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Ultralife's polymer electrolyte rechargeable lithium-ion batteries for use in the mobile electronics industry

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Abstract

Ultralife Polymer™ brand batteries for cellular phones as made by Nokia Mobile Phones Incorporated were introduced in July 2000. Characteristics of the UBC443483 cell and UB750N battery are described and related to the power and battery requirements of these cellular phones and chargers. Current, power, and pulse capability are presented as functions of temperature, depth of discharge, and storage at the cell level. Safety protection devices and chargers are discussed at the battery pack level, as well as performance in cellular phones under various wireless communication protocols. Performance is competitive with liquid lithium-ion systems while offering opportunity for non-traditional form factors. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Lithium-ion batteries; Polymer electrolytes; Mobile telephones

1. Introduction

The ever increasing and aggressive power demands of portable electronic devices continue to challenge battery design and performance. Lithium-ion polymer batteries are an emerging force in this marketplace [1],¹ addressing needs for high energy and for thin and lightweight batteries with customizable shapes and sizes. Ultralife batteries is a leader in the development and manufacture of a wide range of lithium-ion polymer cells and battery packs to meet these needs in consumer, commercial, and military markets.

Ultralife Polymer™ brand after-market batteries for 51xx, 61xx, and 71xx series cellular phones from Nokia were introduced in July 2000. Characteristics of one production polymer cell used in these batteries, the UBC443483, and one battery, the UB750N, are described below. Power and battery requirements of several models of cellular phones and chargers from Nokia are also presented and related to UBC443483 and UB750N design, performance and safety characteristics. Performance for cells under development, both in form factor and chemistry, are also described.

2. Cell design and manufacture

Ultralife Polymer™ brand cells described in this paper use a stacked electrode architecture [2], polymer electrolyte, and fabrication procedures based on Bellcore's plastic lithium-ion (PLion™) technology [3]. Ultralife commercial cells use LiCoO₂ as the cathode active material, graphite as the active material for the anode, and Al-laminated film packaging. Higher energy cathode and anode materials are being developed under a NIST ATP award [4]. Ultralife can also manufacture polymer cells using Li_{1+x}Mn_{2-x}O₄ as the active cathode [2]. Cells are made in a variety of form factors up to 15 Ah in capacity. High volume manufacturing facilities are in place for the UBC443483 (725 mAh) and UBC543483 (930 mAh). These cells are 34 mm wide, 83 mm long, and 4.4 and 5.4 mm thick, respectively. Cells as thin as 0.9 mm thick can be made in this form factor using central anode electrodes. An example of the C rate capacity distribution for a typical production lot of UBC443483 at ambient temperature is shown in Fig. 1. The average C rate capacity is 717 mAh. One standard deviation is 16 mAh. The cells are conservatively rated at 725 mAh at 0.2C as sold, typical average capacity is 735 mAh. Unless noted otherwise, UBC443483 cells are rated at 725 mAh at C rate in this paper. Cells are tested with or without a Raychem® LR4-380 PPTC (polymer positive temperature coefficient) device as noted. Ambient temperature is taken as 23 ± 2°C.

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¹ Approximately 50% of the battery papers were lithium-ion polymer.

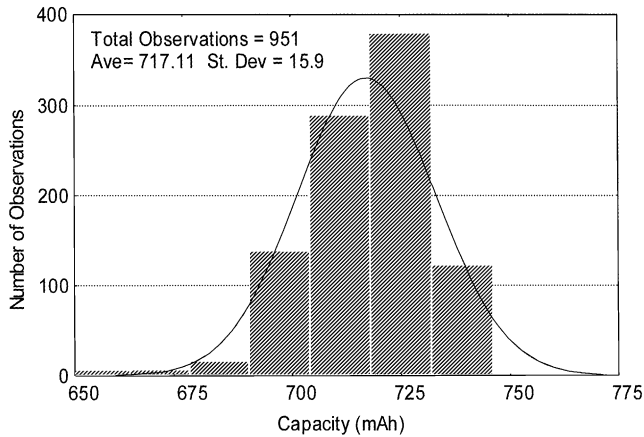


Fig. 1. Distribution of capacity for a typical production run of UBC443483 cells at C rate, cells discharged at 725 mA at ambient temperature.

3. Cell performance

3.1. Charge and discharge characteristics at ambient temperature

Typical charge characteristics for the UBC443483 with a PPTC are shown in Fig. 2. Constant current charge to a specified voltage limit, followed by constant voltage charge at the voltage limit to a specified current limit cut-off is recommended. The constant current charge rate is a function of the electrode coat weights, 350 mA for the UBC443483, having seven electrodes in parallel as described in this paper. A charge limit of 4.2 V is recommended for LiCoO_2 cathodes. Typical current limit cut-offs in the constant voltage charge are $C/10$ to $C/20$. A lower voltage cut-off of 3.0 is recommended during active discharge, drift to lower voltages on stand do not appear to be detrimental to cell performance.

The rate capability from 1 to 10C at ambient temperature of the UBC443483 with a PPTC is shown in Fig. 3. The cells deliver 91% of 1C capacity at 3C rate. Constant power discharges provide flat discharge profiles even at high power rates, such as 2.8 W, where the current reaches 1.3C at end of discharge. Typical constant power discharges for cells with a PPTC are shown in Fig. 4.

3.2. Charge and discharge characteristics below ambient temperature

Low temperature performance of the UBC443483 with a PPTC device was measured from -20 to $+20^\circ\text{C}$ under group special mobile (GSM) simulated pulse discharges. Charges were at ambient temperature with a 4 h soak at the discharge temperature. The discharge consisted of a 1.64 A current pulse of 550 μs duration every 4.6 ms on a background current of 0.2 A. The voltage during the high current pulse is shown in Fig. 5. Resistance measured during the pulse, measured as the difference in the pulse and background voltages divided by 1.44 A, is stable over a wide temperature range. There is little to no performance dependence on state-of-charge.

Rate performance of the UBC443483 cell at -20°C is shown in Fig. 6. Capacity at 1C approaches 65% of the 1C capacity of 725 mAh at ambient temperature, while 0.2C rate delivers 98% of ambient 1C capacity.

Low temperature charge of the UBC443483 is excellent, with fully discharged cells charging at 0°C after 4 h soak at temperature to over 96% of the ambient 1C capacity. The charge was 350 mA constant current to 4.15 V, followed by a constant voltage charge at 4.15 V until the current fell to 72.5 mA (see Table 1).

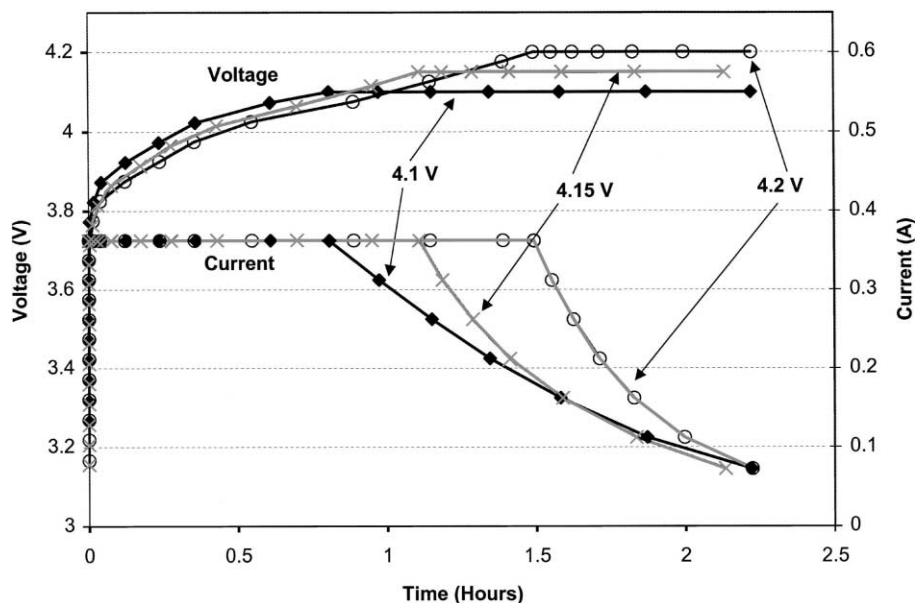


Fig. 2. Typical charge profiles for UBC443483 cells with a PPTC charged at 362.5 mA to specified voltage at ambient temperature.

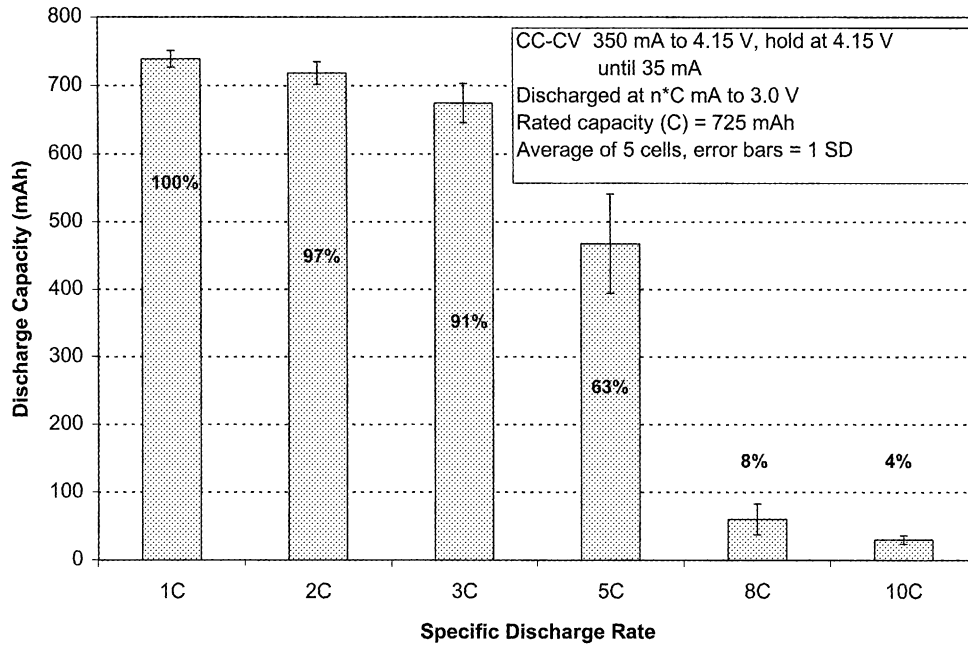


Fig. 3. Constant current discharge capacity vs. rate at ambient temperature for UBC443483 with PPTC.

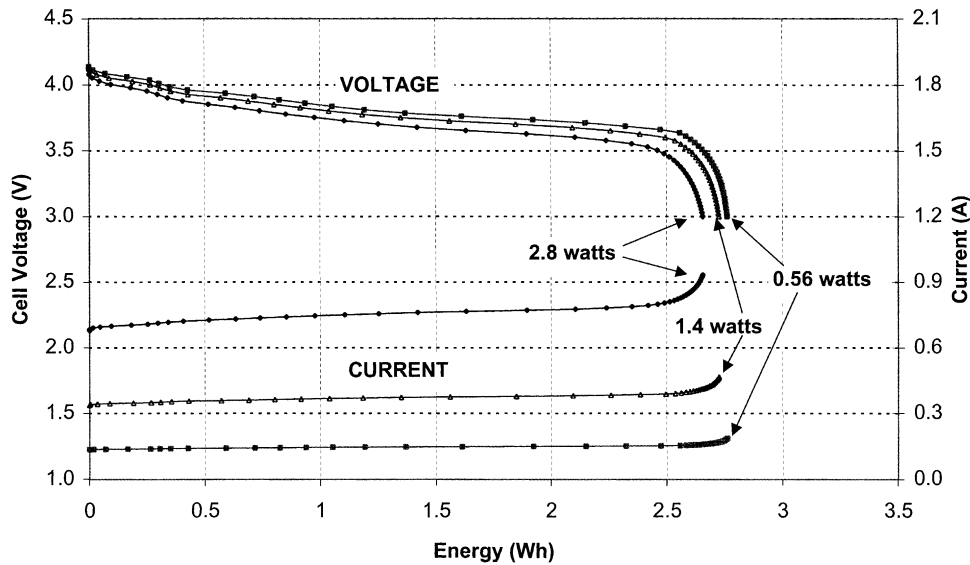


Fig. 4. Constant power discharge profiles for UBC443483 with a PPTC at ambient temperature.

3.3. Long-term cycling: discharge at constant current and constant power

Ambient and 45°C life cycle characteristics are comparable with liquid lithium-ion systems.² Both constant current, Fig. 7, and constant power, Fig. 8, interrupted long-term cycle performances (with 30 min rests between half cycles)

typically exceed 300 cycles to 80% of ambient 1C capacity. Fig. 9 shows comparative information for UBC443483 cells with a PPTC undergoing continuous cycling at ambient and 45°C. Figs. 10 and 11 show the voltage versus time discharge curves for various cycles of a single cell at the temperatures in Fig. 9.

3.4. Long-term cycling: GSM discharge

Long-term cycling, with 30 min rests between half cycles, was performed at ambient conditions using the same GSM simulated pulse discharges described above. Retained capa-

²For example, see specification sheets for Sony US063048G3 (700 mAh), UP383562 (540 mAh) and US18650G3 (1800 mAh) at www.world.sony.com and Panasonic CGP30486 (630 mAh) and CGR18650H (1500 mAh) at www.panasonic.com.

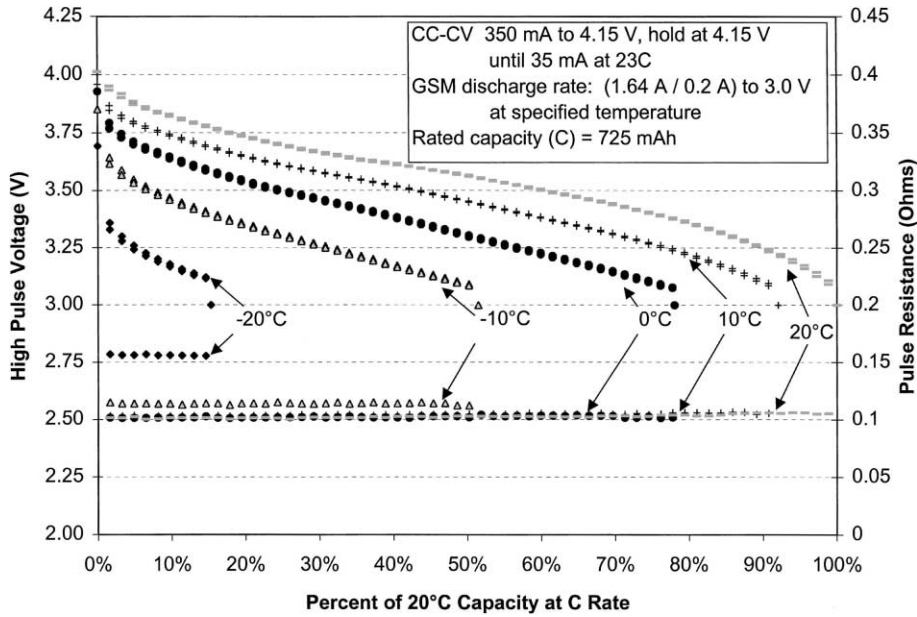


Fig. 5. GSM pulse discharge characteristics of UBC443483 with a PPTC. Ambient temperature charge, GSM discharge (1.64 A/0.2 A) at specified temperature.

city is greater than 80% of ambient 1C capacity for over 250 cycles with concurrent resistance growth measured during the pulse changing from 80 to 94 mΩ, a 17% change (see Fig. 12).

3.5. Cycle life as a function of depth of discharge and rate

Cell and battery performance varies widely depending upon usage habits. Since in-field use is so difficult to model and so random, worst case scenarios are often chosen for life

testing of portable power products. This can be extremely misleading regarding the real world application and often misrepresents the actual battery life in the application. This is brought to the forefront when one starts to model the cycle life of batteries in cellular phone applications, taking into consideration depth of discharge (DOD) effects at various discharge rates.

UBC443483 cells were cycled at DOD varying from 10 to 100% under several different discharge rates. To make testing equal, all cells were charged to the specified voltage,

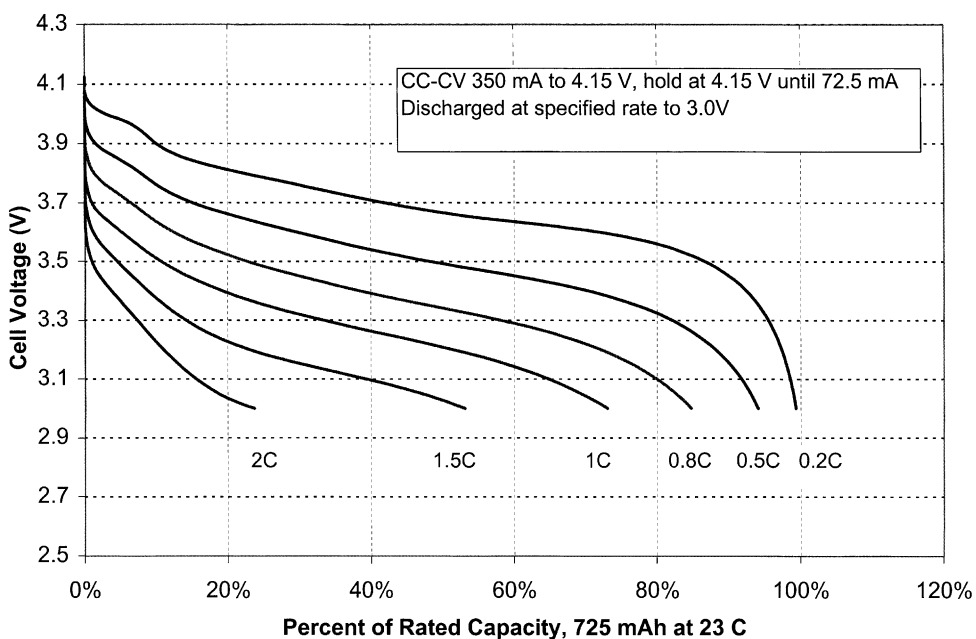


Fig. 6. Constant current discharge capacity vs. rate at -20°C for UBC443483.

Table 1
Capacity obtained during 0°C charge

Samples	Capacity (mAh)	Energy (Wh)
1	717	2.84
2	691	2.74
3	692	2.74
4	697	2.77
5	702	2.78
Average	699.7	2.78
S.D.	10.7	0.04

and then discharged until a percent of rated capacity was removed. If in removing the capacity, the voltage on any cell reached the lower cut-off voltage before the capacity was removed, the test was ended. The exception to this rule was 100% DOD cycling, where cells were discharged to 3.0 V on every cycle. There were three separate tests initiated, each using different discharge rates.

The first test was to charge UBC443483 cells to 4.10 V (column A in Table 2) at 350 mA, or approximately 0.5C (column C in Table 2). The cells were then charged at a constant voltage of 4.10 V until the current fell below 72.5 mA. The cells were then discharged at 350 mA

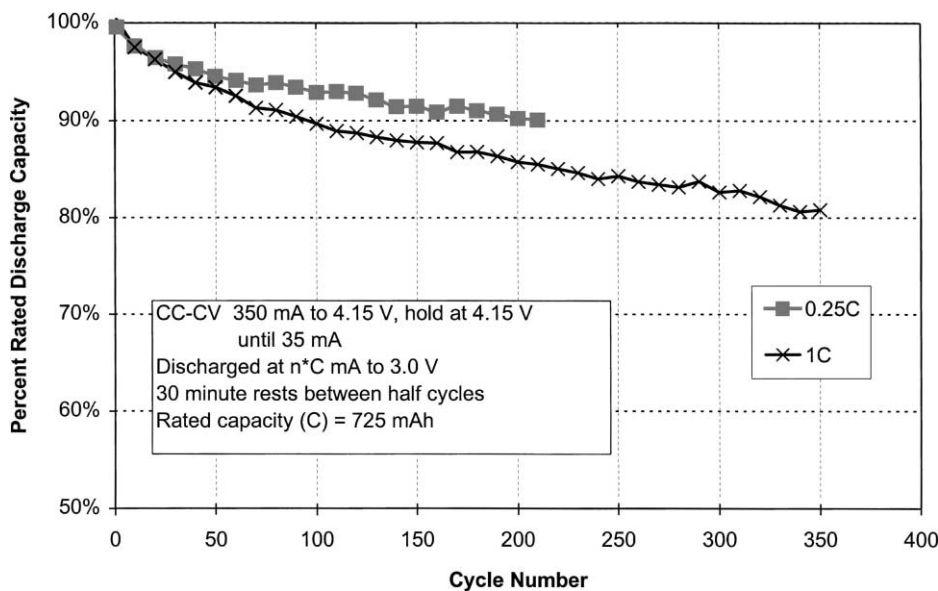


Fig. 7. UBC443483 interrupted constant current long-term cycling at ambient temperature.

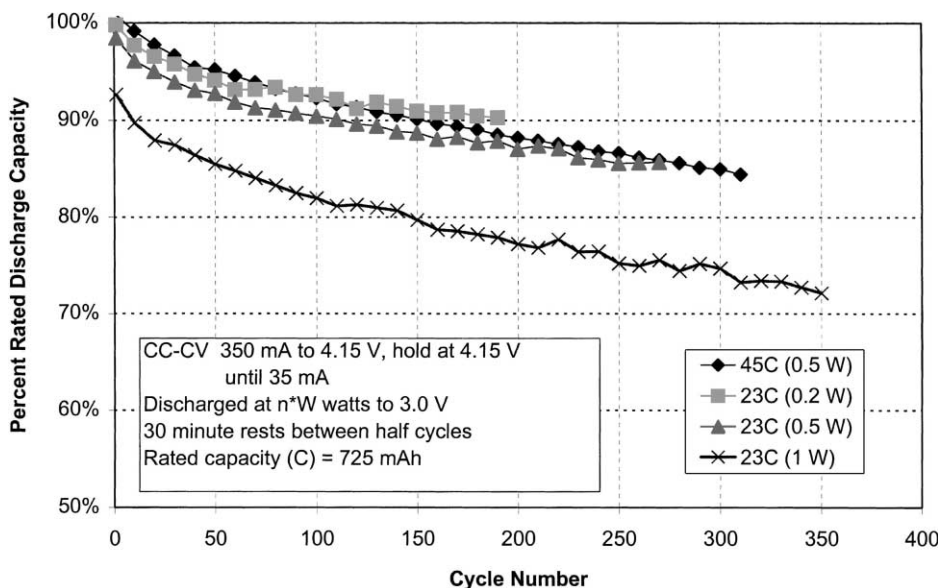


Fig. 8. UBC443483 interrupted constant power long-term cycling at 23 and 45°C. In the figure legend 1W = 2.8 watts.

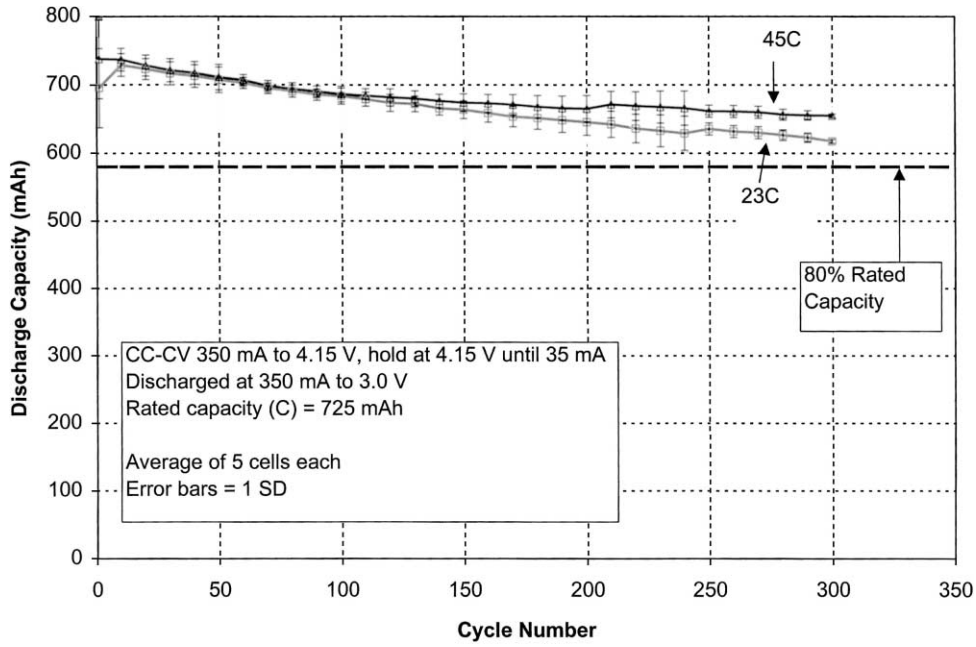


Fig. 9. UBC443483 with a PPTC undergoing continuous constant current long-term cycling at 23 and 45°C.

constant current (column D in Table 2) until the chosen percent DOD was obtained or 3.10 V (column B in Table 2) was reached. Cells were cycled at 10, 20, 40, 60, 80, and 100% DOD. Every 100–500 cycles, cells were charged as above, but only to 4.15 V (column E in Table 2), then discharged at a constant current of 350 mA (column D in Table 2) to 3.0 V (column F in Table 2) to obtain retained capacity information. These conditions were used to parallel the Nokia phone, closely approximating the charge and discharge rates, along with the reduced voltage window (vide infra). Several variants of this test were performed, see Table 2’s figure numbers and related test differences.

When results are examined from the test conditions above, it becomes clear that the number of cycles expected to a given level of retained capacity for a cell is extremely dependent upon DOD. As shown in Fig. 13, a cell cycling at 100% DOD at 1C charge, 1C discharge, would be expected to average 330 cycles to 80% retained capacity. A decrease to 80% DOD increases the number of cycles to 450 — an over 25% improvement. The effect continues as one decreases the DOD cycle percentage, with 1000 cycles at 1C charge, 1C discharge possible to 80% retained capacity at 20% DOD. When a logarithmic trend line is plotted against the 90 and 80% retained capacity lines, a strong

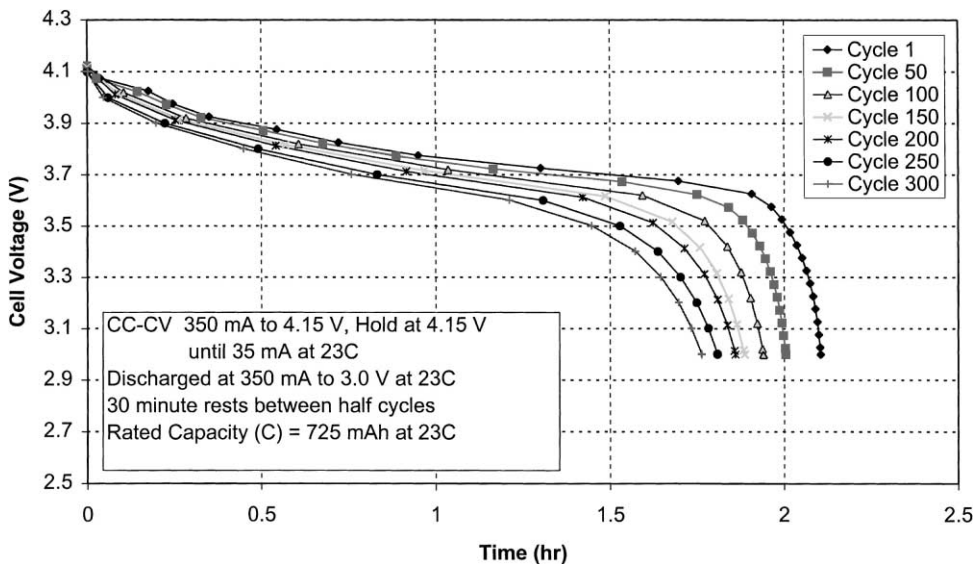


Fig. 10. UBC443483 with a PPTC discharge curves as a function of cycle number at 23°C.

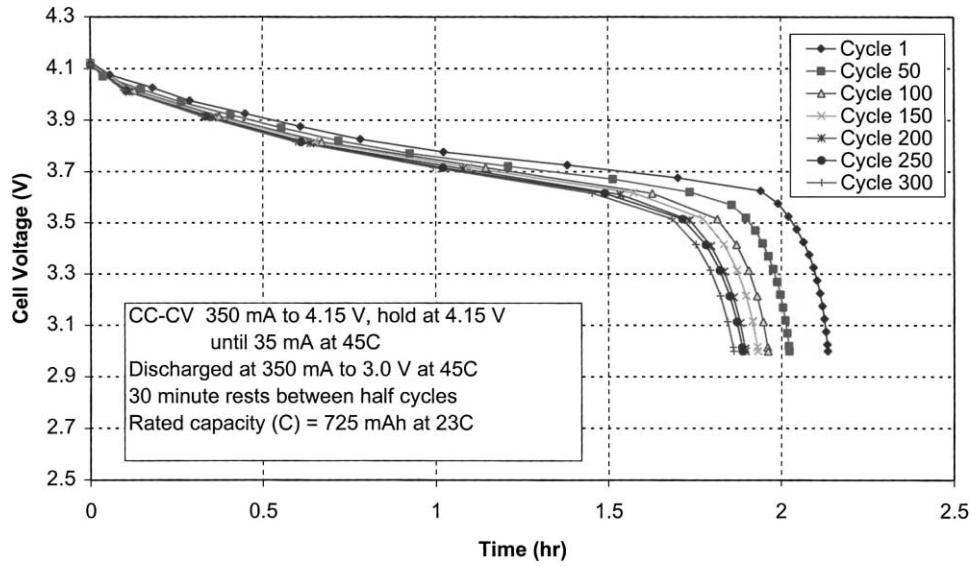


Fig. 11. UBC443483 with a PPTC discharge curves as a function of cycle number at 45°C.

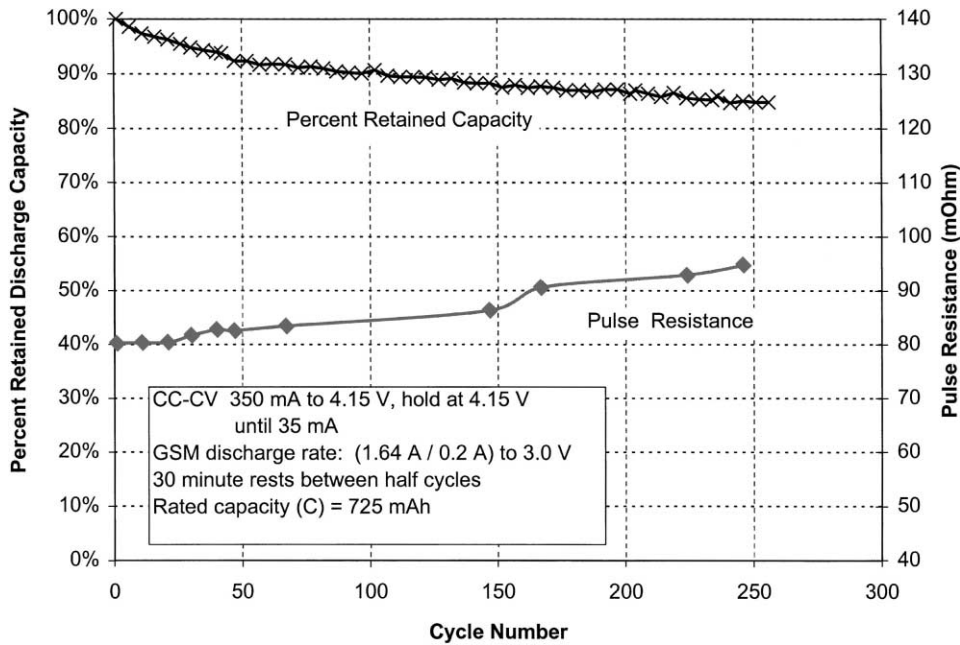


Fig. 12. UBC443483 with a PPTC interrupted long-term GSM discharge characteristics. Ambient temperature charge, GSM discharge (1.64 A/0.2 A) at ambient temperature.

Table 2
Depth of discharge experimental matrix

Figures	A DOD cycle charge voltage	B DOD cycle end test voltage	C DOD charge rate (mA)	D DOD discharge rate	E Retained capacity charge voltage	F Retained capacity discharge voltage
13	4.10	3.1	350	350 (mA)	4.15	3.0
14	4.15	3.0	725	725 (mA)	4.15	3.0
15	4.15	3.0	725	2.8 (W)	4.15	3.0

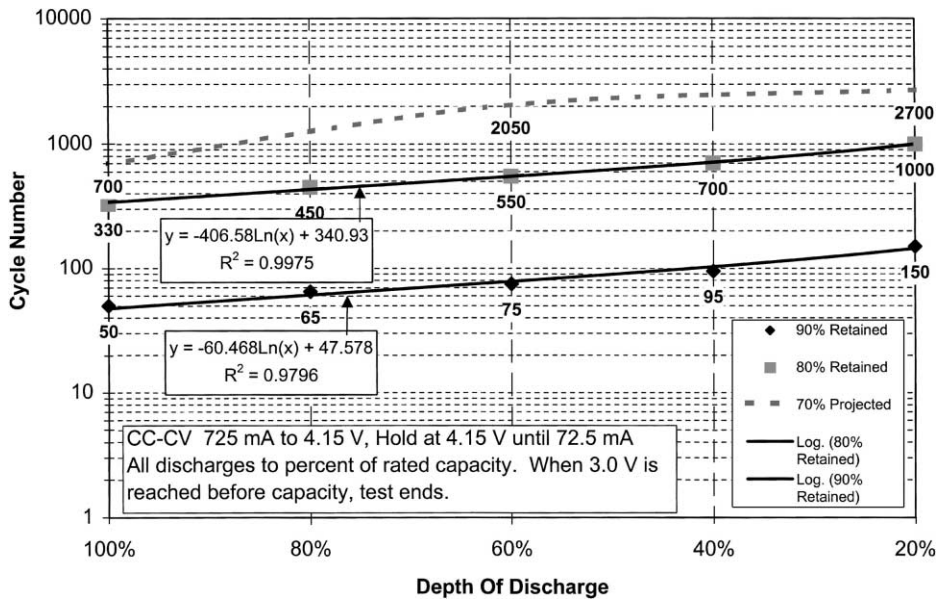


Fig. 13. UBC443483 with a PPTC cycle life vs. depth of discharge at ambient temperature. Constant current discharge at 1C. 100% DOD at 1C discharge every 100–500 cycles.

correlation with R^2 values of 0.97 and 0.99, respectively, is present between DOD and cycle number. A linear projection based on fade between the most recent two full DOD cycles has been added to estimate the number of cycles to 70% of retained capacity.

With examination of the lower rate and constant power test conditions in Table 2, the effect of rate on cycle life is evident. As shown in Fig. 14, the decrease in the charge and discharge rate to 350 mA from 1C charge 1C discharge dramatically increases the number of cycles to 80% retained capacity. At 80% DOD, the number of cycles increases from

450 at 1C charge, 1C discharge, to 600 cycles at 350 mA charge, 350 mA discharge. At 60% DOD, the number of cycles increases dramatically from 550 to 1150. The 20% DOD cycling is enhanced as well, with the number of cycles to 80% retained capacity increasing from 1000 to over 4800. The data obtained in Fig. 14 were obtained from an experimental cell using a doped nickel oxide cathode, but similar results are expected for LiCoO_2 cathodes.

Cycling the cells at constant power also supports the rate relationship, as shown in Fig. 15. Using the 0.2C rated power of 2.8 W, the cells being cycled are exposed to a varying

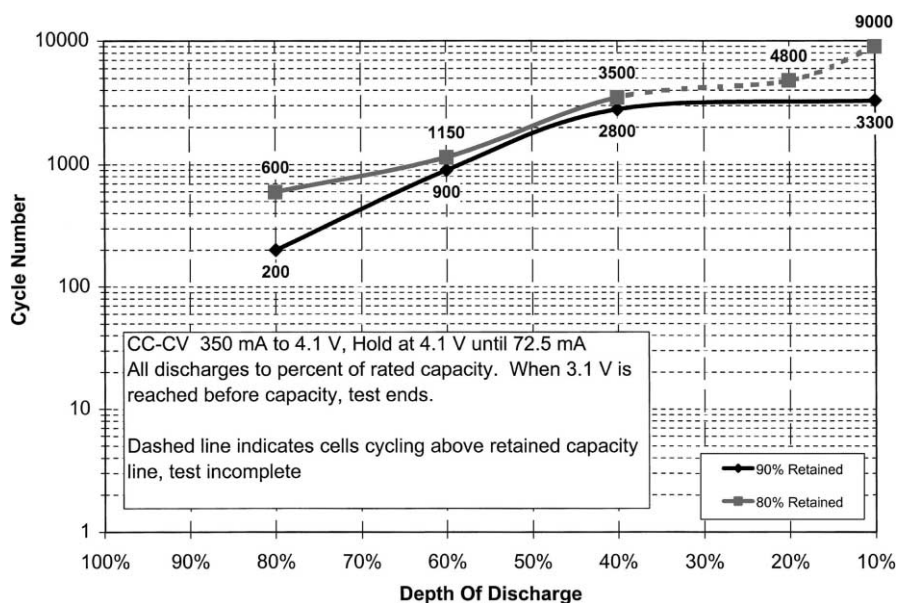


Fig. 14. Cycle life vs. depth of discharge at ambient temperature. Constant current discharge at 350 mA ($C = 685$ mA). 100% DOD at 350 mA discharge every 100–500 cycles.

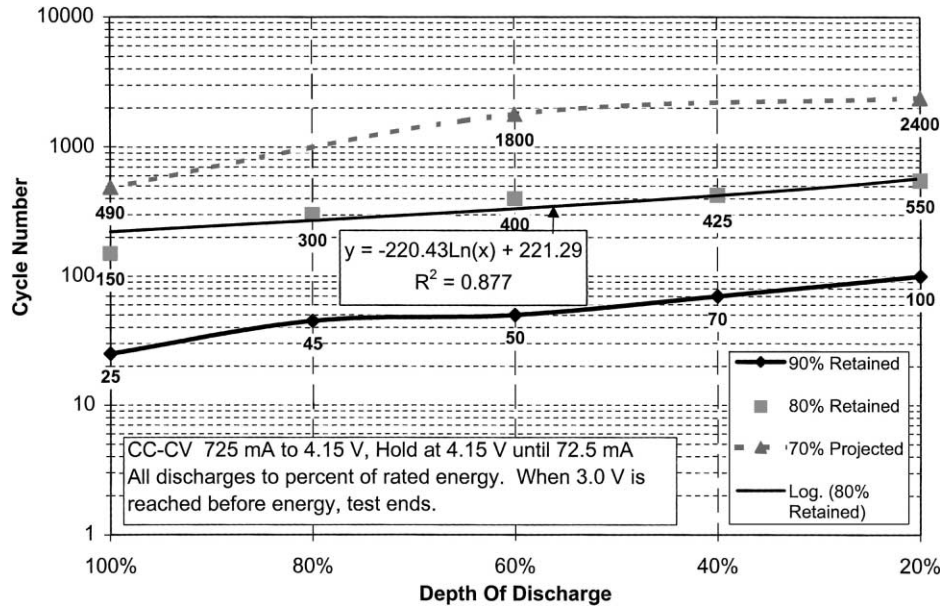


Fig. 15. UBC443483 with a PPTC cycle life vs. depth of discharge at ambient temperature. Constant power discharge at 2.8 W. 100% DOD at 2.8 W every 100–500 cycles.

current throughout discharge. To make results comparable to the other test conditions, the DOD percentages are based on the rated cell capacity, in mAh, and retained capacity is measured by constant power discharges every 100–500 cycles. At low DOD the cells cycle near the 1C rate, while at higher depths of discharge the current can approach 1.3C at end of discharge as illustrated in Fig. 16. Cells cycling at constant power discharges to various DODs have decreased performance when compared to the cells cycling at 1C charge, 1C discharge. A linear projection based on fade between the most recent two full DOD cycles has been added to estimate the number of cycles to 70% of retained capacity.

3.6. Temperature storage studies

Testing was conducted in what is expected to be extreme storage conditions for cells in cellular phone packs under normal usage. This testing used a temperature cycling regime that varied the cell temperature from 0 to 60°C. Cells with a PPTC were held at each temperature for 6 h, then transitioned to the alternate temperature over 6 h. Total temperature cycle was 24 h. Cells were stored at 0 and 100% state of charge (SOC). The cells were removed periodically and tested for impedance growth at 1 kHz frequency and cycled to determine reversible capacity. The cells were charged to 4.1 V and discharged to 3.1 V to closely simulate

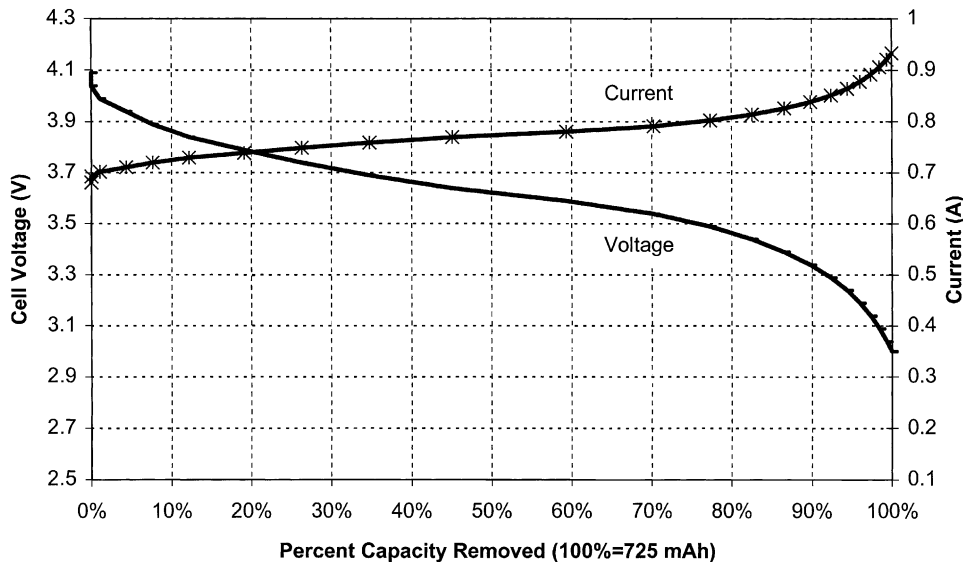


Fig. 16. UBC443483 with a PPTC at 2.8 W constant power discharge to 3.0 V at ambient temperature.

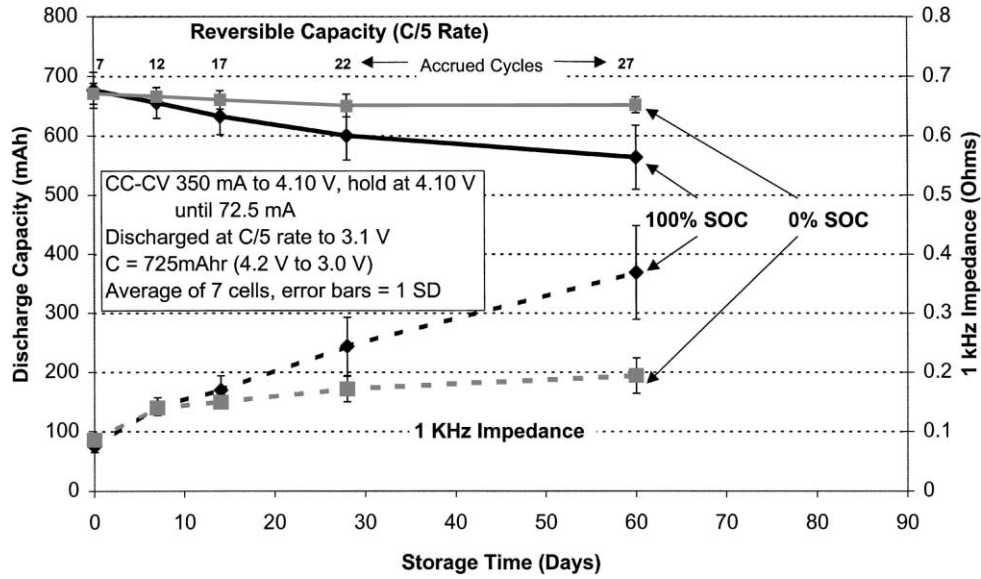


Fig. 17. The 0–60°C temperature cycle storage data for UBC443483 with a PPTC. Temperature cycle: 0°C for 6 h, 6 h ramp to 60°C; 60°C for 6 h, 6 h ramp to 0°C, repeat.

a cellular phone operational voltage window. Results are shown in Fig. 17. There is a charge state dependence on retained capacity and impedance growth at 1 kHz. All impedance measurements were performed prior to storage in the storage charge state, so all are charged to a similar voltage level.

Comparative data has been gathered at a continuous 60°C temperature storage on the UBC443483 cell in 100% SOC as shown in Fig. 18. These cells do not contain PPTC devices, so impedance is decreased by 35 mΩ at the start and throughout the test compared to cells in Fig. 17. Similarity in the results of Fig. 17 (temperature cycling, so

reduced time at 60°C) and 18 (continuous 60°C), suggests that thermal shock is a harsher test.

3.7. Float charge

Cells with PPTC devices were put on ambient temperature float charge at 1.075C rate for 1 week intervals. The voltage was set at 3 levels: 4.1, 4.2, and 4.3 V, while the maximum current was set at 780 mA. The cells were discharged at 780 mA to 3.0 V after each week of storage and the float test repeated. A total of 7 weeks of float charge

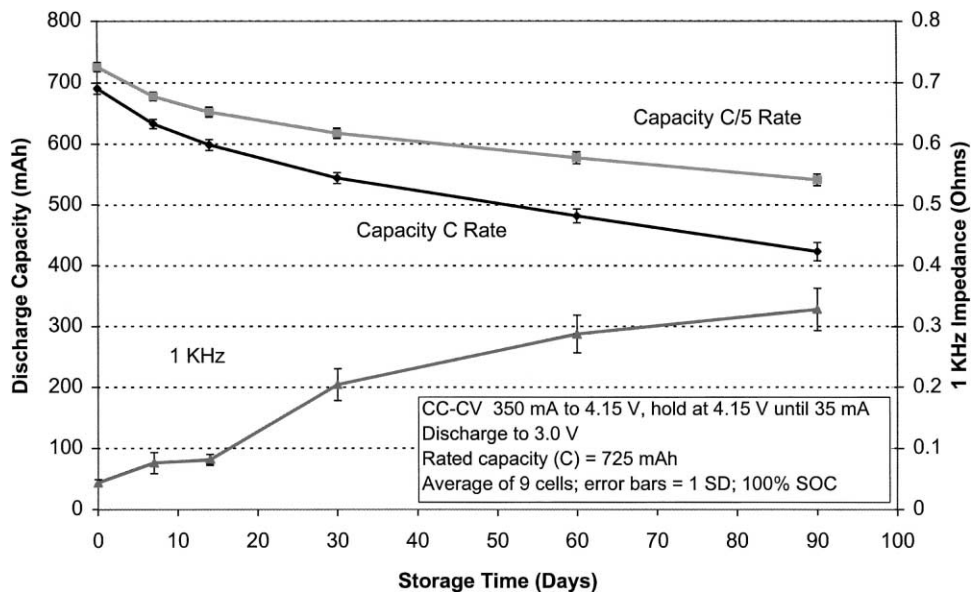


Fig. 18. The 60°C temperature storage data for UBC443483.

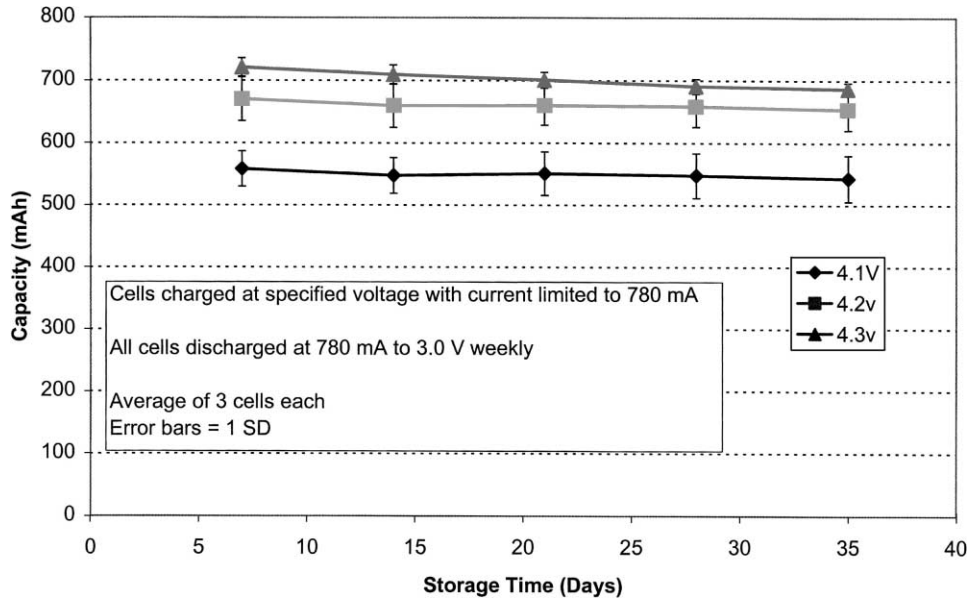


Fig. 19. UBC443483 with a PPTC on float charge at various voltages.

show little degradation of initial capacity and no safety problems, as shown in Fig. 19.

3.8. Advanced product development

Several energy density improvements are expected over the next few years and several prototype and commercial-scale builds are in testing [4]. One such development, yielding a 10% volumetric energy density improvement over current production product has been cycled to over 300 cycles. The cycle profile was a 0.5C charge to 4.15 V,

hold at 4.15 V until current drops below 0.1C, and discharge at 1C to 3.0 V. A non-packaged energy density comparison to the current product can be found in Fig. 20.

3.9. Advanced form factors

One of the key advantages of the Ultralife Polymer™ brand cell is that the form factor can be manipulated. The designer is no longer limited to a round or prismatic shape for powering a consumer device. Many shapes and sizes are possible with the advent of lithium polymer technology.

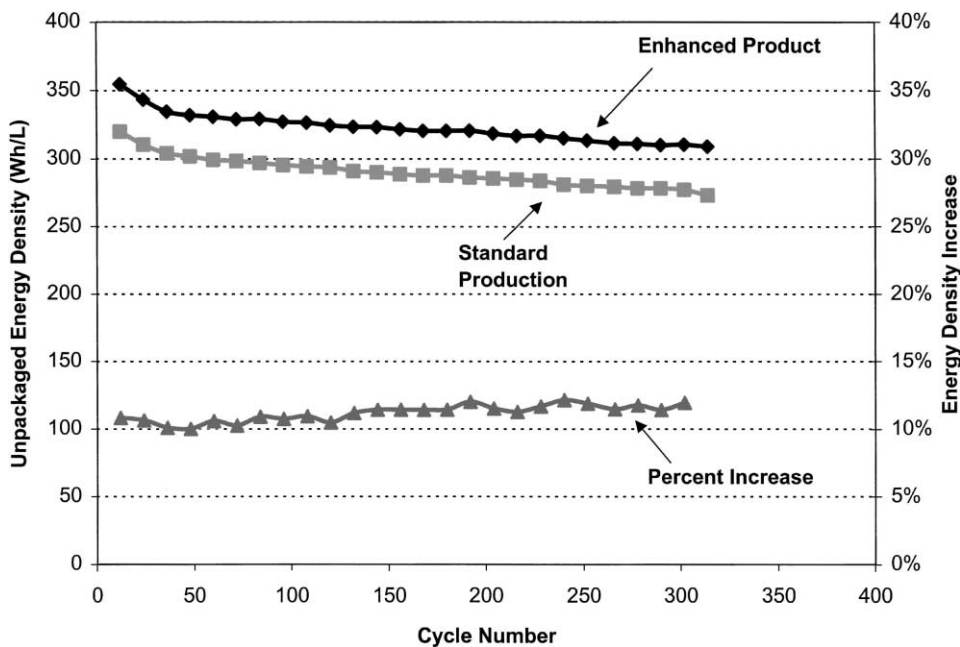


Fig. 20. Enhanced product comparison to current production product in a UBC093562 form factor.



Fig. 21. Array of prototype and commercial Ultralife Polymer™ brand cells. The UBC443483 is the cell without the white label and with the bar code.

Two-dimensional shapes such as triangles, parallelograms, trapezoids, and tori could be easily accommodated with present processing methods, three-dimensional shapes can be envisioned or constructed from two-dimensional building blocks. This will allow designers in the future to more freely take advantage of design options available with shaped power sources. An example of this technology is the triangle cell viewed in Fig. 21. This cell has dimensions of 102 mm × 102 mm × 154 mm, a thickness of 3.1 mm, a capacity of 1130 mAh, and an energy density of 268 Wh dm⁻³.

4. Battery pack design

There are several design considerations that are instrumental in the development of a battery pack system. These include the type of housing, interconnects, and series and parallel combinations of cells used to achieve, respectively, the required voltage and capacity. Thermal management, safety devices, and specialized chargers may also be required. For safety, lithium-ion cell manufacturers usually recommend use of protection circuitry to prevent cell overcharge and overdischarge, as well as PTC devices or fuses to limit current. Impedance, assembly cost, and availability all factor in the final pack design. Ultralife Polymer™ brand batteries incorporate a charge control circuit and a PPTC device (vide supra) for pack protection and safety for the consumer. The incorporation of a protective circuit and a

PPTC device is important to protect against non-specified aftermarket chargers that can charge cell packs in an extremely harsh manner. Some aftermarket chargers tested at Ultralife have extremely high pulse and average charge currents, approaching 3C with the UBC443483. This is much higher than the specified cell charge rate of C/2 for the UBC443483, thus necessitating the need for charge control circuitry.

The charge control circuitry in use by Ultralife in cellular phone packs limits charge voltage to no more than 4.25 V at the cell. If the cell voltage reaches 4.25 V, the charge control will open the charge circuit, disallowing further charge. On discharge a similar protection is in place, where the charge control circuit will open and stop any overdischarge when the cell voltage is below 2.3 V.

The use of charge control circuitry and a PPTC does add impedance to the battery system, thus reducing the average voltage of the battery pack, as shown in Fig. 22. This directly results in lower capacity and, therefore, talk and standby times when going from a cell to a completed battery pack. This results in a need to produce cells with as low impedance as possible to offset some of the impedance associated with protective devices, thereby increasing available capacity and talk time.

5. Battery pack performance

There are varying power requirements for cellular phones across the world, based upon infrastructure setup, network

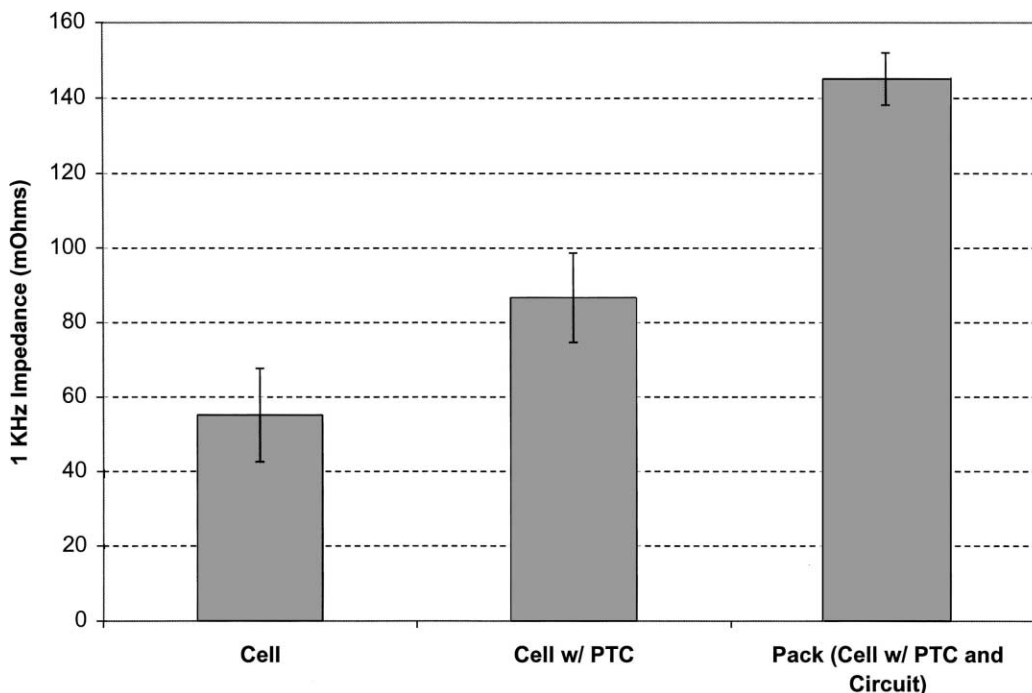


Fig. 22. Impedance comparison of UBC443483 cells with and without a PPTC device and with and without PPTC/circuit elements.

system, phone type, manufacturer, and usage habits. When evaluating several cellular phone types from Nokia in upstate New York using the UB750N battery pack, it is apparent that some of the inherent differences in power requirements are dependent on service provider's type of system. Service providers and system types tested included Sprint personal communication system (PCS), Verizon code division multiple access (CDMA), Frontier time division multiple access (TDMA), Cellular One Analog, and Cellular One Digital.

The analog system places the most aggressive power requirement on the battery. During standby the power consumption is pulse based, with a 100 mA high current for 50 ms every 1.25 s. While talking the system consumes 800 mA constant current, with 1 A μ s pulses. The discharge current is constant whether a user is quiet or talking.

Digital systems are more power friendly. For example, a Verizon 5180 Nokia CDMA phone uses a standby profile that consists of a 200 mA pulse for 150 ms of duration every 2.5 s which does not differ much from the example above. Compared to analog, digital systems conserve power by reducing power levels during periods of inactivity (quiet), and raising power levels during active periods (talking). The talking current profile of the CDMA digital phone determined by test was 500 mA background current with 600 mA μ s pulses, every 300 μ s, while the profile during quiet time periods reduced to 250 mA, with 300 mA high pulses every 5 ms.

Although European phone systems were not actually characterized for average current usage, most European

phones are GSM phones with well-known power requirements [5]. Actual usage tests were performed in Europe. The tests used a Nokia phone and confirms the decreased power consumption and increased talk time over United States systems. Results are summarized in Table 3 for the UB750N battery pack.

The cellular phones were also tested for low battery and cut-off voltage ranges. The phone ceases to operate and the display will not light if the pack voltage is below 3.2 V. The phones start going into low battery alarm below 3.6 V. Due to the high current drain and corresponding voltage drop in the pack, analog phone operation is limited once the low battery alarm sounds. The digital phones are slightly better, with roughly 10–15% of talk time available after low battery alarm sounds.

One of Ultralife's main goals is to produce the lightest, highest capacity, polymer cell phone battery. To this end, several original equipment manufacturer (OEM) and competitor products were tested for specific energy. The results are favorable for the Ultralife cellular phone product, as shown in Fig. 23.

Table 3
Average actual talk times associated with three different cellular phone service provider systems

System	Phone	Location	Talk time (min)
Cellular One Analog	5120	US	44–48
Sprint PCS Digital	6185	US	110–125
European GSM	6110 GSM	UK	200–210

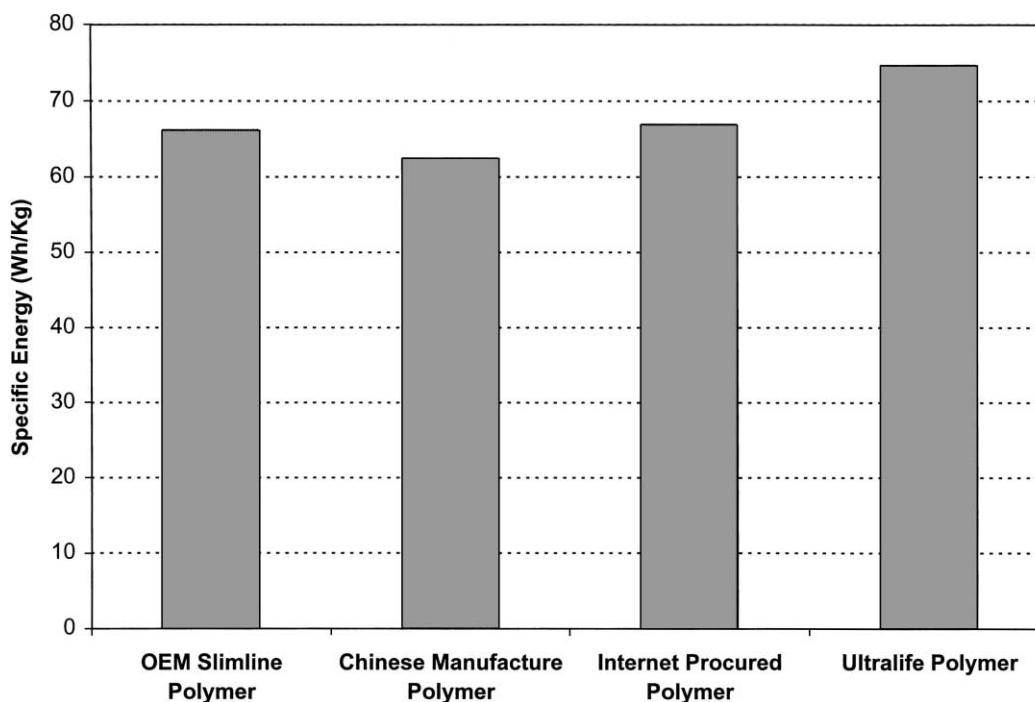


Fig. 23. Comparison by energy density of various polymer battery packs available on the market. Nokia 51xx, 61xx, and 71xx platforms.

Table 4
Comparison of various currently available charge devices

Power supply	Connected to	Method	I_{P-P}	I_{AVE}	I_{RMS}
ACP-7U	Phone model: 6185	Pulse	718.7	216.8	333.3
ACP-7U	DCH-9 base	Pulse	662.5	180	240
ACP-9U	Phone model: 6185	Constant current	NA	729	NA
ACP-9U	DCH-9 base	Constant current	NA	270	NA
LCH-9U (car)	Phone model: 6185	Constant current	NA	776	NA

6. Battery pack charger

Standard Nokia chargers were evaluated for charge currents and voltages. The standard power supply that comes with most Nokia phones is the ACP-7U. This power supply is relatively low rate, and when attached to the phone for charging, uses a peak current nearing 720 mA, with an average current of 220 mA. The charge method is a pulse

width modulation method, whereby as the pack reaches full charge, the period between pulses increases. Several power supplies were evaluated in the same manner.

The fast charge models, ACP-9U and LCH-9U, differ from the ACP-7U in that a constant current charge method is used. These chargers charge at relatively high rates of 720–770 mA until the voltage reaches 3.9 V. The charger then enters a trickle charge mode for the remaining charge. When

Table 5
Various 350 mA ambient discharge capacities at cycle 50 for UBC443483 cells

Description	High voltage cut-off	Low voltage cut-off	Discharge capacity (Ah) at cycle 50	Notes
No PTC	4.20	3.00	0.700	Cell in normal cycle voltage range
With PTC	4.20	3.00	0.683	PTC influence on cell in normal range
No PTC	4.10	3.10	0.580	Cell in "phone" cycle range
With PTC	4.15	3.00	0.572	Cell between normal and "phone" cycle range + PTC is similar to cell without PTC cycling at 4.10–3.0 V
With PTC	4.10	3.10	0.540	Cell in "phone" cycle range with PTC
With PTC and circuit	4.10	3.10	0.526	Cell in "phone" cycle range with PTC and protection circuit board

the ACP-9U is attached to the DCH-9 base, the charge current is reduced to 270 mA at the rear slot. The maximum charge voltage was 4.101 V at the pack for all charge combinations (see Table 4 for the testing matrix).

The maximum charge voltage is important, as a voltage of 4.2 V must be obtained at the cell to fully charge a LiCoO₂ lithium-ion cell. When the pack is charged to 4.1 V, greater than 10% reduction in capacity from the rated cell capacity is possible. Impedance losses due to circuit protection, fuses, and connections further reduce available cell capacity at the pack level. This can be seen in Table 5, which compares the capacity of a cell and a battery pack cycling at the same rates over various voltage windows. The battery pack has reduced capacity due to the reduction in voltage at the cell by the additional circuit and protection devices.

7. Summary

One of the most aggressive and varied power requirements is in the application of today's cellular phones.

Ultralife is a leader in providing next generation portable power for cellular phones and other wireless devices. Current generation Ultralife technology is a significant step forward in the portable power area, and future developments will allow Ultralife to continue to be competitive in this market segment.

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