Comprehensive improvements in Li-ion batteries for demanding applications

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ABSTRACT

Several new electrode materials and electrolyte additives have been tested at Yardney in various combinations in order to improve the performance of LIB at elevated temperature and to extend the calendar life performance. The cell cycling results with new electrode/additive combinations were compared to the lithium-ion systems that normally work well at low temperatures. The goal of this effort was to enhance the cells' cyclability at elevated temperature (70 °C) without losing the performance at −20 °C.

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1. Introduction

Lithium-ion batteries' (LIBs) state of the art has been advanced tremendously over the past decade and advanced LIBs have been steadily gaining market prominence. However, there is still room for improvement in several aspects of performance of commercial cells, especially in their ability to consistently deliver power and capacity after prolonged storage or use, especially at temperatures above 60 °C. In order to develop more durable high-energy, long life power sources, a systematic approach must be taken and several cell components must be optimized. Focus shall be on the electrode active materials, but also, the physical design of the cell must be addressed.

Yardney Technical Products, Inc. for several recent years has been working on established and emerging programs to develop and test a variety of the next generation, long life, high energy, and high power anode and cathode materials for high-performance lithium-ion cells and batteries. Parallel efforts were directed at enhancing cell design in order to maximize such parameters as cell level specific energy. These efforts were undertaken to support Yardney's diverse military and aerospace customer base, to ensure design heritage, and to provide demonstrated performance enhancements for new applications. One of the goals of this study was to greatly improve lithium-ion cell performance after exposure to very high operating temperatures without losing the cells'

ability to perform at −20 °C. These ambitious cell performance requirements called for comprehensive improvements in cathode and anode chemistry, electrode formulations, electrolyte additives, etc. The tested cathode candidates included lithiated mixed metal oxide (LMMO, e.g.: $LiNi_{0.8}Co_{0.2−x}M_xO_2$, where M = Al or Mg, with $0 \geq x \geq 0.15$) materials, whereas the anode enhancements focused on implementation of materials that were less sensitive to SEI layer side-reactions occurring at elevated temperatures and had more controlled particle size distribution (PSD). In addition to the active materials improvements, electrolyte enhancements were also extensively tested. The end result of the above efforts was a cell design that demonstrated very little degradation with extensive cycling up to 70 °C, while retaining performance at −20 °C that is comparable to the start of life performance of the baseline chemistry.

2. Experimental

2.1. Lithiated mixed metal oxide (LMMO) cathode/electrolyte system experiment

Significant part of the electrode/additive systems was tested in NCP7-type cells. This type of cell is comprised of multiple anode–cathode pairs encased in stainless steel can, with current collecting tabs leading to separate positive and negative terminals placed on the top of the casing. Depending on the design details, such as number of electrode pairs, the NCP7 cells normally range in capacity from 10 Ah, for high energy applications, to 5 Ah for high power applications. In this study, 2 Ah polypropylene-shimmed cells in NCP7 casing were used for reproducible, yet facile

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(M. Gulbinska).

Table 1
LMMO cell testing conditions.

Cycle	Regime charge/discharge	End of discharge voltage [V]	Temperature [°C]	Description
1	$C/20$–$C/20$	3.0	25	Formation
2–3	$C/10$–$C/10$	3.0	25	Formation
4–6	$C/5$–$C/5$	3.0	25	Cell acceptance test
7–9	$C/5$–$C/2$	3.0	25	Cell acceptance test
10–12	$C/5$–$1C$	3.0	25	Cell acceptance test
13	$C/5$–$C/5$	3.0	25	72 h stand
14	DC resistance test[a]	3.0	25	Full test
15	$C/2$ and DC resistance test[b]	3.0	25	Baseline
16–18	$C/5$–$1C$	2.0	−20	Low temperature
19–68	$C/2$ and DC resistance test	3.0	25	25 °C life
69–71	$C/5$–$1C$	2.0	−20	Low temperature
72–96	$C/2$ and DC resistance test	3.0	70	70 °C life #1
97–99	$C/5$–$1C$	2.0	−20	Low temperature
100–124	$C/2$ and DC resistance test	3.0	70	70 °C life #2
125–127	$C/10$–$C/5$[c]	2.5	−20	Low temperature
128–130	$C/5$–$1C$[c]	2.0	−20	Low temperature
131–155	$C/2$ and DC resistance test		85	85 °C life
156–158	$C/10$–$C/5$[c]	2.5	−20	Low temperature
159–161	$C/5$–$1C$[c]	2.0	−20	Low temperature
162–164	$C/5$–$C/5$		25	Cell acceptance test
165–167	$C/5$–$C/2$		25	Cell acceptance test
168–170	$C/5$–$1C$		25	Cell acceptance test
171	$C/5$–$C/5$		25	72 h stand
172	DC resistance		25	Full test

[a] In DC resistance test cells are charged at $C/5$ then discharged at $C/10$. Every hour (10% SOC) the cells are discharged at $1C$ for 1 s. The change in voltage divided by the change in current yields the effective DC resistance of the cell.

[b] $C/2$ and DC resistance test indicates $C/2$ cycle life testing with a modified DC resistance test. Cells are cycled at $C/2$. During the discharge of every fifth cycle, after 1 h (50% SOC) the cells are discharged at $2C$ for 1 s. The change in voltage divided by the change in current yields the effective DC resistance of the cell.

[c] The low temperature testing later in the experiment required a lower voltage limit because cells were polarizing to below 3.0 V before delivering any capacity. For the $C/5$ discharges, the lower voltage limit was 2.5 V. For the $1C$ testing, the lower voltage limit was 2.0 V.

assembly. All cells were tested on the Maccor 4000® test system in the same Test Equity® temperature chamber. All charges were to 4.1 V with a current taper to $C/50$. Unless otherwise noted, all discharges were to 3.0 V. The cells were cycled according to Table 1. Charge, discharge and rest steps were all done at temperature values listed in Table 1. Typically, cells were allowed to reach the target temperature during the first $C/5$ charge, immediately after temperature change. Selected cells performed the 85 °C and subsequent testing. Each experimental cell lot contained at least four cells.

2.2. Next generation lithiated mixed metal oxides testing (LMMO-Gen2)

LMMO-Gen2 materials were tested in coin ½-cells, against Li/Li⁺ anodes. Three coin cells were made per each experimental sample. Standard carbonate and LiPF$_6$-based electrolyte and polyolefin separator were used in all tested coin cells. Typical LMMO-Gen2

cathode testing protocol conditions are summarized in Table 2. After undergoing the formation protocol, all cells were tested at current rates ranging from $C/5$ to $2C$ at 20 °C. Then, all cells underwent the 160 h charged stand, and the testing was completed with two recovery cycles at $C/10$ rate. All charges were to 4.1 V and all discharges were to 3.0 V. Current taper rate was $C/50$ in all charge cycles. The dependant variables for comparative analyses were: specific capacity, voltage loss on charged stand, power fades at different temperatures, and $2C$ vs. $C/5$ capacity ratio.

2.3. Advanced anode testing

In parallel to cathode and electrolyte improvements, work was done at Yardney on advanced anode materials and formulations. Anode materials with custom particle size distributions (PSD) were tested. All anode candidates were tested in full pouch cells against commercial LMMO cathode and underwent the same testing protocol, as described in Table 3.

Table 2
Next generation LMMO-Gen2 testing conditions.

Cycle	Testing step	C-rate	Temperature
1–3	Formation	$C/20$, $C/10$	20 °C
4–15	Cell acceptance testing (CAT)	$C/5$, $C/2$, $1C$, $2C$	20 °C
16	Charged stand	160 h duration, $C/5$ charge/discharge	20 °C
17–18	Recovery cycles	$C/10$	20 °C

Table 3
Pouch cell testing conditions for anode study.

Cycle	Testing step	C-rate or pulse current [A]	Temperature
1–3	Formation	$C/10$, $2 \times C/5$	25 °C
4–8	Cycles 4–8	$C/2$	25 °C
N/A	Pulses part 1	$1C$ (24 s), $4C$ (16 s), $3.75C$ (25 s), $8C$ (10 s), $8C$ (55 s), $8.5C$ (15 s), $5C$ (10 s)	25 °C
N/A	Pulses part 2	$1C$ (24 s), $4C$ (16 s), $3.75C$ (25 s), $8C$ (10 s), $8C$ (55 s), $8.5C$ (15 s), $5C$ (10 s)	0 °C

3. Results and discussion

3.1. LMMO cathode/electrolyte system testing results

To date, the principal reason for using electrolyte additives in lithium-ion cells has been stabilizing the anode's solid electrolyte interface (SEI) that is critical to cyclability of LIBs, because at elevated temperatures SEI deteriorates due to the reaction with $LiPF_6$ based electrolytes [1–4]. The loss of capacity and power from LIBs stored at elevated temperature has been attributed to the presence of thermal decomposition products of the electrolyte in the anode SEI [4]. On the other hand, additives that inhibit the thermal decomposition of $LiPF_6$ electrolytes would improve the capacity retention and decrease resistance in thermally abused cells. Thus, the inhibition of the thermal reactions between the anode SEI and $LiPF_6$ electrolytes would lead to improved high temperature performance of LIBs. Since different families of additives have varied mechanisms of high temperature performance enhancement, it is likely that combinations of the two (or more) different additives would have a cooperative effect. The LMMO cathode/electrolyte system takes a systematic approach to testing the combinations of cathode, anode, respective binders with single or multiple electrolyte additives in order to maximize the performance of lithium-ion cell at $-20\,°C$ after thermal storage and/or cycling at $70\,°C$.

The NCP7 cells built for LMMO testing all used the same proportions of active materials, conductive diluents and binder. Experimental lots differed in cathodes, anodes, cathode binders and anode binders. The materials used were down selected based on previous work comparing the state of the art in each area. For example, over 10 cathodes were evaluated before choosing C2 as the best. Commercial polyolefin separators were used in all cells. Lot 6 utilized a polyolefin separator with much higher porosity than the other cell lots. All cells had the same number of pairs of electrodes and were filled with the same amount of electrolyte. The cells were rated at 2 Ah for the purpose of establishing the 1C rate. The cells were then separated into nine lots based on their components, as seen in Table 4.

Cathodes C1 ($LiNi_{0.8}Co_{0.2}O_2$) and C2 (trade secret) were both of LMMO chemistry. Binders: CB1 (Kynar Flex), CB2 (trade secret), AB1 (Kynar Flex), and AB2 (trade secret) were all PVDF-based, with varying molecular weight and polymer cross-linking degree. Anodes: A1 (MCMB-series from Osaka Gas) and A2 (trade secret) were both graphitic with similar particle size distribution. Electrolyte E1 was the baseline for all electrolytes consisting of $LiPF_6$ in a mixture of carbonates (e.g.: ethylene carbonate – EC, dimethyl carbonate – DMC, and diethyl carbonate – DEC). The electrolyte additives were added to E1 to obtain the E2 formulation. The additives were similar to vinylene carbonate (VC) in the sense that their function was to undergo the sacrificial reaction on the electrode's surface, thus protecting the active material. E3 was the same as E2, with an additional electrolyte additive (trade secret, low temperature additive). All of the Lot 1 materials were the baseline (heritage) materials.

Table 4
LMMO cell lots.

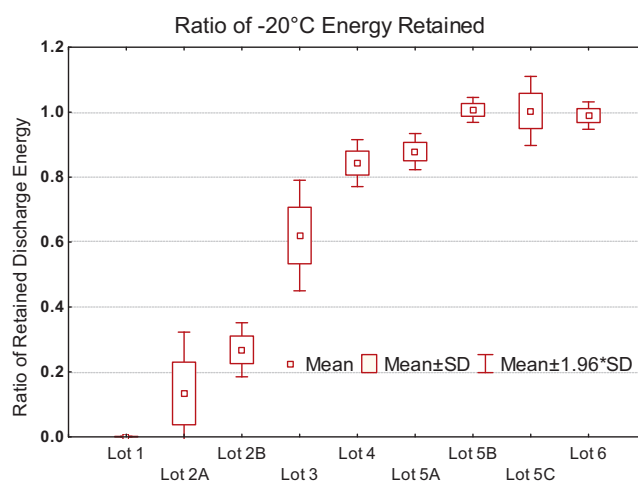| Lot	Cathode	Cathode binder	Anode	Anode binder	Electrolyte
1	C1	CB1	A1	AB1	E1
2A	C2	CB1	A1	AB1	E1
2B	C2	CB1	A1	AB1	E2
3	C2	CB1	A2	AB1	E2
4	C2	CB2	A2	AB1	E2
5A	C2	CB2	A2	AB2	E1
5B	C2	CB2	A2	AB2	E2
5C	C2	CB2	A2	AB2	E3
6	C2	CB2	A2	AB2	E2

Fig. 1. Retained energy, cycle 99 vs. cycle 21 (Table 1).

Each subsequent lot had only one individual material changed in order to allow for stepwise evaluation against the baseline and the previous lots.

All cells in this experiment were tested according to the cycling regimen given in Table 1. In this testing protocol, a brief formation procedure (a charge/discharge cycle at the current rate of $C/20$ cycle, and two cycles done at charge/discharge $C/10$-rate) is followed by the cell acceptance test (CAT), where $C/5$ charge steps are combined with varied C-rate discharges ($C/5$–$1C$ discharge rates). After the CAT, cells undergo the extended cycling (cycles 13–155) at varied temperature conditions, interspersed with the DC resistance tests (as described in footnotes to Table 1) that serve as the means for the cell "state of health" diagnostics. During the extended cycling, temperature ranges from $70\,°C$ (two rounds of testing) to $-20\,°C$ (several rounds, see Table 1).

Fig. 1 compares the initial $-20\,°C$ energy to that delivered after the first round of $70\,°C$ cycling (see Table 1 for testing profile details). Dramatic differences are apparent. The Lot 1 cells no longer deliver any usable energy above 3.0 V at the $1C$ rate. The Lot 2A to Lot 1 comparison demonstrates that Cathode 2 outperformed Cathode 1. Lot 2B to Lot 2A comparison shows the electrolyte additives also improved energy retention. The most dramatic improvement comes in the comparison of Lot 3 to Lot 2B. The energy loss is reduced by 50% with change from Anode 1 to Anode 2. Lot 4 to Lot 3 demonstrates the improvement from Cathode Binder 1 to Cathode Binder 2. The change represents an increase in retained energy from 60% to 82%. It is worth noting that all experimental lots were comparable on the initial 25 °C test and that in the $-20\,°C$ test results the differences between experimental lots were more pronounced than at ambient temperature.

A very slight improvement is seen in comparing Lot 5A to Lot 4 but with a p-value of only 0.16. The final large improvement comes in comparing Lot 5A (no additives) to Lot 5B and Lot 5C (both lots with electrolyte additives). The effect of the additives to stabilize the system is evident, with Lot 5B showing a more visible improvement over Lot 5A than the one observed in Lot 5C.

Fig. 2 displays the mean discharge energy for Lot 1 vs. Lot 5A from cycle 90 through to the end of testing a cycle 172. Clear performance differences exist between the lots. Shown again is that Lot 1 failed to deliver any energy above 3.0 V at $-20\,°C$ after the first round of $70\,°C$ cycle life testing, but does deliver energy for cycles 125–130 after the second round of $70\,°C$ cycling, when the lower voltage limits were set to 2.5 V and 2.0 V (Table 1). After 85 °C testing, Lot 1 only delivers energy at $-20\,°C$ when the discharge rate is $C/5$ or lower. Meanwhile, Lot 5B continues to deliver energy throughout testing, even at $1C$ and $-20\,°C$.
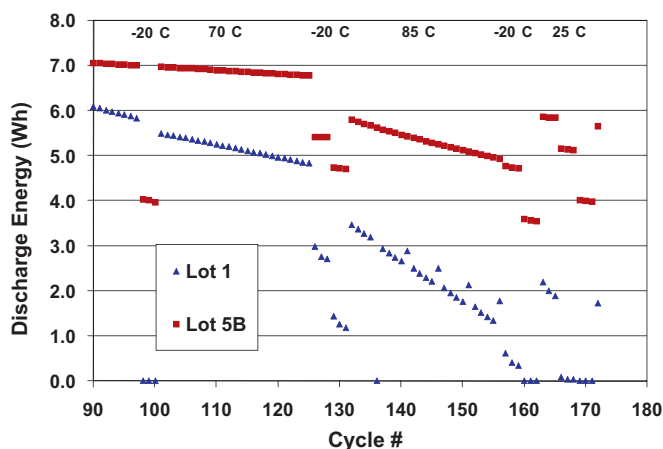
Fig. 2. Mean discharge energy, Lot 1 vs. Lot 5B.

Lot 5B retained over 94% of its initial discharge energy at 1C and −20 °C to 3.0 V after 50 cycles at 70 °C. Lot 5B utilized all five of the material changes identified in Table 1 with respect to the baseline, Lot 1 cells. These material changes represent a significant improvement in high temperature stability with respect to low temperature performance, a key requirement in most demanding lithium-ion applications.

3.2. LMMO-Gen2 cathode testing

LMMO-Gen2 samples (Fig. 3) represent the materials with similar mixed metal oxide chemical compositions as the commercial LMMO material (i.e.: $LiNi_{0.8}Co_{0.2−x}M_xO_2$, where M = Al or Mg, with $0 \geq x \geq 0.15$), but with smaller average particle size. Improved rate capability of these materials is therefore expected, however the first cycle efficiency and voltage retention upon charged stand ought not to be sacrificed.

All LMMO-Gen2 preliminary data was first analyzed for performance variables, such as charge and discharge capacity, rate capability (defined as the ratio of capability retained between C/5 and 2C cycles), and voltage relaxation after the first 2 h of stand time and after 160 h stand time. After the initial data analysis, sample Lot 1, Lot 2 and Lot 3 were selected for further analysis for the specific capacity at the end of each cycle, first cycle efficiency and voltage loss characteristics. This data was then compared to the C2 cathode, which was the best-performing LMMO cathode utilized in previous experiments.

The results of LMMO-Gen2 testing in coin ½-cells are shown in Fig. 3. Each plot represents an average of three cells per experi-
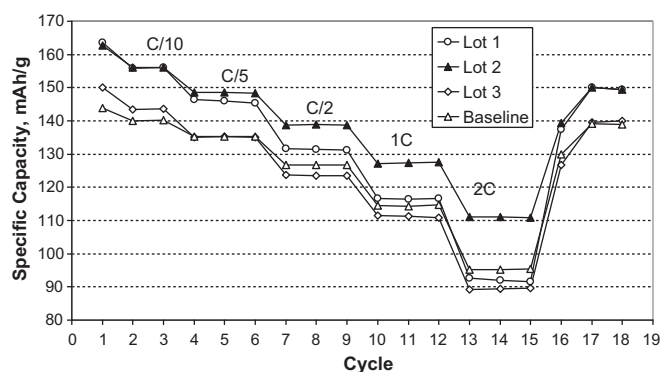

Fig. 3. Specific capacity at the end of each cycle for baseline LMMO sample and the three best experimental LMMO-Gen2 cathodes.
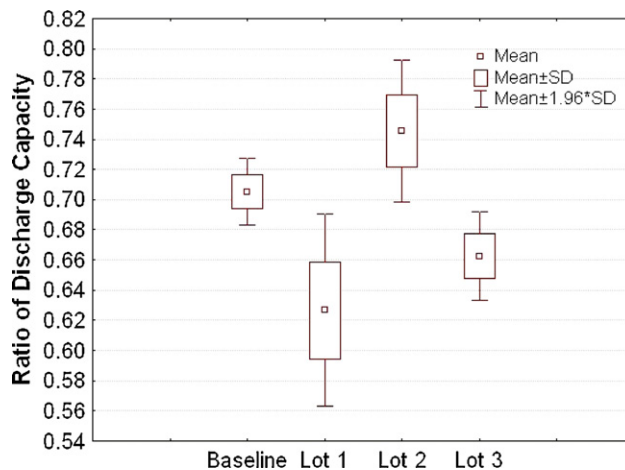

Fig. 4. Rate capability retained between C/5 and 2C cycling.

mental lot. Capacity was normalized per mass of active material. As seen in Fig. 3, all four experimental lots differ in capacity delivered on the first cycle and/or in their rate capability. Lots 1 and 2 both deliver more than 160 mAh g^{-1} on the first discharge, whereas Lot 3 discharges at 150 mAh g^{-1}. The baseline, commercial LMMO cathode starts modestly at about 145 mAh g^{-1} but it is rate performance eventually exceeds that of Lot 1 and Lot 3. The poor rate performance of Lot 1 cathode is very pronounced, especially at 2C rate. Clearly, Lot 2 has a better rate capability than Lot 1, but, in order to have a global comparison between all four lots; the initial capacity needs to be taken out of equation.

Fig. 4 illustrates different values of retained rate capability, compared between three experimental lots of LMMO-Gen2 materials and the baseline LMMO cathode. The ration of retained capacity between 2C and C/5 discharge cycles has been taken, which is one way of normalizing the results of all four experimental lots. Fig. 4 plot shows in a definitive way that experimental Lot 2 has the best rate retention between 2C and C/5 cycles of all lots, baseline material comes second and the remaining lots underperform with respect to commercial LMMO, with Lot 1 exhibiting the worst rate retention.

Another important performance metrics, the first cycle charge/discharge efficiency, is plotted in Fig. 5. Again, the experimental Lot 2 is the most efficient at 91% charge/discharge efficiency, followed by the baseline LMMO that has 88% efficiency. Here, Lot 3 has marginally better charge/discharge capacity ratio than Lot 1,
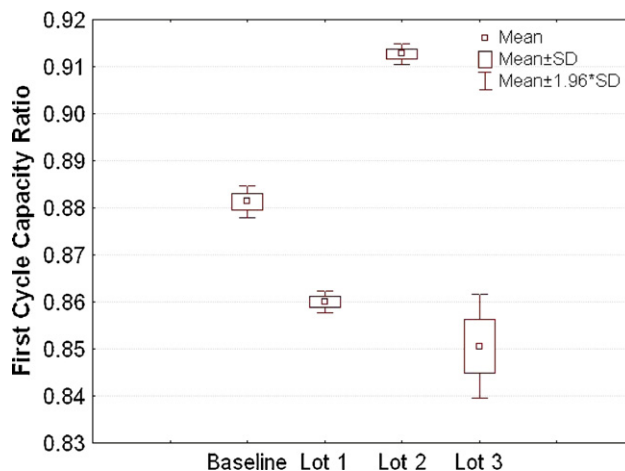

Fig. 5. First cycle efficiency for baseline LMMO sample and Lots 1–3.
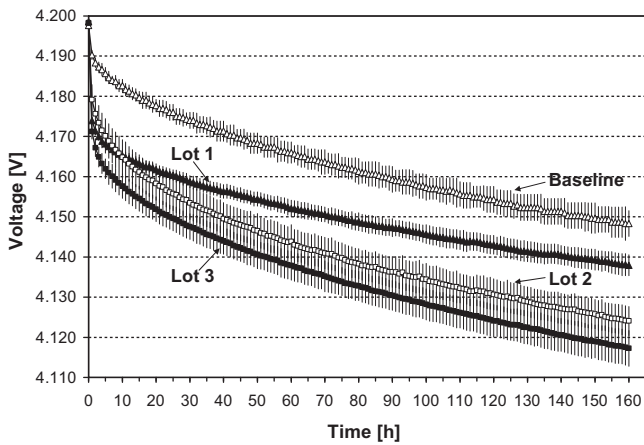
Fig. 6. Voltage relaxation curve during charged stand (160 h) plotted vs. time. Averages of three cells were taken for each lot (standard deviation values are marked as Y-error bars).

Fig. 8. Cell testing results at various temperature conditions.

which is the reversal of their results for rate capability, however both still perform worse than baseline.

Self discharge is a very important factor to consider in lithium-ion cells, especially when small particles of electrode materials are considered. Therefore, voltage relaxation curves (Fig. 6) were plotted vs. time of the charged stand, performed for 160 h, with 4.2 V starting voltage condition. As evidenced in Fig. 6, initial polarization of Lots 1–3 (25–30 mV range, taken in the second hour of the stand) differs significantly from the baseline LMMO cathode (about 10 mV, also measured in the second hour). After the similar initial polarization-related voltage drop, the shape of voltage relaxation curves is very different in Lots 1–3, from 2 to 160 h of stand duration. Lot 1 shows much slower voltage decline during the extended charged stand time (about 62 mV voltage loss after 160 h) than Lots 2–3 (75–85 mV). However, all the experimental lots still exhibit worse self discharge characteristics than the baseline LMMO material (52 mV after 160 h). Lot 1 shows the most promising self discharge behavior, with the voltage loss slope more favorable than the baseline, which in enough time (>200 h) could cross the voltage relaxation of the baseline sample. However, the superiority of Lot 1 needs to be confirmed in further studies. Taking into account a poor discharge rate performance of Lot 1, large average particle size or agglomeration of active material particles are very possible. When all testing results are taken into consideration, self discharge behavior and rate performance ought to have assigned a proper level of "desirability", in order to select the best LMMO-Gen2 candidates for further pursuit.
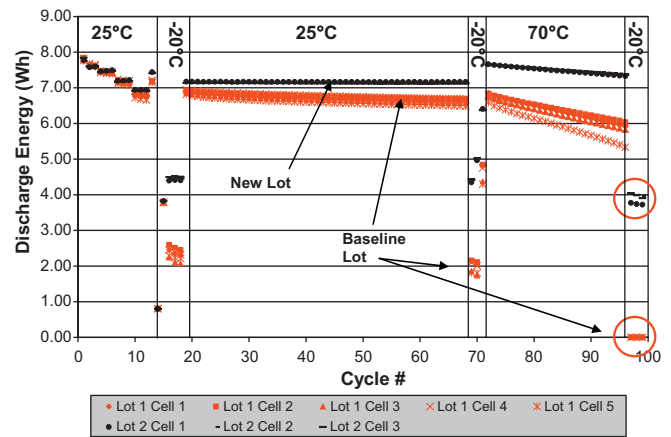
3.3. Advanced anode testing

In addition to the extensive cathode/electrolyte system testing, anode materials with custom particle size distributions (PSD) were also investigated. All anode lots (1–3) selected for further testing in pouch cells had initial reversible capacity higher than 300 mAh g^{-1} and first cycle efficiency of greater than 93% obtained in coin ½-cell preliminary measurements (not shown here).

Fig. 7 represents one aspect of the pouch cell testing of anode candidates. In Fig. 7a, the box-whisker statistical plot for 8C pulse (10 s duration) at 25 °C is shown. Fig. 7b illustrates the box-whisker statistical plot for 8C pulse (10 s duration) at 0 °C. The y-axis represents voltage (in volts) observed after the pulse in the three experimental pouch cell lots. The three experimental lots shown in Fig. 7a and b could not be statistically resolved at this point of testing. However, the cell Lot 2 exhibited narrow statistical distribution and cells from the Lot 3 showed the widest distribution of the three lots. In addition, two cells from Lot 3 did not finish the testing protocol, whereas all cells from Lot 2 completed testing successfully. These observations lead us to the conclusion that the Lot 3 anode material showed the least promise for further development. Compared to the historical performance of the "old" anode material (not shown here) the new material candidates all performed on par or slightly better than the baseline anode material.

3.4. Final cell design

The final cell design resulted from the systematic R&D studies of cathode, anode and electrolyte components. The resulting LIB
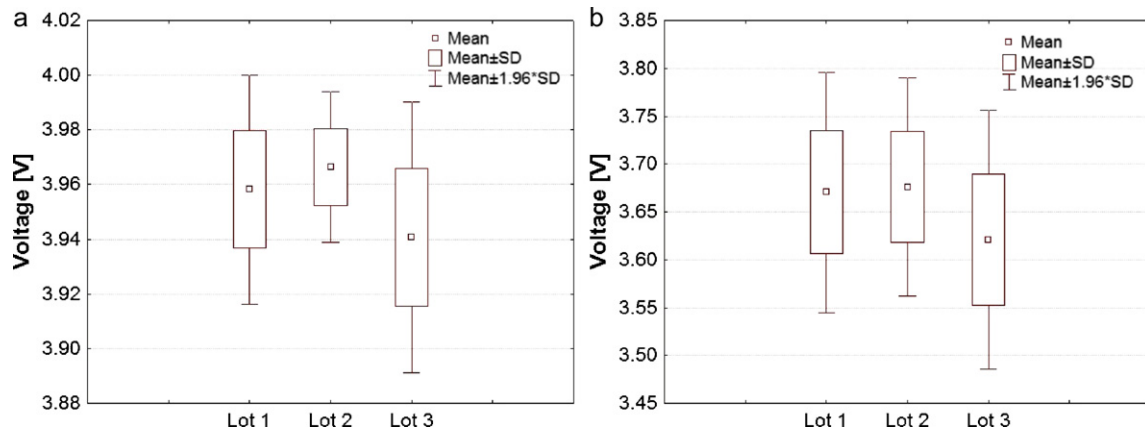

Fig. 7. Pulse discharge results for 8C rate, 10 s: (a) at 25 °C and (b) at 0 °C.

system is showing only minor degradation upon prolonged cycling at 70 °C and robust performance at −20 °C, comparable to that at the start of life of the baseline chemistry is shown in Fig. 8. As it is clearly illustrated in Fig. 8, the "baseline lot" initially tracks with the performance of the "new lot" (the new cell chemistry that encompasses several material and/or formulation changes). However, the two lots separate quickly and after low and elevated temperature testing intervals, the new cell lot clearly outperforms the baseline cells.

4. Conclusions

After a series of comprehensive testing of cathode, anode, electrolyte additives and binder candidates, lithium-ion cell chemistry and electrode formulations were developed that withstand the prolonged exposure to 70 °C temperature and retain impressive performance at −20 °C.

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