Pulses Plus Battery System for High Energy High Power Applications

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Introduction

Over the past decade there has been an increased interest for high energy density primary power sources which are capable of delivering high current pulses for applications such as: emergency call systems, portable defibrillators, GPS tracking devices, oceanographic transponders etc. Several types of electrochemical systems are currently used for this type of applications. However, none of these are optimized for the applications requirements: The bobbin type $Li/SOCl_2$ cells have the highest energy density and lowest self discharge rate but cannot deliver the desired power. The jelly roll cells of this system do have the power capability to deliver the pulses but they are not safe enough for these applications. Another disadvantage of the jelly roll cells in comparison to the bobbin type cells is shorter operating life. The Li/SO_2 system has the best current capability especially at low temperature however, the self-discharge rate of Li/SO_2 cell while discharged at low current is relatively high. In addition, the cell has pressurized SO_2 which reduces the safety of the cells and limits its use. The Li/MnO_2 and Li/CFx technologies have moderate energy density and power capability. However, at low temperature the power capability is relatively low. Consequently, these systems are very marginal for the mentioned applications either from energy or from power requirements viewpoints.

A few years ago Tadiran Batteries Ltd. developed a new power source (Pulses Plus battery) capable of delivering high energy density at high power. It has very low self-discharge rate and wide operating temperature range. This power source combines the bobbin type $Li/SOCl_2$ cell with hybrid layer capacitor (HLC). The electrical and safety characteristics of this system were previously described [(1)]. The aim of this paper is to disclose further features of this system.

Experimental

The bobbin type $Li/SOCl_2$ cells used to assemble the Pulses Plus batteries are the Tadiran standard lithium cells. The HLC's used are of two types: the small size- model HLC -14200 and the large size - model HLC - 14500. Both are hermetically sealed and their construction was described previously [(1)]. Pulse discharge tests were carried out by using Tadiran pulse discharge data acquisition system. Charge- discharge tests of the HLC were conducted on Maccor 4000 tester. Study of the self discharge rate of the HLC, the $Li/SOCl_2$ cells and the Pulses Plus batteries were performed using long term discharge tests, microcalorimetric measurements and quantitative determination of residual lithium in $Li/SOCl_2$ cells [(2,3)].

Results and discussion

Power Capability

Figure 1 describes voltage -time curve of HLC-14500 discharged at constant currents of 1.0 A, 2.0 A, 3.5 A and 5.0 A to 2.8 Volt cut off at RT. The total capacity delivered by the HLC at 5A is as high as 75% of the capacity delivered at 1.0 A discharge.

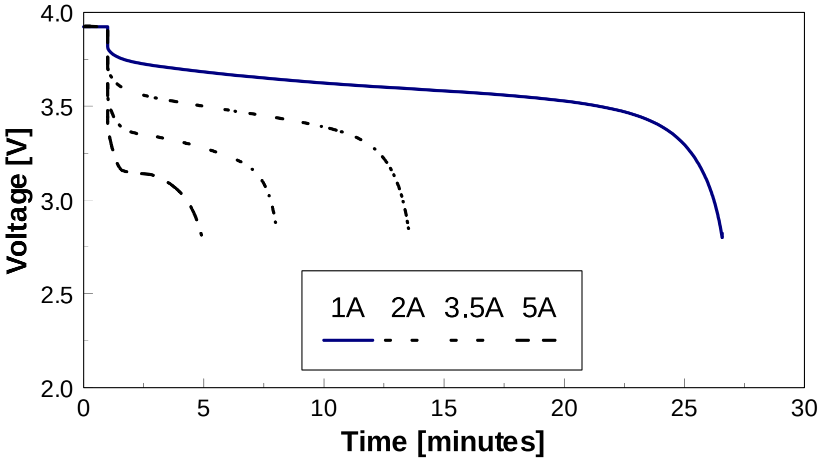

Figure 1: Voltage-time curve of HLC-14500 at 1.0, 2.0, 3.5 and 5A at RT

Figure 2 describes discharge of Pulses Plus battery comprising of AA sizes Li-SO_2Cl_2 cell and HLC-14500 under 10A 1sec pulse every 10 seconds. The minimum voltage at the beginning of the test is 2.85 Volt. The minimum voltage increases to 2.95V within 10 minutes. The slight increase of the minimum voltage with time at the 10 A pulses is attributed to the temperature rise of the battery as a results of high current discharge and not to any passivation of the anode. The results shown at figures 1 and 2 clearly indicate that the Pulses Plus battery can operate at relatively high power.

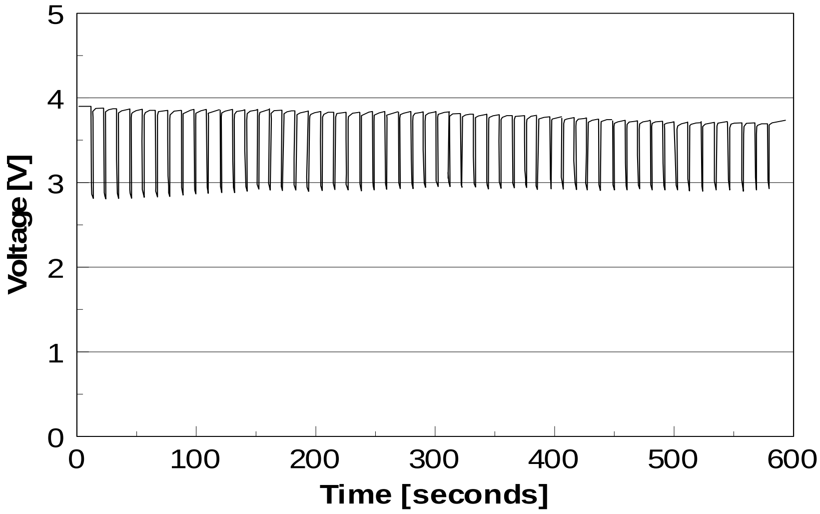

Figure 2: 10A 1 sec pulses every 10 sec. to AA size Li-SO_2Cl_2 and HLC-14500 at RT.

Energy and cell Capacity

Pulse discharge tests carried out on Pulses Plus batteries indicate that the batteries can deliver high voltage at high current as long as the open circuit voltage of the battery prior to applying the load is high enough to carry the discharge. Pulse discharge tests carried out on AA size primary cell and HLC-14200 show that the battery can deliver 17496 pulses of 500 mA for duration of 1 seconds each. The time interval between the pulses is 500 seconds and the cut off voltage is 2.80 Volt. The total net discharge capacity is 2430 mAh. This value is about 95% of the known available capacity for AA size cell at low rate discharge. Figure 3 describes long term discharge test of AA size Li/$SOCl_2$ and HLC-14500 discharged under constant load of 33kOhm (average current of about 110μA) and 1 sec. pulse of 500mA once per week. Capacity of 2.19 Ah was obtained after 27 months of continuous pulse and background current discharge.

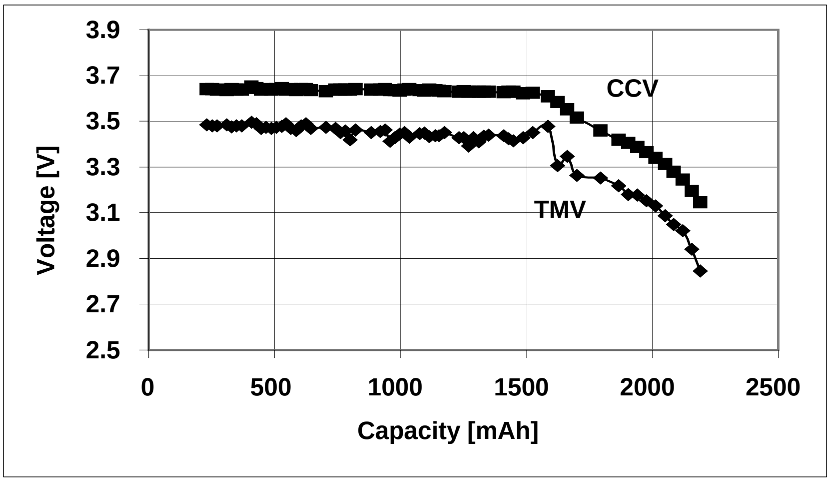

Figure 3: AA size Li/$SOCl_2$ and HLC-14500 battery pack discharged at pulses of 500mA 1sec once per week (average current - 110μA).

Small size HLC's were subjected to charge/ discharge cycles at constant current of 110/50 mA respectively. The charge step was terminated either at 3.67 Volt or at 3.9 Volt. The discharge step was terminated at 3.0 Volt in both cases. The discharge capacity versus the cycle number is shown in figure 4. Both tests have not ended yet. On charging to 3.67V the HLC delivered (up to the preparation of this paper) about 6100 pulses of about 10mAh each. On charging to 3.90 Volt the HLC delivered (up to the preparation of this paper) about 1200 cycles of 100mAh each. The total accumulative capacity is 51 Ah and 98Ah for the 3.67 and 3.90V respectively. It seems from this test that even one single small HLC can deliver the pulses through the entire life of the largest Tadiran lithium cell (38Ah for a DD size Li/$SOCl_2$ cell).

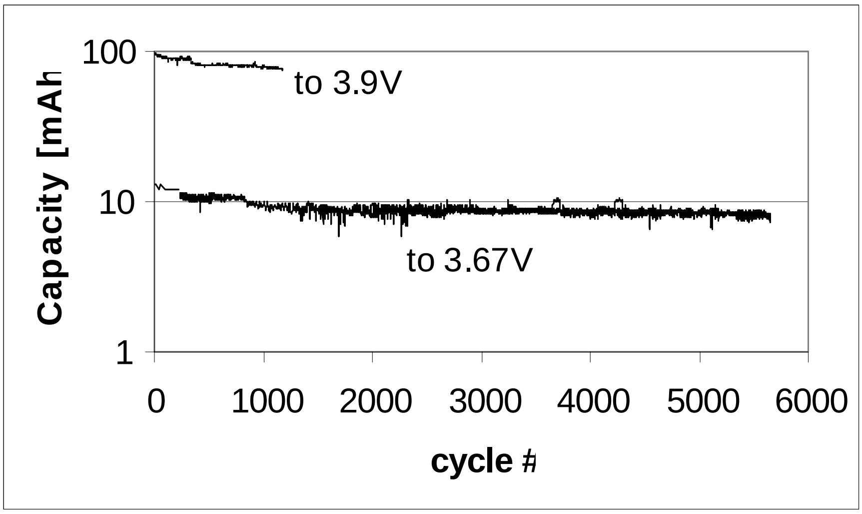

Figure 4:Discharge capacity vs. cycle # to 3.67V and to 3.9V of HLC-14200

Temperature Characteristics

Figure 5 describes minimum voltage during 500mA 1 second pulse discharge at various temperatures. The batteries comprise of AA size Li/$SOCl_2$ cell and large HLC. The battery was connected to background current of 20μA and measurements were taken once per week.

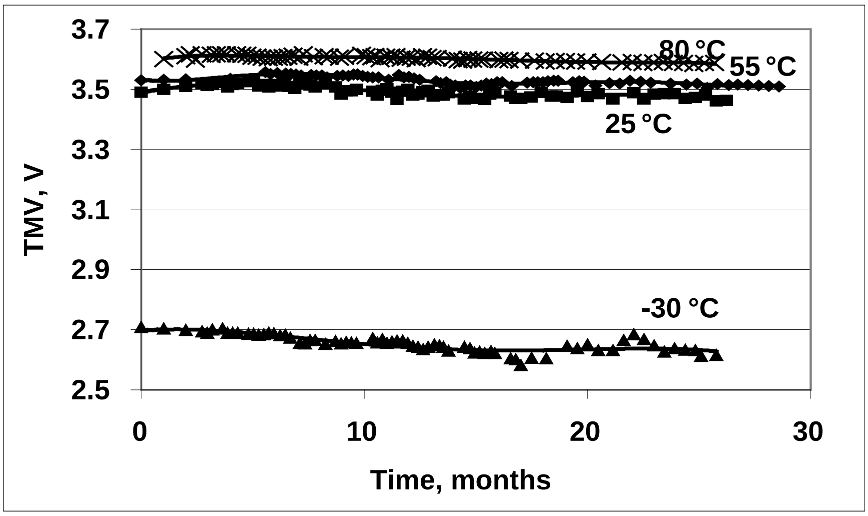

Figure 5: Minimum voltage under 500mA sec. pulse for AA size Li-$SOCl_2$+ HLC-14500

Figure 6 describes discharge curve at 125°C of DD size Li/$SOCl_2$ and HLC-14200. The battery was discharged at peak current of about of 350mA for 1.4 seconds each 5 seconds (average current of 100 mA). The minimum voltage during the peak current and the maximum voltage obtained under OCV conditions are shown in the curves. The battery delivered total capacity of 22.5 Ah to 3.0 Volt cut off.

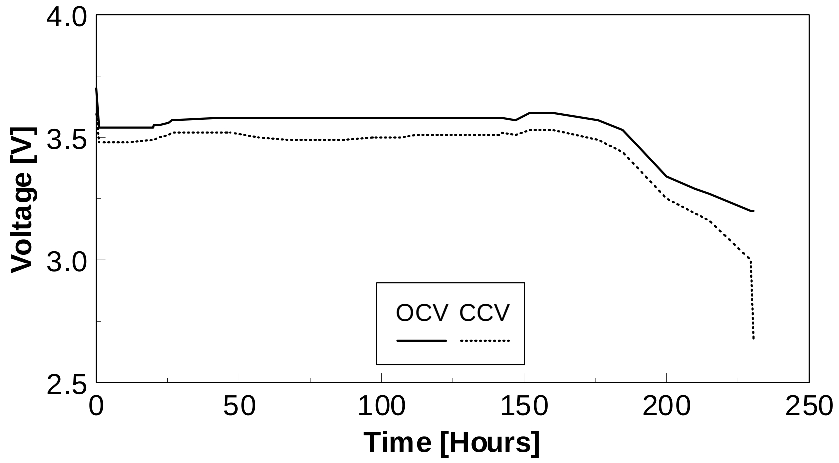

Figure 6: OCV and the minimum voltage during 1.4sec 350mA every 5 seconds pulses at 125°C of DD size Li/$SOCl_2$ and HLC-14200.

Operating life study

One of the most important characteristics of a battery for long term application is its capacity loss. Several techniques were used to evaluate the self-discharge rate of the Pulses Plus battery. Figure 7 describes microcalorimetric measurements under OCV conditions of a Pulses Plus battery comprising of AA size Li/$SOCl_2$ cell and a small HLC.The heat dissipated by the battery, the primary cell and the HLC are shown.

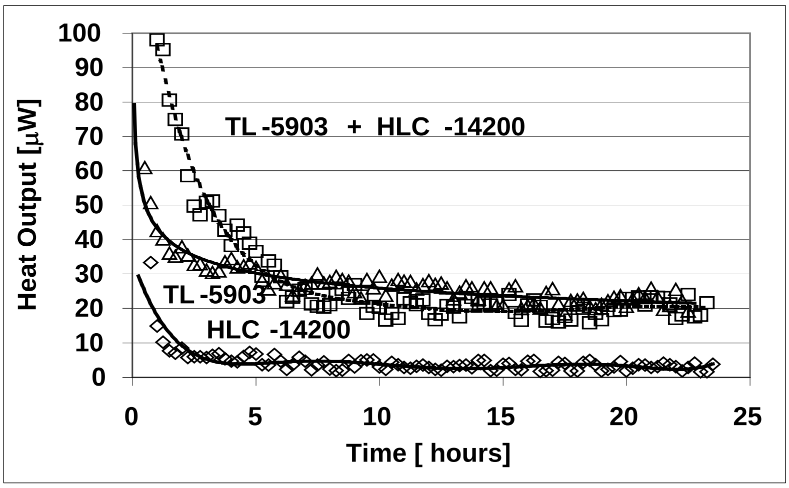

Figure 7. Microcalorimetric measurement under OCV conditions of Pulses Plus battery comprising of AA Li/$SOCl_2$ cell and HLC-14200 after 8 months at RT

As can be seen the heat dissipated by the battery is found to be the sum of the heat dissipated by the HLC and the primary cell. This indicates that under steady state conditions, negligible heat, if any, is exchanged between the cell and the HLC. The thermoneutral potential for the chemical reaction of the HLC is not known, therefore we estimate the self-discharge rate from the heat dissipation and the open circuit voltage of the battery assuming no entropy changes. In addition, the heat dissipated by the HLC is about one fourth of the heat dissipated by the battery. This indicates that the self-discharge rate of the HLC is very low under the test conditions.

Table 1. Self discharge in μA determined by various methods

Test method	**Pulses Plus**	**HLC**	**Cell**
Long term discharge at 100μA	9.2	2.6	6.6
Quantitative determination of residual lithium after 2 years	6	1.7	4.3
Voltage decay of the HLC under OCV	-	2.2	-
Microcalorimetry of HLC, Cell and Pulses Plus battery	5.7	1.2	4.5

Table 1 describes the self discharge rate of Pulses Plus battery based on AA $Li/SOCl_2$ cell and small size HLC. The difference between the discharged capacity of the Pulses Plus battery and the primary cell indicates that under 110μA discharge the battery lost about 7.0% of its capacity. 2 % is due to the HLC and 5% due to the $Li\text{-}SOCl_2$ cell. The residual lithium test indicates total self-discharge rate of 6.0μA for the battery. The capacity loss calculated from voltage decay of the HLC during 11 months of storage at room temperature indicates an average self discharge current of 2.2 μA. Microcalorimetric heat output measurements indicate 1.2 μA for the HLC and 5.7μA for the Pulses Plus battery. In summary of this section it appears that the self discharge rate of the HLC is relatively very low. This finding can also be concluded from the long term operation of the battery at high temperature.

Discharge Data

Comparison with other technologies.

The following figures describe available capacity and operating life of various C-size lithium technologies in comparison with Pulses Plus battery based on bobbin type $Li/SOCl_2$ cell and small size capacitors. The capacity of each system was estimated from manufacture data catalogues together with our base data. Figure 8 describes the available capacity versus pulse current amplitude at room temperature of pulses applied for 5 seconds under average current of 70μA. The available capacity of the Pulses Plus battery was extrapolated from 2 years discharge and microcalorimetric data. As can be seen the capacity and the operating life of the bobbin type cell decrease with the increase of the pulse current amplitude. At pulse current of about 8mA and average current of 70μA the battery can operate for 9.5 years and deliver net capacity of 5.8 Ah. The capacity decreases to 1.5Ah at 150mA pulse current amplitude mainly due to impedance losses. The capacity and the operating life of the jellyroll cell are relatively constant with the current amplitude. At 70μA average current the operating time of jelly roll cell is limited by the self-discharge losses. The maximum operating time is about 4.5 years at low current amplitude and about 3.5 years at 150mA pulse currents. The capacity of the Pulses Plus battery does not change at all with the pulse

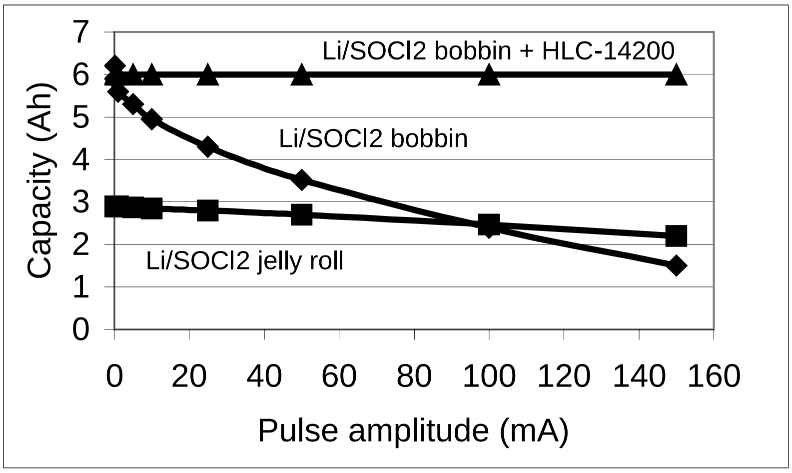

Figure 8. Available capacity to 2.5 V cut off versus current amplitude for C-size cells under 5 sec pulse at RT (average current – 70 μA)

current amplitude due to its high power capability. The operating life and the available capacity are determined by the average current and the self-discharge currents of the C-size cell and HLC. At the given above discharge conditions the battery is expected to operate about 10 years at each of the pulse currents shown in the curve.

Figure 9 describes estimated capacity versus current amplitude for various C- size cells to 2.0 Volt cut off. The average discharge temperature was taken as 25°C with 5% of the time at the extreme temperature end of 70°C and –25°C.

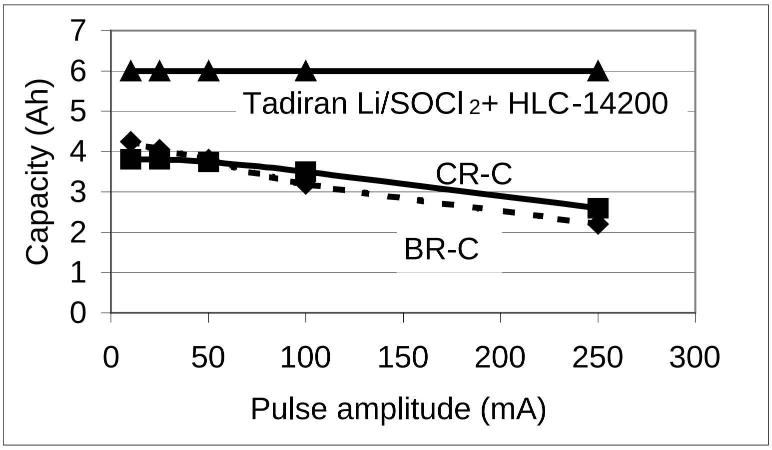

Figure 9. Available capacity to 2.0 V cut off versus current amplitude for C-size cells under 5 sec pulse at –25°C to 70°C (average current – 70 μA)

Capacities were estimated from Tadiran base data and manufacturer catalogues. The capacity of the CR-C and the BR-C cells are limited at the high pulse currents end mainly due to impedance loss at the low temperature even for the cut off voltage as low as 2.0 Volt.

Summary

A new power source based on bobbin type Li/$SOCl_2$ cell and Hybrid Layer Capacitor has been presented. This power source is capable of delivering up to 10A current pulses for long term applications without any passivation or delay problems. Discharge data between –30°C to 125°C verify the wide operating temperature range of this system. Microcalorimetry and long term discharge indicate very low self- discharge rate.

The Pulses Plus battery combines the power capability of jelly- roll cells with the self-discharge rate and the safety level of bobbin type Li/$SOCl_2$ cell.

References

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2. M. Pallivathikal, H. Yamin and U. Zak, Electrochemical Soc. Fall Meeting, Hollywood, Florida, 1989.
3. H. Yamin, M. Pallivathikal and E. Elster, Proceedings of the 35th International Power Sources Symposium, Cherry Hill, New Jersey, 1992.