High Power, Gel Polymer Lithium-Ion Cells with Improved Low Temperature Performance for NASA and DoD Applications

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Abstract:

Both NASA and the U.S. Army have interest in developing secondary energy storage devices that are capable of meeting the demanding performance requirements of aerospace and man-portable applications. In order to meet these demanding requirements, gel polymer electrolyte-based lithium-ion cells are being actively considered, due to their promise of providing high specific energy and enhanced safety aspects. In pursuit of these objectives, high rate, gel-polymer lithium-ion cells from Compact Power, Inc. (Monument, CO) are being actively evaluated to determine their applicability to meet ARMY and NASA needs. These cells, consisting of $LiMn_2O_4$ cathode material, graphite anode material, and a proprietary gel polymer electrolyte, were primarily developed to target the automotive industry (EV and HEV applications). In addition to evaluating baseline cells, a number of prototype cells were fabricated with the incorporation of a low temperature liquid electrolyte developed at JPL, consisting of 1.0 M $LiPF_6$ EC+DEC+DMC+EMC (1:1:1:3 v/v), which was impregnated into the polymer matrix. To evaluate the performance of these cells, a number of characterization tests were performed including: determining the rate capacity as a function of temperature (both charge at room temperature and low temperature), the cycle life performance (both 100% DOD and 30% DOD LEO), the pulse capability, and the impedance characteristics at different temperatures.

Keywords: Lithium-ion high-power cells; Gel polymer electrolytes; Low temperature electrolytes.

Introduction

NASA and DoD possess similar performance requirements for energy storage devices and share a common interest in developing the needed technology to meet their applications.[1] Perhaps the most challenging of these requirements is the ability to successfully operate over a wide temperature range. For military applications, the energy storage device should be capable of operating from –40° to + 70°C, whereas, for unmanned planetary exploration the desired range of operation is from –40° to +40°C. In addition to displaying the ability to operate over a wide temperature range, other performance attributes that are desireable include high energy density, high specific power, and long life. More specifically, the U.S. Army Land Warrior Program is targeted at obtaining cost effective, high energy density batteries and hybrid power sources for training and dismounted soldier applications.[2] NASA is interested in enabling future Rover and Lander missions which require batteries that can operate at temperatures as low as -40°C and planetary Penetrators that require operation at temperatures as low as -60°C.[3] In addition to extreme operating temperature requirements, high specific energy (>60 Wh/Kg) and long cycle life (< 500 cycles) are generally necessary for these applications.

In order to meet these demanding requirements, gel polymer electrolyte-based lithium-ion cells are being actively considered, due to their promise of providing high specific energy and enhanced safety aspects. In pursuit of these objectives, high rate, gel-polymer lithium-ion cells from LG Chem/Compact Power are being evaluated to determine their applicability to meet ARMY and NASA needs. [4] These cells, consisting of $LiMn_2O_4$ cathode material, graphite anode material, and a proprietary gel polymer electrolyte, were primarily developed to target the automotive industry. In addition to evaluating baseline cells, a number of prototype cells were fabricated with the incorporation of a low temperature liquid electrolyte developed at JPL [5,6], consisting of 1.0 M $LiPF_6$ EC+DEC+DMC+EMC (1:1:1:3 v/v %), which was impregnated into the polymer matrix.

To evaluate the performance of these cells, a number of characterization tests were performed including: determining the rate capacity as a function of temperature (both charge at room temperature and low temperature), the cycle life performance (both 100% DOD and 30% DOD LEO), the pulse capability, and the impedance characteristics at different temperatures.

Experimental

A number of 7 Ahr prismatic, pouch design cells were fabricated by Compact Power, Inc. (LG Chem), consisting of $LiMn_2O_4$ cathode material, graphite anode material, and a proprietary gel polymer electrolyte and delivered to JPL for performance characterization. As mentioned above, these cells possessed two different liquid electrolytes including a baseline electrolyte and a low temperature ethylene carbonate (EC)-based quaternary electrolyte. The cells were evaluated in terms of: i) the room temperature rate capability; ii) cycle life performance at room temperature (30% DOD low-earth-orbit [LEO] test and 100% DOD test), iii) the discharge characteristics at low temperature (with both charging at room temperature and at low temperatures), iv) the impedance characteristics over a wide temperature range, and the v) polarization behavior of the cells as a function of temperature. Charge-discharge measurements and cycling tests were performed with a Maccor battery cycler. A Tenney environmental chamber was used to maintain the desired temperature within $\pm 1^{\circ}C$ for the cells.

Cycle Life Performance

The first batch of cells fabricated and delivered to JPL, consisting of the baseline electrolyte formulation (Jan. 2002) in a high-power cell design, were subjected to a number of generic performance characterization tests with the intent of evaluating their attributes over a wide range of conditions. As illustrated in Fig. 1, excellent cycle life performance was obtained when the cells were tested according to a standard 100% DOD test regime (C/5 charge to 4.1V and C/5 discharge to 3.0V) at room temperature. As shown, the cell has completed over 1600 cycles with minimal capacity fade (0.010 %/cycle), corresponding to over 83% of the initial capacity (~88% @ cycle #1,000). During the course of this test, very stable performance continues to be observed with high columbic efficiency (>99%) and excellent watt-hour efficiency (98.4%) delivered after 1600 cycles have been delivered (over 2 years of operation).

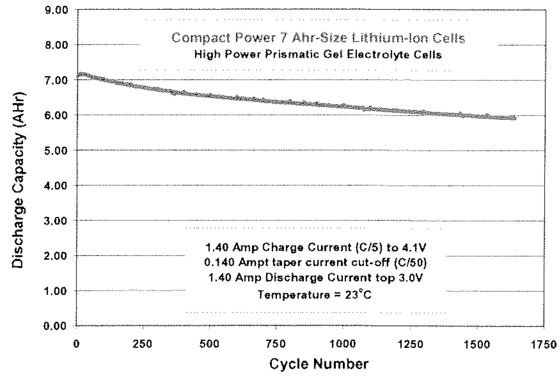

Figure 1. Room temperature cycle life (100% DOD) performance of 7 Ahr cells with the baseline electrolyte.

In addition to evaluating the performance under 100% DOD conditions, cells were also subjected to 30% DOD low-earth-orbit (LEO) cycle life testing to determine the viability of the technology to meet the requirements of planetary orbiter applications. This test consists of a 60-minute charge period (0.4C inrush charge current to 4.0V) and a 30-minute discharge period (0.6C discharge rate). As illustrated in Fig. 2, excellent performance has been obtained to-date with over 10,000 cycles being delivered with minimal decay in the end of discharge voltage observed (~ 132 mV). Throughout this test, 100% DOD capacity checks have been performed, to determine the loss in capacity as a result of cycling, with over 81% of the initial capacity being realized after 10,000 cycles.

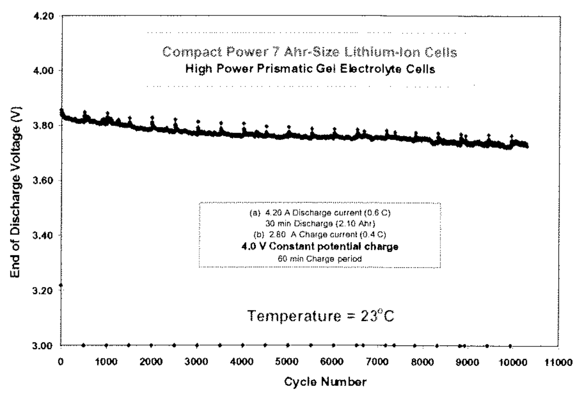

Figure 2. Low-earth-orbit (LEO) cycle life (30% DOD) performance of 7 Ahr Compact Power cells.

Discharge Characteristics at Low Temperature

Since many of NASA missions require good performance at low temperature, emphasis was placed upon evaluating the discharge characteristics of the cells at low temperatures (-20 to –60°C), using conditions of charging at both ambient and low temperatures. When the rate capability of one of the cells containing the JPL quaternary liquid electrolyte, impregnated into the gel matrix polymer, was evaluated at –20°C (with both charge and discharge performed at low temperature), good performance was obtained with over 94% of the room temperature capacity delivered at a C/2 rate (6.636 Ahr). In order to obtain full state of charge prior to discharge, long charge periods were necessitated due to the low temperatures, a characteristic typically displayed by most lithium-ion cell chemistries and designs. Improving the charge acceptance characteristics, especially at low temperature, remains to be a focus of future development. Excellent performance was also obtained at –30°C, with over 76% of the room temperature capacity being delivered using a C/2 discharge rate (3.50 A), with the cell also being charged at low temperature.

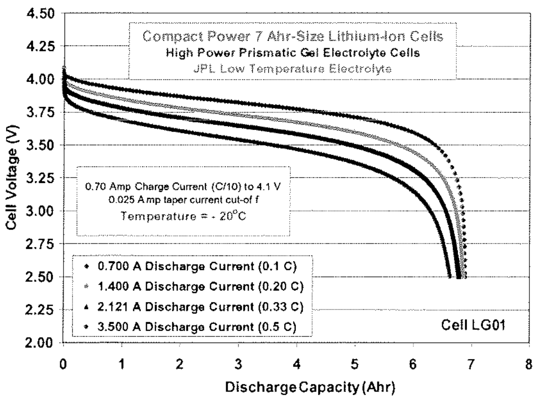

Figure 3. Discharge capacity as a function of discharge rate at –20°C of a 7 Ah cell containing 1.0 M $LiPF_6$ EC+DEC+DMC+EMC (1:1:1:3 v/v).

For temperatures below –30°C, the discharge characterization tests were performed utilizing a room temperature charge methodology, due to the slow charge kinetics and the possibility of lithium plating occurring, which can lead to premature cell degradation.[7] As illustrated in Fig. 4, when a cell was charged at room temperature and discharged at –40°C, excellent capacity was delivered using a C/10 discharge rate with nearly full capacity (>99% of the room temperature value) being delivered when a low end-of-discharge voltage is used. In addition, over 94% of the room temperature capacity is delivered using a C/5 discharge rate, with a substantial portion of the capacity being delivered with an operating cell voltage of above 2.50V. Good performance was also obtained at temperatures as low as –50 to –60°C, albeit using lower rates (C/20-C/50).

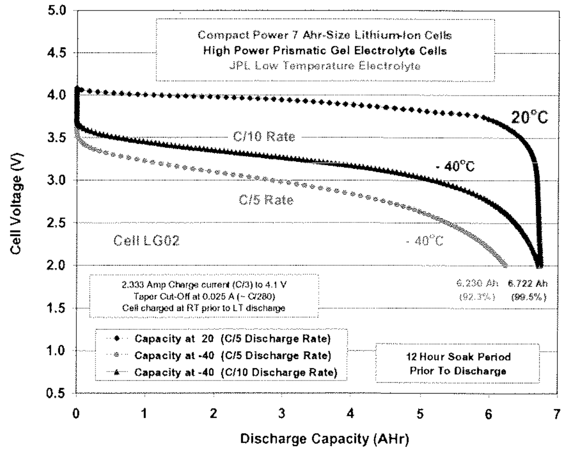

Figure 4. Discharge capacity (Ahr) of a 7 Ah cell containing 1.0 M $LiPF_6$ EC+DEC+DMC+EMC (1:1:1:3 v/v %) electrolyte at –40°C using C/5 (1.40A) and C/10 (0.70 A) discharge rates.

High Rate and Pulse Capability at Various Temperatures

In the course of our studies, we also placed emphasis upon evaluating the high rate and pulse discharge characteristics as a function of temperature. As illustrated in Fig. 5, good high rate capability was obtained with the cells containing the quaternary low temperature electrolyte at ambient temperatures, with nearly full capacity being delivered at a 6C rate (42A). A notable aspect of these findings is that the results were obtained on an aged and cycled cell, and even better performance is anticipated with a fresh cell in which the impedance growth is minimized.

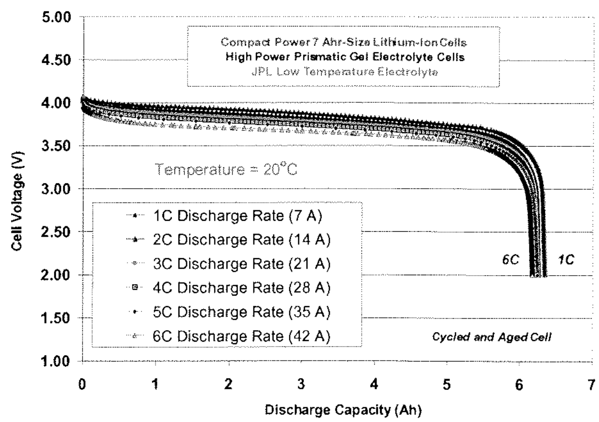

Figure 5. Discharge capacity (Ahr) of a 7 Ah cell containing 1.0 M $LiPF_6$ EC+DEC+DMC+EMC (1:1:1:3 v/v %) electrolyte at 20°C using high discharge rates (C rate to 6C rate).

In addition to evaluating the performance of the cells under continuous discharge conditions, effort was focused upon determining the pulse discharge characteristics at various temperatures and state-of-charge. As illustrated in Fig. 6, excellent pulse rate capability was demonstrated at temperatures as low as –30°C, in which 5C pulses (each 2 seconds in duration) are supported at various states-of-charge (100, 80, 60, and 50% SOC). This test helps to illustrate that the technology has great promise to support hybrid electric vehicle applications, specifically demonstrating the capability to provide adequate "cold-cranking" performance at low temperature.

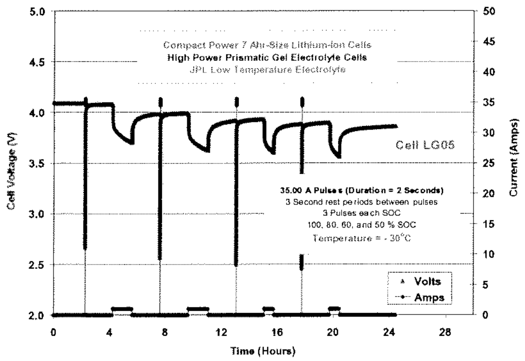

Figure 6. High rate pulse discharge performance at –30°C of a 7 Ah cell containing the 1.0 M $LiPF_6$ EC+DEC+DMC+EMC (1:1:1:3 v/v %) electrolyte.

Conclusions

In this paper, we have evaluated high rate, gel-polymer lithium-ion prototype cells (fabricated by Compact Power, Inc) to determine their viability for a number of NASA and DOD applications. We have demonstrated that the cells possess: i) good cycle life performance (100% and 30% DOD), ii) excellent discharge characteristics at low temperature, and iii) excellent pulse discharge behavior over a range of temperatures. With cells containing a low temperature quaternary electrolyte formulation, excellent performance was obtained at –40°C using a C/10 discharge rate (room temperature charge), with nearly full capacity being delivered. Excellent high rate pulse discharge behavior was also observed over a wide range of temperatures, with 5C pulses being able to be supported at temperatures as low as –30oC. In addition to the studies described, a number of current-interrupt impedance measurements have been performed as a function of temperature in an attempt to further understand the factors governing the performance, especially at low temperatures.

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