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Medical batteries for external medical devices

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Abstract

A miniature 10 mAh, 3.75 V Li-ion battery (button cell) has been developed for external medical application. The miniature cells (0.2 cm^3) show excellent performance in terms of cycle life, energy and power. Life tests have exceeded 2700 cycles at 60% DOD and discharge rates of 1–3 mA. Full discharge tests (100% DOD) have shown very good performance with more than 90% of the capacity delivered at the *C*-rate. Pulse discharge tests indicated excellent pulse capabilities of up to 100 mA over low-level background currents of 10–100 μA. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

External medical devices have been widely used to treat a variety of medical disorder. For example, scoliosis has been treated by periodic muscle stimulation, pain may be alleviated through transdermal electrical nerve stimulation (TENS), and impaired hearing may be assisted by the common hearing aid devices (HAD). New fields of application are also emerging.

Transdermal application of drugs (TAD), for example, is a field of growing interest in medical therapy. Iontophoretic (transdermal) drug delivery has been reviewed in 1991 by Theiss et al. [1] who cite the definitive work of Leduc, 1908 [2]. However, the first reference to the principals of iontophoretic delivery of drugs is found in the work of Veratti (1747), in Italy, at the University of Bologna, over 250 years ago. Professor Veratti described the principle of forcing charged particles through the skin, by use of an electric current. Surprisingly, this was some 50 years before Volta first described an electrochemical cell (1800).

Implantable applications such as the total artificial heart (TAH) and left ventricular assist devices (LVAD), presently under development, also make use of an external battery pack as the main source of energy. These devices are implanted with a small 1 h battery, but most of the operation of the devices is powered from an external battery pack worn like a camera bag. The energy is transferred through the skin via electromagnetic induction.

It has been estimated that over 25 million persons in the United States suffer hearing loss and approximately 7 million use a hearing aid device (HAD). The majority of the hearing aids are powered by Zn/air cells. A typical HAD user will replace this battery every 5–15 days so approximately 150–250 million of these small button cells are consumed annually in the United States. Such a high replacement rate is the source of several problems that include the following:

1. Cost: 10–100 replacement batteries each year per hearing aid.
2. Environment: disposal of 150–250 million used batteries annually, in the United States alone.
3. Health hazard: the proliferation of millions of small batteries annually leads to cases of the accidental ingestion of cells or the insertion of cells into the ear or nose, especially by children and the elderly.

Each of these problems can be mitigated by a user friendly rechargeable hearing aid. One of the major reasons that rechargeable HAD are not widely used is the limited performance found in the commercially available rechargeable button cells of appropriate size. Although large sizes of Li-ion cells are under development for medical devices [3] no small button cells are currently available.

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We [4,5] developed a small 3.6 V Li-ion button cell to overcome the problems cited above, and to offer a high energy density, low impedance cell as an alternative to small NiCd and NiMH button cells.

2. Battery and testing hardware

The button cells developed for the HAD have a typical lithium-ion chemistry schematically depicted as

$$\text{Cu/graphite//1 M LiAsF}_6\text{ in EC}-\text{DMC//LiCoO}_2\text{/Al}$$

where copper (foil) and aluminum (foil) are the current collectors and the electrolyte is 1 M lithium hexafluoroarsenate in ethylene carbonate–dimethyl carbonate (50:50 by volume). The graphite and the lithium cobalt oxide are Li^+-ion intercalation compounds. The battery design including the container, the battery stack and other components, was developed to fulfill the power requirements of a HAD but is scalable to most of the sizes required for external medical devices. The approximate weight of the batteries was about 0.45 g (±0.02 g) and the cell external volume was 0.18 cm^3. The case and the lid were the two terminals of the battery. A complete description of the battery has been reported elsewhere [4,5].

Component preparation and handling as well as battery assembly were performed in a dry room (R.H. < 1%). The weight loss determination was performed by using a four-digit (±1 mg) electronic balance. The electrochemical tests were run with a fully computerized Arbin battery cycler.

To perform the safety tests, the batteries were placed in a stainless steel tube, 2 in. wide and 6 in. long, with one end sealed. The hot plate test was performed by placing the battery directly on a hot plate. Omega thermocouples connected to an A/D card on a Macintosh computer were used to measure the temperature of the batteries during the tests. The temperature-measurement system was calibrated in ice/water (0°C) and boiling water (100°C). The calibration gave accuracy on the temperature measurements of about +2°C with a fast response (a few seconds) upon temperature changes of 100°C.

3. Electrochemical tests

The initial charge or formation of a Li-ion battery is a critical point that influences the entire performance life of the lithium-ion, rechargeable battery. To investigate the effect of the first charge–discharge cycle on the batteries we selected three different current values (0.375, 0.75 and 1.5 mA) to charge the batteries in nominal times of 24, 12 and 6 h, respectively. After two full cycles, with voltage limits of 2.75 and 4.1 V, the cells were charged and discharged at the intermediate current value (0.75 mA) for eight more full cycles (same voltage cut-off). The results of the battery formation test are shown in Table 1 as the discharge capacity and the cycle efficiency (Q_{dis}/Q_{ch}) for the first and the 10th cycles. Also indicated in the table are the maximum, the minimum and the average capacities observed in a set of about 20 cells. Although some variance in the data points is observed in the initial cycle, no significant differences are seen at the 10th cycle. All batteries showed a low cycle efficiency at the first cycle (0.85–0.88) as a result of the irreversible formation of a passive layer at the anode–electrolyte interface. However, the cycle efficiency rose quickly with cycling, approaching unity (99%) by the 10th cycle. In addition, independent of the current selected in the formation cycle, all batteries delivered a similar capacity with an average of 8.6 mAh (Table 1). These results indicate that the batteries can be activated in the above-indicated range of current with no significant differences in performance.

Engineering prototype batteries were further tested to characterize the design and the electrochemical performance in terms of capacity, cycle life, and pulsed discharge performance.

A series of tests were performed to evaluate the effect of the charge voltage cut-off limit on the energy content. Two different test protocols were used. The first one was intended to show the effect of the charge voltage cut-off on the capacity delivered by the batteries. The batteries were charged with a constant current (CC, 3 mA) until the cell voltage reached a prefixed voltage upper limit value (V_{UL}), and then the cells were fully discharged. This

Table 1
Effect of the current on the formation of the Li-ion batteries developed for external medical device applications[a]

Formation charge and discharge current (mA)	Discharge capacity at first cycle (mAh)	Discharge/charge efficiency at first cycle	Discharge capcity at 10th cycle (mAh)[b]	Discharge/charge efficiency at 10th cycle
0.375	9.19	0.856	8.90	0.992
0.375	9.19	0.886	8.88	0.997
0.750	8.04	0.869	9.35	0.995
0.750	8.95	0.882	8.64	0.996
1.500	7.79	0.870	7.94	0.995
1.500	8.53	0.866	8.64	0.995

[a] The cells were formed at different currents (indicated) but from the third cycle all cells were charged and discharged with a 0.75 mA current. Voltage cut-off limits = 2.75–4.1 V.

[b] The maximum, minimum and average capacities delivered in a generic cycle of a battery in a set of about 20 batteries are reported as 9.40, 7.90 and 8.60, respectively.

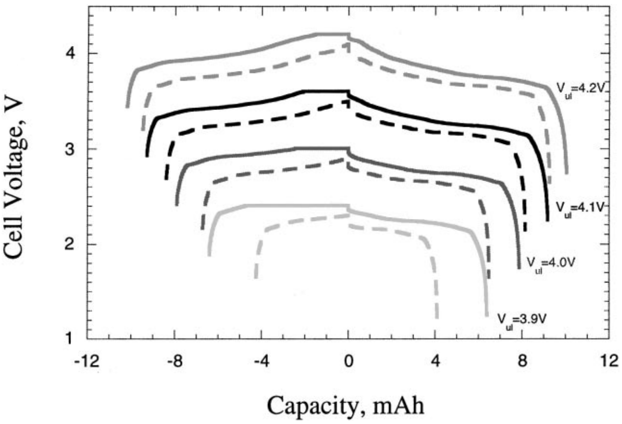

Fig. 1. Cell voltage vs. capacity behavior of the Li-ion batteries as a function of the charging protocol (CC/CO and CC/CV/CO) and the upper voltage cut-off (V_{UL}). For clarity, the curves are shifted down 0.5 V as V_{UL} decreases. Also an additional shift of 0.1 V has been applied to the CC/CO voltage curves (dashed lines).

test protocol is referred to as CC/CO (constant current/cut-off).

The second test protocol evaluated the effect of adding a final constant voltage step in the charging schedule. In this test, the voltage of the Li-ion batteries, after the constant current charge, was held at the V_{UL} until the current decreased down to 1/20 of the CC current. It will be referred to as CC/CV/CO (constant current/constant voltage/cut-off).

The results of these tests are illustrated in Fig. 1, where the cell voltage versus capacity behavior is reported as a function of the test protocol and the upper cut-off voltage limit, and are summarized in Table 2. The average capacity for a given charge protocol is expressed as a percentage of the maximum capacity obtained, i.e. the average capacity (10.35 mAh) delivered by a few batteries when tested with the schedule CC/CV/CO at 4.2 V. The results shown in the figure indicates two main features: the capacity delivered by the batteries depends on the V_{UL} independent of the schedule used, and the delivered capacity is always larger for the batteries tested with the CC/CV/CO schedule than for the ones tested with the CC/CO schedule. The difference in delivered capacity is at least 10%.

The cycle efficiency detected during the CC/CV/CO test protocol (Table 2) is very high (>99%), i.e. in the same value range obtained from constant current cycles between 2.75 and 4.1 V (see Table 1). This supports the conclusion that the cells exhibit a complete reversibility of the process over the largest voltage range.

Summarizing, the results indicate that the delivered capacity of the batteries can be significantly increased both by increasing the anodic cut-off limit and by holding the batteries at the upper voltage until the current decreases below a fixed fraction of the initial current. The Li-ion batteries can be charged with the CC/CV/CO up to a 4.2 V schedule without any damage.

The rate performance was evaluated by discharging the same battery in consecutive cycles at *C* and *C*/12 rates. The largest capacity (9.5 mAh) was obviously obtained with the lower discharge rate. However, even at *C*-rate, the battery delivered 8.7 mAh in 54 min. This corresponded to 86% of the maximum capacity at an average power of 36 mW. This result is very positive. It compares well with commercial, large-size, lithium-ion batteries [6].

Tests were performed to evaluate the performance of the Li-ion batteries during high power current pulses, similar to the duty cycle of a defibrillators. The test consisted of alternately loading and unloading the battery with a constant ohmic load. The battery, initially in open circuit conditions, was connected to the ohmic load (30 Ω) for 10 s and then it was left to relax on open circuit for 15 s. These latter two steps were repeated four times. The results of the test, illustrated in Fig. 2, clearly show the capability of the battery to sustain repeated current pulses of as high as 100 mA (3 V output over 30 Ω load) for 10 s. This current corresponds to a discharge rate of greater than 10*C*. The load voltage during such high current pulses decreased less than 1 V, relative to the open circuit potential.

The cycle life of the Li-ion batteries has been investigated on two batteries by discharging the batteries with a 1 mA current (*C*/9) until a capacity of 5 mAh (about 60% of the

Table 2
Average capacity and cycle efficiency of Li-ion batteries as a function of the charging protocol (CC/CO and CC/CV/CO) and the upper voltage cut-off (V_{UL})[a]

V_{UL} (V)	CC/CO	CC/CV/CO		
	Capacity (%)	Capacity (%)	Efficiency	
			Q_{dis}/Q_{ch}	Q_{VUL}/Q_{tot}
4.2	90	100	0.998	0.15
4.1	77	91	0.996	0.23
4.0	58	80	0.992	0.31
3.9	30	64	0.989	0.75

[a] The capacity is expressed as a percentage of the average maximum capacity (see text). The fraction of charge inserted in the CV step is also indicated.

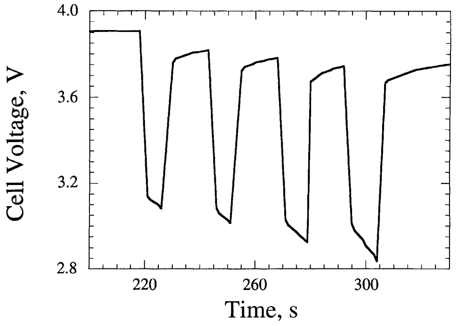

Fig. 2. Constant resistance pulse tests: 312 A cell voltage behavior during nominal 100 mA pulse discharge (10 s) on 30 Ω constant load. The 10 s pulses were alternated with open circuit rest periods of 15 s.

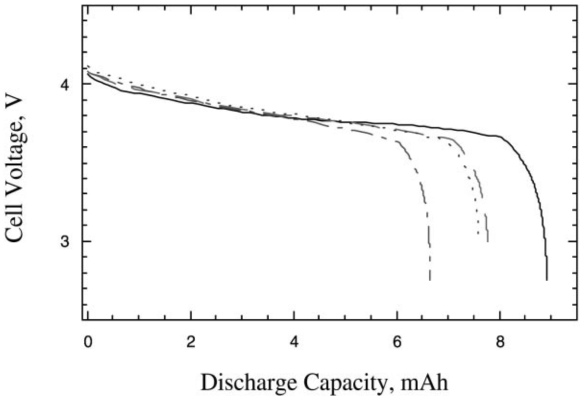

Fig. 3. Delivered capacity versus cell voltage behavior in the full charge–discharge cycles during a prolonged 5 mAh cycle life test, at the first (solid line), 1559th (dashed line), 2000th (dotted line) and 2700th (dashed-dotted line) cycles. Voltage cut-off limits: 2.75–4.0 V (first discharge); 2.75V–4.1 V (other discharges).

tested battery capacity) was delivered. Sporadically a full charge–discharge cycle was performed to evaluate the battery available capacity.

The battery, tested for about 3 years, has performed more than 2700 cycles always delivering the 5 mAh capacity required. Fig. 3 shows the cell voltage versus capacity behavior in different full charge–discharge cycles. After 1559 cycles, the battery was still able to deliver more than 87% of the initial capacity. In the 2000th and 2700th full capacity cycles, the battery was still able to deliver 85 and 75%, respectively, of the initial capacity. The battery is now completing the 3 years of cycling approaching 3000 cycles. This result gives a direct evidence that the cells are capable of powering a hearing aid (or any other device with similar energy and power requirements) for 7 years on a daily use cycle.

It is noteworthy that in the cycle life test the batteries were charged in 2 h or less (at 3 mA). Such a fast charge time is certainly significant for hearing aid applications. In only 10 min, it is possible to quick charge the battery for 2–3 h of normal operation.

4. Safety tests

The safety of lithium-ion batteries is a very important issue that becomes critical for medical applications. Two different sets of safety tests have been performed: in normal operative condition (electrolyte leakage by weight loss measurements) and for the most common battery misuses.

The integrity of the seal of the developed batteries was tested over an extended storage period (>1 year) at two different temperatures. Two batteries were stored on a shelf in air at 22°C (±2). Three more batteries were stored in an oven (in air) at 60°C (±2), to increase the vapor pressure of the solvent (bp of EC = 248°C; bp of DMC = 89−91°C), well above the normal operating temperature range of a hearing aid. The batteries were weighed during this storage period to detect any weight change. In addition, the batteries were visually checked with the help of an optical microscope. No mechanical damage or deformation of the sealing region was detected.

Table 3
Weight loss of batteries versus storage time at 22 and 60°C[a]

Storage (days)	22°C		60°C		
	1	2	3	4	5
1	0.0	0.0	0.0	0.0	0
2	0.0	0.2	0.0	0.2	0.2
5	0.2	0.2	0.4	0.2	0.2
10	0.2	0.4	0.7	0.6	0.4
20	0.0	0.2	1.1	0.6	0.9
50	0.0	0.2	2.4	1.3	1.5
100	0.2	0.4	4.0	2.8	3.0
350	0.4	0.7		8.2	8.2

[a] The weight loss is reported as the percentage of the initial battery weight.

The results of the weight measurements of the five batteries are reported in Table 3. The weight loss is reported as the percentage of the initial battery weight versus the storage time. The batteries stored at 22°C did not loose any significant weight over 350 days of storage. The three batteries stored at 60°C did loose from 3 to 4% of the initial weight within 100 days of storage and slightly over 8% after 350 days. By assuming that it is due to the leakage of the electrolyte solvents (the only volatile components in the batteries), it is possible to calculate that about 60% of the electrolyte is lost over the 350 days storage at 60°C.

The results indicate that the sealing system of the battery is appropriate for storage and use at temperatures around or slightly above ambient temperature, i.e. the operating temperature of external medical devices. In addition, the battery design of the cell appears to possess intrinsic safety features. The batteries stored at 60°C were able to self-release internal overpressure without any damage or disruption of the external structure. This aspect was further investigated in the most common battery misuse tests summarized in Table 4. Although the tests performed were only a fraction of those required to verify the safety of a lithium-ion battery for commercial purposes, the results of these preliminary safety tests indicate that the battery design is also intrinsically safe with respect to the most common types of abuse. None of the batteries under test ignited or exploded with fragments. Rapid ejection of the case and the lid was observed only during the hot plate test. Even in this case no fire was seen. The short circuit test did not cause any damage to the case or the gasket. The battery voltage recovered after the test and no weight loss was detected. In all the other tests, the gas evolving from the electrolyte decomposition was released through the sealing gasket without any major deformation of the battery case. In a few cases, the lid assumed a dome-like shape and this facilitated the release of the internal pressure.

Table 4
Safety evaluation tests performed on developed Li-ion batteries

Test type	Action	Observations	
		During the test	After the test
Thermal	Hot plate (150°C)	Temperature up to 70°C in 5 s	Battery disassembled after 110 s at 130°C
Electrical	Overcharge		
	100 mA	Temperature up to 63°C, cell voltage up to 5 V	Battery disassembled, no voltage, infinite dc resistance
	10 V	Temperature up to 85°C, current up to 0.05 A	No battery disassembling, weight loss: 37 mg, cell voltage: 0.2 V, infinite dc resistance
Electrical	Overdischarge		
	−100 mA	Temperature up to 51°C, cell voltage down to −7 V	Battery disassembled, no voltage, weight loss: 5 mg, 300 Ω dc resistance
	−10 V	Temperature up to 80°C, current up to 1.5 A	No battery disassembling, no voltage, weight loss: 14 mg, 3000 Ω dc resistance
Electrical	Short circuit	Temperature up to 38°C, current up to 0.85 A	No battery disassembling, cell voltage: 2.5 V, no weight loss

5. Conclusions

The new design, lithium-ion batteries have shown very good performance in terms of energy density and specific energy. With an average discharge voltage of 3.6 V and a capacity of about 10 mAh, the Li-ion batteries give an average energy density of 200 Wh/l and a specific energy of 75 Wh/kg. These values compare extremely well with large-size commercial, lithium-ion batteries (250 Wh/l and 110 Wh/kg) [6–8]. These small Li-ion button cells developed offer about 80% of the energy density and 70% of the specific energy of large-size, commercial lithium-ion batteries. This performance is considered exceptional taking into account the large fraction of the cell weight and volume that are taken by the case and hardware. The batteries also exhibited very good performance during pulse-discharge tests. The batteries satisfied all of the requirements for powering HAD including the battery life under operating conditions.

The overall conclusion from the tests performed on the Li-ion cells is that they meet the requirements of a rechargeable hearing aid. The Li-ion battery technology is now available to enable the realization of greatly improved rechargeable external medical devices that would combine higher safety, ease of use, cost savings and improved performance.

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