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Performance characteristics of Ultralife's solid polymer rechargeable batteries

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Abstract

Ultralife Batteries delivered the world's first commercial shipments of solid polymer rechargeable batteries in 1997. The battery consists of a $Li_xMn_2O_4^-$ based cathode, graphite anode and proprietary polymeric separator. Energy density of the batteries exceeds 120 W h kg^{-1} and 200 W h dm^{-3} at the C rate. Pulse capability up to 5 C has been demonstrated. More than 90% of the initial C rate capacity remains after 500 continuous cycles at room temperature. These solid polymer rechargeable batteries also show good low and high temperature performance and have good safety characteristics.

Keywords: Lithium-ion solid polymer electrolyte batteries; Lithiated transition metal oxides

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1. Introduction

Since the first successful commercialization of the secondary lithium-ion rechargeable battery by Sony in 1991, this new generation of batteries has established a leading position in consumer electronic devices and is widely accepted as a power source by most original equipment manufacturers (OEMs). As successful as liquid lithium-ion batteries have been in the area of consumer electronics, there are still many unfulfilled promises. Today's fast growing portable electronics market demands higher energy, safer, thinner and lighter batteries. Developed to satisfy these demands, the solid polymer lithium-ion battery is the newest member of the rechargeable lithium battery family. Several companies and academic institutions are intensively engaged in the research and development of this new product. Ultralife Batteries is the first company to commercialize solid polymer rechargeable batteries. These products were delivered into the Japanese market in late 1997. This new battery technology enabled the breakthrough of a thin notebook computer produced by Mitsubishi Electric, which is around 19 mm in thickness and weighs only 1.4 kg [1]. The flat-format battery offers design engineers advantages in weight, thinness, and improved safety, without sacrificing high energy density, long cycle life and other favouable characteristics. These attributes make solid polymer lithium-ion batteries an ideal power source for the next generation of portable electronics devices, such as mobile phones, laptop computers, and other portable devices.

Subsequent to the first delivery of solid polymer rechargeable batteries in 1997, scientists and engineers at Ultralife have made many significant technical advances in the area of energy density, rate performance, cycle life, high temperature storage, pulse capability and impedance control.

Ultralife has also established high-volume manufacturing facilities for mass production of the solid polymer rechargeable batteries. Samples of these batteries produced by an automated production line have been delivered to many prospective customers including OEMs and value-added distributors.

2. Design of the battery

Ultralife's solid polymer cell adopts a central anode configuration. Two separator films alternately separate two cathodes from a common anode. The assembled cell plate is about 0.64 mm thick. Multiple plates are tabbed together, according to the capacity and thickness require-

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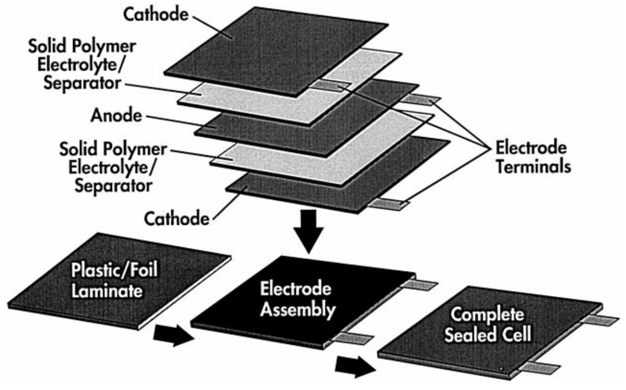

Fig. 1. A schematic illustration of Ultralife's solid polymer rechargeable cell.

ments defined by a specific application, and sealed in a plastic laminate. Fig. 1 shows a schematic construction of the cell. All of the electrode and separator films are being manufactured using production scale facilities located in Newark, NY. $Li_{1+x}Mn_{2-x}O_4$ is used as cathode material for improved safety, low production cost and benign environmental impacts. A graphite anode offers the flat voltage profile that is desired by many consumer applications. Ultralife's proprietary separator significantly enhances the structural integrity of the batteries, while a new electrolyte formulation has further improved cycle life, rate capability, and capacity retention at both low and high temperature. More general characteristics of Ultralife's solid polymer rechargeable batteries have been described in a previous publication [2].

3. Performance of the battery

3.1. General characteristics

Fig. 2 shows typical charge characteristics. A cell rated at 800 mA h is charged using constant current at the C rate to 4.2 V. The full capacity of the cell is obtained by keeping the charge voltage constant at 4.2 until the current drops to $C/10$.

For most cells, the useable capacity obtained at the C rate of discharge is greater than 96% of the total capacity, which is defined as the effective $C/10$ rate capacity using the signature curve discharge method. Rate capability is comparable to that of liquid lithium-ion cells. With the optimal formulations for electrodes and separator films, ionic conductivity of the specific electrolyte system becomes the rate-determining factor. For example, Fig. 3 illustrates an 800 mA h cell that has been discharged at room temperature using $2C$, C, $C/2$, $C/5$ and $C/10$ rates, all to an end voltage of three. Close to 100% of cell capacity can be withdrawn at C rate or lower, and about 90% of total cell capacity is available at $2C$ rate. The most recent version of these cells, using improved chemistry, has demonstrated that over 94% of total cell capacity can be withdrawn at $2C$ rate.

3.2. Variation of discharge capacity with temperature

Operational characteristics of a solid polymer lithium-ion cell are determined in large part by the composition

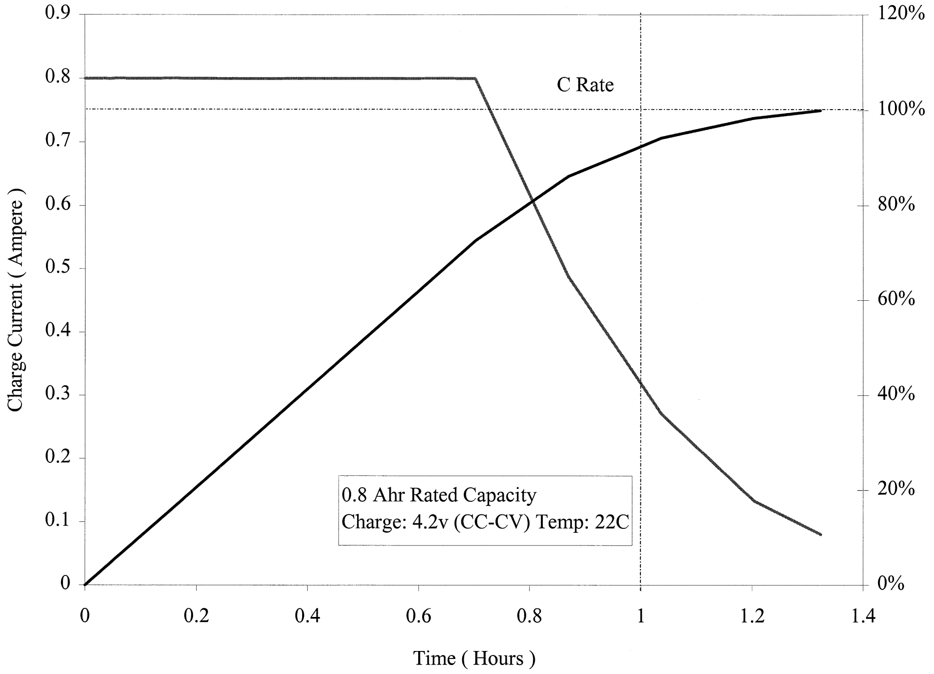

Fig. 2. Typical current–time and charge acceptance characteristics of an 800 mA h cell charged at 4.2 V until current fell to 0.8 A, then 0.8 A constant.

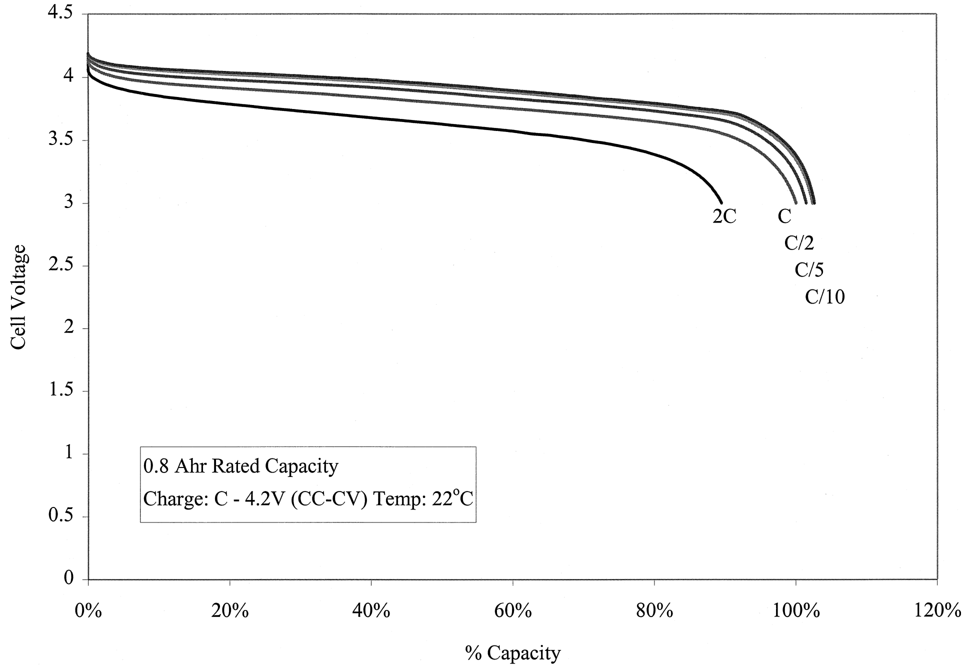

Fig. 3. Discharge performances of an 800 mA h cell at rates between 2*C* and *C*/10.

and nature of the electrolyte used in the cell, including the various solvent combinations in which ionic lithium salts are solvated. It is difficult, however, to provide an 'all purpose' electrolyte that can provide good discharge rate capability at both high and low temperatures. The traditional electrolyte for polymer lithium-ion cells (electrolyte 1 in Fig. 4) has a composition of 1 M LiPF$_6$ in EC:DMC (2:1) [3]. It demonstrates good high temperature characteristics. But this electrolyte is also well known to have poor characteristics at low temperature. In order to overcome this pitfall, Ultralife developed a proprietary electrolyte (electrolyte 2 in Fig. 4), which is able to perform well at

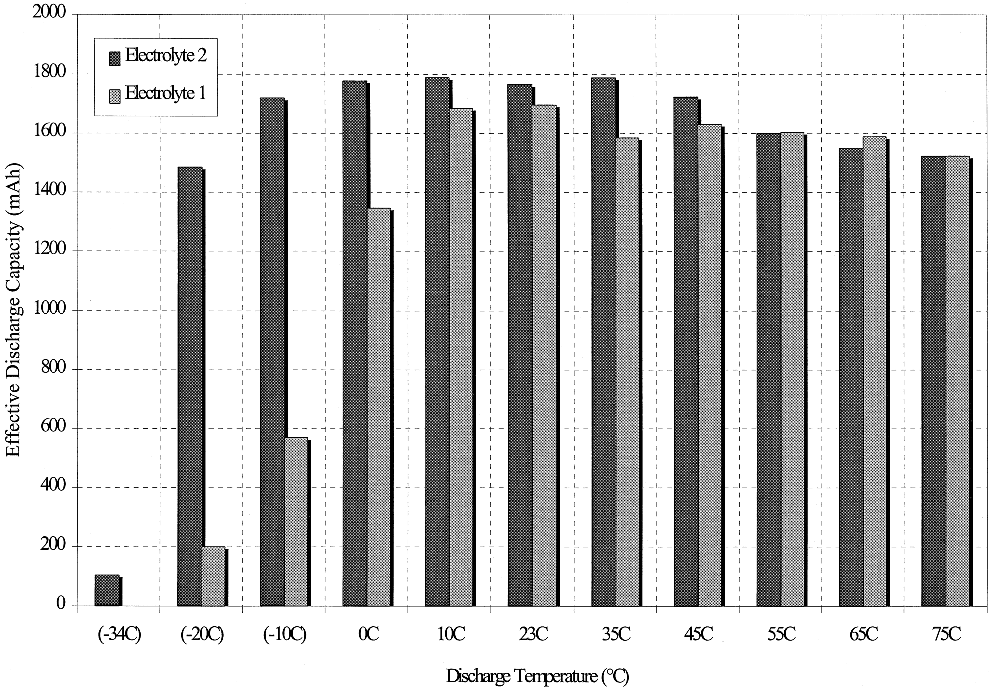

Fig. 4. Discharge capacity as a function of temperature of 1.6 A h cells containing either electrolyte 1 or 2.

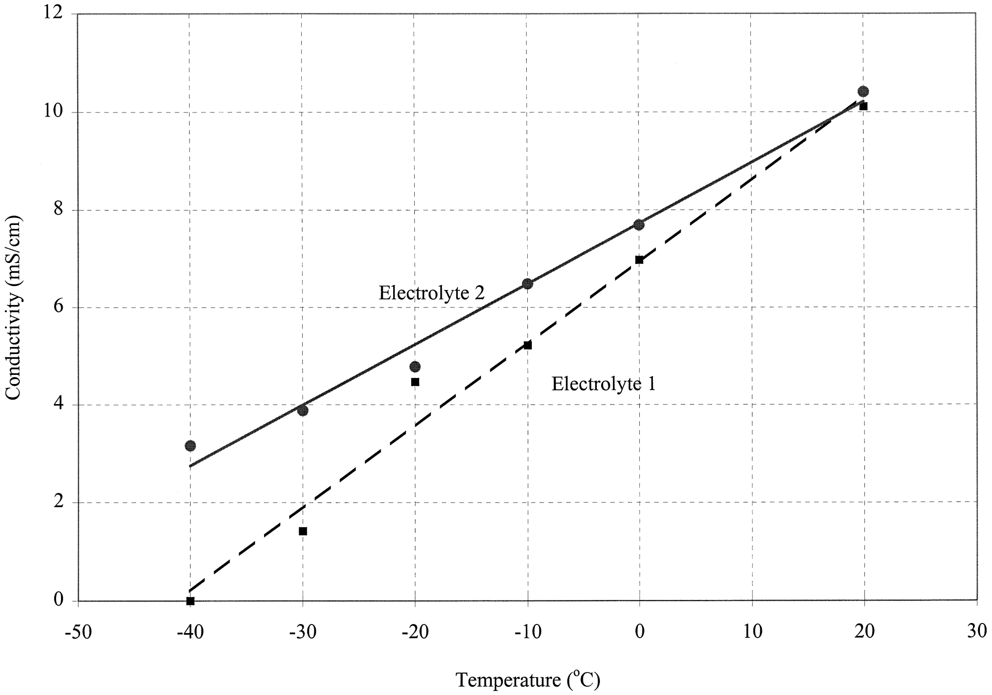

Fig. 5. Conductivity of electrolytes 1 and 2 as a function of temperature.

both high and low temperatures. Fig. 4 shows that comparable performance of 1.6 A h cells can be obtained at high temperatures using either electrolyte. However, at −10°C, electrolyte 2 offers a three-fold increase in useable capacity at $C/5$ rate compared to electrolyte 1, and about a five-fold increase at −20°C. A higher rate capability is consistent with the higher conductivity of electrolyte 2 at temperature as shown in Fig. 5.

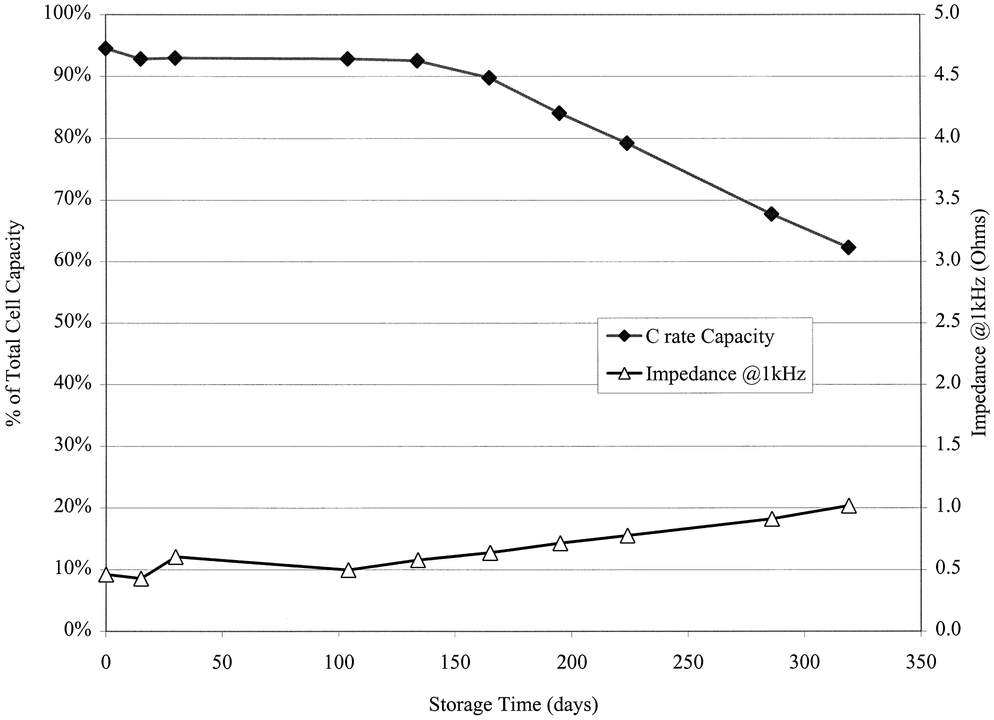

Fig. 6. Capacity retention and impedance growth of a 110 mA h cell during storage at room temperature from a fully charged state for 325 days. Discharges at the C rate.

3.3. Performance after storage

The stability of cell components is a major factor affecting the shelf life of solid polymer lithium-ion batteries. Fig. 6 shows charge retention and rise in impedance of a typical cell stored at room temperature. After being stored in a fully charged state at room temperature for nearly a year, the cell retains over 60% of its initial capacity, while the impedance has grown to about double its initial value. For cells stored at 55°C in the charged state for 3 months, there is about 29% capacity loss, as shown in Fig. 7. At $C/5$ rate, however, cell capacity remains around 80% of its initial value and impedance doubles from 0.48 to 0.9 Ω. Intensive research and development work has conducted to enhance the high temperature storage capability of solid polymer batteries.

By using improved chemistry, 85% of initial C rate capacity can be retained after 45 days storage at 55°C and about 75% retained after 20 days at 71°C. Ultralife expects continuous improvements in both rate and high temperature performance.

3.4. Long-term cycling

A typical solid polymer rechargeable battery exhibits excellent charge/discharge cycling performance both at room and elevated temperatures. Fig. 8 shows the cycling behaviour at ambient temperature of an 800 mA h cell. The cell was continuously cycled to 100% depth of discharge (DOD) at the $C/5$ rate. After 800 cycles, about 80% initial capacity remained. By incorporating several chemical modifications in these cells, Ultralife was able to reduce the capacity loss of the cells during cycling to about 8% after 500 cycles, as shown in Fig. 9. A $C/5$ rate for one charge and discharge was used after every 11 C-rate cycles so that any loss in rate capability or impedance growth could be monitored. Similar cells have been cycled continuously at an elevated temperature (45°C) for 1.5 months. Fig. 10 shows that more than 80% of initial C rate capacity remains after 300 cycles. The capacity loss in this case may be attributed to the cumulative effect of both high temperature storage and, to a lesser extent, long-term cycling.

3.5. Discharge testing to the GSM cellular phone regime

Fig. 11 shows the voltage profile of a cell rated at 800 mA h, discharged to a simulated GSM pulse discharge. This 4.6 ms pulse discharge had a background current of 0.2 A and included a 550 ms 1.2 A pulse. The discharge capacity removed by pulse discharge was equal to the cell's rated capacity. This translates into a talk time of greater than 3.5 h.

The typical d.c. resistance of a cell of this size as measured under this GSM load is less than 80 mΩ. These characteristics will enable Ultralife's solid polymer rechargeable batteries to be competitive in the cellular phone market, which is forecasted to rise from 250 million subscribers in 1998 to more than 500 million subscribers

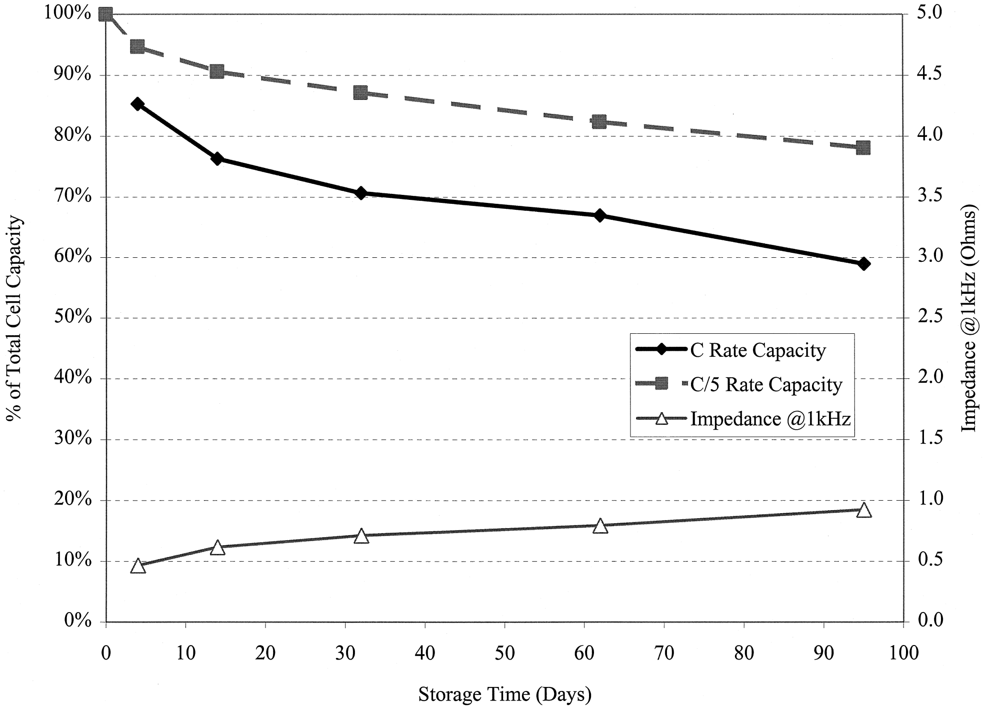

Fig. 7. Capacity retention and impedance growth of a 110 mA h cell during storage at 55°C from a fully charged state for 100 days. Discharges at the C and $C/5$ rates.

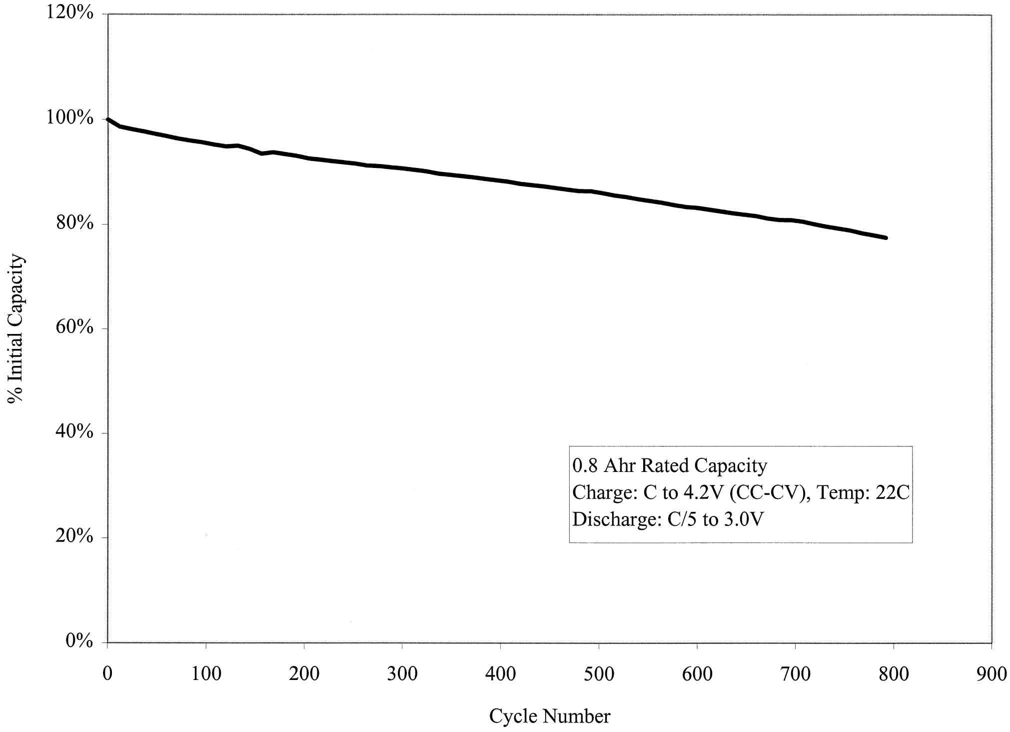

Fig. 8. Capacity decline to 80% of initial value during 800 cycles of CC–CV charge: $C/5$ discharge to 3.0 V.

by the year 2002 [4], doubling the number of batteries required over the next three years.

3.6. Safety characteristics

Various safety tests have been conducted on these batteries using the guidelines specified by UL1642 and the Japanese Storage Battery Association (JSBA). Tests included pressure, short-circuit, overcharge, over-discharge, nail penetration, crush, vibration, and exposures to high temperatures in ovens The most severe tests are overcharge/overdischarge, short circuit, and nail penetration. Solid polymer cells were overcharged at voltages as high

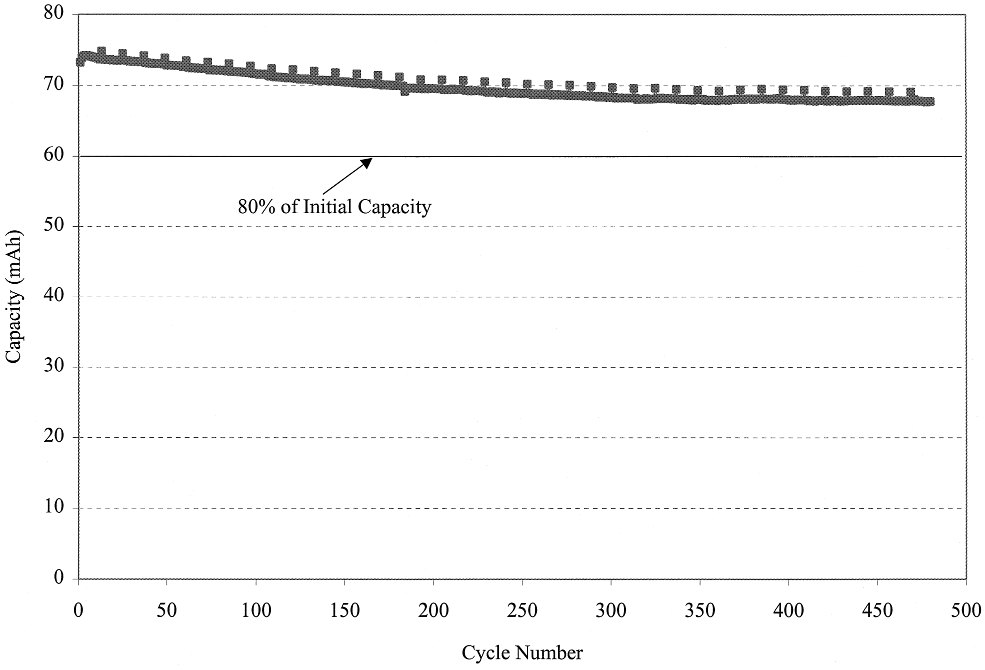

Fig. 9. Capacity decline at room temperature to 93% of initial value during 480 cycles of CC–CV charge: C rate discharge, with a $C/5$ charge: discharge every 11 cycles.

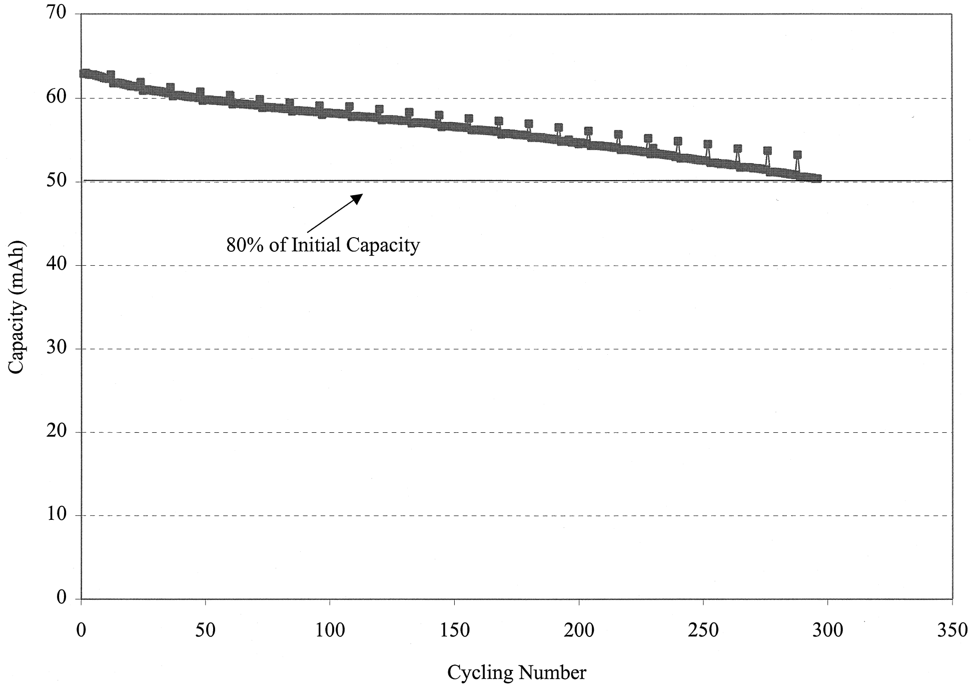

Fig. 10. Capacity decline at 45°C to about 80% of initial value during 300 cycles of CC–CV charge: *C* rate discharge, with a *C*/5 charge: discharge every 11 cycles.

as 20 V, at up to the 3*C* rate, and over-discharged at up to the 3*C* rate. The cells stopped functioning, but no flaming or any other hazard occurred. Fig. 12 shows the behaviour on short circuit of a 4 A h cell at room temperature.The cell current peaked at 3.2 A and had dropped to 500 mA after 3 min. A maximum surface temperature of 53°C was reached, also after 3 min. When a positive thermal coefficient (PTC) device was incorporated into those cells, no adverse effects were observed. The nail penetration was conducted by firing a nail, 3 mm in diameter, through the

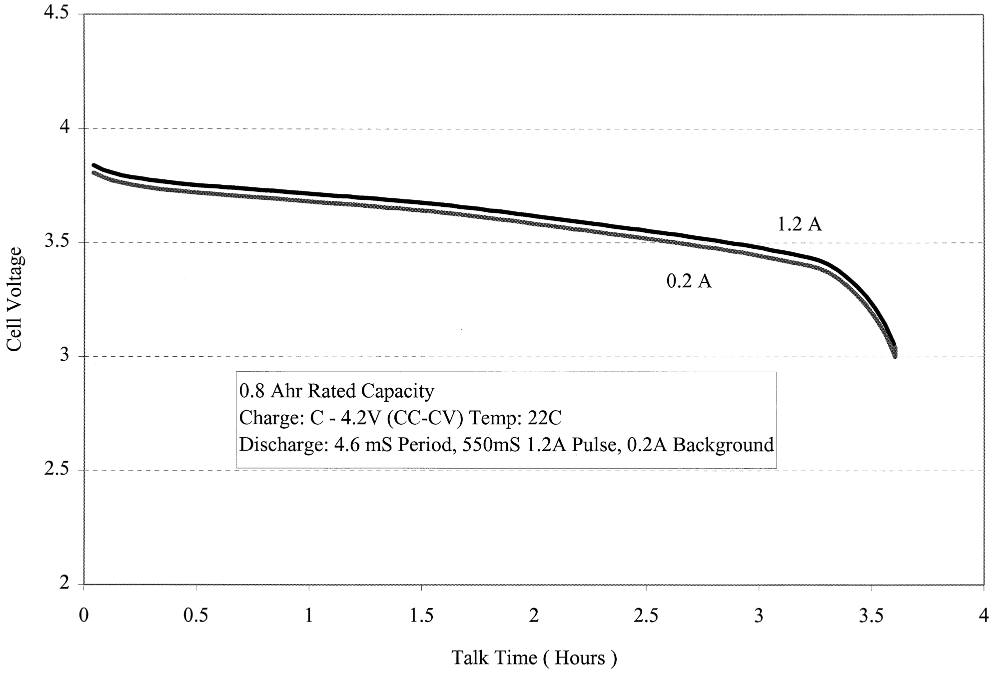

Fig. 11. Simulated GSM discharge characteristics of a 800 mA h rated capacity polymer lithium-ion cell.

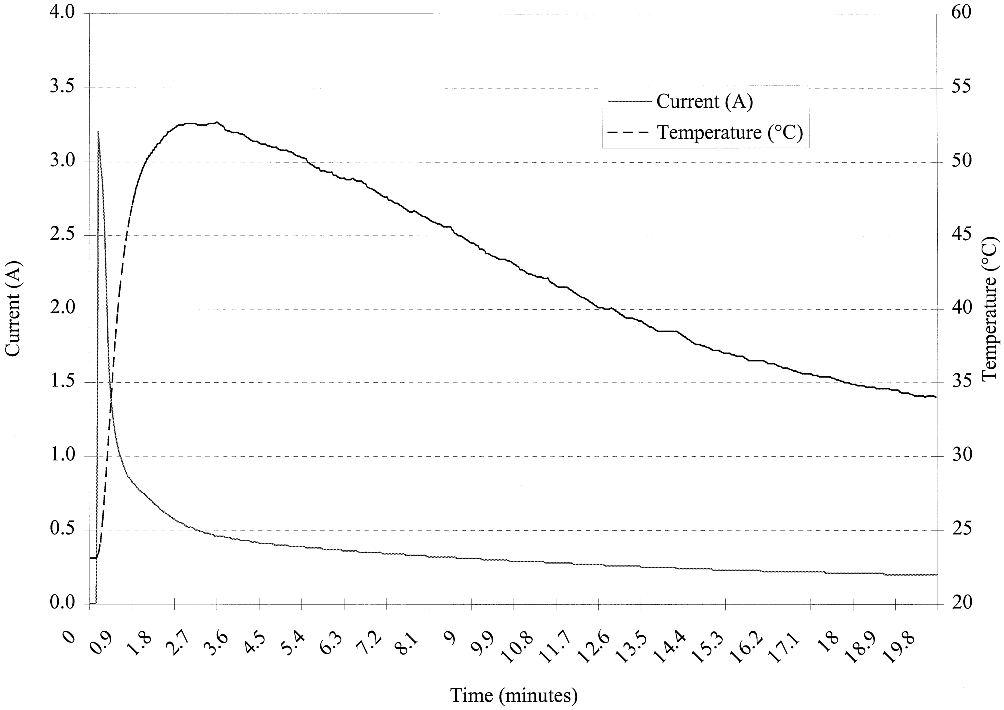

Fig. 12. Behaviour of a 4 A h cell when short-circuited at room temperature.

centre of a fully charged 4 A h cell. Fig. 13 the cell voltage and temperature after penetration. A maximum temperature of 73°C was reached after 10 min from penetration. After a brief dip in output voltage at the moment the nail penetrated the multiple plates of the cell stack, most cells showed a voltage recovery, followed by a continuous drop in potential. Interestingly, a number of cells showed a levelling off in voltage profile after the

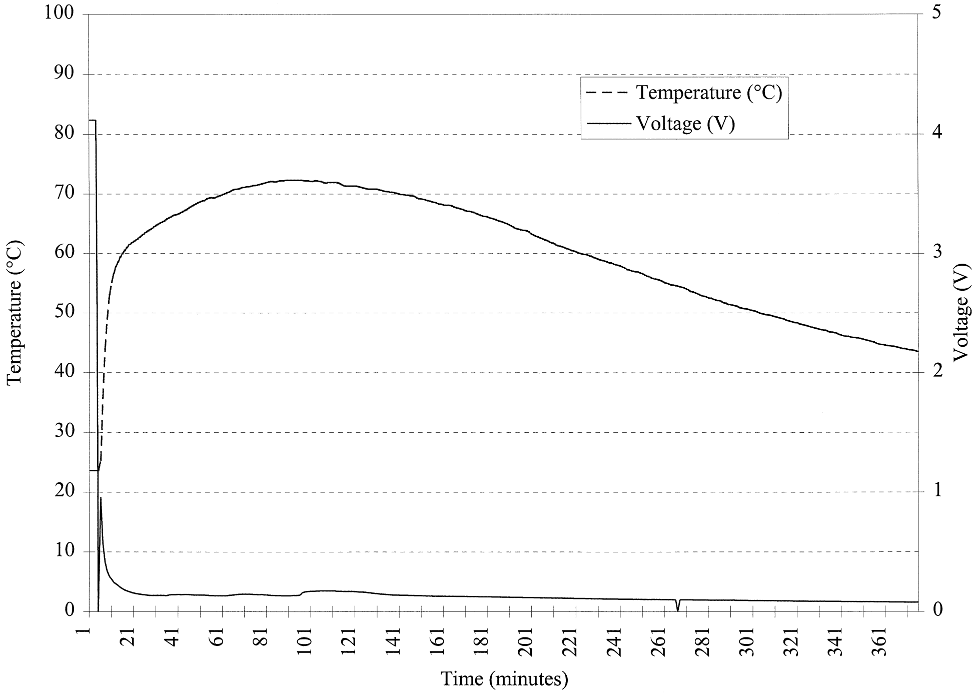

Fig. 13. Behaviour of a 4 A h cell after penetration by a nail.

voltage rebound. This phenomenon is probably due to a self-repairing mechanism, whereby the polymer material melts and forms an insulating layer around the nail. This superior safety feature distinguishes solid polymer rechargeable cells from their liquid lithium-ion counterpart.

3.7. Energy density

The energy density of lithium-ion batteries is influenced primarily by form factor, specific capacity of the cathode material, and packaging efficiency. The design flexibility of solid polymer rechargeable batteries is an advantage when tailoring products to various thicknesses and shapes as dictated by customers' specifications. By using manganese chemistry, Ultralife is able to achieve specific energies between 110 and 120 W h kg^{-1} at the *C* rate and energy densities ranging from 180 to 200 W h dm^{-3} for packaged cells, and 260 to 300 W h dm^{-3} for unpackaged cells. If a higher capacity cathode material, such as a nickel-based material were utilized, a specific energy increase of between 30–40% can be expected. Further optimizations of cell construction parameters will continue to yield higher energy densities.

4. Summary

Since supplying the world's first commercial solid polymer rechargeable batteries in 1997, Ultralife has made significant improvements in energy density, cycling rates, impedance control, long term cycling, and high temperature storage. These batteries show competitive characteristics to cylindrical and prismatic lithium-ion batteries that use liquid electrolytes, with significant advantages in energy density, safety, lightness and thin format. With continuous advancements through research and development, Ultralife is making its solid polymer rechargeable battery an ideal power source for the next generation of consumer electronics.

References

[1] Portable Design, 1998, p. 12.
[2] J.S. Xue, J.A. Read, E.A. Cuellar, M. Wittman, B. Coffrey, R.D. Wise, Proc. 5th Workshop for Battery Exp. Dev., Burlington, VM, 1997, p. 211.
[3] D. Guyomard, J.M. Tarascon, U.S. Patents 5,192,629 and 5,422,203.
[4] Communication from Dataquest, 1997.