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# Performance of the Sony Lithium-Ion Rechargeable Battery

George Au and Martin Sulkes

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#### 1. INTRODUCTION

Rechargeable lithium batteries which contain free lithium metal have exhibited safety problems which jeopardize their widespread usage. To date, they have short cycle lives and the high reactivity of cycled lithium metal is a prime safety concern. Rechargeable batteries which contain lithium intercalation compounds, instead of the free lithium metal, should be much safer and have a greater cycle life. Such systems are called "rocking chair" types, since the lithium-ions move back and fort between the cathode and anode on charge and discharge. The Sony Corp produced a lithium-ion rechargeable battery which is incorporated cellular phone equipment only in Japan. Each battery into consisted of two 5/4 C<sub>s</sub> size cells. Sony claimed that cell type 20500 has a rated capacity of 1080 milliampere hours when discharged at C/3 rate. But this phone battery is rated at only 900 milliampere hours. Eighteen batteries and two chargers were obtained and subjected to the evaluation described in this report.

#### 2. APPROACH

The Sony battery packs which were manufactured 12/91 were dismantled and the cells recovered. They were then subjected to testing and evaluation as follows:

- o Visual and mechanical inspection
- o Discharge at various rates and temperatures
- o Various charging conditions
- o Storage
- o Cycle life

3. TEST PROCEDURES AND CONDITIONS

3.1 Visual and Teardown Inspection

Cells to be evaluated were weighed and examined to insure their physical integrity. Dimensions were recorded. The cells were then dissected and an analysis performed to determine their internal composition.

#### 3.2 <u>Electrical</u> <u>Testing</u>

### 3.2.1 Charging.

(1) Sony Charging Method. It consists of essentially a constant potential charge with a 1.1 ampere limit to 4.1 volts. Charge temperatures tested were  $-30^{\circ}$ C,  $0^{\circ}$ C,  $25^{\circ}$ C and  $50^{\circ}$ C. The capacities in ampere hours were recorded. This data is the benchmark for comparing the Sony charging method with the multistep constant current charging methods described below. (2) Multistep Constant Current Charging. Constant current charging was performed at various temperatures, to a cutoff voltage on each step of 3.9, 4.1 and 4.25 volts:

First step: 700 mA Second step: 200 mA Third step: 50 mA

#### 3.2.2 Discharging.

(1) Constant Current. After being charged by one of the above methods at  $25^{\circ}$ C, the cells were then discharged at a constant current of 500 mA, at various temperatures, to a 2.5 volt end point. Additional discharges were conducted at 0.5, 1, 2 and 3 amperes at  $25^{\circ}$ C using the standard charge cutoff voltage of 4.1 volts.

(2) Pulse Discharge. Cells were charged to 4.1 volts and then discharged on a cycle consisting of 5 amperes for 5 seconds, then off for 25 seconds to a 2.5 volt cutoff at 25°C. The test was repeated using a charging cutoff voltage of 4.25 volts and a pulse of 4.5 amperes.

#### 3.2.3 Storage.

Cells were charged to three voltage levels: 3.9, 4.1, and 4.25 volts. They were then stored at  $45^{\circ}$ C for 14 days. The cells were subsequently discharged at  $25^{\circ}$ C at 0.5 ampere to 2.5 volts. Several charge/discharge cycles were run to establish whether a temporary or permanent loss occurred as a result of the storage. Afterwards the same cells were charged and stored for 20 days at 50°C. The cells were then discharged at 0.5 ampere to 2.5 volts at 25°C and recharged.

3.2.4 Cycle Life.

Cells were cycled on a regime consisting of a multistage constant current charge, as indicated in paragraph 3.2.1(2) above and then discharged at a constant current of 0.5 ampere to a 2.5 volt cutoff. The cells were to be cycled until they reached 60% of their initial capacity.

#### 3.2.5 Test Equipment.

Cells were charged and discharged using a Techware Automatic Battery Cycler.

#### 3.2.6 <u>Recorded</u> Data.

The following data were recorded: voltage and current during charge/discharge, ampere-hours, and watt-hours during both charge and discharge.

4. TEST RESULTS

4.1 External and Internal Cell Examination.

Cells were weighed and dimensioned. They were then cut apart to examine the internal components. The results of the examinations are as follows:

4.1.1 External Dimension

Diameter	2.1 cm
Height	5.2 cm
Volume	$18.0 \text{ cm}^3$
Weight	41 gm
Cell type	20500 lithium-ion (5/4 SUB C)

4.1.2 Internal Construction

Electrode configuration	Spirally wound
Outside electrode	Anode
Mandrel	3.5 mm diameter
	stainless steel tube
Outer separator fastener	Green tape
Polarity	Case negative
Anode lead weld point	Bottom of case

#### 4.1.3 Electrode and Separator Dimension

Anode thickness	0.0095 inch (0.24 mm)
Anode length	24.75 inches (62.9 cm)
Anode width	1.63 inches (4.14 cm)
Anode area:	520 cm <sup>2</sup>
Cathode thickness	0.0075 inch (0.19 mm)
Cathode length	23.5 inches (59.7 cm)
Cathode width	1.585 inches (4.03 cm)
Cathode area	$480.6 \text{ cm}^2$
Separator thickness	1 mil isotactic
_	polypropylene (Celgard)

### 4.2 Analytical Results (see Reference 1)

## 4.2.1 Cathode

Active MaterialLiCoO2Active Material Loading10.46 gm (total)Active Material Capacity1.43 Ah (LiO.5COO2)BinderUndefinedCurrent collector0.001 inch thick A1 foilLeadAluminum tab

## 4.2.2 Anode

Active MaterialCarbon (polyfurfuryl<br/>alcohol-derived carbon)Active Material Loading6.56 gm (total)Active Material Capacity1.22 Ah (Li<sub>0.5</sub>C<sub>6</sub>)Binder(Polyvinylidene<br/>fluoride)Current collector0.001 inch thick Cu foil<br/>Aluminum

#### 4.2.3 ELECTROLYTE SOLUTION

Solute	LiPF <sub>6</sub>
Solute concentration	Undefined
Solvents	PC (70 volume percent) DEC (30 volume percent)
Total electrolyte weight	4.05 gm

4.2.4 CELL CASE

Material

Nickel-plated steel

4.3 Sony Charger Characteristic.

The Sony charger, Model No. JC2-H211 has two channels for charging two BA2-H211 cellular phone batteries at the same time. Each channel has four contact pins directly connected to the battery. Although the charger has a capability to access each cell in the battery, it does not charge or control each cell in the battery separately. It had been reported that earlier models of this charger did control the voltage on a single cell, rather than a battery basis. The two cells are charged in series with a constant potential limit of 8.2 volts. The JC2-H211 charges at a constant current of 1.1 amperes until the battery voltage reaches approximately 7.9 volts and starts to taper off to 70 milliamperes. It will completely shut off the current after two and a half hours of charge. The charger has three indicator lights:

(1) A green light for AC power.

(2) One red light each for each channel to indicate the battery is being charged. A steady red light indicates current limiting at 1.1 amps.

(3) A blinking red light indicates that the battery is partially charged and in the voltage limited mode. When the red light is out, no current is flowing and charge is completed.

4.4 Electrical Results

4.4.1 Charging.

Figures 1 through 3 are the curves for a 3-step constant current charging to 3.9, 4.1 and 4.25 volts respectively, at different temperatures. Table 1 summarizes the charging input in amperehours under the various charging scenarios.

(1) Charge Curves for Charging to 3.9, 4.1 and 4.25 Volts at Different Temperatures. Figures 1-3 show that the total time to charge the cell is decreased as the temperature is increased. As the charging cutoff voltage is raised, the total time to fully charge the cell is increased because of the significantly higher capacity. At the lower temperatures, charging requires a high voltage to overcome increased impedance, and thus full charge is not obtained. Figures 4 through 7 give the discharge curves obtained after charging at different charge voltages and varying temperatures using a discharge end voltage of 2.5 volts and a discharge constant current of 0.5 ampere.

(2) Charging Input at Indicated Temperature. Table 1 shows that higher charge input is obtained at the high temperature of  $50^{\circ}$ C. The charge input is greatest for the highest charging cutoff voltage of 4.25 volts. As the temperature gets lower, the charging input drops, until at  $-20^{\circ}$ C and below only a very small portion of the charge is inputted at 0.7 and 0.2 ampere. The importance of lowering the charge rate at the lower temperature

is evident regardless of the charge cutoff voltage. Therefore, at low temperatures the cell can only accept a low rate of charge. This is attributed to the higher impedance at low temperature.

#### 4.4.2 Discharging.

(1) Effect of Charging Voltage on Discharge. The higher the charging cutoff voltage used, the higher the average closed circuit voltage on discharge, as seen in figure 4. The capacity is approximately doubled in going from a charging voltage of 3.9 volts to 4.4 volts. Table 2 summarizes the effect of charge voltage on discharge capacity at various temperatures. The higher charge voltage, together with high temperature, gives the highest capacity. However, when the cell is operating at high temperature  $(50^{\circ}C)$ , it will have the highest permanent loss (see the storage discussion, para. 4.4.2(5), for detail).

Effect of Temperature on Discharge. Figures 5 through 7 (2) give the curves obtained at different temperatures with a discharge of 0.5 ampere to a 2.5 volt endpoint. Charging conditions were as previously stated in para. 3.2.1(2). Charge and discharge temperatures are the same. Compared to the 25°C discharge capacity, the 50°C result was approximately 7% higher, while at 0°C and -20°C it was lower by 18.0% and 64.0%, respectively. The discharge capacity is affected by both the charge and discharge temperatures. However, the major factor in obtaining greater output capacity was by increasing the charge cutoff voltage and charging at room temperature or higher. This is not only demonstrated by comparing the discharges of Figures 5-7, but even more vividly by comparing figure 8 with figure 7, when discharging the cell at -20°C after a room temperature charge (figure 8) and after a -20°C charge (figure 7). The discharge capacity can be increased 45% at -20°C after charging at room temperature and using the 4.25 volt cutoff.

(3) Effect of Discharge Rate. Figure 9 depicts the discharge curves obtained for discharges at the 0.5, 1, 2 and 3 ampere rates. Capacity drops off steeply as the discharge rate is increased above 1 ampere, with much lower average operating voltages as well. The Li-ion cell does yield almost full capacity for a 1C rate discharge.

(4) Pulse Discharge. Figure 10 shows that at a 4.25 volt charge voltage cutoff, a capacity of 0.773 ampere-hour was obtained on the subsequent discharge cycle of 4.5 amperes for 5 seconds, then off for 25 seconds to an end voltage of 2.5 volts at 25°C. This indicates that lithium-ion cells are capable of relatively high current pulses as long as the average discharge rate is not excessive.

(5) Storage. The data obtained on cells subjected to storage are in Table 3. The initial loss in capacity on the first cycle after storage and the permanent loss are higher as the charge cutoff voltage is increased. This was also confirmed for the subsequent storage and cycling at 50°C of the same cells. Figures 11 and 12 (charge cutoff voltages of 4.1 and 4.25, respectively) compare the discharge curves and capacities before storage for the first discharge immediately after storage, and after recharge.

(6) Cycle Life. One cell shown in figure 13 was subjected to a regime consisting of a charge cutoff voltage of 4.1 volts and discharge of 0.5 ampere to 2.5 volts. It has reached 400 cycles to date. Initially, the cell gave 0.85 ampere-hour then dropped to 0.75 ampere-hour at 75 cycles and gradually decreased to 0.73 ampere-hour at 400 cycles. For the first 40 cycles and again at around 125 to 165 cycles there were big dips in capacity. After that the cell recovered to give normal capacity. The reason for the dips has not been substantiated, but it is attributed to an intermittent contact in the circuitry for short periods of time. In figure 14, where the charge voltage was 4.25 volts, the initial capacity is approximately 12% higher than for the 4.1 volt charge cutoff voltage. However, capacity does drop more quickly until the same capacity is reached as for the 4.1 charge cutoff voltage cell. At 350 cycles, the capacities are about equal, after which the capacity for the 4.25 charge cutoff voltage cell dropped below that of the 4.1 volt one. The cells are still being cycled until they reach 60% of their initial capacity. The cells are still Additional cell cycling at these and slightly higher voltages should establish the charging voltage to achieve optimum capacity and cycle life.

#### 5. CONCLUSIONS

(1) The advantages of the Sony lithium-ion rechargeable cell are in its carbon anode which when combined with a high voltage cathode (such as LiCoO<sub>2</sub>) makes for a high voltage, high cycle life and a very safe cell compared to other types of lithium rechargeable cells.

(2) The Sony lithium-ion cell was well built. It was similar in construction to other types of spirally wound electrode/separator constructions.

(3) Charging the Sony lithium-ion cell in accordance with Sony instructions and/or using the Sony charger, produced the capacity and energy density close to their battery rated values, but not their original claimed values. Cells typically gave 20% less capacity than claimed and the same capacity as rated. (4) The Sony charger can recharge the cellular phone battery in one hour to about 90% of capacity. It will fully charge within two and a half hours. It was demonstrated that using a multi-step (3 steps: 700 mA, 200 mA, 50 mA) constant current method of charge gave equivalent capacities to that using the Sony method of charge. Salient results for this charging are:

(a) Temperature. The highest temperature (50°C) of charge gave the highest charge input. No excessive overcharge was noted even with a 4.25 volts charge cutoff.

(b) Charging cutoff voltage. The highest charging cutoff voltage gave the highest charge input and discharge output. Energy density is increased about 13% per 0.1 volt rise in charge cutoff.

(c) At the lower temperature of charge, more charge is inputted at low charge rates. Practical charge temperature limits are 0°C to 40°C, because below 0°C only low current is accepted, and, at 50°C and above, data indicated that there is high permanent loss in capacity.

(5) Storage. For the 14 day storage at  $45^{\circ}$ C, a higher charging cutoff voltage (prior to storage) resulted in a higher initial loss and a permanent loss in capacity after storage. For the 20 days storage at 50°C, a loss of 1.2% per day was measured. 80% of that capacity loss was permanent and not recoverable with cycling. This indicates that 50°C and higher temperatures can significantly reduce the capacity and cycle life of the Sony cell.

(6) Cycling. Although a higher charge voltage cutoff (4.25 volts versus 4.1 volts) produced higher initial capacity, a greater drop off in capacity is noted when cycling with the higher charge cutoff voltage cell until around 350 cycles. At that point, the lower charge cutoff voltage (4.1 volts) cell began to outperform the higher charge cutoff voltage (4.25 volts) cell. Cycle life can be extended by limiting charge voltage but at the expense of initial capacity. However, voltages as high as 4.25 volts appear to yield an acceptable cycle life.

(7) The performance obtained for the Sony lithium-ion rechargeable cell was compared to that of other rechargeable systems. Data are presented in table 4. They show that the Li-ion rechargeable cell, using the highest charge cutoff voltage, gives greater energy densities than the present aqueous systems [nickel-cadmium (NiCd) and nickel-metal hydride (NiMH)], but lower than the LiNiO2 system. However, its cycle life is much better and it has given indication of being safer than metallic lithium rechargeable systems. (8) Of extreme importance was the fact that for the charge/discharge conditions imposed on the Sony lithium-ion rechargeable 5/4  $C_s$  cells, no safety incidents were encountered. This is very encouraging and positive information which should give the go ahead for a more thorough evaluation of the Sony lithium-ion battery (two cells or more) under more stringent conditions and full characterization of its performance, cycle life, storage and safety features.

#### 6. RECOMMENDATION

Based on the promising preliminary data collected to date, it is recommended that a more complete evaluation be conducted to further characterize the performance of the Sony and other "rocking chair" (RCT) lithium-ion rechargeable cells and batteries. At the present time the RCT is one of the most promising lithium rechargeable batteries for military use. The data have indicated:

- High cell voltage (fewer cells to produce a given battery voltage)
- o High cycle life
- o Quick recharge capability
- o Reasonable storage
- o Safe operation

#### 7. REFERENCE

1. Rayovac Corporation, "Ultrasafe High Performance Rechargeable Ambient Temperature Battery." Program Review, Contract DAAL01-92-C-0221, Nov. 18, 1992.

























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TABLE 1. CHARGING INPUT AT INDICATED TEMPERATURE

CHARGE ACCUMULATIVE CAPACITIES IN AMPERE HOURS
CHARGE VOLTAGE & CURRENT

-30°C -20°C 0°C 25°C 50°C

	1				ì				ł				
500		0.479	0.626	0.662		0.664	0.810	0.850		0.717	0.880	0.927	
		0.371	0.551	0.603		0.560	0.753	0.812		0.595	0.793	0.853	
		0.144	0.386	0.491		0.253	0.557	0.680		0.276	0.587	0.709	
		0.001	0.095	0.258		0.011	0.156	0.379		0.018	0.195	0.420	
		0	0	0		0	0	0		0.000	0.000	0.115	
	ЪЦТ	AMP.	AMP.	AMP.	5	AMP.	AMP.	AMP.		AMP.	AMP.	AMP.	
	3.9 VC	0.70	0.20	0.05	4.1 VO	0.70	0.20	0.05	4.25 VC	0.70	0.20	0.05	

					Chorad of
0.923	0.872	0.739	0.660	0.047	4.25V
0.816	0.804	0.713	0.471	0.044	4.10V
0.668	0.609	0.524	0.363	0.017	<b>3.90V</b>
50°C	s 25°C	ATURE 0°C	TEMPER -20°C	-30°C	CHARGE VOLTAGE
	JRES	MPERATI	RIOUS TEI	ICITY AT VA	

TABLE 2. EFFECT OF CHARGE VOLTAGE ON DISCHARGE

Unarge at 25°C, Discharge at given te aperatures at 0.5A to 2.5V. Capacities in ampere-hours.

AT 45°C FOR 14 DAYS WITIAL LOSS PERMANA ER STORAGE AFTER 5 6.90 2.5 11.1 6.0 12.9 6.4 12.9 6.4 12.9 6.4 12.9 12.9 12.3 14.6 12.3 14.6 12.3 15.1 13.8 24.1 20.2

TABLE 3. STORAGE TESTS AT 45C AND 50C

\* CYCLED SEVERAL TIMES AFTER STORAGE

TABLE 4. CH/	ARACTERISTICS (	JF RECHARGEA	BLE SYSTEMS
SYSTEMS	% AVG LOSS PER CYCLE	ENERGY DENSITY (WH/KG)	VOLUMETRIC DENSITY (WH/LITER)
NICAD	0.02	30	94
HI CAP NICAD	0.03	38	126
HMIN	0.03	55	178
LI-ION@3.9V	0.004	51	116
LI-10N@4.1V	0.04	71	160
LI-10N@4.25	0.07	84	192
LI-ION@4.4V	0.28	107	244
LINIO2	0.43	160	360

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