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High-energy, high-power Pulses Plus™ battery for long-term applications

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Abstract

Pulses Plus™ batteries were developed at Tadiran and introduced into the market few years ago. These batteries combine a primary high-energy bobbin type $Li/SOCl_2$ cell with a hybrid layer capacitor (HLC). The HLC is a battery-like capacitor consisting of lithium intercalation compounds as electrodes with pseudo capacitance of 785 F for standard AA size.

The Pulses Plus™ battery can deliver very high energy at very high-power pulses (above 15 A at RT). Under low temperature conditions, its power capabilities are also very good, as 2 A, 1 s pulses above 2.5 V at −40 °C can be obtained. The stability of performance after elevated temperature storage and its low self-discharge rate make this a battery to operate under high pulse power over 20 years.

Keywords: Pulses Plus™ lithium primary battery; Hybrid layer capacitor; Low temperature performance; Long duration applications

1. Introduction

Due to a trend change in electronic systems technology, there are today many applications that require high-energy density power sources with the capability to deliver very high pulse currents (this is to distinguish from continuous discharge).

Electronic systems such as automatic meter readers (AMR), GPS tracking devices, emergency and alarm systems, portable medical equipments and transponders are examples for such systems.

The power sources available today are not optimized for these electronic systems. Bobbin type cells have high-energy density but their pulse current capabilities are limited. Jellyroll cells do have the pulse power capability, however they have lower energy density and they suffer from relatively high self-discharge and capacity loss.

A few years ago, the Pulses Plus™ battery was developed in Tadiran batteries. This battery is a combination of a primary bobbin type $Li/SOCl_2$ cell and a hybrid layer capacitor (HLC). The HLC is a battery-like capacitor, which consists of lithium intercalation compounds as electrode active materials and organic electrolyte.

The primary cell maximizes the energy and the HLC maximizes the pulse power, so a modular combination of them can meet many of the above applications requirements.

Previous work showed that the Pulses Plus™ battery has high-energy density [1] and high-rate pulse capability [2–4] over a very wide operating temperature range (−40 to 85 °C). It has a high operating voltage (3.6 to 3.9 V for 1 unit), it is free from any passivation and voltage delay problems [2], it has very low self-discharge rate [3] that gives it long shelf life and it is as safe as bobbin type $Li/SOCl_2$ cells [2].

This paper will describe further performance improvements of the Pulses Plus™ battery. Modification of HLC components resulted in an excellent improvement of low temperature performance, higher power capabilities and very low self-discharge rate. The performance was found to be very stable even after long-term storage at RT and at elevated temperatures.

2. Experimental

The primary cells used for the Pulses Plus™ batteries and for self-discharge evaluations are Tadiran standard bobbin type $Li/SOCl_2$ or Li/SO_2Cl_2 cells [1]. The HLC has a jellyroll design as was described previously [2]. HLCs of two different sizes were used: HLC1550 is a standard AA size, and a smaller sized one: HLC1520. The electrodes' active area for the HLC1550 is about 350 cm^2 and 1/4 of this for

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the HLC1520. The HLCs are hermetically sealed by laser welding and glass to metal seal. The electrodes have intercalation compounds as active materials. The anode is based on a novel carbon. The cathode is based on a multi-metal oxide as the active material. Combination of several types of carbons is used as a conductive agent in the cathode. A microporous polypropylene membrane is used as a separator. The electrolyte is $LiPF_6$ dissolved in an ethylene carbonate-based solvent mixture.

Charge–discharge tests were conducted with the MACCOR 4000 battery tester. Microcalorimetric measurements were carried out at 25 °C using a 1 μW resolution Isothermal Microcalorimeter (IMC) made by CNC Corporation.

Pulse and discharge tests at low and high temperatures were carried out after stabilization for at least 16 h at the test temperature.

3. Results and discussion

3.1. Capacity and cycle life of the HLC

Fig. 1 shows the capacity and the cycle life for HLC1550 charged to 3.67 V ($Li/SOCl_2$ potential) and 3.90 V (Li/SO_2Cl_2 potential). These results are obtained under 100% DOD for each potential and at relatively fast charge rate of about *C*/0.75. It can be seen that the capacity obtained for HLC1550 is about 200 and 320 mA h at 3.67 and 3.90 V, respectively. This means that HLC1550 can deliver 200 mA pulse for 60 min when charged to 3.67 V and 96 min when charged to 3.9 V. Cycling at 3.9 V charge shows very good cycle life as the capacity degrades to about 80% of the initial capacity after 1000 cycles and to 75% of the initial capacity after 1500 cycles (an average capacity loss of 0.05% per cycle). For 3.67 V charge excellent cycle life is obtained as no capacity loss was observed even after 2000 full charge–discharge cycles. Until now (the cells are still running), the total accumulated capacity after 2000 cycles is 400 A h for charge voltage of 3.67 V. The capacity of the largest Tadiran DD size $Li/SOCl_2$ cell is about 40 A h. So, one single HLC1550 can support the power capability of at least 10 parallel DD size $Li/SOCl_2$ cells in a battery pack.

Similar behavior of cycle life is obtained for the smaller size HLC. After 1500 charge–discharge cycles at the same current density as for HLC1550 (i.e. 110 mA charge, 50 mA discharge) the capacity dropped from 80 to 60 mA h when cycled to 3.90 V. When cycled to 3.67 V, here again no capacity loss was observed even after 2200 cycles.

3.2. Power capability of the HLC

As mentioned before, the HLC maximizes the power capability of the Pulses Plus™ battery. Fig. 2 shows the discharge curves for HLC1550 charged to 3.67 V for several discharge currents at RT. It can be seen that the capacity obtained under relatively low discharge current (100 mA) is 700 A s. This is equivalent to a pseudo capacitance of 600 F. Increasing the discharge current by one order of magnitude to 1 A led to a minor capacity decrease to 650 A s. Further increasing of the discharge current to 5 A gave capacity of 500 A s (about 70% of the capacity obtained at 100 mA discharge), so HLC1550 can deliver 5 A pulses for 100 s to 2.5 V cut-off voltage when charged to 3.67 V. Fig. 3 shows the discharge results for HLC1550 charged to 3.9 V. It can be seen that higher capacities are obtained for all discharge currents. The capacity at 100 mA discharge is 1100 A s or equivalent pseudo capacitance of 785 F. The capacity obtained at 5 A discharge is 900 A s. This is more than 80% of the capacity obtained at 100 mA.

To demonstrate an extreme power capability, HLC1550 at 3.9 V was discharged at 15 A continuous current. Fig. 4 shows the results for this test. It can be seen that HLC1550 charged to 3.9 V delivers 15 A continuous current for 25 s to 2.1 V cut-off.

Similar results were obtained for the small size HLC. For example: the capacities obtained for HLC1520 at 25 mA discharge (i.e. the same current density as 100 mA for HLC1550) are 175 and 275 A s or 150 and 195 F for 3.67 and 3.9 V, respectively.

These results show that the HLC can deliver pulses at a very wide current range to give most of its capacity. This

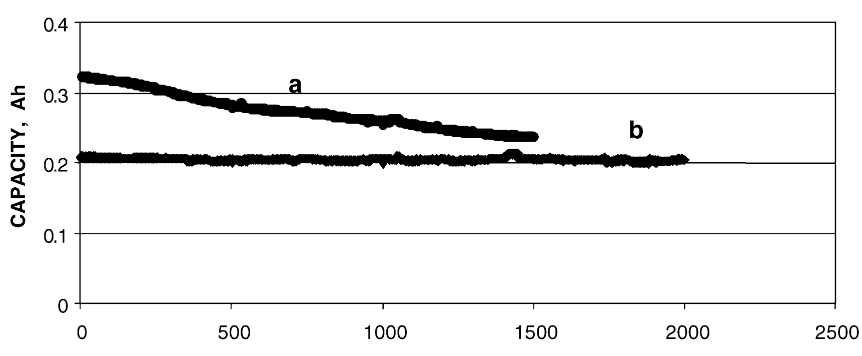

Fig. 1. Cycle life for HLC1550 charged to 3.9 V (a) and 3.67 V (b). Charge: 440 mA (end of charge at 20 mA). Discharge: 200 mA to 2.5 V cut-off.

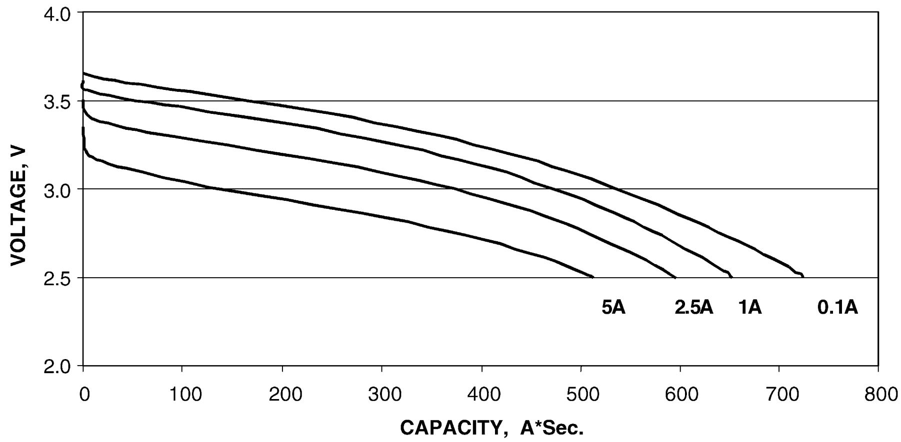

Fig. 2. Discharge curves for HLC1550 at 3.67 V, RT.

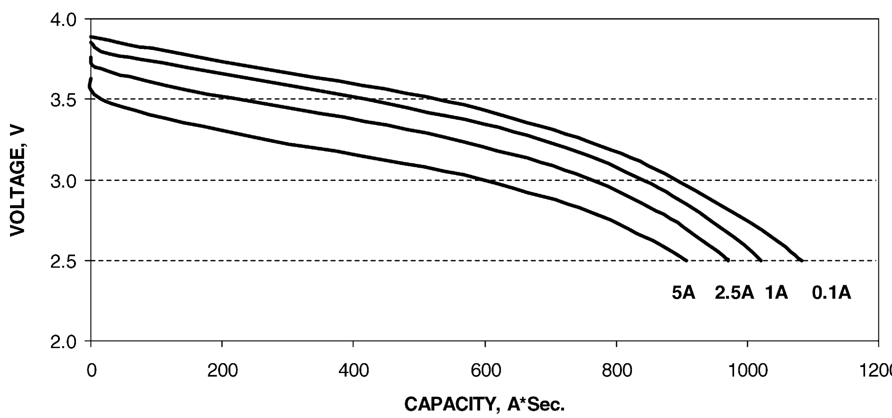

Fig. 3. Discharge curves for HLC1550 at 3.9 V, RT.

current/capacity behavior indicates very good kinetic characteristics of the HLC.

Fig. 5 shows the discharge curve for HLC1550 charged to 3.9 V at RT. This HLC was pulsed at 15 A, 1 s pulse every 10 s to 2 V cut-off voltage. Under these conditions the HLC delivers 80 pulses. The accumulated capacity of these pulses is 330 mA h. This indicates that the HLC can deliver most of its energy even under very high-power pulses at average minimum pulse voltage of 2.6 V.

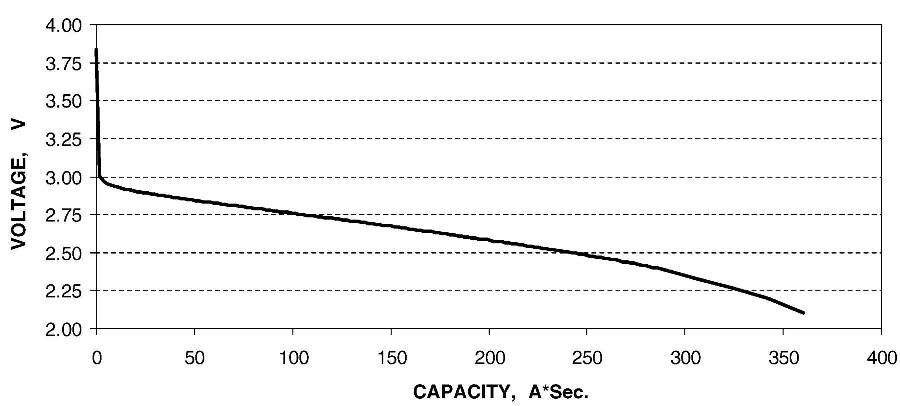

Fig. 4. Discharge curve for HLC1550 at 3.9 V, RT under 15 A continuous current to 2.1 V cut-off.

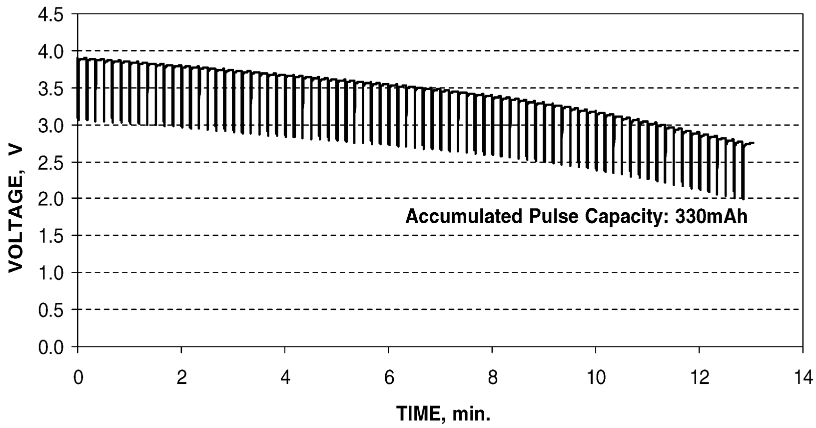

Fig. 5. Pulse discharge curve for HLC1550 at 3.9 V, RT. Discharge: 15 A for 1 s every 10 s to 2 V cut-off.

3.3. Low temperature performance of the HLC

In order to characterize the low temperature capabilities, HLCs were pulsed and discharged at several temperatures under relatively high-rate conditions.

Fig. 6 shows discharge curves for HLC1550 charged to 3.67 V at several temperatures at 1.3 A. It can be seen that the HLC can operate at very wide temperature range from 72 °C down to −40 °C at very high discharge rate (about 7 °C at RT). The pulse capacity of HLC1550 at 72 °C is 200 mA h (9.2 min pulse). This capacity is very similar to the capacity obtained at RT. The HLC can deliver about 50% of its RT capacity at −40 °C: 85 mA h (3.9 min pulse) to 2 V cut-off.

When charged to 3.9 V (Fig. 7) the capacity of the HLC is increased to 280 mA h (or 13 min pulse) at 72 °C. The same capacity was obtained at RT. At −40 °C, the capacity was decreased to only 210 mA h (9.7 min pulse). This means that HLC1550 at 3.9 V can deliver at −40 °C 75% of the capacity obtained at RT and at 72 °C.

For the small size HLC the capacities obtained at 350 mA are 45 mA h (7.7 min pulse) at RT and 15 mA h (2.6 min pulse) at −40 °C when charged to 3.67 V. At 3.9 V charge, the capacities increased to 70 mA h (12 min pulse) at RT and 35 mA h (6 min pulse) at −40 °C.

3.4. Accelerated storage and operating life of the HLC

One of the most important requirements for long-term applications is the ability of a battery to keep its performance capabilities after long storage at RT and at elevated temperatures.

Fig. 8 shows the voltage of HLC1550 under 1.3 A for several pulse durations at −37 °C as a function of storage time at 72 °C. The HLCs were stored while connected to 1/2AA $Li/SOCl_2$ cells at 72 °C. The primary cells were disconnected and the pulses were taken from the HLCs only. From the results of these tests very low voltage degradation for the HLC can be observed: the voltage values after 21 days storage at 72 °C are very similar to the values obtained for a fresh HLC. In addition, even after 81 days storage at 72 °C, the HLC can still operate at −37 °C with very low voltage degradation at very high pulse rate (7 °C).

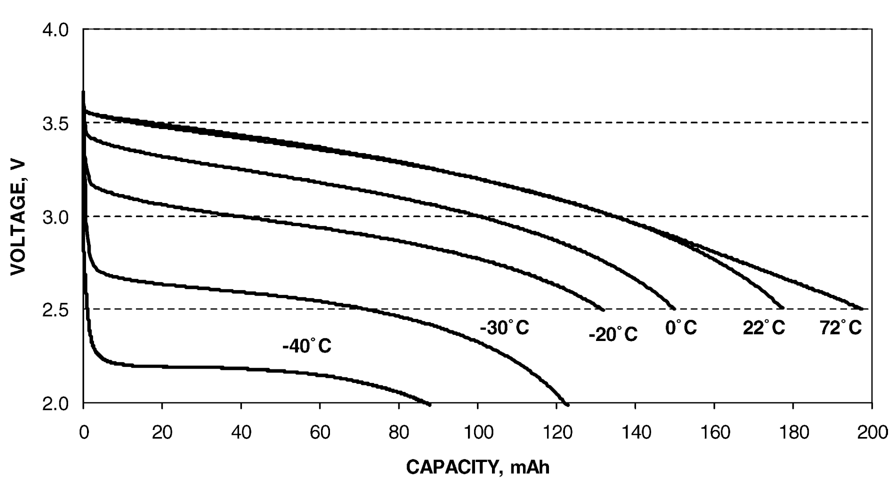

Fig. 6. Discharge curves at 1.3 A for HLC1550 at 3.67 V for several discharge temperatures.

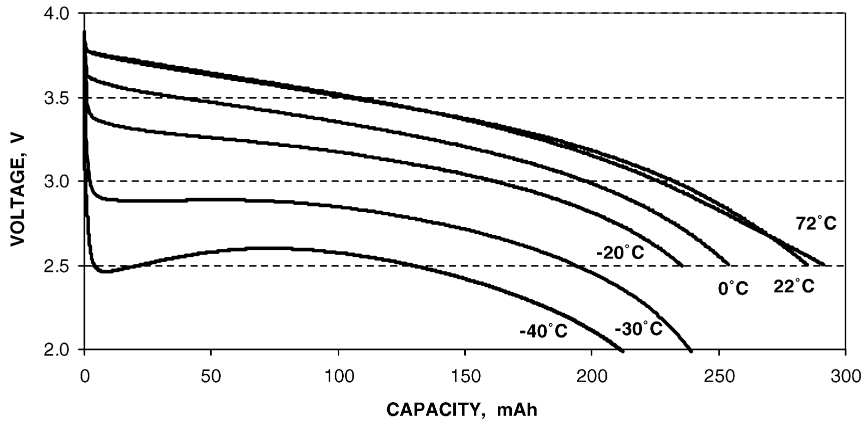

Fig. 7. Discharge curves at 1.3 A for HLC1550 at 3.9 V for several discharge temperatures.

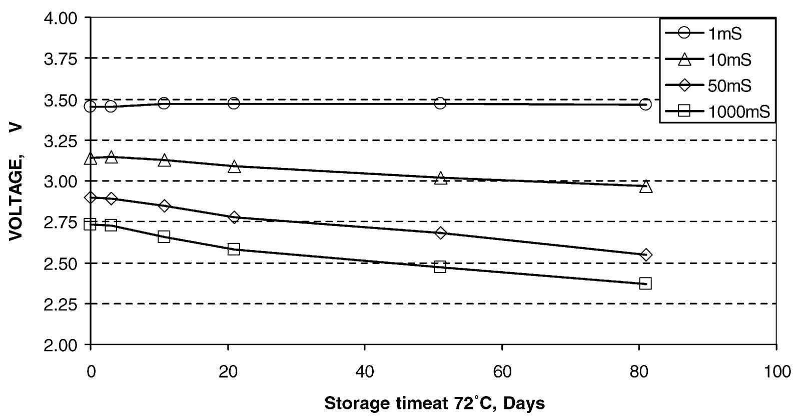

Fig. 8. Voltage values for HLC1550 at 3.67 V under 1.3 A for several pulse durations at −37 °C as a function of storage at 72 °C.

When charged to 3.9 V, 200 mV higher voltage values were obtained, with similar degradation with storage.

Fig. 9 shows voltage curves for 1 s, 2 A pulse for HLC1550 charged to 3.67 V at different temperatures. The HLCs were stored connected to AA/2 Li/$SOCl_2$ cells at 72 °C for 21 days. In order to show the net power capabilities of the HLC by itself, the primary cells were disconnected before the pulse tests. As can be seen, very low over potential was developed at RT and at 72 °C. At low temperatures the over potential was increased, however, the HLC can still support 10 °C rate pulses down to −40 °C above 2.3 V after 1 s.

In addition, no TMV phenomena were observed for all pulse temperatures. This indicates that the HLC is free from

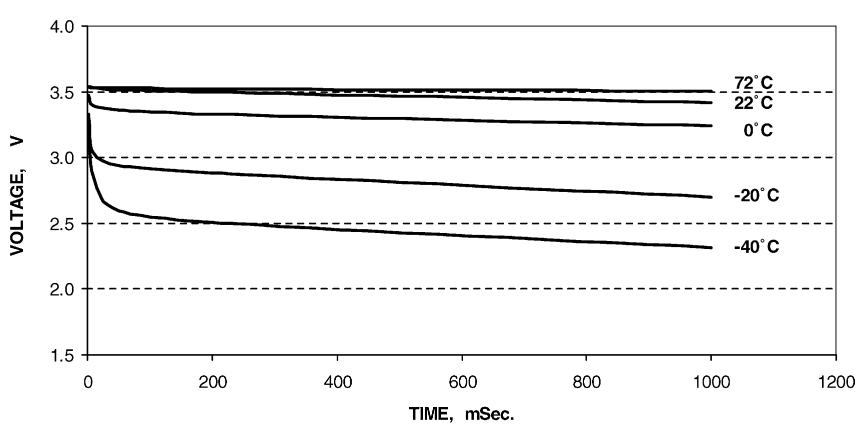

Fig. 9. Voltage curves for HLC1550 at 3.67 V under 2 A, 1 s pulse at several temperatures after 21 days storage at 72 °C.

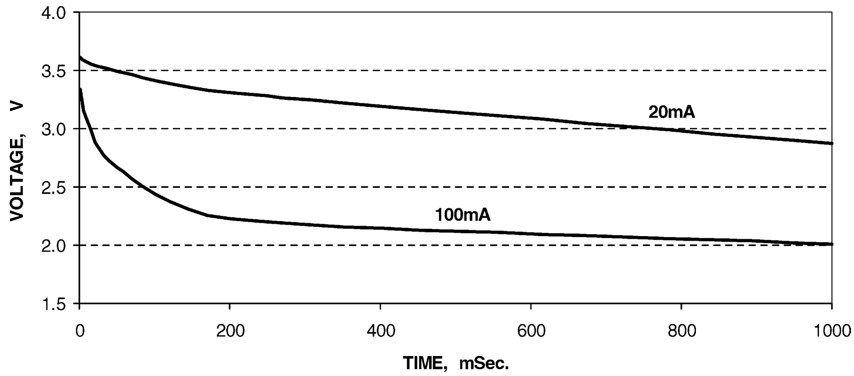

Fig. 10. Voltage curves for HLC1550 at 3.67 V under 20 and 100 mA, 1 s pulse at −70 °C, after 21 days storage at 72 °C.

any passivation problems and high operating voltage can be obtained immediately when current is applied.

At relatively low pulse currents, the HLC can even operate at −70 °C. Fig. 10 shows voltage curves for HLC1550 after 21 days storage at 72 °C tested at −70 °C under 20 and 100 mA, 1 s pulses. It can be seen that even at this very low temperature the HLC can deliver 100 mA pulse for 1 s above 2 V.

Higher voltage values (by 200 mV) for these tests were also observed when the HLC was charged to 3.9 V.

In order to evaluate the stability of the Pulses Plus^{TM} battery, HLC1550 were electrically connected to 1/2AA bobbin type $Li/SOCl_2$ or Li/SO_2Cl_2 cells and stored at 72 °C. Once a week a 1 s, 2 A pulse was applied. Fig. 11 shows the minimum voltage for this test as a function of storage time at 72 °C. As it can be seen from this figure, very good voltage stability was obtained especially for the $Li/SOCl_2$ system during almost 2 years of operation at 72 °C.

In the year 2000, an operating life of 2.5 years at 55 °C for similar Pulses Plus^{TM} batteries at 3.67 V was presented [3]. This test is still running and so far, an operating life of 66 months has been achieved with very stable voltage values.

Again, similar voltage values were obtained for HLC1520 when the same current densities were used for the low and the high temperature tests.

These results show that the Pulses Plus^{TM} battery can operate for very long time, which makes it suitable for use in long-term applications.

3.5. Self-discharge of the HLC

In the past, several techniques were used in order to evaluate the self-discharge of the HLC and the Pulses Plus^{TM} battery. Microcalorimetric studies, long-term discharge and quantitative determination of lithium indicated self-discharge currents of 1.2–2.6 μA for HLC1520 [3]. Self-discharge values of 1–2.2 μA were calculated from the OCV decay of the HLC1520 during long storage at RT [3,4].

Further microcalorimetric tests for self-discharge determination of the HLC were conducted at RT. Several 1520 HLCs were stored, connected to $Li/SOCl_2$ cells, for 3 months at 72 °C. As noted, no passivation was developed during storage at 72 °C. After stabilization of the chemical processes at the HLC was achieved at 72 °C, the batteries were stored for an additional week at RT. After storage, the HLCs were

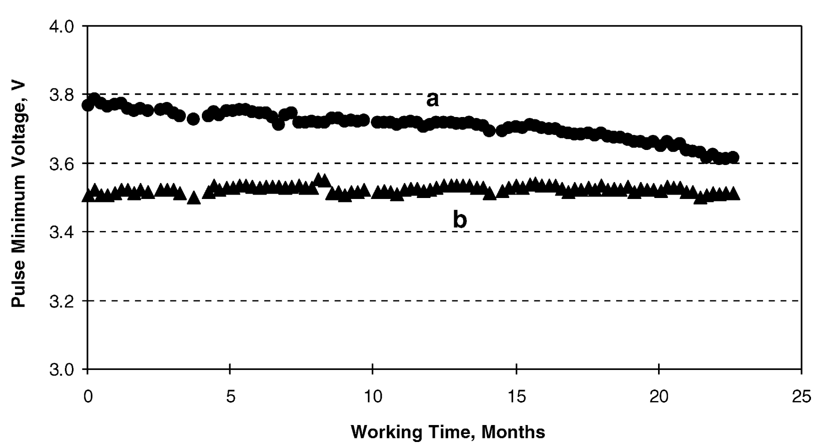

Fig. 11. Typical minimum voltage for Pulses Plus^{TM} batteries under 2 A, 1 s pulse at 72 °C once a week. The batteries combine HLC1550 together with 1/2AA Li/SO_2Cl_2 (a), or $Li/SOCl_2$ (b) primary cells.

disconnected from the primary cells and their heat dissipations were measured at RT using a microcalorimeter. As the thermo-neutral potential for the chemical reaction takes place at the HLC is not known we assume that the heat dissipation due to entropy changes is negligible and the open circuit voltage was used to evaluate the self-discharge current.

In order to evaluate the self-discharge of the HLC at 72 °C, 1/2AA bobbin type $Li/SOCl_2$ or Li/SO_2Cl_2 cells were discharged under load of 6.2 kΩ at 72 °C. Some of the primary cells were connected in parallel to HLC1520 to form Pulses Plus™ batteries. According to the discharge capacity differences between the primary cells, the Pulses Plus™ batteries and the discharge time, the self-discharge for the HLC was calculated.

Table 1
Self discharge of HLC 1520

Test method	HLC potential (V)	Temperature (°C)	Self-discharge (μA)
Long-term discharge at 6.2 Ω load	3.90	72	5.0
Long-term discharge at 6.2 kΩ load	3.67	72	2.5
Microcalorimetric measurements	3.67	25	0.8

Table 1 summarizes the results for these tests. It can be seen that very low self-discharge rates for the HLC were found at 72 °C: the self-discharge for HLC1520 calculated to be 5 and 2.5 μA at 3.9 and 3.67 V, respectively. At RT

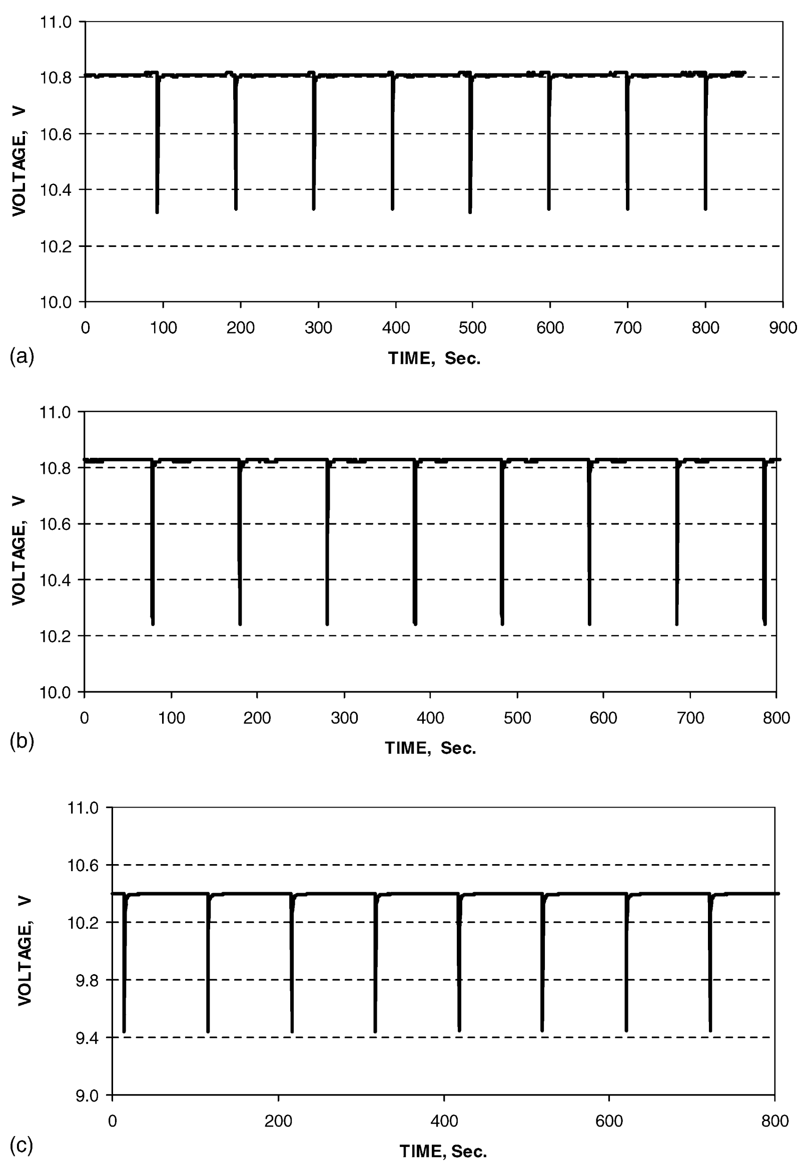

Fig. 12. Pulse discharge for Pulses Plus™ battery pack at 750 mA, 1 s pulse every 100 s at RT: (a) first eight pulses. (b) Another set of eight pulses after 45 A h discharge. (c) Another set of eight pulses after 57 A h discharge.

the self-discharge current for the HLC was found to be only 0.8 μA when charged to 3.67 V.

These results predict very long operating life for the Pulses Plus™ battery.

3.6. *Pulses Plus™ battery*

Last year, the results of a Pulses Plus™ battery were presented [1]. The battery was composed of a HLC1550 and a DD sized $Li/SOCl_2$ primary cell. Three sets of this combination were connected in series to give an OCV of 11 V. This battery was pulse discharged at 750 mA, 1 s pulse every 100 s to 7.5 V cut-off. Under this regime the battery delivered 39 A h—the total capacity of the DD $Li/SOCl_2$ cell.

A similar Pulses Plus™ battery was tested under the same discharge conditions. This time 3D sized $Li/SOCl_2$ primary cells were connected to a HLC1550.

Fig. 12 shows three sets of eight pulses during the discharge of this battery: the first eight pulses, another eight pulses after 45 A h discharge and another eight pulses close to the end of discharge (after 57 A h discharge). It can be seen that the minimum voltage at the beginning of discharge is about 10.3 V (Fig. 12a). After 75% of the theoretical capacity was consumed (Fig. 12b) the minimum voltage had dropped only to 10.25 V. After most of the capacity was consumed (57 A h, Fig. 12c), the minimum voltage was decreased but remained relatively high for this state of discharge (above 9.4 V). This battery delivered almost its all theoretical capacity 58.5 A h to cut-off voltage of 7.5 V.

These results indicate that the HLC can support the primary cells to deliver all its low rate capacity under high pulse discharge currents without any significant capacity loss. This makes the Pulses Plus™ battery a very long-term high-energy high pulse power system.

3.7. *Comparison with other technologies*

Plot in Fig. 13 was taken from the EDN magazine [5]. It can be seen that fuel cells have very high specific energy (up to 1 kW h/kg) but their power density is limited to about 20 W/kg. On the other hand, aluminum capacitors have very high-power densities (up to 10 kW/kg), however their specific energy is very low (about 0.2 W h/kg). Other systems such as Ni/Cd, lithium batteries, ultra and double layer capacitors have moderate power/energy capabilities. Into this plot the power/energy characteristics for the HLC1550 at 3.9 V were added. It can be seen that the HLC has an specific energy of about 70 W h/kg. It can deliver most of its energy at high rates (even at 1 kW/kg). Part of its energy can be obtained even at power density up to 3 kW/kg. These characteristics covers most of the power/energy range includes the Ni/Cd, the double layer capacitors and ultra capacitors, significant part of the lithium batteries and even a part of aluminum capacitors.

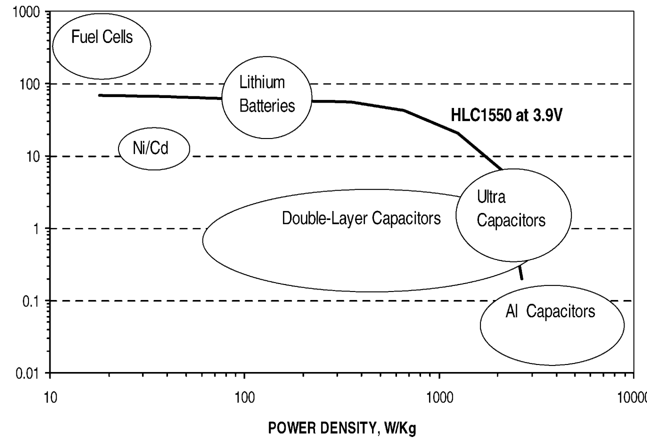

Fig. 13. Ragone plot for several power sources.

The advantage of the HLC over these systems is increased when other parameters such as self-discharge, operating temperature and storage temperature range are taken into considerations.

4. Summary

The Pulses plus™ battery has very good energy/power capabilities. It can operate at very high rates over a wide temperature range—down to −40 °C. Its self-discharge rate is very low and long operating life (up to 20 years) can be achieved.

In addition, several Pulses plus™ units can be combined in serial and/or in parallel to give a wide variety of energy and power requirements.

These characteristics make the Pulses plus(tm) battery very attractive to be used in many applications on the market.

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