

Lithium-ion batteries for hearing aid applications: I. Design and performance

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Abstract

Rechargeable batteries have been designed for powering hearing aid devices (HAD). The cells, based on the lithium-ion chemistry, were designed in a size that is compatible with the existing HAD. The 10 mA h batteries were tested to characterize the design and the electrochemical performance from the point of view of a typical HAD application. Results are presented for constant-current tests, first-cycle conditions, charge voltage cut-off, rate performance, and cycle life. The pulse capabilities and the preliminary safety tests of the batteries will be presented in a following report. The results of the lithium-ion HAD cells developed in this project are compared with other battery chemistries: lithium-alloy and nickel–metal hydride secondary batteries and Zn–air primary batteries. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Lithium-ion; Hearing aid device; Nickel–metal hydride

1. Introduction

Hearing aids play an important role in the treatment of hearing disorders. 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 these miniature sound amplifiers are powered by Zn–air cells. A typical HAD user will replace this battery every 5–15 days, thus, approximately 150–250 million of these small button cells are consumed annually in the United States.

Certain problems associated with the proliferation of such small cells have been reported, including the ingestion of cells and the insertion of cells into the ear canal or the nasal passage [1–3]. Subsequent electrolysis of body fluids can exacerbate the inflammation of the adjoining tissue, causing great discomfort.

A further problem noted particularly by that segment of the elderly population who rely on a HAD for hearing is the problem of restricted manual dexterity and poor vision [4]. This relates to the replacement of a depleted battery. The replacement of the very small hearing aid battery requires some skill in opening the battery compartment latch door on the HAD, removing the depleted cell, and then inserting the fresh cell. Manufacturers have addressed the problems of maintaining proper cell polarity by the design of the compartment and the battery case. However, for some of the hearing impaired, it remains difficult to replace the battery.

To summarize, problems that are related to the use of primary batteries in hearing aids include the following:

1. *Cost.* The typical user must purchase 25–50 replacement batteries each year.
2. *Environment.* 150–250 million used batteries must be disposed of each year, 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 by the elderly.
4. *Unexpected loss of hearing.* During the use of HAD, when the battery becomes depleted, there is loss of hearing and the cell must be replaced.

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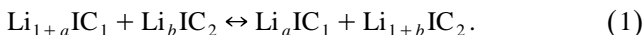
5. *Battery replacement.* Individuals with limited dexterity or vision experience difficulty in replacing the cell in the battery compartment of the hearing aid.

Each of these problems can be mitigated by a user-friendly, reliable, and rechargeable hearing aid. One of the major reasons why rechargeable hearing aids are not widely used is the limited performance found in the present commercially available rechargeable batteries or coin cells of appropriate size. Rechargeable hearing aids with NiCd cells have been available for many years but are not widely used. Larger sizes of Li-ion cells are under development for medical devices [5], but no small button cells are available.

We have developed a small, 3.6 V Li-ion button cell to overcome the problems cited above for the primary battery-powered HAD, and also to offer a high-energy density, low impedance cell as an alternative to small NiCd and NiMH button cells. The present paper describes the characteristics of this cell.

The high level of interest in lithium batteries today is a direct result of the need for lightweight portable power sources and the unique properties of lithium. Lithium is the lightest of the alkali metals, and as a result, it can offer a higher density of energy storage than any other metallic anode material. For this reason, lithium batteries represent the ultimate in advanced, high performance batteries for the growing market in portable consumer electronic products, communications, and other cordless devices, at least in the context of the present battery technology.

Historically, in rechargeable lithium batteries, the metallic lithium was found to cause major safety problems, as well as to shorten the operating life of the battery. The lithium-ion approach was developed to permit a lithium-based battery that contains no lithium metal. This has proven to be an excellent strategy for the solution of the cyclability and, at least partly, the safety problems. Li-ion batteries are composed of two highly reversible intercalation electrodes sandwiched around the electrolyte. Ionic lithium is initially present in one of the two electrodes, and most commonly, in the cathode (positive electrode). It is transferred to the anode during the first charge and then shuttled back and forth between the two electrodes during charge and discharge. No metallic lithium is plated in the cell. This concept was proposed by Scrosati in the mid 1980s [6]. The chemistry of a lithium-ion battery involves the movement of lithium ions from an intercalation compound (IC₁) to a second one (IC₂) as shown generically below:

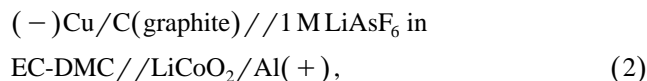


Since the electrochemical potential of the couple $\text{Li}_y\text{IC}/\text{Li}_x\text{IC}$ differs depending on the nature of the intercalation compound, such a system shows an OCV value that will depend on the composition of lithium in both intercalation compounds.

Commercial batteries based on the Li-ion concept have been in production by Sony since 1990 [7]. These cylindrical cells have a specific energy of 110 W h/kg and an energy density of 250 W h/l. Their cycle life has been demonstrated out to beyond several hundred full, 100% depth of discharge (DOD) cycles. Today, several multinational companies produce lithium-ion batteries for commercial purposes [8]. All systems are based on carbonaceous materials (graphite or amorphous carbons) as the negative electrode with lithiated cobalt, nickel or Co–Ni mixed oxides as the positive electrode. One or more layers of plastic film, made of micro-porous polyethylene and/or polypropylene, which are impregnated with an electrolytic solution, separate the electrodes.

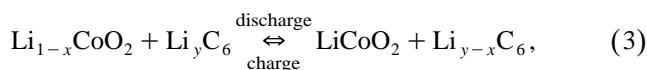
Johnson and White [9] published a complete characterization of commercially available (18650 size) lithium-ion batteries. The comparison examined five batteries from different producers (Sony, Sanyo Electric, Matsushita Electric Industrial, Moli Energy, and A&T Battery). All cells had a jellyroll design with the electrodes and the separator (two layers) tightly wrapped and held together with a tape. Different mixtures of organic solvents (diethyl-, dimethyl, ethylene-, methyl, ethyl-, and propylene-carbonates) were used in the electrolytic solutions.

The HAD batteries developed in this work have a typical lithium-ion chemistry schematically depicted as:



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 the two intercalation compounds.

The electrochemical process that gives energy is:



where $0 \leq x \leq 0.55$, $0 \leq y \leq 1$ and $y \geq x$. Since the electrochemical potential of lithium is larger in the carbon electrode than in the lithium-depleted LiCoO_2 electrode, the reaction proceeds spontaneously toward the right side if a flow of electrons is allowed through an external circuit. In this way, the battery supplies energy (discharge). The difference of the electrochemical potential of lithium in the two electrodes gives an average battery voltage of 3.75 V. If the reaction is forced in the opposite direction, e.g., by supplying energy from the external circuit, the battery is charged. The two processes can be reversibly repeated for several hundred cycles [7].

The comparison of the battery structure (Eq. 2) and the electrochemical process (Eq. 3) shows the uniqueness of this system; initially, the lithium ions reside in the cathode (positive electrode), i.e., the battery is built in the discharged state. The battery as assembled even shows a negative voltage of approximately -0.2 V. This is a clear

advantage of the lithium-ion chemistry because the batteries are assembled in the less reactive state. The batteries, as well as most of the components, do not require any particular environment for handling and assembling in dry conditions, before the electrolyte-loading step. On the other hand, lithium-ion batteries need to be charged prior to any use. The first charge of the battery is a critical step that affects its performance for the whole life of the battery [10]. It involves the formation of a passivation layer at the porous anode–electrolyte interface. This is important because from a thermodynamic viewpoint, lithiated carbonaceous materials are as reactive as metallic lithium. Fully lithiated graphite and amorphous carbon electrodes are within a few millivolts of metallic lithium. The passivation layer that is formed at the anode–electrolyte interface must be uniform and strongly adherent to the anode particles to prevent further reaction of the electrolyte. The first charge/discharge cycle, the formation cycle, has been investigated as part of the present work and the optimum conditions are reported.

Beyond the formation cycle, the batteries were tested to characterize the design and the electrochemical performance as required for the hearing aid application. A typical cycle for a HAD battery consists of a low power (nominal 1 mW) discharge for 16 h (daylight period). Power pulses as high as 10 mW and as long as 1 s, superposed on the low power discharge, are also required. The total capacity required for a day of operation is about 18 mW h. The discharge is followed by an overnight charge from 1 to 6 h at the respective power level from 18 to 3 mW. The use of a battery chemistry that provides an average output voltage of 3.75 V gives the advantage of reducing the current and the capacity by a factor of 3 when compared with the commercially available 1.25-V batteries.

The second important requirement of a rechargeable HAD battery is the cycle life. The target is fixed by the average life of a typical HAD, which is about 4 years. This establishes the battery cycle life goal to be about 1500 cycles.

Engineering prototype batteries were used for the tests. For comparison purposes, commercially available cells based on the lithium-alloy anode/vanadium oxide and Zn–air chemistries, and also, a small developmental nickel/metal hydride (Ni–MH) cell were tested. In this paper, we report the results of the investigations on the capacity, the rate performance, and the cycle life of the new lithium-ion batteries we have developed for HAD applications. Pulsed discharge performance and preliminary safety characterization will be reported later.

2. Experimental

The battery design, including the container, the battery stack and other components, was developed to fulfill the

requirements of a HAD battery. Fig. 1 illustrates the structure of the HAD battery developed in this work. The external shape of the HAD battery developed in this work is a typical squat, cylindrical cell, usually called a button cell. The developmental cell (referred to as 312A) has a diameter of 7.95 mm and a height of 3.6 mm. These dimensions are very close to those of the standard size 312 hearing aid batteries. The battery consists of a metallic case, a metallic lid, a gasket, an insulating layer and the electrochemically active elements, which are described in detail elsewhere [11]. The case and the lid of the battery were formed from 0.15-mm thick, stainless steel 416 foil. The gasket was made by machining a polypropylene rod and the internal insulator was an adhesive polyester tape (3M). The active materials were LiCoO_2 for the cathode and graphite for the anode. Current collectors were Al and Cu, respectively. The electrodes were separated by two layers of microporous polypropylene (Celgard Separator type 2500).

Once formed, the electrode assemblies were inserted into the cases which were then filled with about 60 mg of electrolyte (1 M LiAsF_6 in EC-DMC 50:50). The flooded cases containing the battery stack were subjected to reduced/normal pressure cycles in order to facilitate the penetration of the electrolyte into the pores of the separator and the electrodes. As a final step, the gaskets and the lids were positioned on the cases and the cells were sealed by using a custom cell crimper.

The approximate weight of the 312A 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. The case, electrically connected to the cathode by the cathodic tab, was the positive pole of the battery, while the lid, electrically connected to the anode by the anodic tab, was the negative pole.

Although not always necessary, the component preparation and handling, as well as the 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.

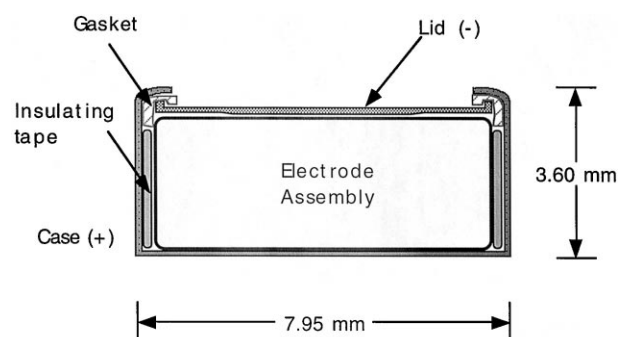


Fig. 1. Schematic illustration of a cross-sectional view of the 312 HAD battery.

3. Results and discussion

3.1. Weight loss determination

The integrity of the seal of the 312A 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 ($\pm 2^\circ\text{C}$). Three more batteries were stored in an oven (in air) at 60°C ($\pm 2^\circ\text{C}$), i.e., to increase the vapor pressure of the solvent (B.P. of EC = 248°C ; B.P. of DMC = $89\text{--}91^\circ\text{C}$) 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.

The results of the weight measurements of the five 312A batteries are reported in Fig. 2. The figure reports the weight loss as the percentage of the initial battery weight vs. the storage time. As can be easily seen from the figure, the batteries stored at 22°C (#21 and #22) did not lose any significant weight over 350 days of storage. The three batteries stored at 60°C did lose from 3% to 4% of the initial weight within 100 days of storage. After 350 days, the weight loss was slightly over 8% of the initial battery weight. 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 were lost over the 350 days storage at 60°C .

The results indicate that the sealing system of the battery is appropriate for the storage and use at temperatures around or slightly above ambient temperature, i.e., the operating temperature of HADs. In addition, this 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 important issue is further addressed elsewhere [12].

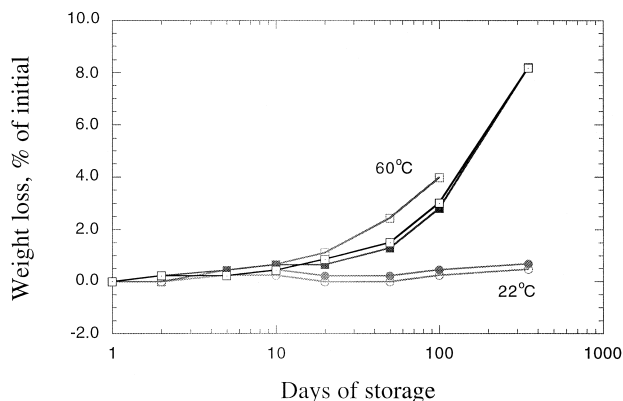


Fig. 2. Weight loss of 312A batteries vs. storage time at 22°C (circles) and 60°C (squares). The weight loss is reported as the percentage of the initial battery weight.

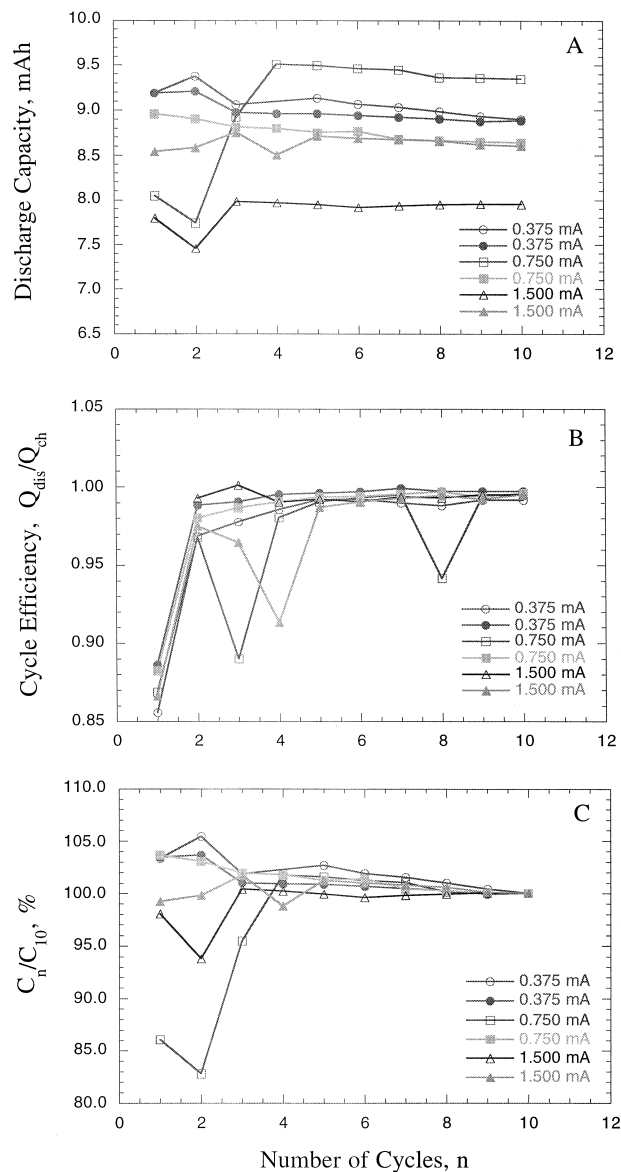


Fig. 3. Effect of the current on the formation of the 312A batteries. The cells were formed at different currents (see legend). From the third cycle, all cells were charged and discharged with a 0.75 mA current. Voltage cut-off limits: 2.75–4.1 V.

3.2. Battery formation

As indicated before, lithium-ion batteries are assembled in the discharged state. In the first charge, some irreversible processes take place. Among these, the formation of a passivation layer around the graphite particles, due to the reduction of the electrolyte, is the most important. The formation of a continuous and compact passive film is a very important requirement for a good battery life because it prevents the occurrence of this irreversible reaction in the subsequent charge/discharge cycles, ensuring good cycle life and high charge/discharge efficiency.

The initial charge or activation of the battery is then a critical point that influences the entire performance life of

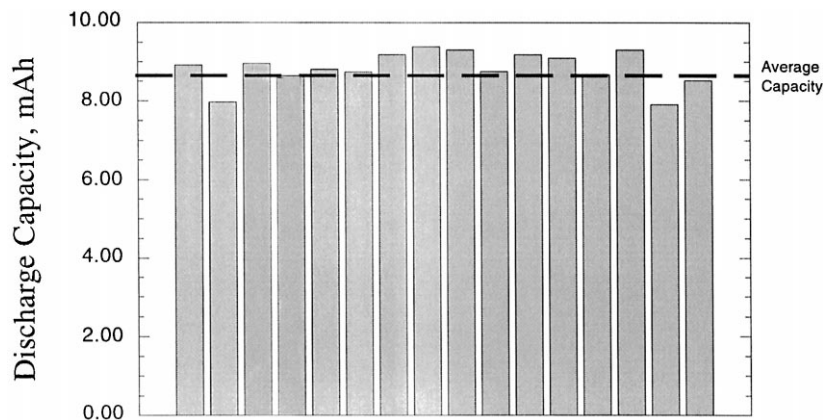


Fig. 4. Capacity delivered in a generic cycle by several 312A batteries. The cells were charged and discharged at $C/12$ rate ($I = 0.75$ mA). Voltage cut-off limits: 2.75–4.1 V.

the lithium-ion, rechargeable battery. To investigate the effect of the first charge–discharge cycle on the 312A batteries, we selected three different current values (0.375, 0.75 and 1.5 mA) to approximately charge the batteries in 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).

Panels A and B in Fig. 3 show the discharge capacity and the cycle efficiency ($Q_{\text{discharge}}/Q_{\text{charge}}$) of the batteries under test. In panel C, the discharge capacity in each cycle is given as the fraction of the capacity delivered by the same battery in the final cycle of the test. This permits a comparison of the behavior of different cells that may have different capacities, due for example, to the differences in the electrode area.

Although some variance in the data points is observed in the initial cycles, no significant differences are seen in the curves of Fig. 3. All batteries showed a low cycle efficiency at the first cycle (0.85–0.88) as a result of the

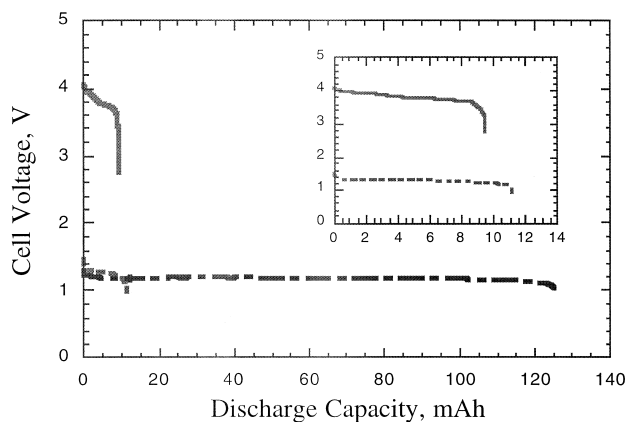


Fig. 5. Delivered capacity vs. cell voltage behavior of 312-sized batteries having different chemistries: Li-ion (solid line), Ni–MH (dotted line) and Zn–air (dashed line). The inset is a magnification of the rechargeable batteries (Li-ion and Ni–MH). The cells were discharged with a constant power of about 3 mW.

irreversible formation of a passivation layer at the anode–electrolyte interface. The cycle efficiency rose quickly on cycling. At the second cycle, it was as high as 97% and it passed 99% at the tenth cycle. These results indicate that the 312A batteries can be activated in the above-indicated range of current with no significant differences in performance.

Fig. 4 shows the discharge capacity delivered by several batteries during a typical cycle. Independent of the current selected in the formation cycle, all batteries delivered a similar capacity with an average of 8.6 mA h. With an average discharge voltage of 3.6 V (see Fig. 5), the 312A batteries give an average energy density of 172 W h/l and a specific energy of 65 W h/kg. These values compare extremely well with large-sized commercial lithium-ion batteries (110 W h/kg and 250 W h/l) [6–8]. The 312-sized batteries developed in the present work offer about 60% of the energy density and specific energy of large-sized 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.

Fig. 5 shows the cell voltage vs. the delivered capacity for three different battery chemistries contained in the 312-sized case, namely, the Li-ion developed in this work, and Ni–MH and Zn–air batteries. The batteries were discharged at a constant power of about 3 mW. The

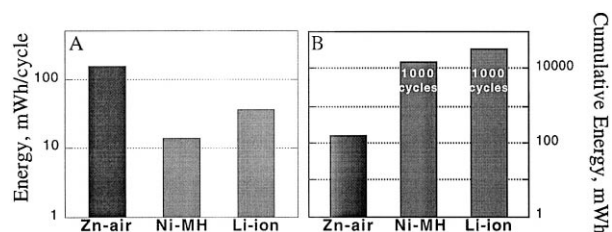


Fig. 6. Comparison of the single cycle energy (panel A) and cumulative energy (panel B) of 312-sized batteries having different chemistries: Li-ion (present work), Ni–MH and Zn–air.

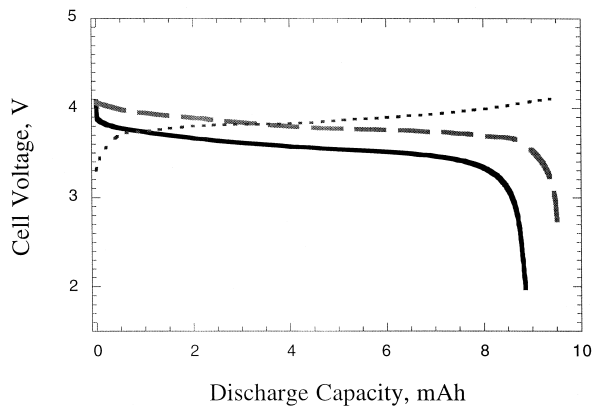


Fig. 7. Delivered capacity vs. cell voltage behavior of a 312-sized battery discharged at two different rates: C/12 (dashed line) and C (solid line). A typical charge cycle at C/12 rate is also shown (dotted line). Voltage cut-off limits: 2.75–4.1 V.

delivered capacities were 9, 11 and 125 mA h, respectively. The 312A battery showed the smallest capacity but it is important to note that the output voltage of the 312A Li-ion battery is three times larger than the other two, and that Zn–air batteries are not rechargeable. Introducing these considerations, it becomes evident that the three battery chemistries have to be compared in terms of stored energy either per single discharge or accumulation over the entire cycle life. These comparisons are shown in Fig. 6. It is evident from these figures that the 312A Li-ion batteries store more energy per cycle than the other rechargeable battery (Ni–MH) and, in terms of the entire battery life, from 220 to almost 350 times the energy stored in a Zn–air primary battery.

3.3. Discharge rate

This test was performed to establish the rate capability of the 312A batteries. Two discharge currents were selected, 10 and 0.75 mA, corresponding to the C and the C/12 rates, respectively. The tests were performed on the same 312A battery in two consecutive cycles. Prior to each discharge, the battery was charged up to 4.1 V with a 0.75 mA current.

The test results are illustrated in Fig. 7, where the cell voltage is shown as a function of discharge capacity for the two rates. The cell voltage behavior during a typical charge is also illustrated (dotted line). The maximum capacity (9.5 mA h) was obviously obtained with the lower discharge rate (dashed line), but the results clearly indicate the very good rate capability of the battery. With the highest current (solid line) equivalent to the C rate, the battery delivered 8.7 mA h in 54 min. This corresponds to 92% of the maximum capacity at an average power of 36 mW. This result is very positive. First, it compares well with commercial large-sized, lithium-ion batteries [8]. Second, and most important, it clearly indicates that the battery developed in the present work can fulfill the power requirement for HAD batteries. In fact, the battery is not only able to supply the required power for a HAD (10 mW) but is able to deliver more than 90% of the full capacity at four times greater average power level.

3.4. Charge cut-off optimization

A series of tests were performed on the 312A batteries to evaluate the effect of the charge voltage cut-off limit on the delivered capacity. Two different test schedules (see Tables 1 and 2) were used. The first test schedule was intended to show the effect of the charge voltage cut-off on the capacity delivered by the 312A 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}), then the cells were fully discharged. To ensure reliable measurements, three charge/discharge cycles were repeated for each V_{UL} selected. This test schedule is illustrated in Table 1. It will be referred to as constant current/cut-off (CC/CO).

The second test schedule given in Table 2 is devoted to the evaluation of the effect of the addition of a further constant voltage step in the charging schedule. In this test schedule, the voltage of the 312A batteries, after the CC charge, is held at the V_{UL} until the current decreases down to 1/20 the CC current. It will be referred to as constant current/constant voltage/cut-off (CC/CV/CO).

Table 1
Constant current charge test schedule

Step	Current (mA)	C rate (nominal)	Iteration	Voltage cut-off (V)
1. Charge	3.0	C/3		3.90
2. Discharge	1.0	C/9	3 cycles (step 1)	2.75
3. Charge	3.0	C/3		4.00
4. Discharge	1.0	C/9	3 cycles (step 3)	2.75
5. Charge	3.0	C/3		4.10
6. Discharge	1.0	C/9	3 cycles (step 5)	2.75
7. Charge	3.0	C/3		4.20
8. Discharge	1.0	C/9	3 cycles (step 7)	2.75

Table 2
CC/CV charge test schedule

Step	Current or voltage	C rate (nominal)	Iteration	Cut-off limit
1. Charge	3.0 mA	C/3		3.90
2. Charge	3.90 V			0.15 mA
3. Discharge	1.0 mA	C/9	3 cycles (step 1)	2.75
4. Charge	3.0 mA	C/3		4.00
5. Charge	4.00 V			0.15 mA
6. Discharge	1.0 mA	C/9	3 cycles (step 4)	2.75
7. Charge	3.0 mA	C/3		4.10
8. Charge	4.10 V			0.15 mA
9. Discharge	1.0 mA	C/9	3 cycles (step 7)	2.75
10. Charge	3.0 mA	C/3		4.20
11. Charge	4.20 V			0.15 mA
12. Discharge	1.0 mA	C/9	3 cycles (step 10)	2.75

The results of the tests on four 312A batteries are illustrated in Figs. 8 and 9. The first figure refers to the 312A batteries tested with the CC/CO test schedule. Fig. 9 illustrates the results for the batteries tested with the CC/CV/CO test schedule. The height of the columns in the figures gives the discharge capacity delivered by the batteries. Above the columns is reported, the V_{UL} to which the 312A cells were recharged. Also indicated are the charge steps (CC or CC/CV). The numbers overprinted on the columns indicate the fraction of the total capacity delivered by the batteries in the second and third cycles of the indicated test schedule. The calculations were done in a somewhat complicated way. First, a capacity of 100% was defined as the average capacity (10.35 mA h) delivered by the two batteries when tested with the schedule CC/CV/CO @ 4.2 V. The average amount of the capacity supplied to these two batteries in the CC step of the CC/CV/CO @ 4.2 V schedule was 9.3 mA h, i.e., approximately 90% of the full capacity (solid part of the columns in Fig. 9). The latter value (90%) was then taken as reference for the capacity of the two batteries tested with the CC/CO schedule. In other words, the capacity delivered by any battery after a CC charge up to 4.2 V was assumed to be 90% of the maximum capacity of the battery. Although the calculation appears to be complicated, it simplifies the interpretation of the results, allowing the comparison of different cells that may have different capacities, due for example, to the differences in the electrode area.

An accurate observation of the results shown in Figs. 8 and 9 indicates three main features cited below.

(i) The capacity delivered by the batteries depends on the V_{UL} independent of the schedule used.

(ii) The fraction of the full capacity delivered by the batteries upon CC/CO up to 3.9 or 4.0 V tests can change substantially (see Fig. 8). This result was indeed expected considering the previously observed cell voltage vs. capacity behavior of these batteries during charge (see Fig. 5). The slope of the voltage is in fact very small in the 3.8–4.0 V voltage range. As a result, a small difference in

the cut-off voltage (V_{UL}) can correspond to a large difference in the charge (and discharge) capacity. On the other hand, if the voltage is held, as in the CC/CV/CO test schedule, this kinetic effect disappears, and a good reproducibility of the capacity delivered by the battery can be attained.

(iii) The delivered capacity is always larger for the two batteries tested with the CC/CV/CO schedule than for the two tested with the CC/CO schedule. The difference in delivered capacity was at least 10%.

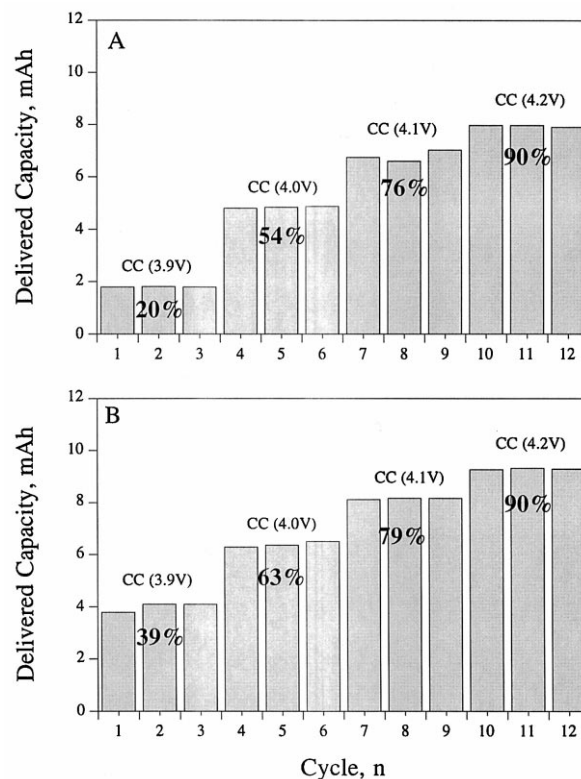


Fig. 8. Delivered capacity as a function of charge voltage cut-off for the two 312A batteries tested with the schedule CC/CO (see Table 2). See text for further details.

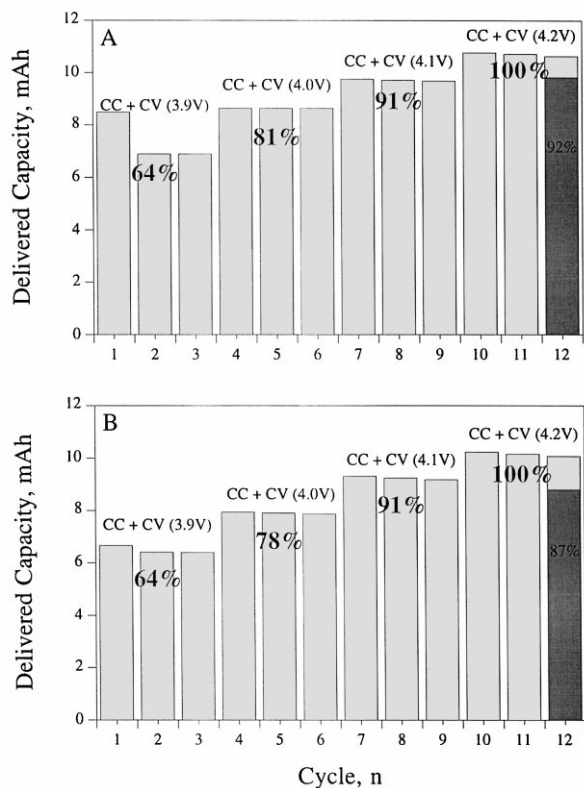


Fig. 9. Delivered capacity as a function of charge voltage cut-off for two 312A batteries tested with the schedule CC/CV/CO (see Table 2). See text for further details.

The cycle efficiency values of the batteries tested with the CC/CV/CO are reported in Table 3. The cycle efficiency gives important information regarding the stability of the battery during the charge/discharge cycle, i.e., it indicates if there is any irreversible process involving the electrolyte or the electrodes. The values reported in Table 2 are very high ($> 99\%$), i.e., in the same value range obtained from the CC cycles in the 2.75–4.1 V (see Fig. 3B and text). This supports the conclusion that the cells exhibit a complete reversibility of the process over the larger 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 312A button cells can be charged with the CC/CV/CO up to a

Table 3
Cycle efficiency ($Q_{\text{discharge}}/Q_{\text{charge}}$) of the 312A batteries

V_{UL}	HARI46 (CC/CV/CO) (%)	HARI48 (CC/CV/CO) (%)
3.90	99.98	99.80
4.00	99.72	99.58
4.10	99.50	99.20
4.20	99.15	98.91

4.2 V schedule without any damage, but with an enhancement of more than 20% of the delivered capacity.

3.5. Load curve tests

Load curve tests were made to verify the maximum load current that the 312A and the reference batteries could sustain. The tests were run by applying a current sweep to the battery until the voltage dropped below a certain value. The current was swept quickly (50 mA/s) in order to perform the whole test without an appreciable change of the battery state of charge. The tests were performed on fully charged (0% DOD) and partially discharged (50% DOD) batteries.

Panels A and B in Fig. 10 show the cell voltage behavior during the current sweep for 312A batteries at the two different states of charge. For comparison, the results obtained for the VL2016 Li-alloy coin cell and the Ni–MH and Zn–air button cells are also reported. The end voltage was fixed at 2.5 V for the 312A Li-ion, at 2.0 V for the Li-alloy coin cell and at 0.5 V for the Ni–MH and the Zn–air button cells. The Ni–MH battery showed the best load performance, sustaining currents as high as 180 and 130 mA, respectively, in the full charge state and at 50%

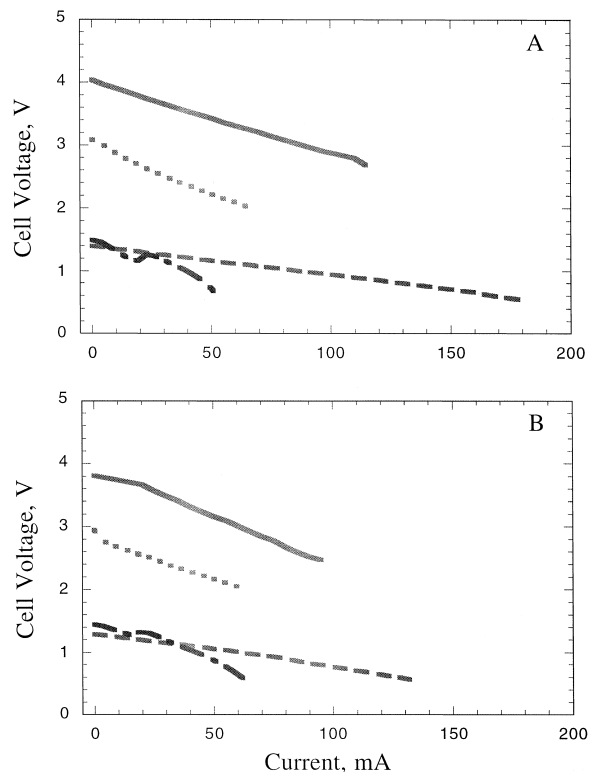


Fig. 10. Comparison of the load curves (cell voltage vs. current) of 312-sized batteries having different chemistries: Li-ion (solid line), Ni–MH (dashed line), Li-alloy (dotted line) and Zn–air (different dashed line). The curves were obtained by applying a current sweep of 50 mA/s to the batteries at the full charge (panel A) and 50% DOD (panel B) states. The end-voltage was fixed at 2.5 V for the 312A Li-ion, at 2.0 V for the Li-alloy and at 0.5 V for the Ni–MH and the Zn–air.

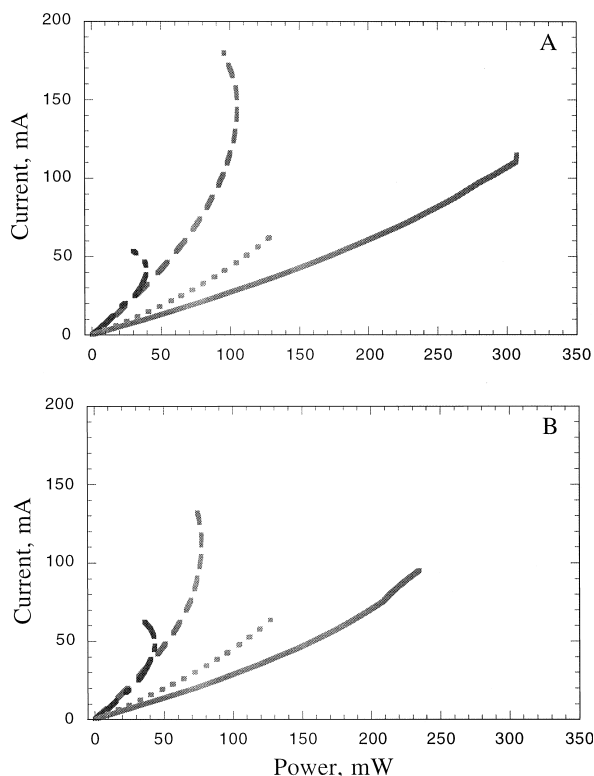


Fig. 11. Comparison of the load curves (current vs. power) of 312-sized batteries having different chemistries: Li-ion (solid line), Ni-MH (dashed line), Li-alloy (dotted line) and Zn-air (dash-dot line). The curves were obtained by applying a current sweep of 50 mA/s to the batteries at the full charge (panel A) and 50% DOD (panel B) states. The end-voltage was fixed at 2.5 V for the 312A Li-ion, at 2.0 V for the Li-alloy and at 0.5 V for the Ni-MH and the Zn-air.

DOD. The 312A battery performance was slightly lower, with the highest currents of 115 and 95 mA in the two stages of charge. Clearly, more limited in rate capability were the Zn-air and the Li-alloy batteries, with maximum sustained currents below 70 mA.

For the same reasons described earlier, the performance of the batteries with different output voltages should be compared only in terms of energy, or as in this case, power. In Fig. 11A and B, the results of the same tests are shown in terms of current vs. power. The current sweep rate used in the tests was high enough to allow the assumption that the calculated power approached the instantaneous power. In terms of power, the 312A battery is superior to the other batteries, delivering energy at a rate as high as 300 mW. The reference batteries barely reached the 100-mW maximum power (the 2016 has a volume almost three times larger than a 312 battery).

3.6. Battery cycle life

The cycle life of the 312A batteries has been investigated on two batteries. The test consisted of discharging the batteries with 1 mA current (C/9) until a capacity of

5 mA h was delivered. With an average cell discharge voltage of 3.7 V (see Fig. 5), this capacity corresponds to more than 18 mW h, i.e., the daily energy requirement of a typical HAD. The delivered capacity (5 mA h) corresponded to about 60% of the full capacity of the batteries used in the test. The batteries were then charged with a CC of 3 mA (C/3) up to a 4.0 V cut-off voltage. The low voltage cut-off was chosen to prevent electrolyte or cathode decomposition. The procedure described above corresponds to an acceleration of at least four times the normal power requirement of a HAD. Four simulated daily cycles are completed in 24 h.

The two 312A batteries were tested for over a year. Since the discharge capacity of the batteries is fixed, important information can be obtained only by comparing the behavior of the cell voltage during the charge and discharge cycles. The cell voltage vs. capacity behavior of the 312A batteries in different cycles is shown in Fig. 12. The two batteries under test performed similarly in the initial 400 cycles. Upon further cycling, the cells behaved differently. By the 1000th cycle, the end voltage of the second battery (panel B) was so low to hit the cathodic

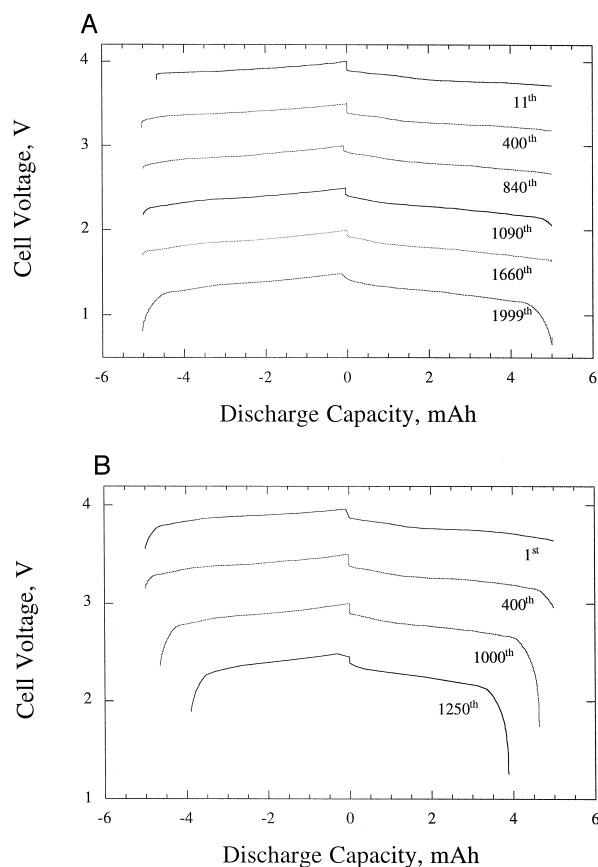


Fig. 12. Cell voltage vs. capacity plots of two 312A batteries in several different cycles (see legend). The cells were discharged to a fixed capacity of 5 mA h. Discharge/charge currents: 1.0/3.0 mA (C/9–C/3 rate). Voltage cut-off limit: 4.0 V. Cathodic safety limit: 2.75 V.

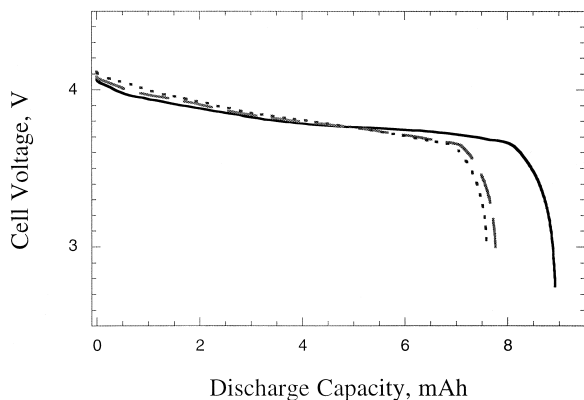


Fig. 13. Delivered capacity vs. cell voltage behavior of the 312A battery shown in Fig. 12 panel A, at the 1st (solid line), 1559th (dashed line) and 2000th (dotted line) cycles. Voltage cut-off limits: 2.75–4.0V (1st discharge); 2.75–4.1 V (1559th and 2000th discharges).

safety limit fixed at 2.75 V, thus, reducing the discharge capacity to less than 5 mA h per cycle. The insufficient charge cut-off voltage is in agreement with the results seen earlier. Unfortunately, when the long-term cycle test was started, the other information on the 312A batteries was not available. The test on the battery with the poorest performance (panel B) was terminated when the delivered capacity went below 80% of the required 5 mA h. However, the battery failure to deliver the required capacity was most likely due to the use of an incorrect charge cut-off voltage as explained later.

The first battery (panel A) performed very well by delivering 5 mA h per cycle up to 1090 cycles. However, the end-discharge voltage begun to decrease after the 1000th cycle indicating that the cell was not fully recharged within the cut-off voltage selected. The battery was then subjected to a full charge/discharge cycle (1559th cycle) up to a voltage cut-off limit of 4.1 V. The voltage vs. delivered capacity behavior of the battery in this full cycle is reported in Fig. 13 (dashed line). The comparison with the discharge curve at the 3rd cycle (solid line in Fig. 13) indicate that the 312A battery was still able to deliver more than 87% of the initial capacity. In the following standard cycle (1660th cycle in Fig. 12A), the 312A battery showed a voltage vs. capacity behavior that is almost identical to the initial one. As a consequence of this evidence, the cycle life test was modified by inserting three full charge/discharge cycles every 100 standard cycles (5 mA h). In this way, the 312A battery was always able to deliver the required 5 mA h up to 2000 cycles (1999th cycle in Fig. 12A). In the 2000th full capacity cycle, the 312A battery was still able to deliver 85% of the initial capacity. The battery is now approaching the third year of cycling and has now completed over 2200 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 5 years on a daily use cycle.

It is worth noting that in the cycle life test, the 312A 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 charge the 312A battery for 2–3 h of normal operation. Thus, if the end user neglected to charge the hearing aid at night, they could charge it in the morning, and in 30 min, put in enough capacity for up to 6 h of use.

4. Conclusion

The new design, lithium-ion batteries developed in this work have shown very good performance in terms of energy density and specific energy (170 W h/l and 65 W h/kg). These values compare well with commercial large-sized batteries. Most important, the 312A batteries satisfied all of the requirements for powering HAD including the battery life in operating conditions. The estimated cost for these batteries is about US\$10 each, in quantity of 1,000,000, i.e., well below the cost of a 5-year supply of the presently used primary Zn–air batteries. A 5-year supply of Zn–air hearing aid batteries is about 125 cells for the typical hearing aid user, and would cost the consumer about US\$125. The 312A, lithium-ion batteries allow the realization of a rechargeable HAD that would combine higher consumer safety, ease of use, lower cost and improved performance.

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