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Development of true prismatic lithium-ion cells for high rate and low temperature applications

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Abstract

Lithium-ion cells are presently being considered for use in a wide range of aerospace applications. Cells for these aerospace applications, such as F-16 and JSF aircraft, are required to operate at rates up to 15 C and at temperatures from −40 to 71°C. To address these requirements, a series of experiments has been undertaken to empirically determine those factors that limit performance. The first experiment compares three different electrode weight loadings and two different anode particle sizes. A chemistry identified from this experiment was able to increase room temperature rate capability by >500%. Pulse discharge rates as high as 70 C and continuous discharge rates of 20 C were demonstrated. Furthermore, cell performance of 1 C at −40°C and 4 C at −30°C has been demonstrated.

A second experiment evaluated the use of non-solid/electrolyte interface (SEI) forming conductive diluents in the anode. This experiment did not identify any advantages to the conductive diluent at temperatures above −20°C. However, at a discharge rate of 1 C at −40°C, the group with the highest level of diluent offers 300% more capacity than the baseline experimental group with no non-SEI forming diluent.

Keywords: Lithium-ion batteries; Electrolytes/non-aqueous

1. Introduction

The majority of research performed in the advancement of lithium-ion chemistry has concentrated on improving aspects of performance for commercial applications such as cellular phones and laptop computers. These devices typically operate at moderate temperatures and rates. In such applications, the primary goal has been to maximize capacity through improvements in the specific capacity of the active materials. However, for some applications it is not the capacity of the battery that is the limiting factor. Specifically, for several aerospace applications the driving force in the sizing of a proposed battery has not been the total energy required, but rather the high discharge power. Batteries with 2–20 times the total required energy, and thus, size have been necessary to support the power requirements.

Whenever the discharge rate, and not the actual rated capacity, drives the cell design, those chemistry changes that may reduce capacity, but increase rate capability, are being evaluated.

The first experiment presented in this paper compares anode particles of 6 μm average size to those with an average size of 10 μm. In addition, several other experimental lots that varied the ratio of anode material to cathode material were constructed. A second experiment evaluated the use of very high amounts of silver powder as a conductive diluent in the anode. The specific selection of these first two experiments was based on previous work [1] done by Lithion in the evaluation of candidate chemistries for the MSP01 Mars Lander program. The results presented in this paper are a continuation of the work presented at the San Diego SAE meeting in November 2000 [2].

2. Experimental

For both experiments discussed in this paper the cells were constructed using a true prismatic design with a nominal capacity, for the baseline chemistry, of approximately 7 Ah. The baseline chemistry is that which was developed and qualified for the MSP01 Mars Lander battery. In order to minimize experimental variation, all cells within each experiment used cathodes and anodes that came from the same slurry mix. All electrode coating was also per-

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formed on the same day. For both experiments, all of the cells used the ternary electrolyte, 1 M $LiPF_6$ in 1:1:1 EC:DMC:DEC, utilized for the Mars 2001 Lander project. All electrical testing on the cells was also performed concurrently, with all cells on the same test system and in the same temperature chamber. The only exception to this was the very high rate cycling for which there were insufficient channels to test all of the cells concurrently.

The first experiment evaluated three different electrode weight loadings. The electrode weight loadings were equally spaced and are referred to as *Medium*, *Low*, and *Very Low*. In addition, two different MCMB particle sizes were evaluated: 6 and 10 μm. This portion of the experiment was fully factorial so all electrode weight loadings were evaluated at both anode particle sizes for a total of six experimental lots. All experimental lots consisted of three individual cells. This first experiment also evaluated the effect of varying the ratio of anode to cathode materials. Specifically, increased ratios of anode to cathode were varied up to approximately twice the baseline ratio. This latter portion of the experiment was added in to evaluate the hypothesis that the anode SEI layer is the limiting factor in low temperature discharge performance. By having "extra" anode, the current density through the anode SEI would be decreased by a factor commensurate with the amount of "extra" anode.

Also based upon previous work performed at Lithion, a second experiment was conducted to evaluate the use of a new type of conductive diluent in the anode. While carbon diluents have been evaluated in the past, these materials still form an SEI layer that somewhat reduces their surface electrical conductivity. Low levels of silver have reportedly [3] been added to the anode by several manufacturers. The major difference is that the quantity of silver used in this experiment was as much as 25,000% higher than levels reported in other manufacturers' cells. At these levels, some degree of alloying is expected. In this experiment, silver powder was added to the anode slurry during the mixing operation. Since the performance of carbon diluents is a function of particle size, as well as other aspects, the same was assumed to be true for the silver diluent. Thus, three different silver particle sizes were evaluated. The smallest size was evaluated at three levels while the two larger particle sizes were evaluated only at the central level. A baseline lot, containing no silver, was also constructed. As with the other experiment presented in this paper, three cells per experimental lot were constructed.

3. Results and discussion

For reference, some of the initial results, presented previously, are given below. The majority of the discussion concerning the first experiment is centered on Lot 1 through Lot 6. The layout of these lots is given in Table 1. Fig. 1 shows how the cell capacity varied with electrode weight loading. The capacities shown in Fig. 1 are those used to determine the C rate of cells. In most tests, however, the cells were cycled at the same current, regardless of initial capacity. This latter situation more closely resembles the real world requirements to which the cells would be exposed.

Since the cell dimensions were held constant, and not cell capacity or electrode surface area, the lower weight loadings have lower capacity and higher electrode surface area. The capacity drop from the medium weight loading to the low weight loading is approximately 8%. The capacity drop

Table 1
Experiment layout

	10 μm anode	6 μm anode
Medium loading	Lot 1	Lot 4
Low loading	Lot 2	Lot 5
Very low loading	Lot 3	Lot 6

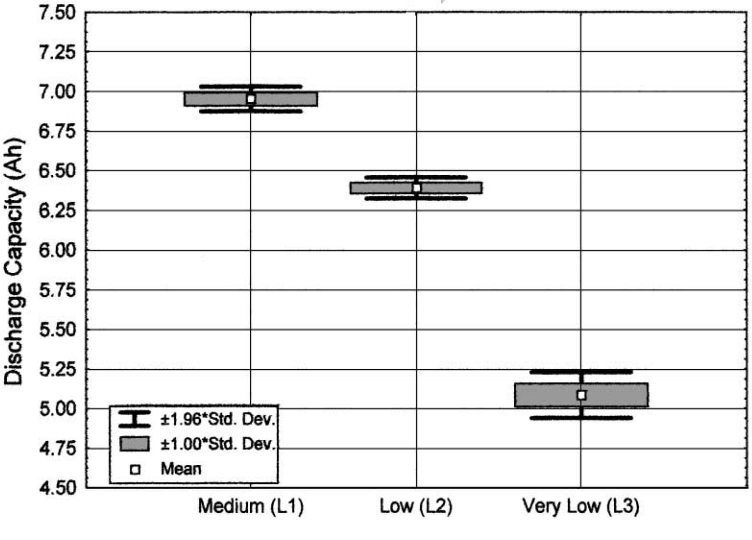

Fig. 1. Capacity at the C/10 discharge rate for the three weight loadings.

Table 2
Lots 1–6[a]

	Cathode surface area (cm^2)	Cell mass (g)
Lots 1 and 4	2700	220
Lots 2 and 5	3500	218
Lots 3 and 6	5700	228

[a] Cell masses and surface areas.

from the low weight loading to the very low weight loading is approximately 18%. Both of these values are in excellent agreement with the theoretical capacities based upon equally sized reductions in loading between the lots. The surface areas and cell masses for first six lots, those in which the ratio of anode to cathode material was held constant, are given in Table 2.

A 25°C voltage profile for a discharge rate of 20 A is given in Fig. 2. Since all cells were discharged at the same rate, the 20 A discharge rate corresponds to between 3 and 4 C, depending on the specific lot. The current density is approximately 7 mA cm^{-2} for the medium weight loading, 6 mA cm^{-2} for the low weight loading, and <4 mA cm^{-2} for the very low weight loading. As can be seen in Fig. 2, the lighter weight loadings do not offer any advantage in capacity even up to the 3–4 C discharge rate.

A full statistical analysis of the results at 20 A reveals that the discharge capacity is a strong function of weight loading (*P*-value approaching 0) with the heavier loadings being preferred. However, when either average voltage or energy efficiency is evaluated, the lots with the lighter weight loadings offer statistically significant improvements.

Fig. 3 shows a marginal means plot, with a 95% confidence interval, that shows the lots with the highest weight loadings have a 33% lower energy efficiency. This implies that the lighter weight loading cells would be of interest for very large cells, if heat generation needed to be minimized.

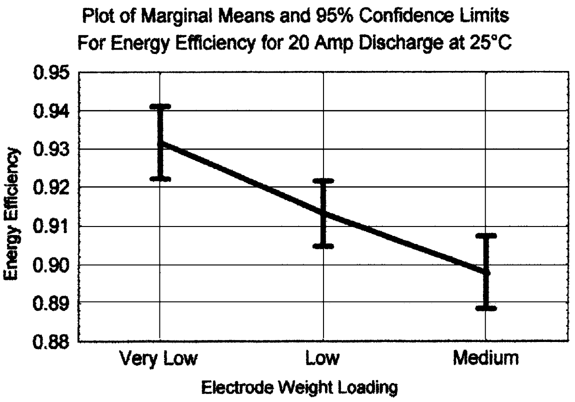

Fig. 3. Energy efficiency for 20 A discharge from the three different weight loadings.

Fig. 4 shows a rate capability plot for the MSP01 Mars Lander cells. This testing was performed at 25°C. This figure shows acceptable performance up to a 5 C discharge rate.

This is well above what is typically obtainable from commercially available cells. In-house testing revealed that

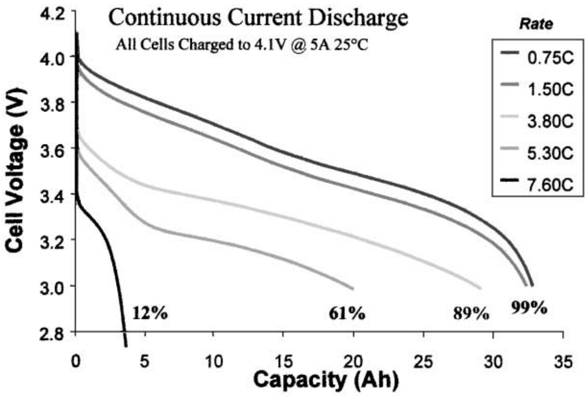

Fig. 4. Discharge capability of baseline chemistry.

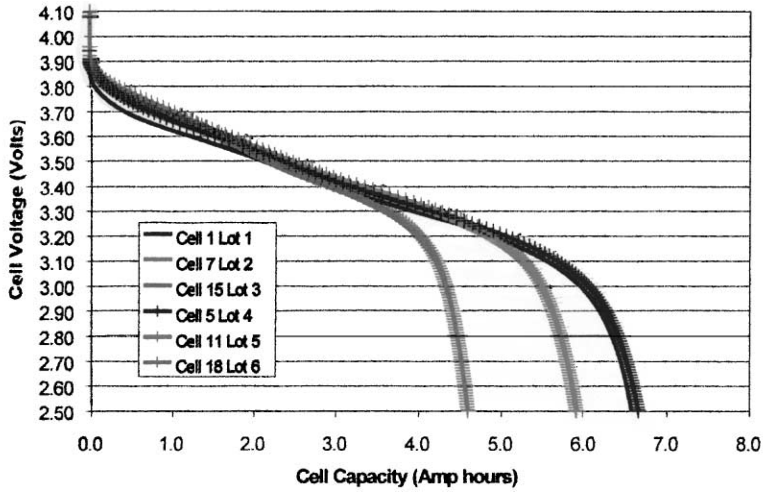

Fig. 2. Voltage profiles for 20 A discharges at 25°C. Highest (Ah): Lots 1 and 4; lowest (Ah): Lots 3 and 6.

the best commercial cells had acceptable performance at discharge rates up to 2.5 C.

Fig. 5 shows the discharge voltage profile for the six lots when subjected to a 50 A continuous discharge between a 7 and 10 C discharge rate, depending on the experimental lot. The current densities are 18 mA cm^{-2} for the medium weight loading cells, 14 mA cm^{-2} for the low weight loading cells and only 9 mA cm^{-2} for the very low weight loading cells. In comparing Figs. 4 and 5, there is excellent agreement between the MSP01 cells and the control cells (Lot 1) constructed with the same chemistry. Both cells show approximately 15% capacity for a 7 C (18 mA cm^{-2}) load.

Fig. 5 clearly shows that the weight loading is the most significant factor in obtaining high discharge rates at 25°C. The experimental lots with the 6 μm cells showed only marginally improved performance compared to their 10 μm counterparts. When the Lot 6 cells were subjected to a 18 mA cm^{-2} continuous discharge load, the cells did not perform as would be expected given the performance of the Lot 1 and Lot 4 cells at this current density. Based upon Fig. 5, the anticipated capacity above 2.7 V would be only 15%. The 13 (75 A) and 18 mA cm^{-2} (100 A) results are shown in Fig. 6.

The Lot 6 cells, at a discharge current density of 18 mA cm^{-2}, or 100 A, delivered in excess of 85% of initial capacity. The true fraction of capacity is somewhat higher since over 200 ‘‘other’’ cycles had occurred after the initial capacity value of 4.9 Ah was determined. A value >90% is more appropriate. The comparable continuous discharge current density of 18 mA cm^{-2} for the baseline chemistry and the Lot 6 cells clearly shows that the Lot 6 chemistry is not limited to the same current density as the baseline cells. This is a result of the decreased electrode thickness with the lighter weight loadings. A useful comparison tool is to

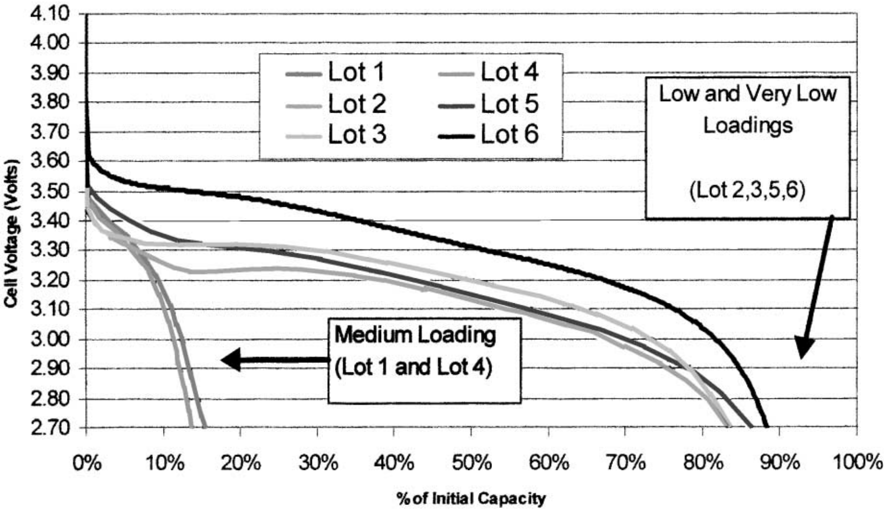

Fig. 5. Voltage profiles for 50 A discharges at 25°C from the six lots.

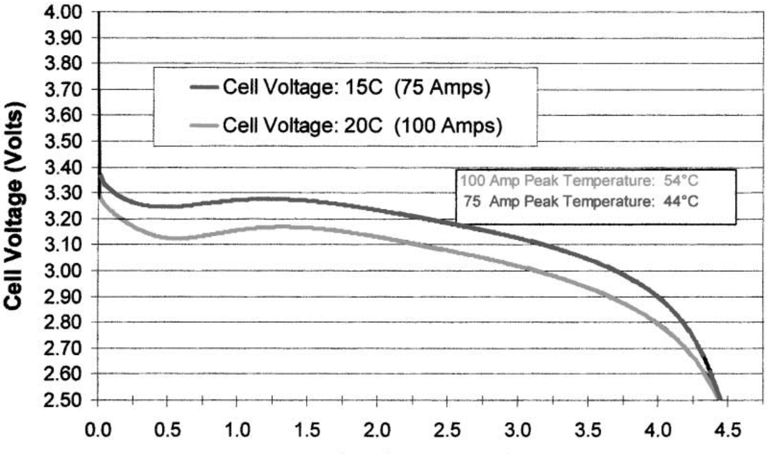

Fig. 6. Voltage profiles for 75 and 100 A continuous discharges.

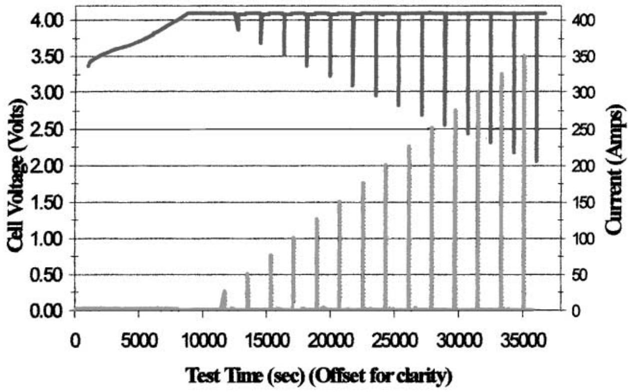

Fig. 7. The 0.100 s discharge pulses at 25°C.

calculate the distance between the center of the cathode coating and the center of the anode coating for each experimental lot. This gives an average distance between the 50% capacity points. The mean diffusion distance for the medium weight loading cells is 2.2 times that of the very low weight loading cells. Thus, because the mean ionic diffusion path is much shorter for the lighter weight loading cells, they are not limited to the same current density. Due to cell construction limitations, continuous discharge testing at rates above 100 A was not viable. Future constructions will incorporate larger terminals and other mechanical improvements aimed at increasing the current carrying capability.

In addition to continuous discharge testing, extensive pulse discharge testing was completed. For brevity, only an analysis of the very low weight loading cells, with the 6 μm anode particles, is presented. Fig. 7 shows the voltage for 0.100 s pulses at various currents.

For clarity on the figure, the voltage is slightly offset in time. The current level in the discharge pulses ranged from 2 (10 A) to 62 mA cm^{-2} (350 A). These pulses translate into specific energy and energy density values of 3200 W kg^{-1} and 7200 W dm^{-3}. If a more gravimetrically and volumetrically efficient cell hardware, such as that for the MSP01 Mars Lander, were used, the same chemistry would easily provide 3700 W kg^{-1}and 9000 W dm^{-3}.

The Lot 6 cells were also subjected to a 0.150 s, 150 A pulse at 25°C. During this pulse, the cells were connected to high-speed data recording equipment. Voltage and current data was recorded every 2 μs. By performing this test, the portions of the total polarization attributable to ionic polarization and ohmic polarization can be determined. For this specific pulse, it is estimated that 55% of the polarization is ohmic while 45% is ionic. A summary chart of the results of this test is shown in Fig. 8. Longer duration pulse testing confirmed that the slope of the voltage near the end of the pulse continues to plateau. Thus, for very high rate pulses of even relatively long duration, large improvements are available in both ionic and ohmic related polarization.

Low temperature testing was also conducted on the cells. Both continuous and pulse discharges were evaluated. For brevity, only the continuous discharges are presented in this paper. Fig. 9 shows a discharge voltage profile comparison for a 2.5 A discharge at −40°C. These cells were charged at −40°C. The figure shows that although the best lot offers twice the capacity of the worst lot, over 80% of the polarization is still present. Of the 20% of the polarization that has been eliminated, only a very small portion is related to the weight loading. Thus, if the electrolyte were responsible for the majority of the polarization, the decrease in bulk ionic current density between the electrodes by a factor of two should have halved the polarization. Instead only a small decrease in polarization is observed suggesting that the electrolyte is not responsible for the main portion of the total polarization at these conditions. This trend exists, to lessening degrees, through the −10°C discharge tests that were conducted. However, this trend is the opposite of the result for the 25°C high rate testing. In the very high rate testing at 25°C, the weight loading effect dominated the

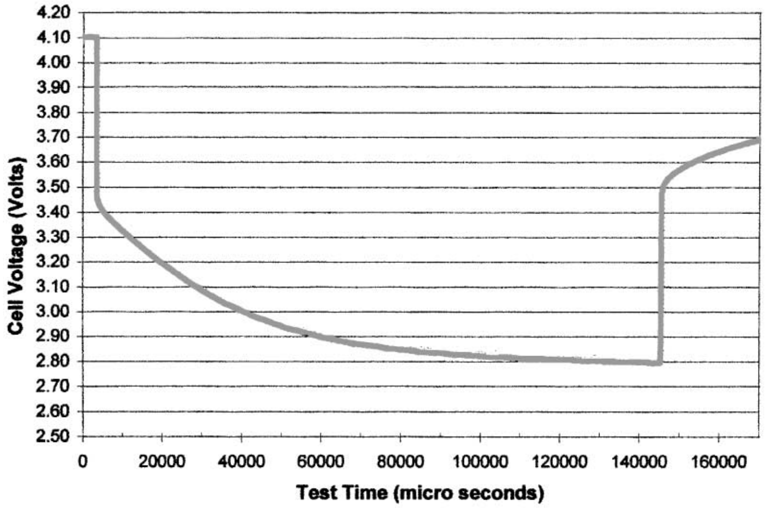

Fig. 8. The 0.150 s, 150 A pulse at 25°C.

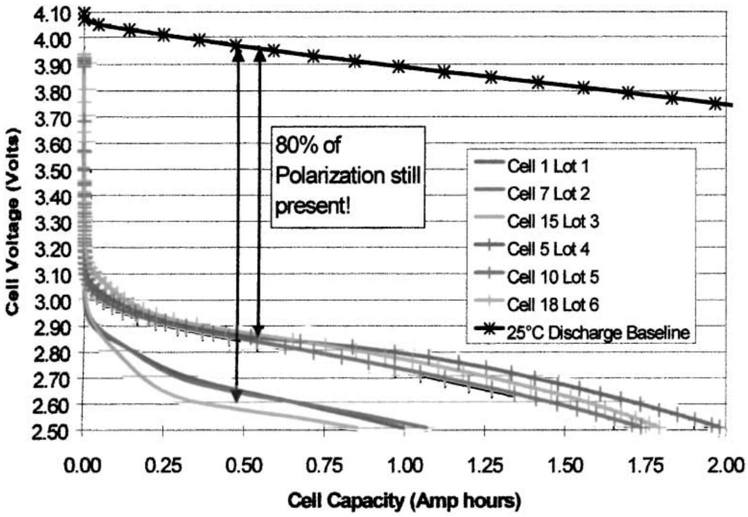

Fig. 9. The 2.5 A discharges at −40°C, showing better capacities from Lots 4–6.

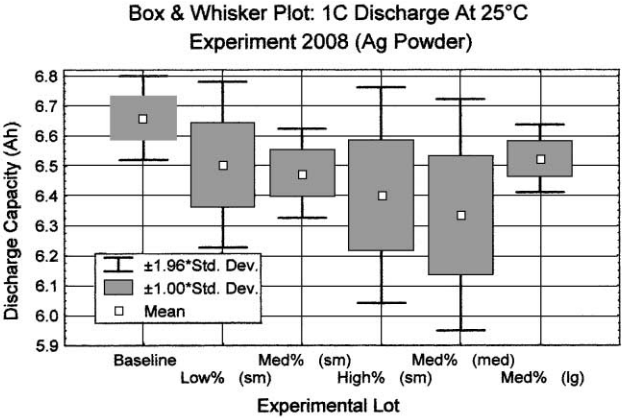

Fig. 10. 1 C discharge capacity at 25°C of cells with anodes containing three different amounts of silver powder in three particle sizes.

polarization. Thus, the rate limiting mechanism is temperature dependant.

A second experiment, to improve high rate and low temperature performance is also underway. As described previously, this experiment involves the doping of the anode with very high amounts of silver. The preliminary results at both 25 and −40°C are shown in Figs. 10 and 11, respectively. All of these cells are constructed with the medium weight loading and 10 μm anode particles. The experiment contains a baseline lot with the MSP01 Mars Lander chemistry. This is also the same chemistry as was used in Lot 1 of the previous experiment. Fig. 10 shows that the addition of silver, in large quantities, depresses the 25°C discharge capacity. This may be due to an unfavorable alloying of the lithium with the silver.

In Fig. 10, three levels of silver are compared: Low, Medium and High %. In addition, three silver particle sizes are evaluated: small (sm), medium (med), and large (lg). For clarity, Fig. 11 shows only the results for the first four lots at a rate of 1 C and a temperature of −40°C.

While the lot with the least amount of silver doping shows a slight depression in performance, the lot with highest amount of silver doping shows three times the capacity of

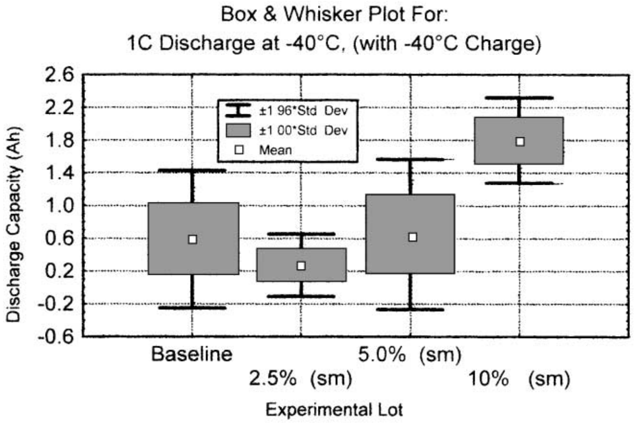

Fig. 11. 1 C discharge capacity at −40°C of cells with anodes containing three different amounts of silver powder of the small particle size.

the baseline lot. The results of the discharge energy are even more dramatic indicating a slightly higher operating voltage for the silver doped lots.

4. Summary

The results of the two experiments presented in this paper show large improvements in lithium-ion performance at both high rates and low temperatures. The most dramatic improvement is the ability of the Lot 6 cells to deliver over 90% of their capacity, above 2.7 V at a 20 C discharge rate. In addition, discharge rates as high as 4 C at −30°C have been demonstrated. The first experiment reveals the individual effects from the anode particle size and the weight loading. Thus, it was determined that the rate limiting factor differs at low and high temperature. Furthermore, it was determined that, at low temperature, the majority of the polarization is the result of a variable not captured in these experiments. The results of the silver doping experiment, while still preliminary, indicate considerable opportunity for this general approach. Future experiments will be aimed at addressing the rate limiting factors not captured in these experiments.

Acknowledgements

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