Hybrid Primary Battery for Applications requiring High Current Pulses

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Abstract

This contribution describes the hybrid PulsesPlus™ primary battery, which comprises of Lithium Oxyhalide system ($Li/SOCl_2$ or Li/SO_2Cl_2) with unique hermetically sealed parallel Hybrid Layer Capacitor (HLC). This hybrid battery combines the advantages of the high energy density, the low self-discharge over wide temperature range and the safety of the bobbin Lithium Oxyhalide system with high pulse power capability. Until now, the high power pulse capability necessitates the use of jelly-rolled cells. In addition, the hybrid PulsesPlus™ battery does not have the passivation phenomenon during storage and during long-term discharge at a wide temperature range.

In this work, we demonstrate the pulse power capability, the low passivation, along with its reliability and safety.

Introduction

The low power version of the Lithium-Oxyhalide (Thionyl and Sulfuryl Chloride) system has the highest gravimetric and volumetric energy densities of all the commercially available systems. Energy densities achieved in the Oxyhalide commercial cells, in their low power, bobbin configuration, are 750 Wh/kg and 1450 Wh/liter [1]. In addition, the bobbin Lithium-Oxyhalide system is manifested by its extremely long life expectancy over a wide temperature range (e.g., low self-discharge and high chemical and electrochemical stability) and by its excellent safety level.

However, due to the low surface area, the rate capability of the bobbin version is relatively low. In addition, the use of the cells in outdoor applications, which expose the cells to extreme temperatures (e.g., -40ºC to 105ºC), decreases further the ability of the cells to deliver high current pulses, due to build up of passivation layer.

Two approaches have been adopted for application that requires high current pulse peak:

1. The use of high surface area primary cells (jelly-rolled configuration). This approach reduces the safety level of the cell, increases self-discharge rate, and decreases the energy density.

2. The alternative approach is to use the bobbin Oxyhalide cells, and to add parallel capacitor. In this case, the parallel capacitor delivers the high current pulse, while the bobbin Oxyhalide cell delivers the energy required.

Electrolytic parallel capacitors are the most commonly used with primary cells. The electrolytic capacitors become bulky when pulse charge exceeds 0.0003 mAh. Parallel super-capacitors are being used to less extent, owing to their relatively high ESR, and high self-discharge especially at high temperatures, which limits the current pulses and the operating life.

Three years ago Tadiran Batteries developed a new battery-based capacitor, HLC, which is capable of supporting the low rate cell during high current pulses. The new HLC capacitor has high energy density, therefore, it is capable of storing high charge values. In addition, the HLC capacitor has low internal resistance and operates over wide temperature range. A comparison between the two conventional types of capacitors and the HLC capacitor is shown below. The HLC capacitor has energy density, which is higher by two orders of magnitude than the conventional capacitors. The cycle life and the power density are given for partial discharge of the HLC capacitor.

Parameter	Electronic capacitor	D.L. capacitor	HLC capacitor
Discharge time	µsec- msec	ms- days	µs-days
Charge time	µsec- msec	ms- minutes	hours
Energy, Wh/L	<0.01	<5	<300
Power, W/L	>10,000	<10,000	>4000
Cycle life	>100 M	<100 M	>1 M

The PulsesPlus™ hybrid battery technology comprises of low-rate bobbin type $Li/SOCl_2$ or Li/SO_2Cl_2 cells with the novel HLC capacitor.

Suitable applications for the PulsesPlus™ hybrid battery are: portable defibrillators, GPS tracking devices, oceanographic transponders, emergency call systems and the like.

The present article deals with power capability of the PulsesPlus™ battery, the lack of passivation, the reliability of the battery operation over wide temperature range, and the safety aspects.

Experimental

Since the HLC capacitor is combined with Oxyhalide system, they should have the capability of operating over a wide temperature range, low self-discharge and same level of safety and reliability. The HLC capacitors are hermetically sealed, similar to Tadiran Oxyhalide cells.

The charge delivering capability of the HLC capacitor, during the current pulse, is determined by its size and by the voltage across its terminals. Tadiran provides either Sulfuryl chloride cells with 3.9V or Thionyl chloride cells with 3.7V. Generally, at 3.9V the capacitor stores about 4 times the capacity of the 3.7V capacitor. Three sizes of cylindrical capacitors are available:

	HLC-14200	HLC-14500	HLC-18500
Capacity- 3.9V	0.10 Ah	0.40 Ah	0.70 Ah
Capacity- 3.7V	0.02Ah	0.10Ah	0.2Ah
Diameter, mm	14	14	18
Height, mm	20	50	50
S.D at 25ºC, µA	1	2	4

The total capacity that can be delivered by the PulsesPlus™ hybrid battery is determined by the capacity of the Oxyhalide cells in the battery. Tadiran Batteries provides cells having capacities ranging from 1Ah for 1/2AA cell to 35Ah for DD size cell. Parallel and serial combinations of cells can further increase the capacity and the voltage of the battery.

Results

1. Power capability

Figure 1 shows the voltage-time curves of HLC-14500 capacitor discharged at currents of up to 15A. The power capability at this rate is 5000 W/L, and the total energy delivered at 15A is 25 mWh (90 joules).

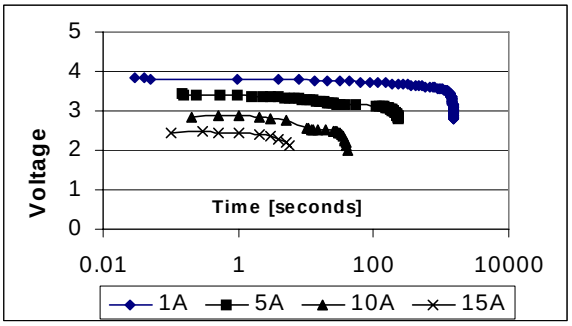

Figure 1: RT Voltage–time curves of HLC-14500

Figure 1 shows that the discharge voltage of the HLC capacitor, at each current, is very stable and does not drop below 2.0V (for 15A). This voltage stability distinguishes the HLC capacitor compared with common electrolytic and D.L. capacitors.

Figure 2 shows pulse capability of PulsesPlus™ battery, comprising low-rate AA Li/SO_2Cl_2 cell (TL-6903) with parallel HLC-14500 to deliver a train of 10A/1s pulse every 10 seconds.

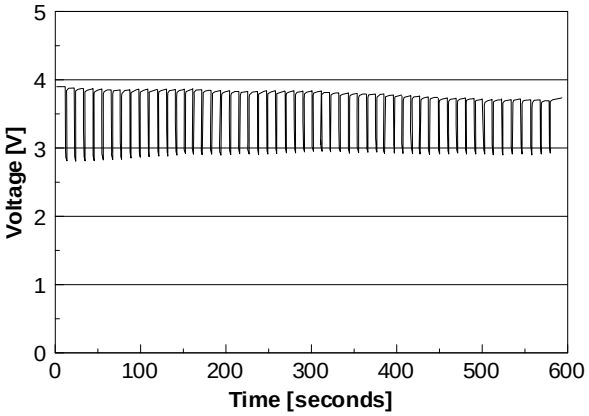

Figure 2: Pulse train of 10A/1s pulses every 10s, delivered by AA Li/SO_2Cl_2 and HLC-14500.

Figure 2 shows that the HLC-14500 capacitor can deliver a train of 10A/1s pulses with minimum voltages above 2.85V. In addition, no voltage delay can be practically seen at the start of these high pulses. The trend of increasing minimum voltages during the late pulses is caused by temperature rise inside the battery due to the high power pulses.

2. Reliability at elevated temperatures

The reliability of common capacitor is tested by placing the capacitors at elevated temperatures, usually for several thousands of hours at 70ºC [2].

This time scale is not sufficient for testing the reliability of PulsesPlus™ hybrid battery, which ought to operate for 10 years, partially at temperatures as high as 100ºC. This requires testing on a scale of ten thousands of hours at elevated temperatures.

Figure 3 shows the behavior of PulsesPlus™ hybrid battery that consists of low-rate AA size Li/$SOCl_2$ (TL-5903) with parallel HLC-14500 capacitor at 80ºC. The battery is being discharged by weekly pulses of 500mA/1s. The CCV (TMV) values, are the minimum voltages during the current pulses.

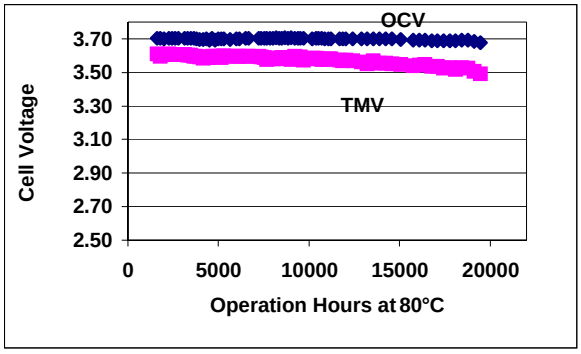

Figure 3: OCV and CCV (TMV) during weekly 500mA/1s pulses, at 80ºC. AA size Li/$SOCl_2$ (TL-5903) in parallel with HLC-14500 capacitor.

Figure 3 shows that the PulsesPlus™ hybrid battery is relatively stable for about 20,000 hours at 80ºC.

The voltage distance between the OCV and CCV curves in Figure 3 is proportional to the internal resistance of the battery. The resistance value obtained is 0.20Ω, reaching 0.37Ω after 20,000 hours at 80ºC.

Figure 4 shows the discharge of PulsesPlus™ that consists of DD size Li/$SOCl_2$ cell (TL-5137) and parallel HLC-14200 capacitor, at 125ºC. The battery was discharged at 350ma/1.4s every 5s (average discharge current is 100ma).

The minimum voltage values during the pulses in Figure 4 are higher than 3.4V. The battery delivered 22.5Ah up to a 3V cut-off voltage, through 220,000 pulses.

In order to test the production reliability of the HLC capacitors, 100 HLC-14200 capacitors from 5 lots, were tested at 85ºC, with a weekly 250ma/1s pulse. Half of the capacitors were

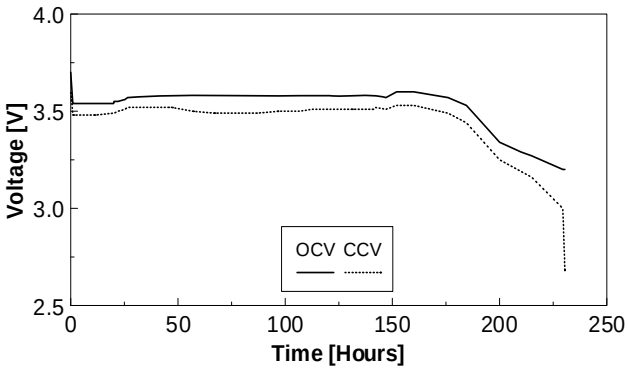

Figure 4: OCV and CCV during 350ma/1.4s pulses every 5s, at 125ºC, of DD size Li/$SOCl_2$ in parallel with HLC-14200 capacitor.

connected to AA size Li/$SOCl_2$ (TL-5903) and the other half to AA size Li/SO_2Cl_2 cells (TL-6903). Figure 5 presents the average, the minimum and maximum CCV values during the pulse of all cells.

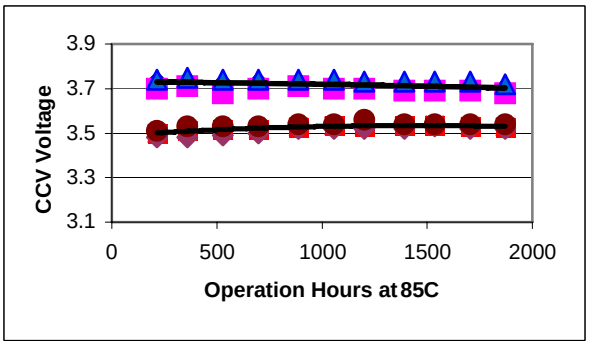

Figure 5: CCV at 250ma/1s weekly pulse, of 50 AA Li/$SOCl_2$ (lower) and 50 AA Li/SO_2Cl_2 cells (higher), in parallel with HLC-14200 capacitor, at 85ºC. The maximum and the minimum CCV values are shown above and below the average CCV values presented by thick curve.

Figure 5 shows that all the 100 batteries behave in a consistent and uniform way, for over 2,000 hours at 85ºC.

3. Self-discharge

Since PulsesPlus™ battery operates as a stand-alone power source, the self-discharge of the battery is a crucial characteristic for long-term applications. The behavior of the PulsesPlus™ hybrid battery at high temperature as was shown above, points to its low self-discharge characteristics.

PulsesPlus™ hybrid battery consisting of AA Li/$SOCl_2$ (TL-5903) with parallel HLC-14500 capacitor that was continuously discharge at a 33kΩ load with weekly 500ma/1s pulse delivered 2.19Ah (27 months). This capacity represents battery maximum self-discharge current of 9.2μA (2.6μA for the HLC and 6.6μA for the Li/$SOCl_2$).

Self-discharge value obtained for the HLC-14500 capacitors from microcalorimeter measurement is 1.2μA [3].

The self-discharge results indicate that the self-discharge rates of HLC capacitors are lower than that of the Oxyhalide cells.

4. Passivation

The results given in Figure 2 indicated that the PulsesPlus™ hybrid battery consisting of AA Li/SO_2Cl_2 cell (TL-6903) and HLC-parallel 14500 capacitor shows no voltage delay even at the 10A pulse.

Figure 6 shows the initial part of the 1.5A pulse at –25ºC on microseconds scale (25μs per division). Upper curve is the battery voltage while the lower curve is the initial part of the current pulse. Figure 6 shows that the voltage curve practically follows the current pulse curve, with no voltage delay. The voltage of the battery after 100μs is 3.4V.

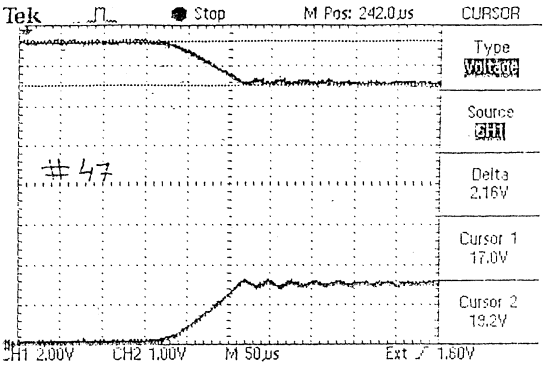

Figure 6: Voltage curve (upper) during the initial part of 1.5A pulse at –25ºC. Time scale is 25μs per division.

5. Safety

We have tested several types of PulsesPlus™ hybrid batteries under abusive conditions, including: crush tests, short circuits at RT and 72ºC, heating to 150ºC, shock and vibrations charging and over discharge. All the batteries showed no safety problem.

The extensive safety and environmental tests program indicated that the safety of the HLC capacitors is similar to that of the bobbin low rate Oxyhalide system.

Conclusions

The data presented show that the combination of low-rate bobbin Oxyhalide system with HLC capacitor, could be a viable alternative to jelly-rolled high power cells, for applications requiring high power pulses for long operation periods, and wide temperature range.

Power density as high as 5000 W/L can be achieved during the pulse currents.

The PulsesPlus™ hybrid batteries show practically no passivation during high power pulses and at low temperatures.

The HLC capacitor has lower self-discharge rate than the Oxyhalide cells of the same size.

The safety level of the PulsesPlus™ hybrid battery family is similar to that of the low-rate bobbin Oxyhalide system.

References

1. H. Yamin, M. Shlepakov, E. Elster and D. Shapira, The 16th International Seminar on Primary and Secondary Batteries, Fort Lauderdale, Florida, 1996

2. M. Aoki, K. Sato and Y. Kobaysahi, 3rd International Seminar on Electrochemical Capacitors and Similar Energy Devices, Fort Lauderdale, Florida (1993).

3. H. Yamin, E. Elster and M. Shlepakov, The 17th International Seminar on Primary and Secondary Batteries, Fort Lauderdale, Florida, 2000.