 135 m Ω . This value is higher than that reported more recently by Sony (95 m Ω) as measured by AC impedance [2]. From our resistance value and the cells' average projected electrode surface area (490 cm²), a value for the area resistance of 66 Ω ·cm² can be determined. The general shape of the curves differs somewhat at higher discharge rates. At the high rate (2C), a rapid decrease in cell voltage occurs in the first 0.05 A·hr, followed by a short plateau, ending in a gradually increasing rate of voltage drop near the end of discharge. This should be contrasted with the nearly constant rate of voltage change with discharge capacity at the low-rate discharges.

Figure 3 is a plot of the delivered cell capacity and specific energy as a function of discharge rate. The discharge rate is plotted as a function of the rated capacity divided by the discharge current, or equivalently, the inverse "C" rate. Substantial decreases in capacity and energy are observed at above a 1C discharge rate. The capacity and energy density approach 0.95 A·hr and 83 W·hr/kg at very low discharge rates.

Figure 4 shows the "round-trip" energy efficiency (energy out/energy in) as a function of discharge rate. A round-trip efficiency of 86% is very good for any cell with a 1 hr discharge and 3 hr charge cycle. For the lower discharge rates, most of the efficiency loss is associated with the ohmic heating during charging, so the efficiencies may be substantially higher at slower charging rates (e.g. 0.4 A rather than 0.9 A charge to 4.1V). From the 30% DOD cell data (i.e. LEO cycling program cell), a round time efficiency of 91% is observed.

The change in efficiency has been very small from the beginning of the LEO test to the cells' present state (0.24% decrease over 3800 cycles) with most of the loss in efficiency occurring during the first 1000 cycles (see cycle life data below).

Figure 5 shows the specific power versus the delivered specific energy for the Sony 20500 cell, as well as equivalent data for a rechargeable commercial NiCd (Panasonic) and primary alkaline (Eveready) "C" cell. The tests were performed under constant power conditions. The results of this figure show that at low C rate discharges, the lithium ion cell delivered in excess of 80 W·hr/kg (consistent with the constant current discharge data), compared to 35 W·hr for the NiCd. The "C" Alkaline cells maximum energy density is perhaps 95 W·hr/kg at very low powers and rates (>1 day discharge). These results indicate that lithium ion batteries' specific power and power density (peak continuous usable power of about 250 W/kg, 610 W/l) ranks with the best available batteries available today. Note that the energy delivered at the peak power point of 200 W/kg is equivalent to the NiCd cells trickle discharge-rate energy.

The "density" of the Sony Lithium ion cells (2.45 g/cc) are less than that of NiMH, NiCd or Pb-Acid cells of the same size. This fact dictates that the lithium ion cell must be able to deliver a higher specific power than other greater mass-density batteries when comparing alternative choices for an application with a given power-density specification.

The effects of repeated high rate discharge on cycle life has not been investigated, but 650 100% DOD cycles have been observed at a 1C rate, which is equivalent to a discharge power range of from 62-92 W/kg (see cycle data below).

4. Cycle Life Data

Lithium Ion cells were charged and discharged continually under constant current conditions to 30, 44, 50 and 100% depths of discharge (DOD) capacity at room temperature (which varied from about 15 to 25°C). The conditions for these tests are given in table 1 below. All cells were

placed in wood containers to minimize any safety hazards. This also helped to insulate the cells from minor fluctuations in the ambient room temperature. The 44 and 100% DOD test cells were charged at a high rate (1.4 A and 0.9A respectively) to the 4.1V cutoff, and were then allowed to "completely" recharge by holding the voltage at that value for an additional 2 hr's. The 30% DOD test cell were performed using a 45 minutes discharge/approximately

45 min. charge program. The discharge conditions correspond to a C/2.5 rate. In order for the inherently slower charging process to keep pace, a recharge program of 0.9 amps to 4.1 volts followed by a 30 min. hold at 4.1V was use. This procedure allowed nearly complete recharging to occur in the approximately 45 min. LEO time window.

**Table 1
Test Conditions and Cycle Life of
the 20500 Sony Lithium Ion Cell**

Depth of Discharge	Discharge Current (Amps)	Cutoff Conditions	Charge Current (Amps)	Const. Voltage Charge Time	Cycle Life ^a
100	0.9	2.75 V	1.4	2 hrs	650 (650) ^b
44	0.9	0.395 A•hr	1.4	2 hrs	3800 (2250) ^c
50	0.36	0.450 A•hr	0.36	2 hrs	14000 (900) ^c
30	0.36	0.270 A•hr	0.9	30 min	40000(4100) ^c

a The numbers in parenthesis are the actual number of cycles to date.

b To a capacity of 25% of the first cycle capacity at the given rate.

c Cycle life projections are based on linear interpolations of capacity to a 2.75V EODV.

4.1 100% DOD Test

Figure 6 shows the discharge capacity of the 100% DOD cell as a function of cycle number. The cell lost 25% of its initial capacity after approximately 650 cycles. This is the point that we arbitrarily defined as the cells' end-of-life. Initially the capacity falls off rapidly, but later the rate of decay declines and is nearly linear. This appears to be a general characteristic of the Sony cells. It was found that the same cell lost only 17% of its rated capacity at a C/5 charge/discharge rate at the end of life (i.e. at the end of 650 cycles). This difference indicates that a major contributor to the cell "capacity" degradation is an increase in the cell ohmic resistance. The ohmic change could be due to an increase in the electrolyte resistance (polymerization or dry out), a change in the electrode/current collector contact (e.g. as the carbon electrode material expands and contracts during the intercalation process) or some other cause rather than the chemical degradation of the

cell components, and is consistent with data presented by Sony[1].

The residual end-of-charge current (i.e. the current at the end of the 2 hour, 4.1 V potentiostatic charge step) and the cell resistance (measured by the instantaneous voltage drop on discharge) for the 100% DOD test are shown in Figure 7. Both parameters increase linearly with cycle number until the end of the test. Most likely these parameters are at least partially interrelated.

An estimate of the reduction in the cell capacity associated solely with the increase in cell resistance can be made by assuming a linear relationship between cell voltage and capacity. The initial and final (650 cycle) cell voltage range is from 3.99V to 2.75V, and 3.88V to 2.75V respectively. Purely ohmic contributions would result in a capacity reduction of 8.9%. This value is consistent with the difference in the cell capacity at the end of life (650th cycle) at the 1C and C/5 rates (25%-17% = 8%).

Incomplete charging, as indicated by the residual end-of-charge current, may have a cumulative effect. Since the charging process is slower than the discharging process, continued cycling at a high rate could result in the reduced utilization of "hard to access" intercalation sites in the carbon anode. Ignoring this possibility and using the difference between the 1st and 650th cycles residual end-of-charge current for an estimate of capacity loss results in a value of about 3% capacity fade.

4.2 44% and 50% DOD Tests

Figures 8 and 9 show the end-of-discharge voltage (EODV) versus cycle number of the 50% and 44% DOD cell tests, respectively. The 50% DOD test was started later than all the other tests after the results from the 44% DOD cell (charged at a 1.56C rate to the 4.1V cutoff) showed a faster-than-expected capacity fade (see Figure 8). Comparison of the data in the two figures shows an unexpected result that the EODV of the lower (44%) depth-of-discharge cell is substantially lower. The significant difference between the two cells is their different charging and discharging currents (see table 1).*

As with the 100% DOD results, only a portion of the lower EODV (comparing Figure 8 with Figure 9) is due to strictly ohmic effects. Changes in cell resistance with cycle number for the 44% DOD test are shown in Figure 10 (determined by the instantaneous voltage drop from the end of charge to the beginning of discharge). Initially the cell resistance increases linearly with cycle. Later, the rate of increase appears to decrease. It may be that the cells kinetic and/or diffusion resistances are substantially changing during the cycling, and that substantially larger capacity fade of

* The literature on the appropriate charging conditions for these cells is confusing. Various charge rate (from 0.3 to 1.4A) followed by a 2 hour potentiostatic hold are discussed. As indicated in table 2, two of our tests were run at the maximum 1.4A charge rate, one test at 0.9A, and a last test at 0.3A.

the high charge/discharge rate, 44% DOD cell is due to something other than simple electrolyte breakdown, polymerization, or electrode contact resistance changes. Substantial changes in the structure of the solid electrolyte interfacial layer, reduction in the carbon microsphere or lithium cobalt oxide capacity for lithium, or anode/cathode impedance mismatch during higher rate charging (forcing lithium metal deposition onto the anode) could be causes for premature cell failure.

In contrast to this the slower rate, the 50% DOD cell is performing very well. Using a simple linear extrapolation through the data to date results in a projected cycle life of over 14,000 cycles. The discharge rate is the same as the 30% DOD LEO test discussed below, but the charging rate is slower.

4.3 30% DOD/LEO Test

EODV data for the 30% DOD LEO cycle test is shown in Figure 11. Sixteen (16) cycles are completed every day. Presently, the cell has been cycled 4100 times (only 3300 cycles are shown in Figure 11 because of computer plotting memory limitations). No change in the projected trends has been observed. As in the other cycle tests, initially the EODV falls rapidly. In this case, a change in slope is note observed until after about 1200 cycles. Later the rate of EODV-decrease diminishes. Based on a linear extrapolation of the data from the 1500th cycle to the 3250th cycle, the cell will reach an EODV voltage of 2.75V after 68000 cycles. We therefore project that the cell should deliver over 40,000 cycles (6.85 years).

4.4 Cycle Life Test Discussion and Future Work

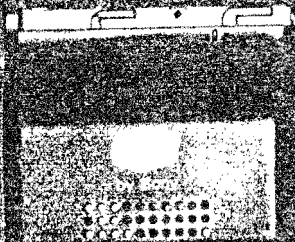
Figure 12 is a log plot of the projected cycle life of the Sony lithium-ion cells as a function of the depth-of-discharge. We note that the cycle conditions and (in the case of the 100% DOD test) end-of-life conditions for these test are all different. We conclude from the data that, within reasonable operating limits, the cycle life of these cells can be very long at low DOD's. Based on our limited data, cycle life is

substantially improved with decreasing charge and discharge rate (below a 1C rate). However, neither a physical model or enough quantitative data are available to further aid in our interpretation of the results at this time. A more thorough analysis of the cells' degradation mechanism is needed. The effects of series cell connections and capacity mismatch, overcharge, and temperature on life should also be investigated.

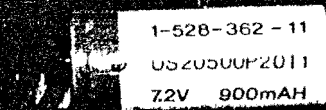
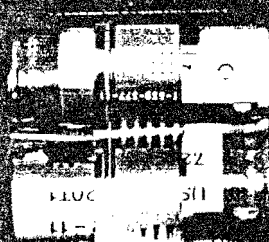
In addition, extensive testing of these cells should be performed under vacuum and across the specified temperature range. Reports from other space users of commercial NiCds indicate that some minor performance degradation may be associated with cell outgassing during initial exposure to vacuum, followed by stabilization.

REFERENCES

- 1) Ozawa, Kazunori, and Masaaki Yokokawa, "Cycle Performance of Lithium Ion Rechargeable Battery", presented at The Tenth International Seminar of Primary and Secondary Battery Technology and Applications, March 1-4, 1993, Deerfield Beach, Florida. Florida Educational Seminars, Inc. Boca Raton, Florida.
- 2) Dr. T. Nagaura, Sony Energytec, Inc., Fukushima, Japan. Product announcement literature, "A Lithium Ion Rechargeable Battery".
- 3) Sony Energytec Inc. Lithium Ion Rechargeable Battery US-61 Series Technical information packet. (Some information from this source is photocopied and given in Appendix B).



SONY Lithium Ion Battery
for Cellular Phone



Sony 20500 Lithium Ion Battery Performance at Various Discharge Rates

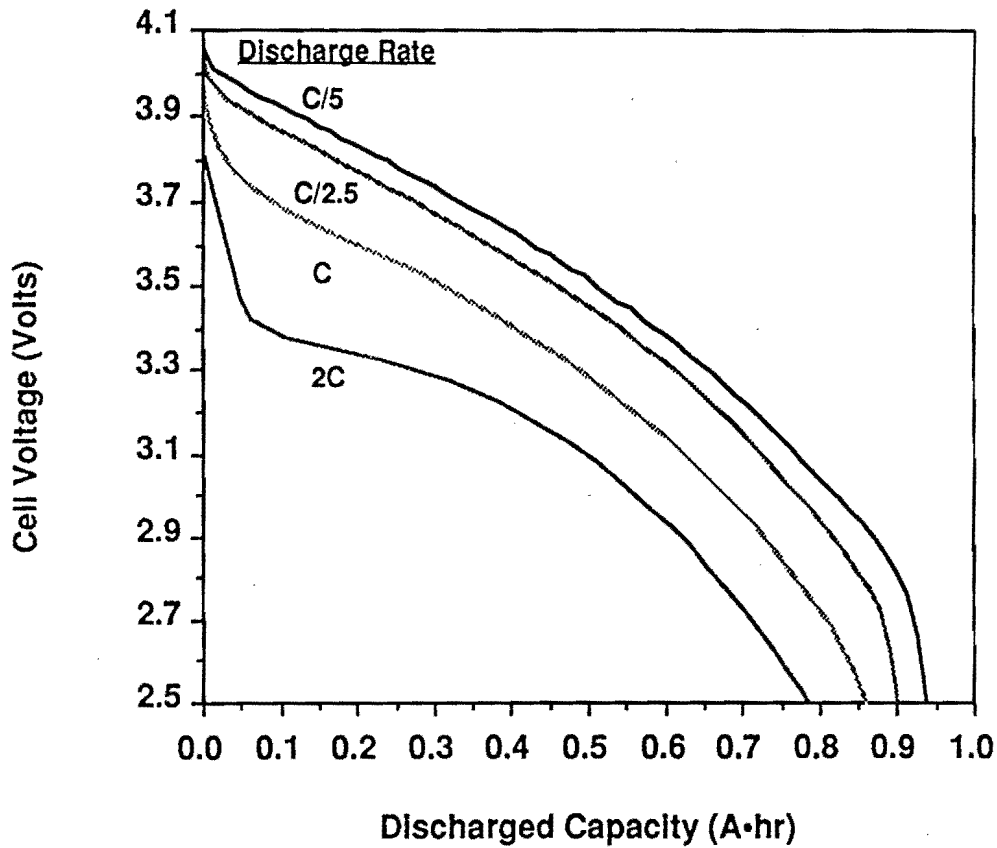


Figure 2

Sony 20500 Lithium Ion Battery Performance at Various Discharge Rates

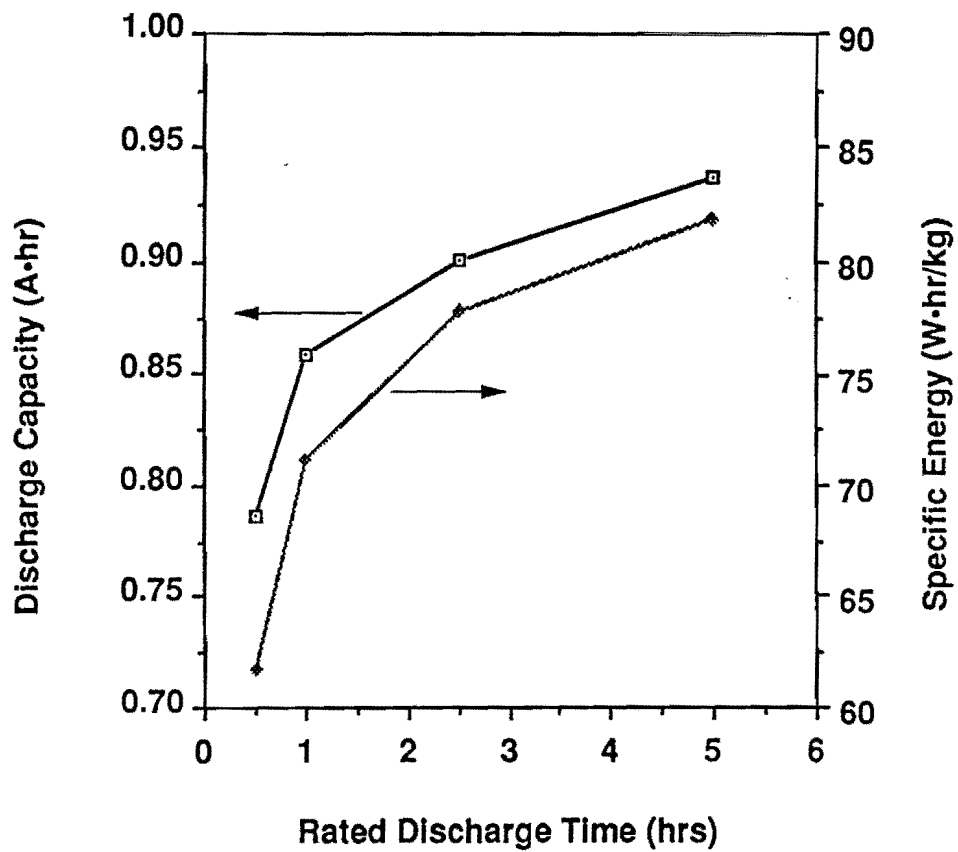


Figure 3

Sony Lithium Ion Round Trip Efficiency

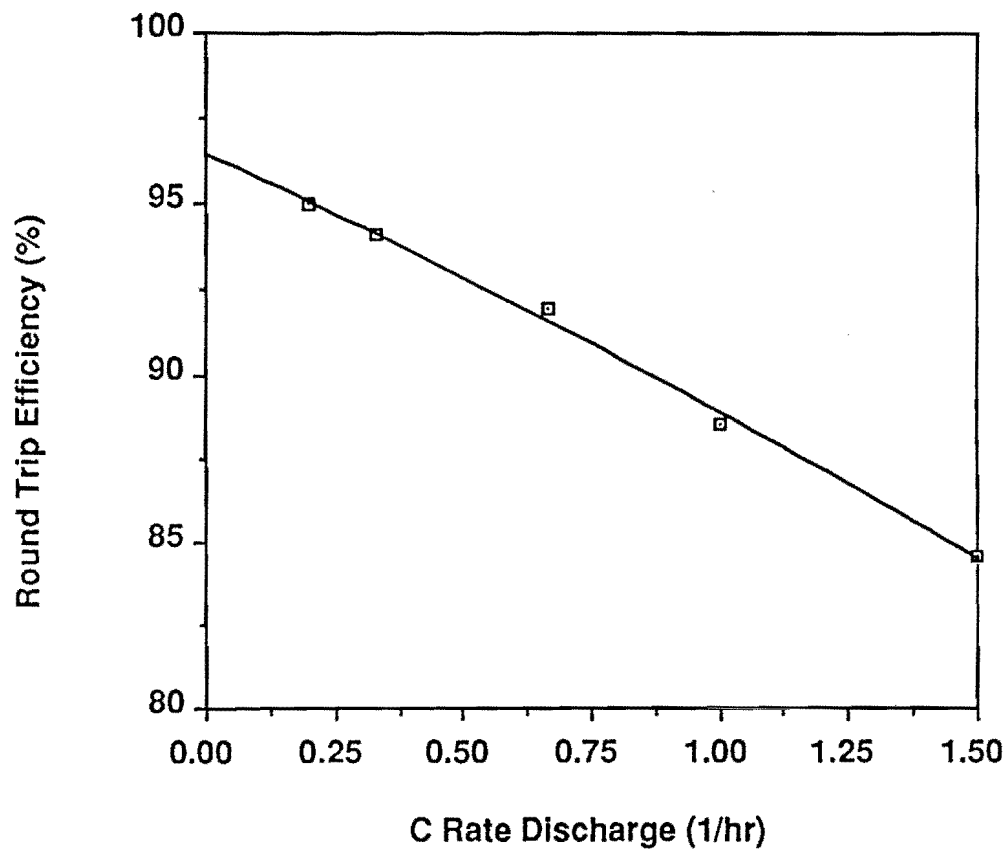


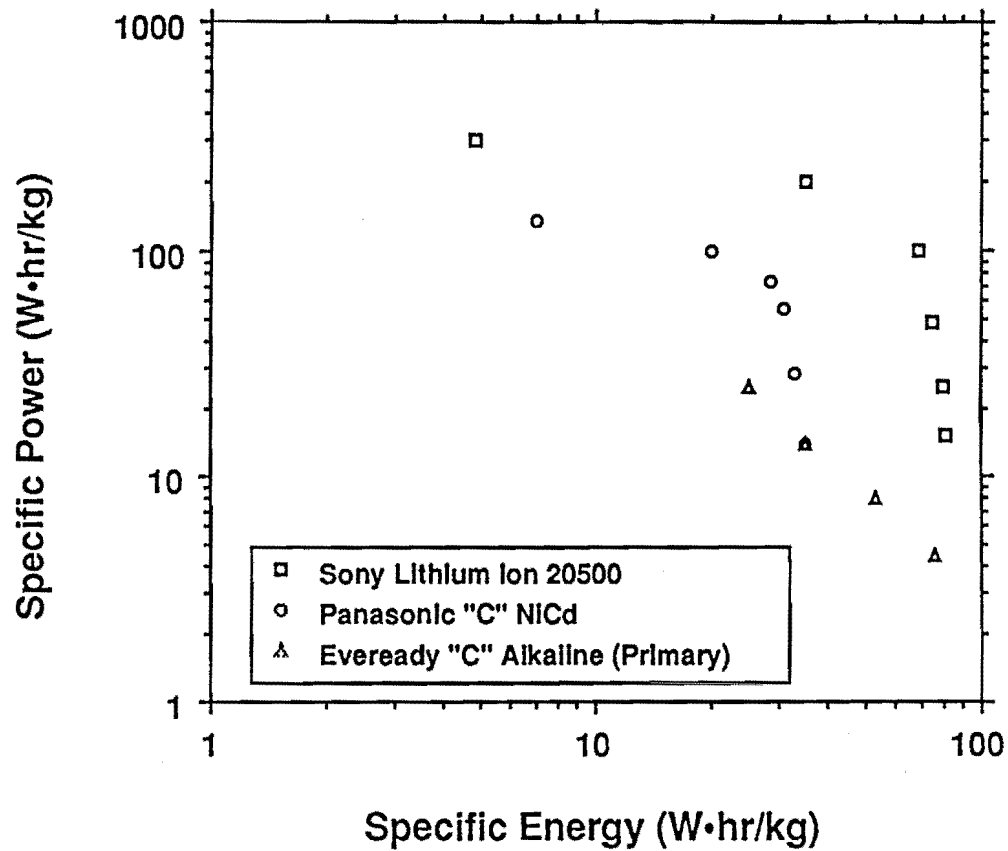
Figure 4

Charge Conditions
0.9A to 4.1V
Then 4.1V for 2 hrs

Power/Energy Performance of Small Cells



Figure 5



Sony Lithium Ion 100% DOD Cycle Life

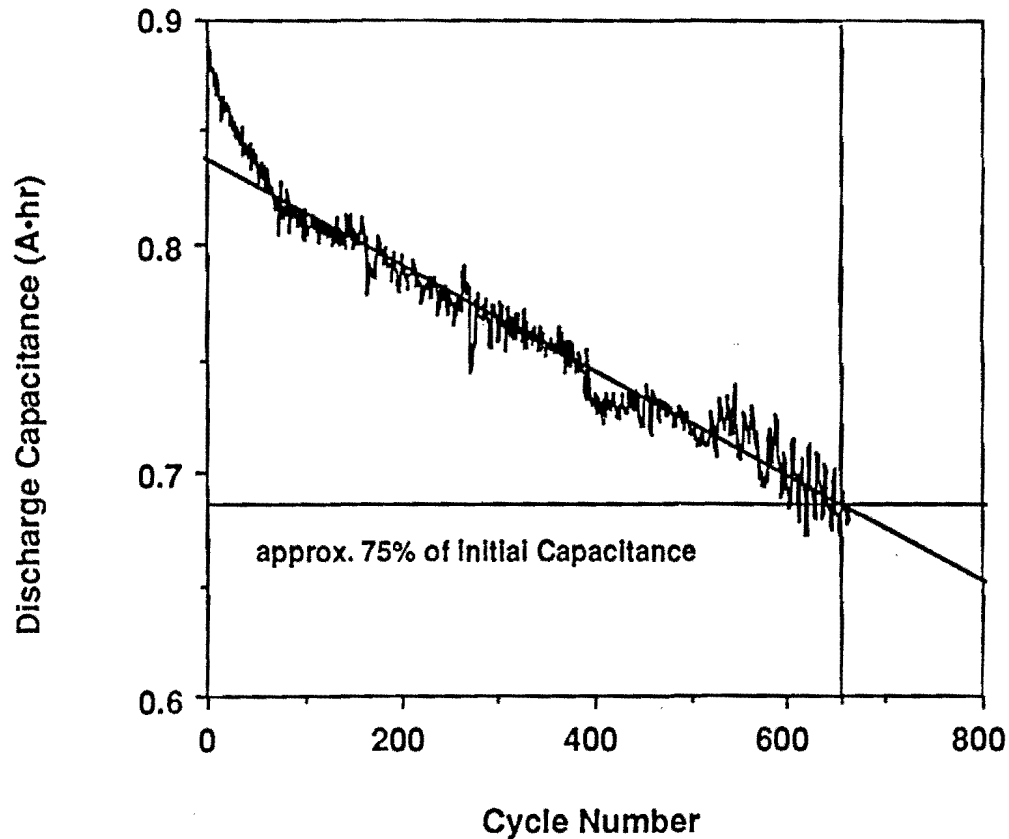


Figure 6

20050 Cell Test Conditions

Discharge

0.9A Discharge to 2.75 V

Charge

0.9A charge to 4.1V, Then 4.1 V for 2 hrs

Change in Cell Performance with Cycle Number-100% DOD

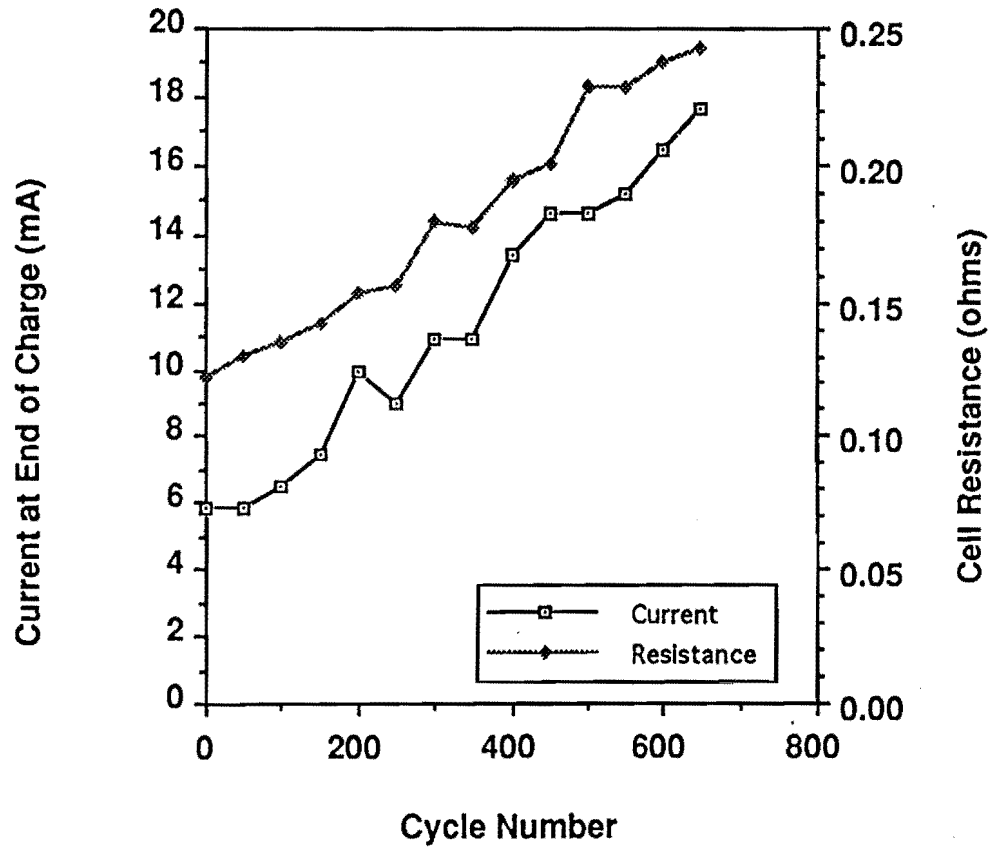
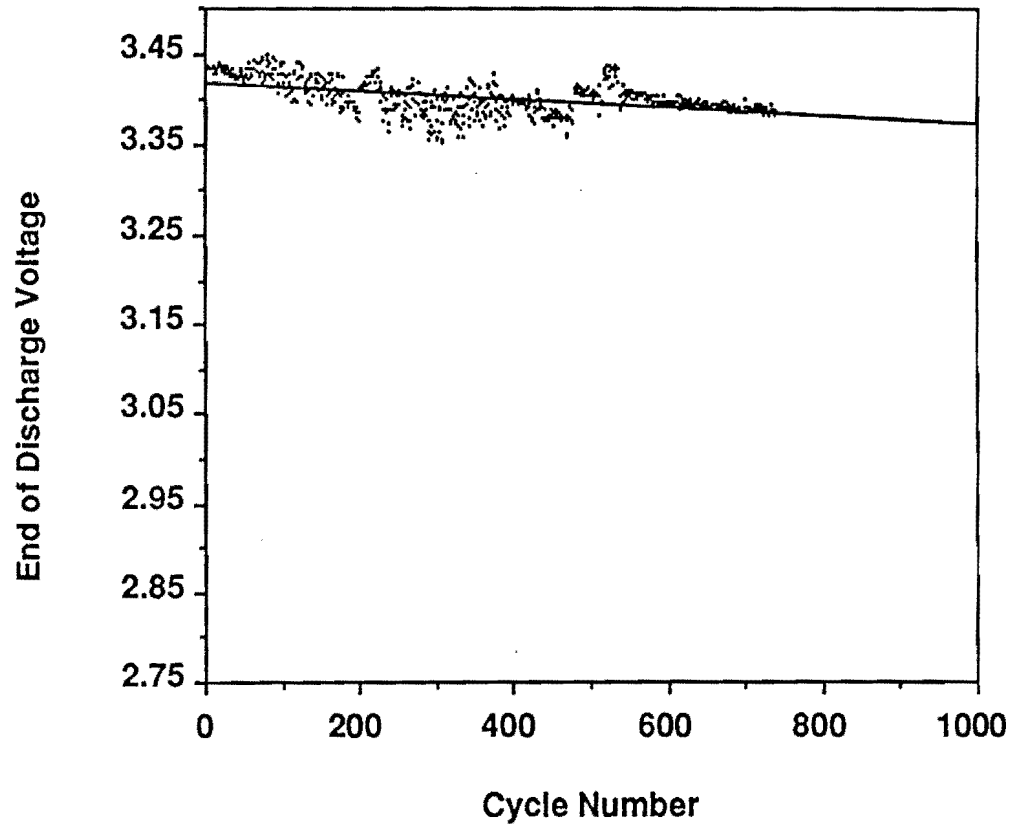


Figure 7

Sony Lithium Ion 50% DOD Cycle Life



0.36 A Charge to 4.1V, then 2 hrs hold at 4.1V
0.36A Discharge to 0.45 A·hr Capacity

Figure 8

Sony Lithium Ion 44% DOD Cycle Life

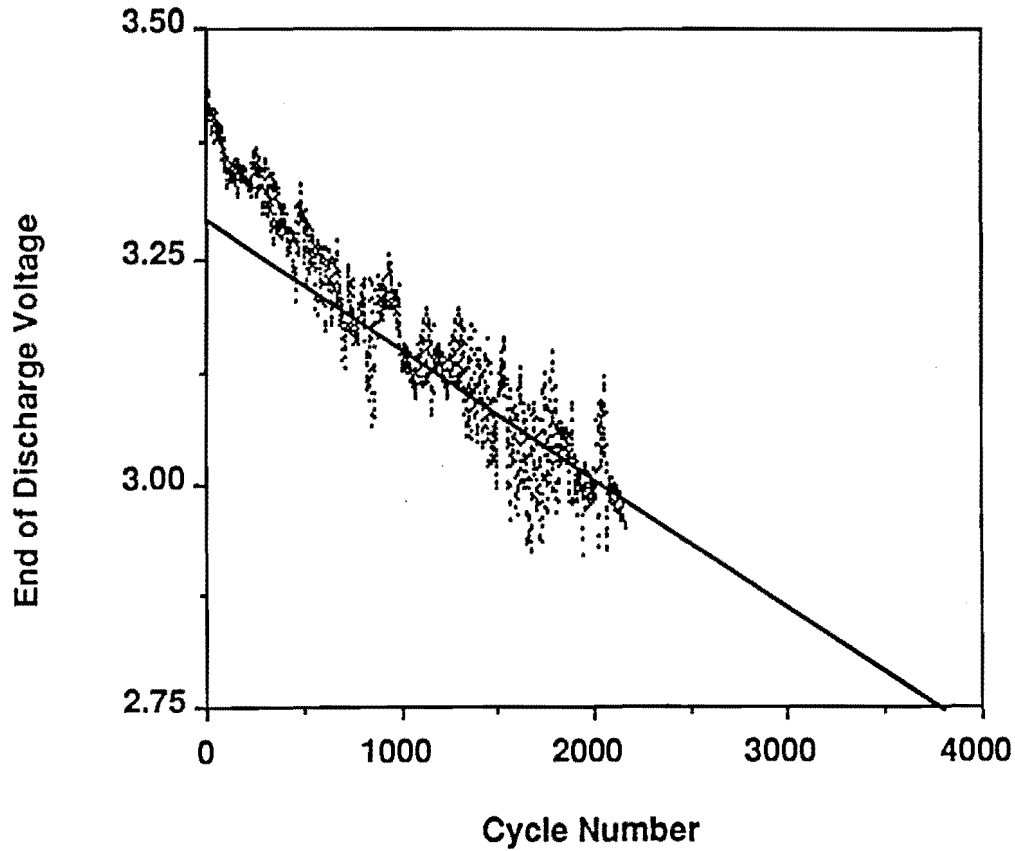
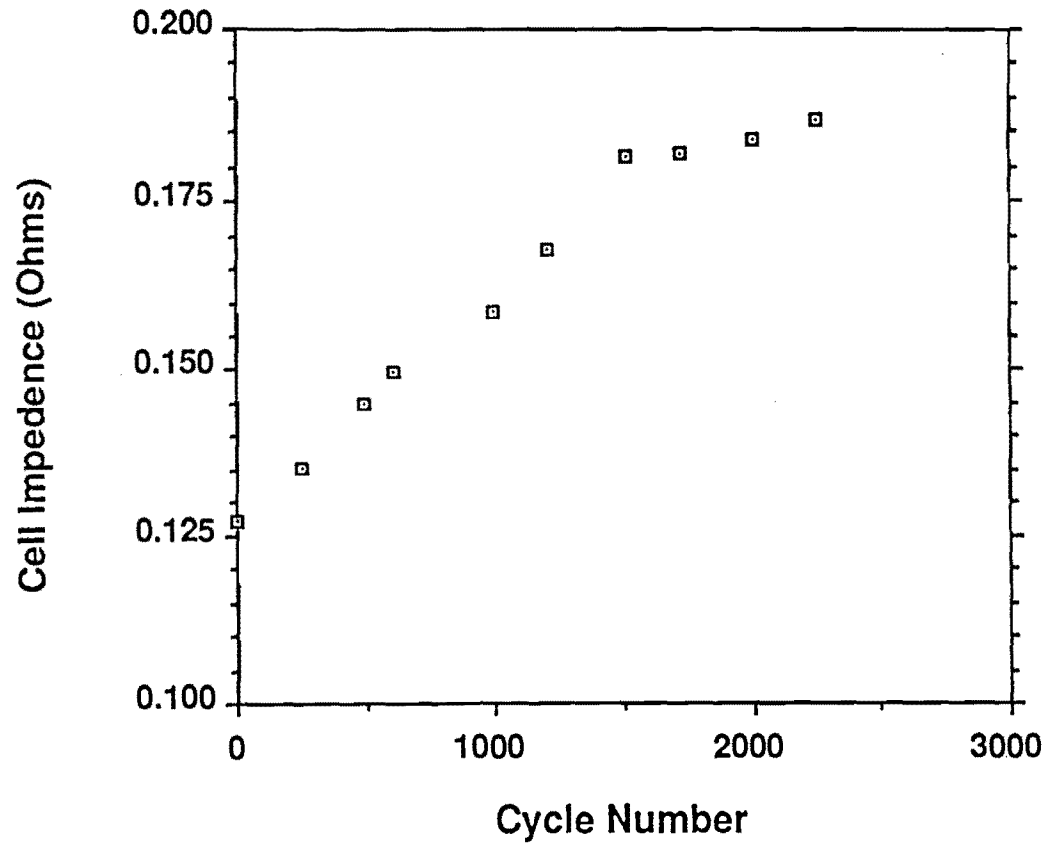


Figure 9

Cycle Conditions
1.4A Charge to 4.1 V
Voltage Hold 4.1V for 2 hrs.
Discharge at 0.9A for 0.395A·hr



Cell Resistance- Changes With Cycle Number



44% DOD
1.4A Charge to 4.1V, then 2 hour Hold
0.9A Discharge for 26 minutes

Figure 10

Sony Lithium Ion 30% DOD Cycle Life

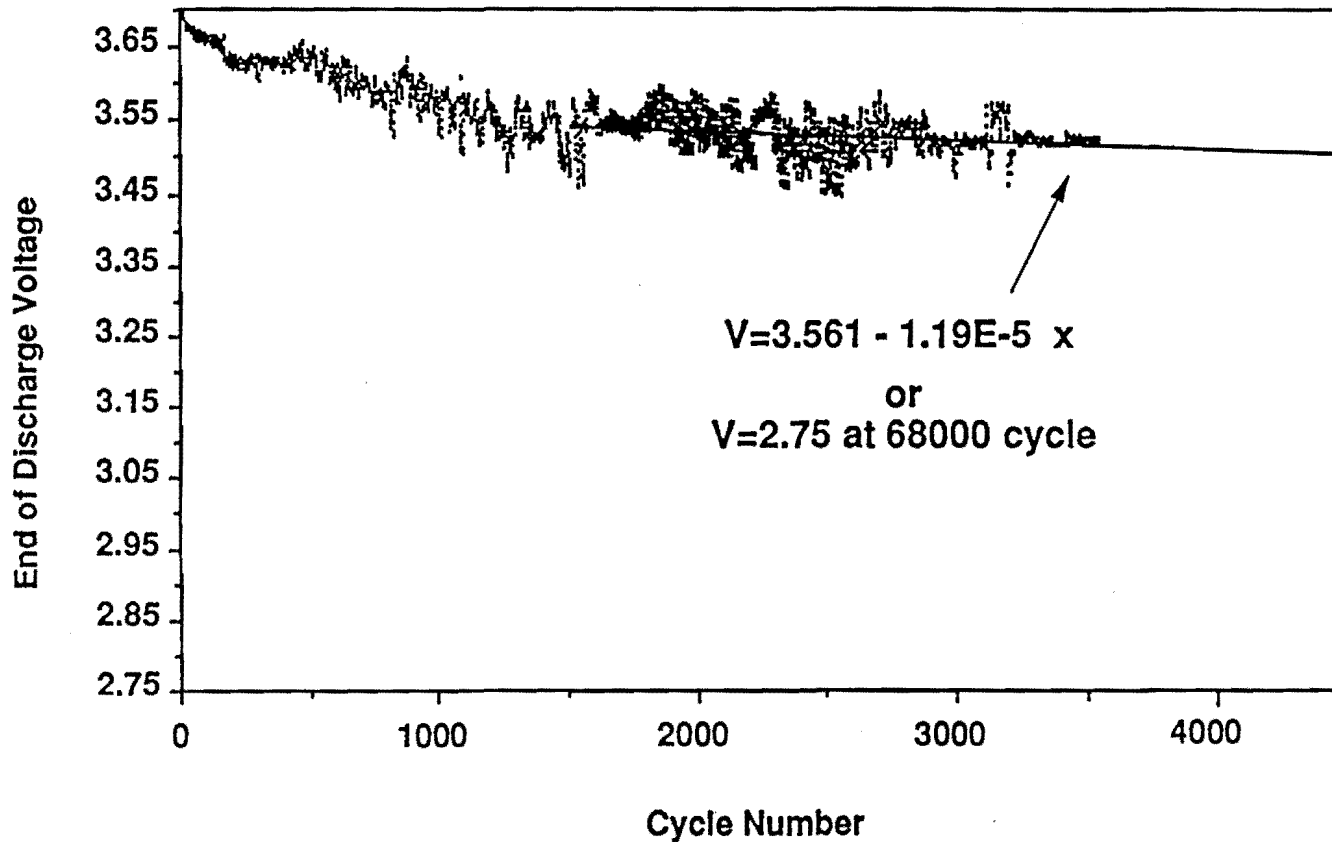


Figure 11

Cycle Conditions
Discharge- 0.36A for 45 min
Charge- 0.9A to 4.1 V (about 15 min)
then 4.1 V for 30 min

Cycle Life Projections of Sony Lithium Ion Batteries

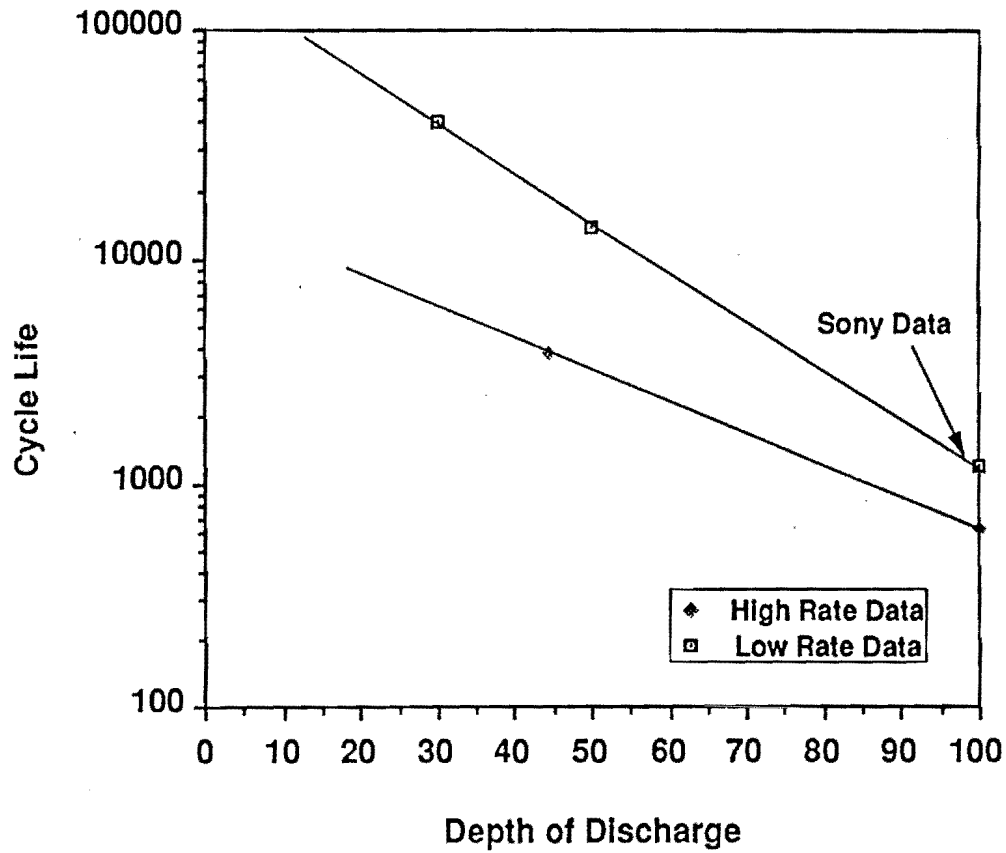


Figure 12

APPENDIX A

SONY Initial Performance
Announcement

Performance Comparison of Lithium Ion Rechargeable Battery
and
Typical Conventional Rechargeable and Primary Batteries

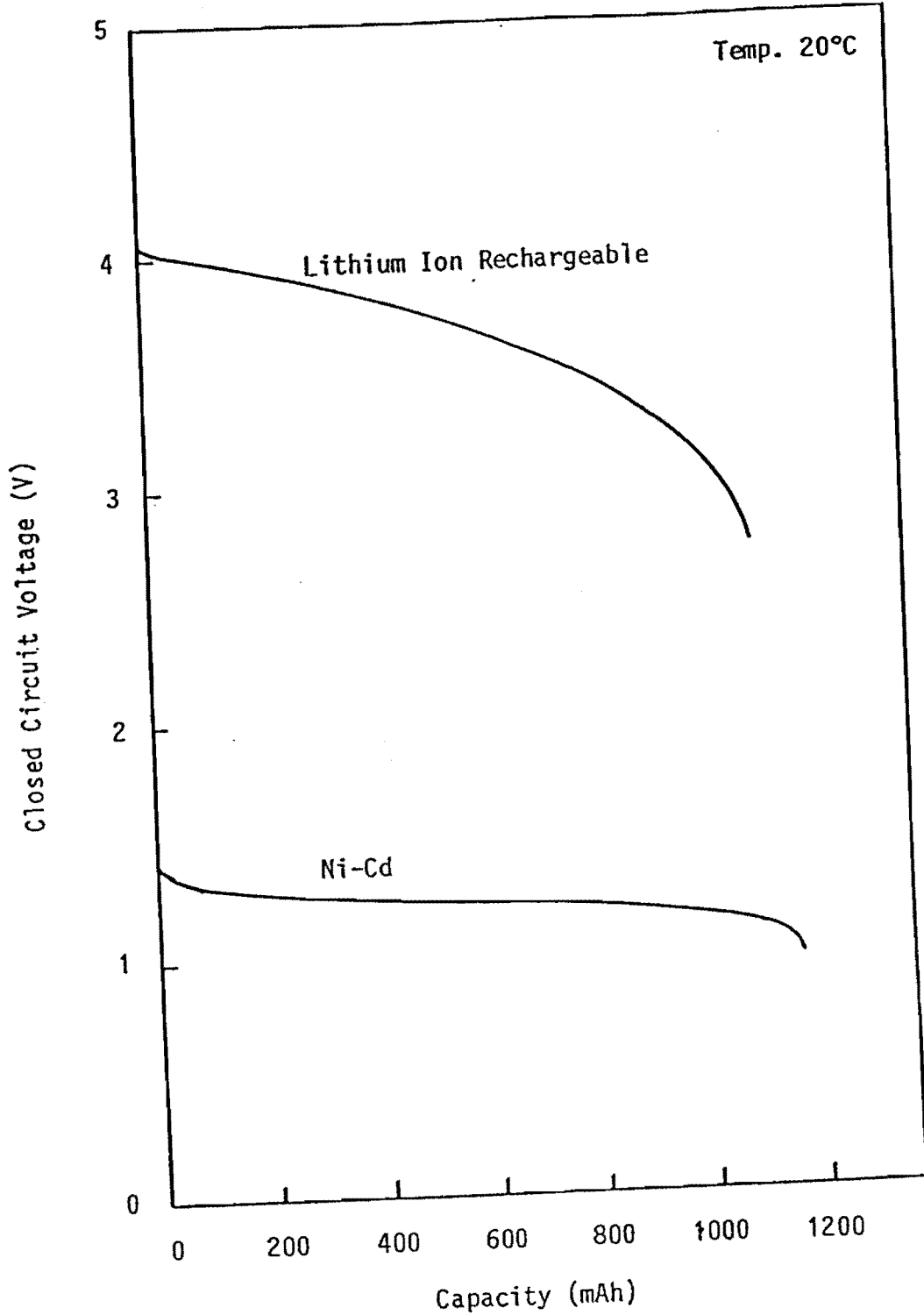
Type of Batteries	Lithium Ion (D size)	Ni-Cd (D size)	Portable Sealed Load Acid Battery (P86-1A)	Primary Alkaline Cells (D size)
Volume	55.4 cm ³	65.4 cm ³	61.7 cm ³	55.4 cm ³
Weight	122 g	160 g	180 g	137 g
Operating Voltage	3.6 V	1.2 V	6.0 V	1.1 V
Energy Capacity	14.0 Wh	4.80 Wh	4.56 Wh	11.0 Wh
Energy Density per-Volume per Weight	253 Wh/l 115 Wh/kg	87 Wh/l 30 Wh/kg	74 Wh/l 25.3 Wh/kg	199 Wh/l 80.3 Wh/kg
Cycle Life in 100%D.O.D.	1200 cycles	800 cycles	200 cycles	1 time discharge (non rechargeable)
Self Discharge After 1 month After 3 month After 6 month	12 % 21 % 30 %	25 % 40 % 60 %	5 % 10 % 20 %	- - 1 %
Temperature for Charge for Discharge	0° C ~ 45° C -20° C ~ 60° C	0° C ~ 45° C -20° C ~ 60° C	0° C ~ 40° C -20° C ~ 50° C	- -20° C ~ 60° C
Accumulated Discharge Energy per Volume per Weight	14.6 kWh 264 kWh/l 120 kWh/kg	3.5 kWh 63.2 kWh/l 22.1 kWh/kg	0.81 kWh 13.1 kWh/l 4.5 kWh/kg	0.011 kWh 0.2 kWh/l 0.08 kWh/kg

APPENDIX B

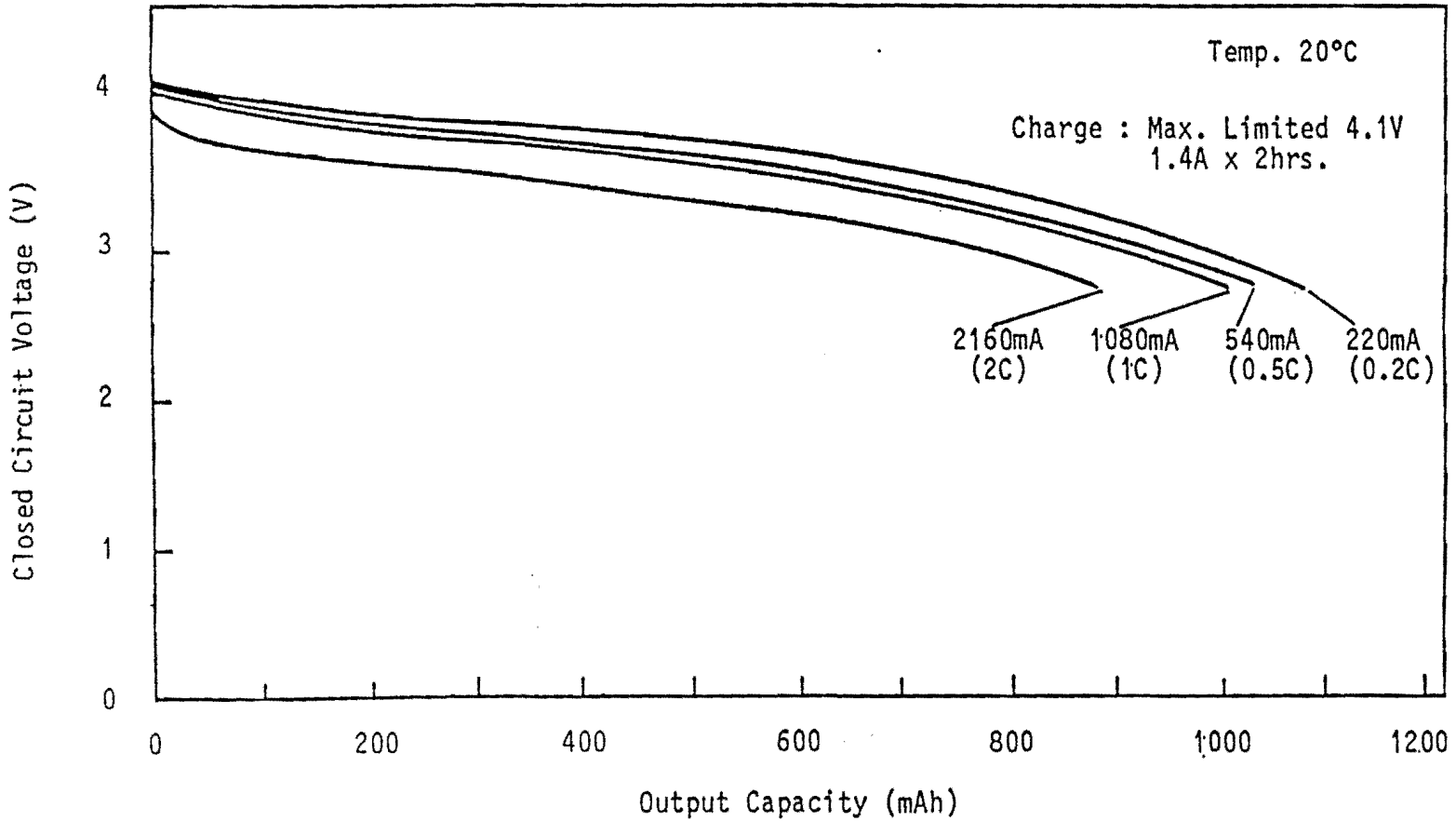
Sony Specification for US-61 Series Cells and Sony Data for the 20500 Cell

Type of Batteries	US-61 (AA) 14500	US-61 16530	US-61 20420	US-61 20500
Volume	7.5 cm ³	11.3 cm ³	13.9 cm ³	16.5 cm ³
Weight	18 g	28 g	32 g	39 g
Operating Voltage	3.6 V	3.6 V	3.6 V	3.6 V
Capacity	400 mAh	640 mAh	860 mAh	1080 mAh
Energy Capacity	1.44 Wh	2.30 Wh	3.10 Wh	3.89 Wh
Energy Density per volume per weight	192 Wh/l 78 Wh/kg	204 Wh/l 83 Wh/kg	223 Wh/l 98 Wh/kg	236 Wh/l 99 Wh/kg
Cycle Life in 100% DOD	1200 cycles	1200 cycles	1200 cycles	1200 cycles
Self Discharge after 1 month after 3 months after 6 months	12 % 21 % 30 %	12 % 21 % 30 %	12 % 21 % 30 %	12 % 21 % 30 %
Temperature for charge for discharge	0°C ~ 45°C -20°C ~ 60°C	0°C ~ 45°C -20°C ~ 60°C	0°C ~ 45°C -20°C ~ 60°C	0°C ~ 45°C -20°C ~ 60°C
Accumulated Dis. Energy per volume per weight	199 kWh/l 81 kWh/kg	212 kWh/l 86 kWh/kg	231 kWh/l 102 kWh/kg	245 kWh/l 103 kWh/kg

APPENDIX B (Sony Data)

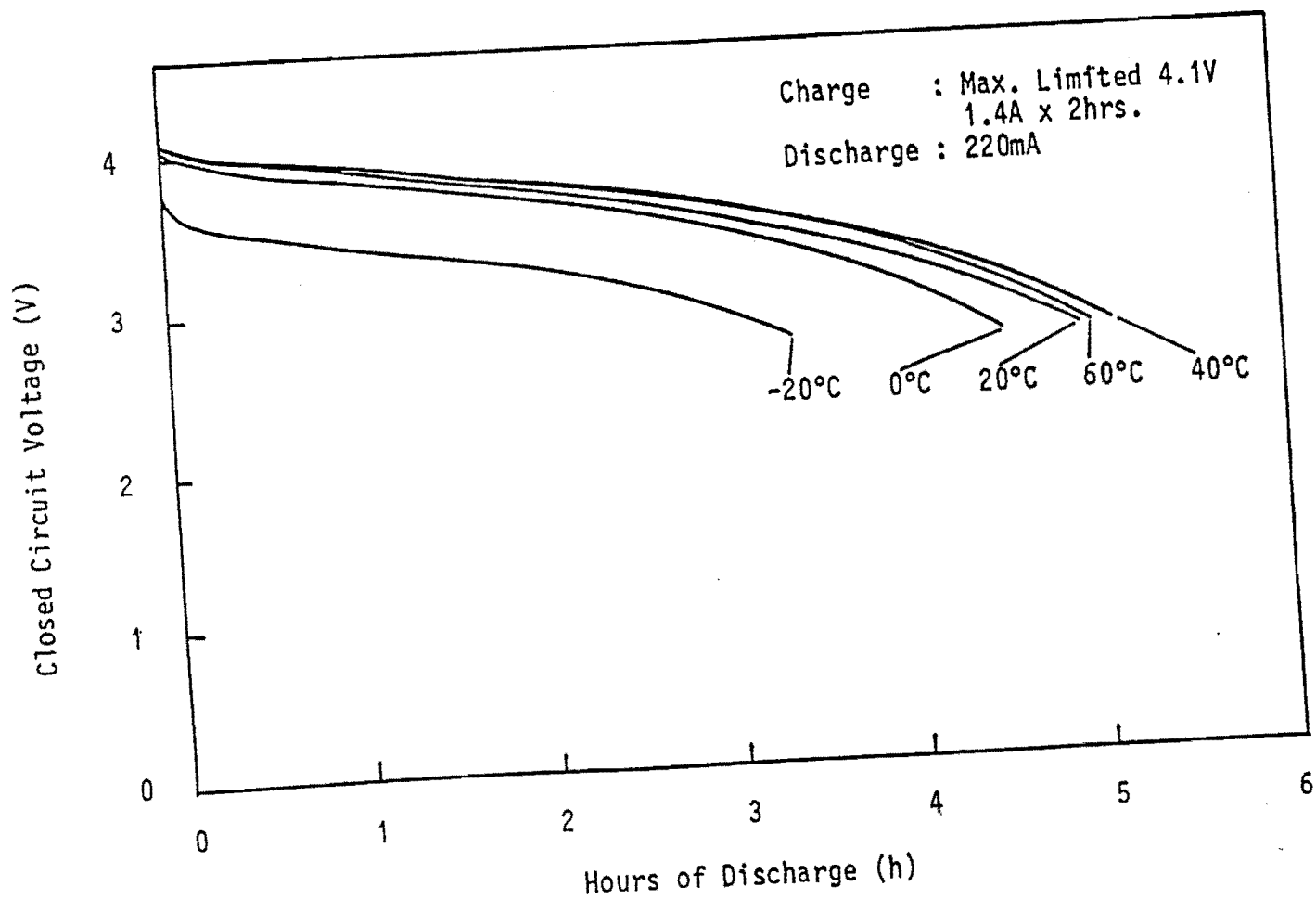


Discharge Curve of 20500 Size Cells
Discharge Current : 220 mA



APPENDIX B (Sony Data)

Discharge Curves of Lithium Ion Rechargeable Battery 20500 Size Cell
at Various Drains



APPENDIX B (Sony Data)

Discharge Curves of Lithium Ion Rechargeable 20500-size Cell
at Various Temperatures