

PULSES PLUS™ Battery System for Long Term and Wide Operating Temperature Range Applications.

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Introduction

Over the past few years there has been an increased interest for high energy density primary power sources which are capable of delivering high current pulses (to distinguish from continuous discharge) for applications such as: emergency call systems, electronic meters (Gas, Water etc.), portable defibrillators, GPS tracking devices, oceanographic transponders etc. Several types of electrochemical systems are currently used for these applications. However, none of these are optimized for the applications requirements: Bobbin type cells have the high energy density and low self discharge rate but cannot deliver the desired power. The jellyroll cells do have the power capability to deliver the pulses but they have less capacity and higher self-discharge rate.

A few years ago, Tadiran Batteries Ltd. developed a new power source (Pulses Plus™ battery) capable of delivering high energy density at high power. This power source remarkably increases the pulse rate capability and the operating voltage of the bobbin type Li/SOCl₂^(1, 2). It has very low self-discharge rate and wide operating temperature range. This power source combines the bobbin type Li/SOCl₂ cell with hybrid layer capacitor (HLC).

The aims of this work were:

1. To increase the rate current capability of the Pulses Plus™ battery at low temperature (down to -40°C).
2. To increase the pulse discharge capacity of the pulses plus™ battery.

Experimental

The primary cells used for the pulses plus™ batteries are Tadiran standard bobbin type Li/SOCl₂ or Li/SO₂Cl₂ cells. Two types of HLC's were used: HLC1550 is a standard AA size, and HLC1520 is a small size HLC. The construction of the HLC was described previously⁽¹⁾. The electrodes active area for the HLC1550 is about 350cm² and ¼ of this for the HLC1520. The HLC's are hermetically sealed by lazer welding and glass to metal joint. The electrodes are consisted of intercalation compounds as active materials. The electrolyte is based on LiPF₆ salt dissolved in a carbonates solvent mixture.

Charge-discharge tests were conducted with the MACCOR 4000 battery tester.

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

Results and discussion

Capacity and cycle life of the HLC

Figure 1 shows the capacity and the cycle life for HLC1550 charged to 3.67V (Li/SOCl₂ potential) and 3.90V (Li/SO₂Cl₂ potential). It can be seen that the capacity obtained for HLC1550 is about 200mAh and 400mAh at 3.67V and 3.90V respectively. This capacity is very stable for hundreds of cycles, for both charge potentials (the cells are still running). The total accumulated capacities after 1500 cycles are 570Ah and 300Ah for charge voltage of 3.90V and 3.67V respectively. As the largest Tadiran DD size Li/SOCl₂ cell has a capacity of about 40Ah, one single HLC can support the capacity of parallel packs consisted of about 8 DD size Li/SOCl₂ cells.

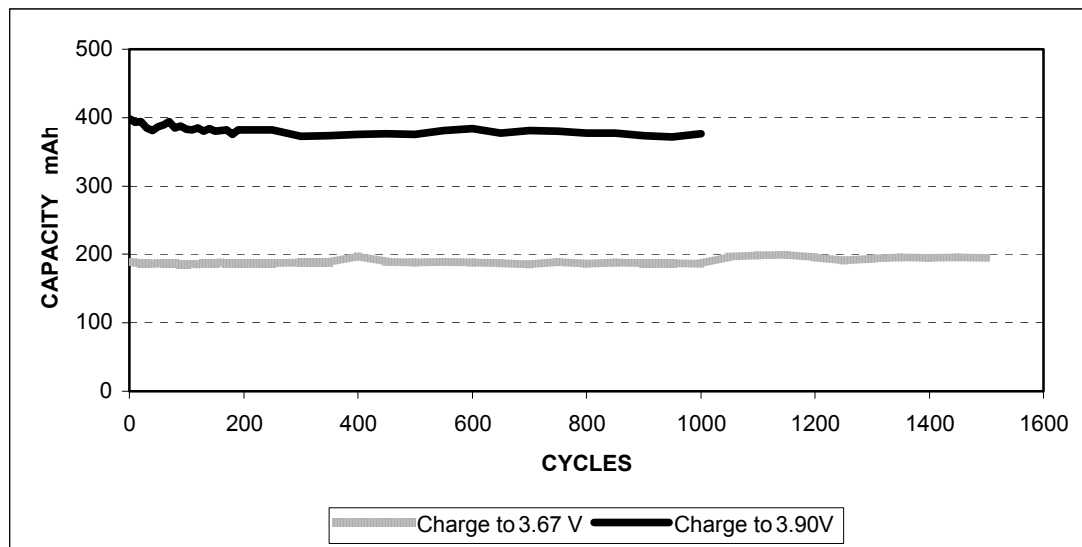


Figure 1: Capacity vs. cycles at RT for HLC1550 charged to 3.67V and 3.90V. Charge - 440mA (end of charge 20mA). Discharge - 200mA to 3V.

The same behavior obtained for the smaller size HLC (1520). After 2000 charge-discharge cycles at the same current density as for HLC1550 (i.e. 110mA charge, 50mA discharge) the capacity dropped from 100mAh to 90mAh when cycled to 3.90V and from 50mAh to 48mAh when cycled to 3.67V.

Figure 2 shows the discharge curve for HLC1550 charged to 3.67V for several discharge currents at RT. It can be seen that the cell can operate at a very wide current range up to 5A continuous discharge. So, a fully charged HLC1550 can deliver long pulses at various currents. For example, HLC1550 can deliver 5A pulse for 0.6 minutes with working voltage above 2.8V.

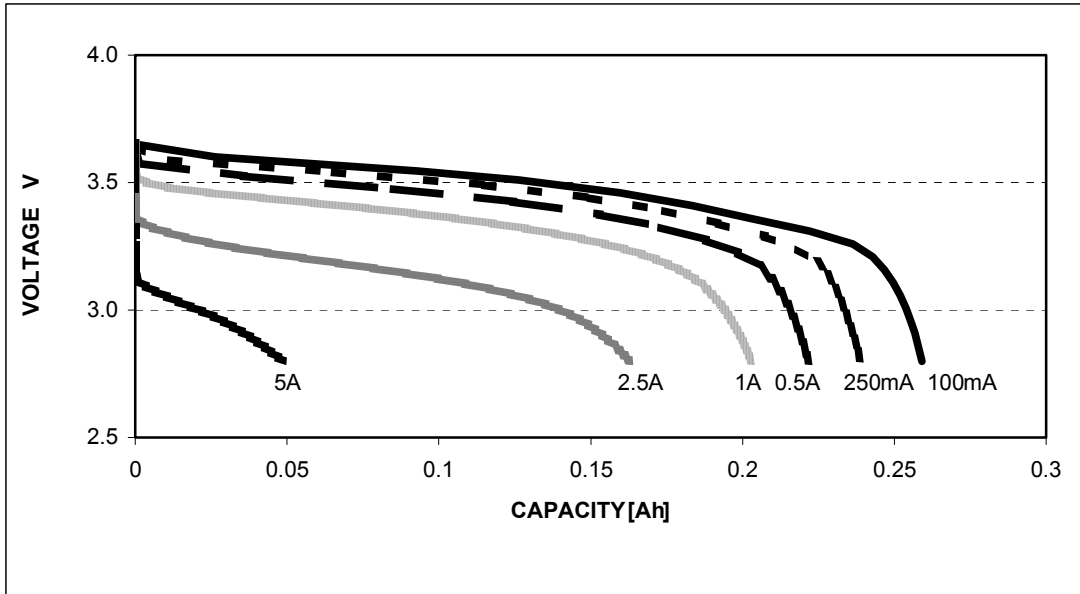


Figure 2: Discharge curves to 2.8V cut-off voltage as a function of current at RT for HLC1550 charged to 3.67V.

Figure 3 shows discharge curves for the small size HLC1520 charged to 3.67V at different temperatures. It can be seen that the HLC can operate at very wide temperature range from 72°C down to -37°C at very high discharge rate (about 7C at RT). The pulse capacity at 72°C is 230A*sec. The HLC can deliver 15A*sec. even at -37°C.

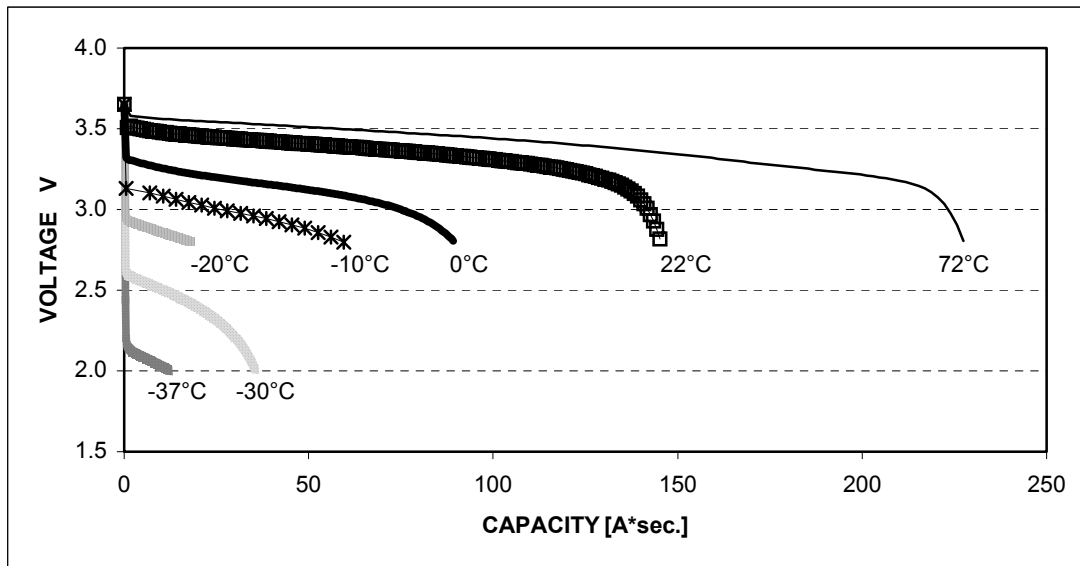


Figure 3: Discharge curves at 350mA for HLC1520 charged to 3.67V at different temperatures. Cut-off voltage: 2.8V for temperature above -30°C and 2.0V for -30°C and lower.

Figure 4 shows voltage curves for 1 second, 350mA pulse for the small size HLC1520 charged to 3.67V at different temperatures. From these results it can be seen that the HLC can operate at relatively high current for short pulse time even at low temperatures (down to -40°C).

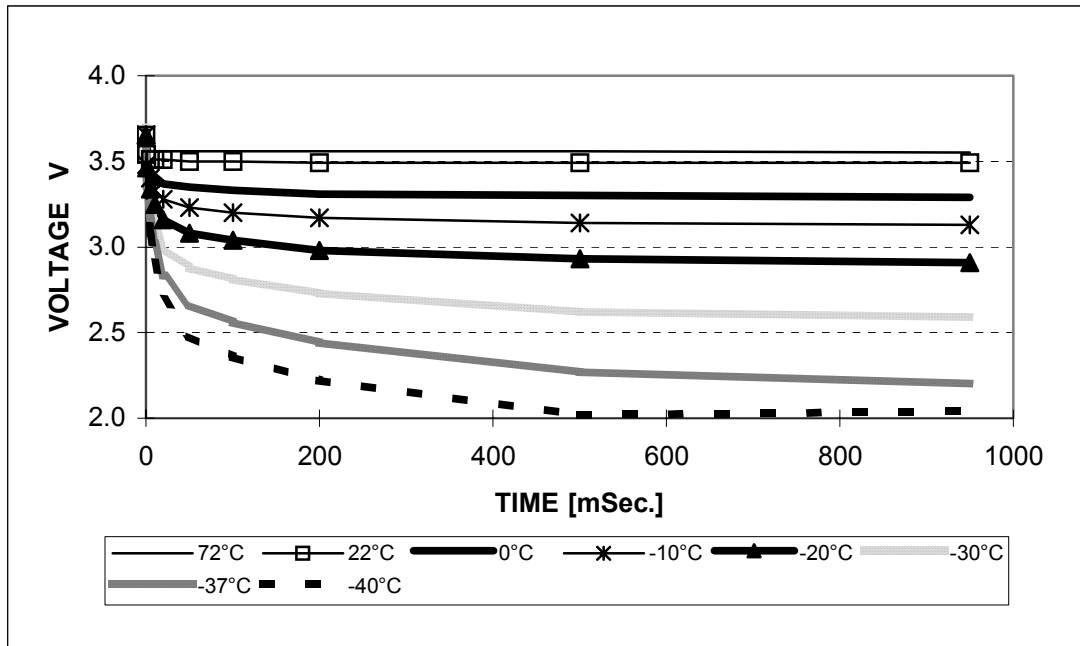


Figure 4: Voltage curves at different temperatures for 350mA, 1 second pulse for HLC1520 charged to 3.67V.

Figure 5 shows the voltage curve for 50mSeconds, 500mA pulse for the small size HLC1520 charged to 3.67V at 72°C, RT and -30°C respectively. As can be seen, very low over potential was developed at RT and at 72°C. Despite of the increase in over potential at -30°C, the HLC can still support 10C rate above 2.5V.

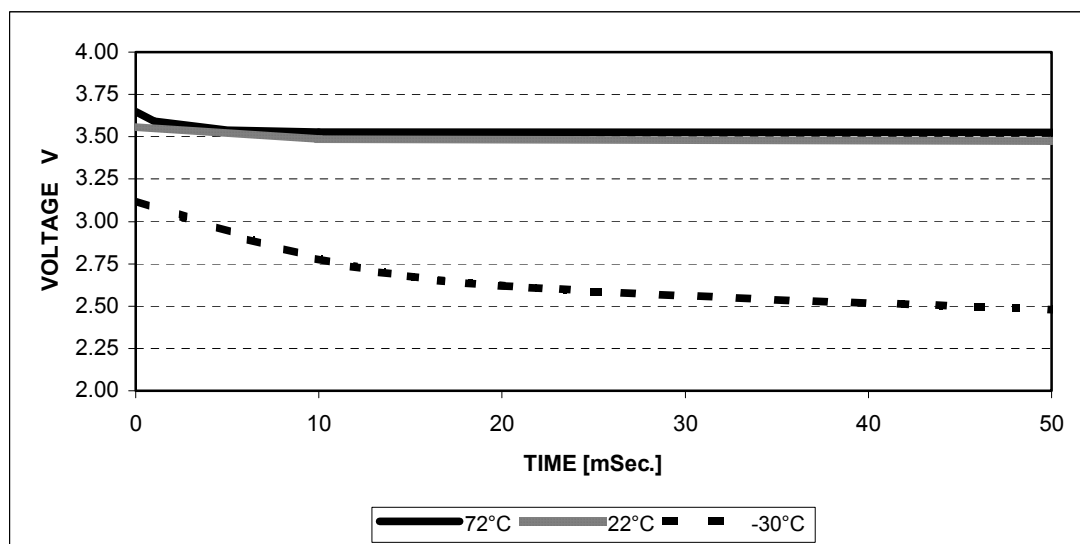


Figure 5: Voltage curves at 72°C, RT and -30°C at 500mA, 50mSec pulse for HLC1520 at 3.67V.

Accelerated storage and operating life

As Tadrian's bobbin type Li/SOCl₂ cells have a very long operating life (up to 10 years), very low self-discharge and very good stabilization of performance with storage time of the HLC are required.

Figure 6 shows the voltage of HLC1520 under 350mA for several pulse durations at -37°C as a function of storage time at 72°C. While on storage, the HLC was being connected to AA/2 Li/SOCl₂ cell. The primary cell was disconnected prior to the pulse 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, it can be seen that even after 51 days storage at 72°C, the HLC can still operate at -37°C with very low voltage degradation at very high discharge rate (7C).

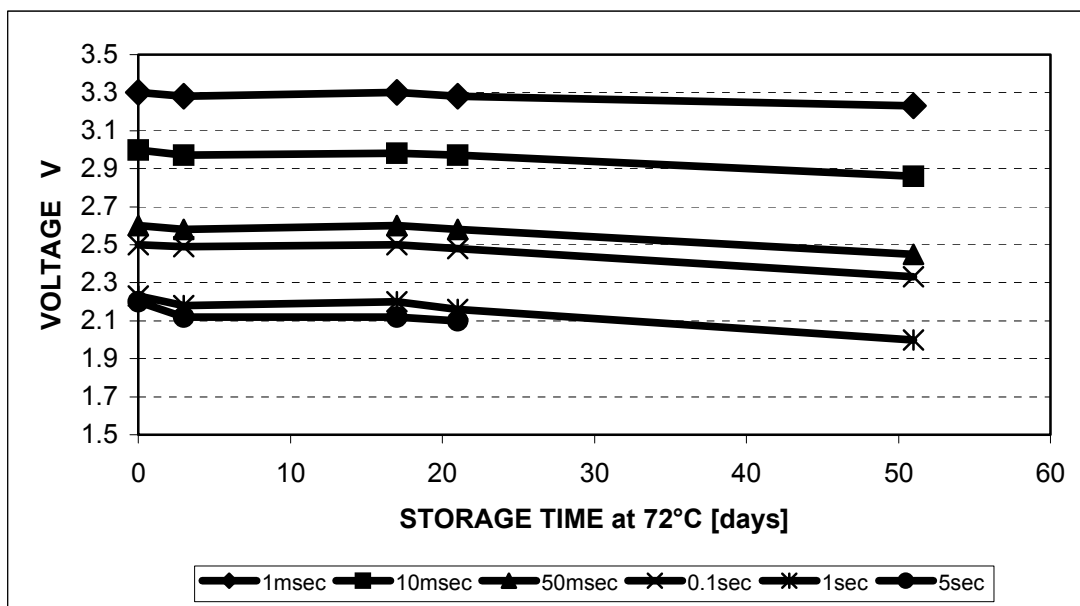


Figure 6: Voltage values at -37°C under 350mA pulse for HLC1520 at 3.67V vs. storage time at 72°C.

In order to evaluate the stability of the Pulses Plus™ battery, HLC1520 electrically connected to AA/2 bobbin type Li/SOCl₂ or Li/SO₂Cl₂ cells and stored at 72°C. Once a week 1 second, 500mA pulse was applied. Figure 7 shows the typical minimum voltage (TMV) for this test as a function of storage time at 72°C. As it can be seen from this figure, excellent TMV stabilization was obtained for both types of batteries during 7.5 months storage at 72°C.

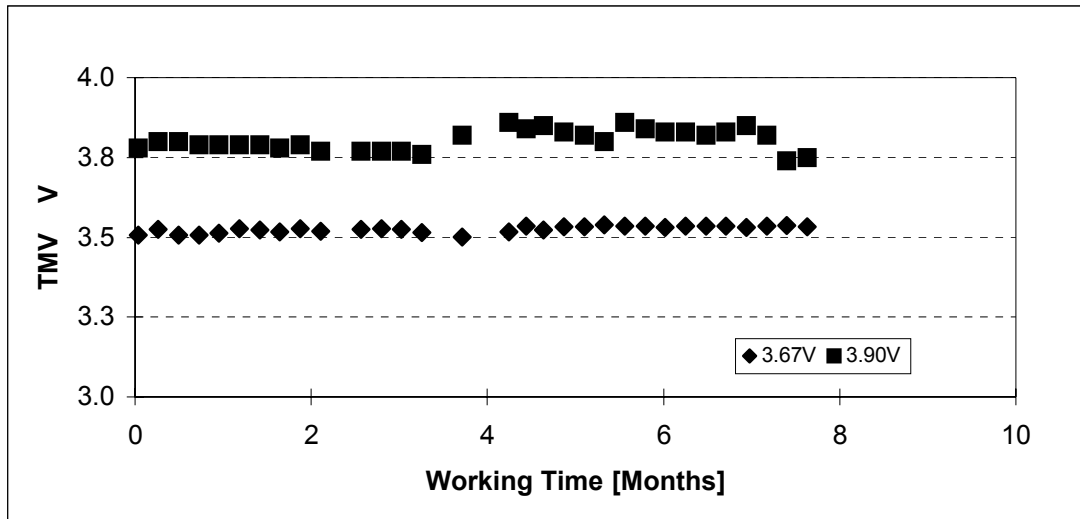


Figure 7: TMV (Typical Minimum Voltage) for Pulses Plus™ batteries Pulsed at 500mA, 1 second at 72°C once a week. The batteries combine HLC1520 together with AA/2 Li/SOCl₂ or Li/SO₂Cl₂.

After 7.5 months of tests at 72°C, the HLC's were disconnected from the primary battery and discharged at RT at 250mA. Discharge curves for the two HLC1520 that were connected to the AA/2 Li/SO₂Cl₂ and the AA/2 Li/SOCl₂ are shown in figure 8. The discharge capacities obtained are 92mAh and 54mAh for 3.90V and 3.67V respectively. The capacities of fresh HLC at the same discharge conditions are 95mAh and 54mAh for 3.90V and 3.67V respectively. So, after storage at the above conditions, the HLC charged to 3.90V lost about 3% of its initial capacity, while the HLC charged to 3.67V did not loss any capacity.

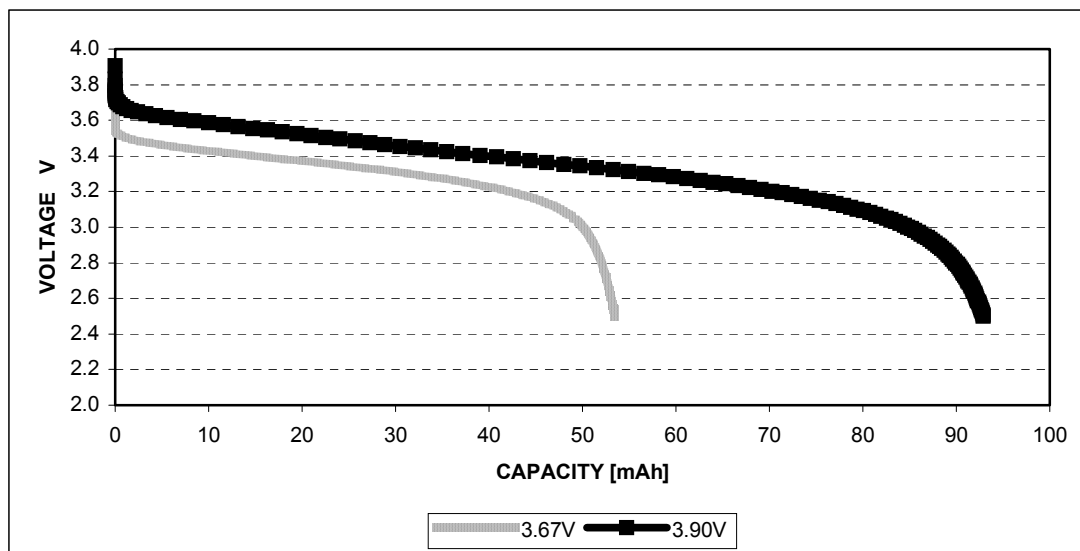


Figure 8: Discharge curve at 250mA, RT for HLC1520 at 3.90V and 3.67V, after 7.5 months storage at 72°C connected to AA/2 Li/SO₂Cl₂ primary cell.

Self-discharge of the HLC

In order to evaluate the self-discharge of the HLC, long term storage at room temperature and at accelerated storage at 90°C were conducted.

After 1-year storage at RT, HLC1520 lost about 10mAh. The average self-discharge current at room temperature calculated for the HLC is about 1µA.

To accelerate the storage time, the self-discharge of the HLC was studied at 90°C: 1520 HLC's were cycled 5 cycles at constant current of 25mA between potential range of 2.75 – 3.90V or 2.75 – 3.67V at RT. After the 5th charge, the cells were stored for 7 days at 90°C, followed by two more charge-discharge cycles. The OCV and the Impedance at 1Khz were measured at RT before and after storage. Table 1 summarizes the results for this test. As it can be seen, the capacity loss after 7 days storage at 90°C was 10mAh for HLC's stored at Li/SO₂Cl₂ potential and 8mAh for HLC's stored at Li/SOCl₂ potential. The self-discharge current at 90°C for the HLC calculated from these results are 60µA and 50µA at 3.90V and 3.67V respectively. All of this capacity loss is reversible, as the capacity obtained at the 6th discharge (after storage) is similar to the 5th charge capacity (before storage).

Several techniques were used in order to evaluate the self-discharge of the HLC when connected to a primary cell⁽²⁾. It was found that the self-discharge of the HLC when connected to a primary cell to form a hybrid battery is lower than that of a single HLC.

Table 1: Storage tests at 90°C for HLC1520 charged to 3.90V and 3.67V.

Charge potential	Before storage			After storage 7d at 90°C			
	5 th charge capacity [mAh]	OCV [V]	Z1khz [ohm]	OCV [V]	Z1khz [ohm]	5 th discharge capacity [mAh]	6 th discharge capacity [mAh]
3.90V	100	3.855	0.16	3.800	0.24	90	98
3.67V	50	3.610	0.20	3.590	0.28	42	50

Pulses Plus™ Battery

In order to demonstrate the energy and power capabilities of the combination of a primary cell and HLC, Pulses Plus™ batteries combines HLC1520 together with AA bobbin type Li/SOCl₂ were pulsed at 100mA to 3V cut-off voltage every 5h at RT. During the 5h, the HLC is charged by the primary cell. Figure 9 shows the pulse capacity as a function of pulses number. The capacity of the first pulse was 60mAh. This capacity decreased and stabilized at about 18mAh. The capacity starts to drop sharply after 100 pulses. This is due to a decrease in the current capability of the primary cell. However, the HLC can still function at 100mA. The total capacity after 200 pulses is 2Ah whereas the total capacity after 1000 pulses (after working time of 6 months) is 2.5Ah: this is the theoretical capacity of the primary cell! The pulse capacity of the last pulse is 1.8A*sec. Post mortem of the primary cell showed completely discharged cell as all the electrolyte was consumed and only traces of lithium were left.

Two main conclusions were drawn from this test:

1. No practical capacity loss was caused by the HLC.
2. The HLC can support the primary cell to deliver all its low rate capacity under high pulse discharge currents.

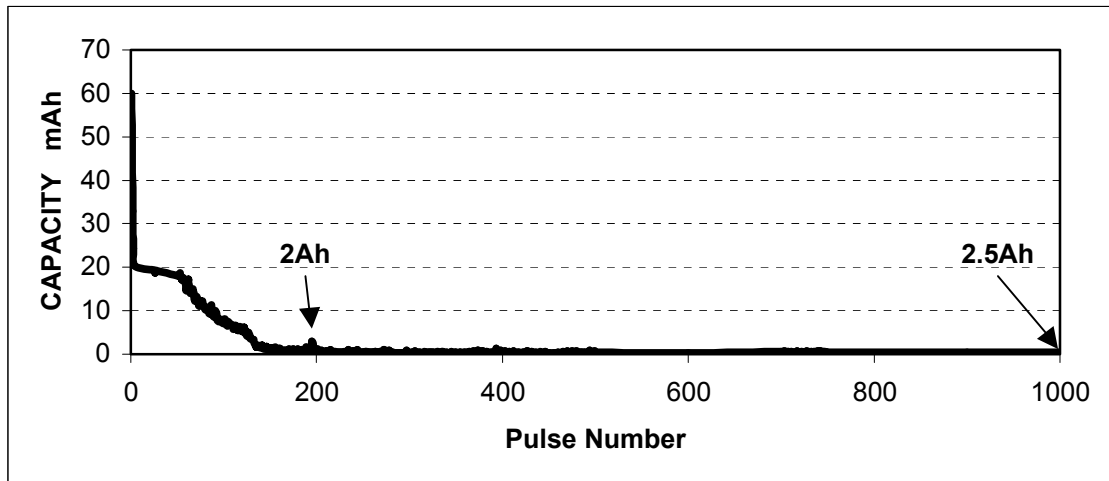


Figure 9: Pulse capacity vs. number of pulses for Pulses Plus™ battery combined of HLC1520 and AA Li/SOCl₂ primary cell. The battery Pulsed at 100mA to 3V cut-off every 5h at RT.

Summary

The Pulses plus™ battery has very high energy and power capabilities. It can operate at very high rates over a wide temperature range down to -40°C . Its self-discharge is very low and long operating life of the battery (more than 10 years) can be achieved. The performance described in this work are improvements by factor of two in the current capability at low temperature and 5 times increase in the pulse discharge capacity at 3.67V in comparison to the previous design⁽²⁾.

These improvements were achieved mainly by electrolyte optimization and cathode material modification.

The improvement in performance can be cost effective as less number of HLC's and/or smaller HLC's are needed to meet a certain application requirements.

References

1. H. Yamin, S. Luski, J. Carmely, E. Elster and M. Shlepakov: "High Energy and Power Densities Pulses Plus™ Battery". The 16th international Seminar on Primary and Secondary Batteries, Fort Lauderdale FL. March 1999.
2. H. Yamin, E. Elster and M. Shlepakov: "Pulses Plus™ Battery System for High Power Applications". The 17th international Seminar on Primary and Secondary Batteries, Fort Lauderdale FL. March 2000.