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Short communication

Studies of 18650 cylindrical cells made with doped $LiNiO_2$ positive electrodes for military applications

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Abstract

We studied GP 18650 cylindrical cells made with doped $LiNiO_2$ positive electrode for military application. The studied cells should deliver about 184 Wh/kg according to the military specification MIL-PRF-320521 while it delivers about 201 Wh/kg according to the general commercial standard. The difference in the cell specific energy is mainly caused by the difference in the charging voltage. It is 4.1 V in the military specification compared to 4.2 V in the general commercial standard. Clearly, to take full advantage of the commercial lithium-ion cell, either the military increases the voltage limit to 4.2 V from 4.1 V or the cell manufacturers redesign their cells according to the 4.1 V charging voltage limit.

The studied cell exceeds all major military requirements including high rate discharging, high current pulse discharging, low temperature discharging, cycle life, high temperature storage, and abuse tolerances such as the overcharging, forced discharging, and external short. Specifically, the capacity of the cell exceeds the requirement by 51% at a high discharging rate (3.3 A) and by 39% with a high current (6 A) pulse. The cell can discharge not only ∼62% of the expected capacity at −30 °C but also ∼47% at −40 °C and at 0.67 A, which means that the military can extend their specification to −40 °C. The cell still retained 1.97 Ah (or 92%) after 224 cycles, which exceeds the requirement by ∼9%. The cell retained 1.95 Ah (or 95%) after one-week storage at 50 °C and at 4.1 V, which exceeds the requirement by 8%. The abuse tolerance is also very high. The maximum cell temperature ranged only from 62 to 70 °C during overcharging, external short, and forced discharging. Directions for the improvement are also discussed.

Keywords: Li-ion; Military; $LiNiO_2$ positive; Low temperatures

1. Introduction

The study in lithium ion cell for military application is an active area in recent years [1–6] because the lithium ion cell has the potential to achieve the highest specific energy among all conventional secondary battery chemistries except a lithium metal based rechargeable battery. It is believed that the lithium ion cell will lead to not only a lightweight military devise but also an overall cost reduction for the military in the years to come.

The military application is very different from the general commercial application in operation conditions, performance, and abuse tolerance. For instance, the military unmanned underwater vehicle battery operates with a nominal voltage of 4.1 V while 4.2 V is the general commercial standard [4]. The military require a very high current pulse for several seconds while it is rare in the other applications [7]. The military needs good performance down to −40 °C [2] while the general application only needs good performance at −20 °C. The military requires the cell to pass a 0.5 C overcharge test with a 24 V power supply while the specification from Underwriters Laboratories is that the cell must pass an overcharge at three times the current specified by the cell manufacturer [1,7,8]. In view of these differences, it is conceivable that the lithium ion cell designed for the general commercial application may not meet all military requirements or targets.

To explore the challenges in the military application, we have designed and studied a GP 18650 cell using a doped $LiNiO_2$ positive according to the critical requirements of the military specification MIL-32052/1 (CR). There are two purposes for this work. First of all, we want to explore the capability of the lithium ion cell according to the military standard by studying the GP 18650 cell which meets the long term goal of the Department of Energy (200 Wh/kg) and the military FY-07 goal (>200 Wh/kg) at the general commercial condition [2,10]. Secondly, we hope that our

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work will provide directions for future improvement in the commercial lithium ion cell for use in military applications. The following is our detailed report.

2. Experimental

All cells were made at Gold Peak Battery Technologies in San Diego. Two or three cells were evaluated in each test. Most tests were done with Firing Circuit BRT 2000 except the storage test at 50 °C, where the cell capacity check was done using Maccor equipment. The following are the detailed military test conditions except ones indicated otherwise.

(1) Full capacity discharge: the cell was (i) charged at 0.5 C rate for 2 h to 4.1 V at room temperature and (ii) discharged to 2.5 V at 0.67 A. For a typical general commercial conditions, the cell was (i) charged at 0.8 C to 4.2 V for 2.5 h and (ii) discharged to 2.8 V at 0.2 C rate.
(2) High rate discharge: the cell was (i) charged at 0.8 C to 4.1 V for 2 h at room temperature and (ii) discharged to 2.5 V at 3.33 A.
(3) Discharged at −30 and −40 °C: the cell was charged at room temperature to 4.1 V at 0.8 C for 2 h first, and then held at the target low temperature for 4 h, and finally discharged to 2.5 V at 0.67 A. The MIL-PRF-320521 requires 16 h at the target low temperature prior to the discharge. We hold 4 h at the target low temperature because (i) our temperature chamber cannot provide 16 h at −30 and −40 °C and (ii) we believe that 4 h is enough for the cell to achieve the equilibrium state.
(4) Pulse discharge: The cell was charged to 4.1 V for 2 h at 0.8 C and room temperature, and then discharged for 5 s at 6 A and rest for 25 s until the cell discharge voltage decreased to 2.5 V.
(5) Storage at 50 °C and 4.1 V for one week: the cell capacity of three cells at 0.67 A was measured first, then all cells were charged at 0.5 C to 4.1 V for 2 h and subsequently were put into a 50 °C oven. After one week at 50 °C, all cells were first discharged to 2.5 V at 0.67 A and room temperature to check the capacity retention, and then charged back to 4.1 V at 0.5 C for 2 h and discharged to 2.5 V at 0.67 A to check the irreversible capacity loss.
(6) Military cycling test: the procedure is: (i) cycle 1: step 1: charge the cell to 4.1 V for 2 h at 0.5 C rate and RT; step 2: rest for 5 min; step 3: discharge at 0.5 C to 2.5 V; step 4: rest for 20 min; (ii) cycles 2–26: step 1: charge the cell to 4.1 V for 2 h at 0.8 C rate; step 2: rest for 5 min; step 3: discharge at 0.67 A to 2.5 V; step 4: rest for 20 min; step 5: repeat steps 1–4 for 24 times; (iii) cycle 27: step 1: charge the cell to 4.1 V for 2 h at 0.8 C rate; step 2: rest for 2 h; step 3: discharge at 0.67 A to 2.5 V; step 4: rest for 20 min; (iv) cycle 28: step 1: charge the cell to 4.1 V for 2 h at 0.5 C rate; step 2: rest for 2 h; step 3: discharge at 0.67 A to 2.5 V; step 4: rest for 20 min; (v) repeat cycles 1–28 until 224 cycles are achieved in total.
(7) GP acceralated cycling test: the procedure is: (i) charge the cell to 4.2 V for 2.5 h at 0.8 C, (ii) rest for 5 min, (iii) discharge at 1 C rate to 2.8 V, (iv) rest for 5 min, (v) discharge at 0.2 C rate to 2.8 V, (vi) rest for 20 min, and repeat steps (i–vi) for 300 times.
(8) Overcharge test: the cell was charged at C/2 rate for 8 h with 20 V power supply. (We only charged the cell to 20 V because we do not have 24 V power supply which is required by the military specification.)
(9) Forced discharge: the cell is forced to discharge completely. For detail, please see reference [7].
(10) External short: the cell is shorted externally with a low resistance lead. For detail, please see reference [7].

3. Results

3.1. Cell discharge capacities at various conditions

Fig. 1 shows the typical cell capacity versus the cell voltage for the cell charged according to the military and general commercial conditions. The military charging protocols lead to not only a lower discharging capacity but also a lower discharging voltage. The cell capacity is about 2.04 Ah with the military charging condition 4.1 V at 0.5 C for 2 h and about 2.15 Ah with 0.8 C military charging protocol. For comparison, the cell capacity is about 2.30 Ah with a typical general commercial condition 4.2 V at 0.8 C for 2.5 h.

Fig. 2 shows the typical cell capacity versus the cell discharging voltage at 3.33 A for the cells charged with both 4.1 V at 0.8 C for 2 h and 4.2 V at 0.8 C for 2.5 h. The cell charged to 4.1 V delivers about 2.05 Ah while the cell charged to 4.2 V shows around 2.2 Ah at 3.33 A.

Fig. 3a shows the typical cell capacity versus the cell voltage during the 6 A pulse discharging for the cell charged to 4.1 V for 2 h at 0.8 C rate. The cell can deliver 222 pulses, which corresponds to 1.86 Ah. Fig. 3b shows the pulse voltage profiles of the 1st, 136th, and 222nd pulses.

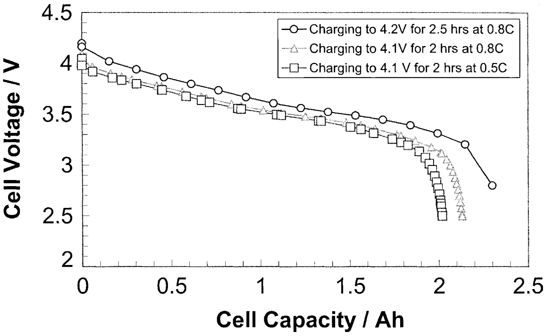

Fig. 1. The typical cell discharge voltage-capacity profiles at 0.67 A (military) and 0.46 A (C/5, general commercial condition) for the cells charged according to the military charging protocol 4.1 V and the general commercial standard 4.2 V.

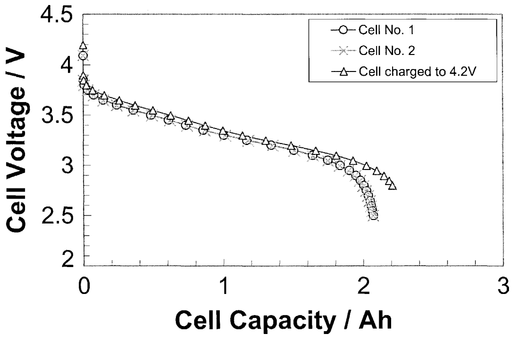

Fig. 2. The typical cell discharging voltage-capacity profiles at 3.33 A (or 1.43 C) for the cells charged with the military charging protocol 4.1 V for 2 h at 0.8 C and the general commercial condition 4.2 V for 2.5 h at 0.8 C.

3.2. Cell discharge capacity at low temperatures

Fig. 4 shows the typical cell capacity versus the cell voltage at −30 and −40 °C and 0.67 A for the cell charged to 4.1 V for 2 h at 0.8 C rate and at room temperature. The cell delivers about 1.35 Ah at −30 °C and 1.0 Ah at −40 °C. There is an increase in the cell voltage in the beginning of the discharging at −40 °C, which indicates that there may be some effect from the cell self heating in the beginning of discharging.

3.3. Cell stability at high temperature

Table 1 lists the cell capacity before and after one-week storage at 50 °C for the cells being charged at 0.5 C to 4.1 V for 2 h. The cell still retained about 1.945 Ah (or ∼95%) and only lost about 1.6% permanently.

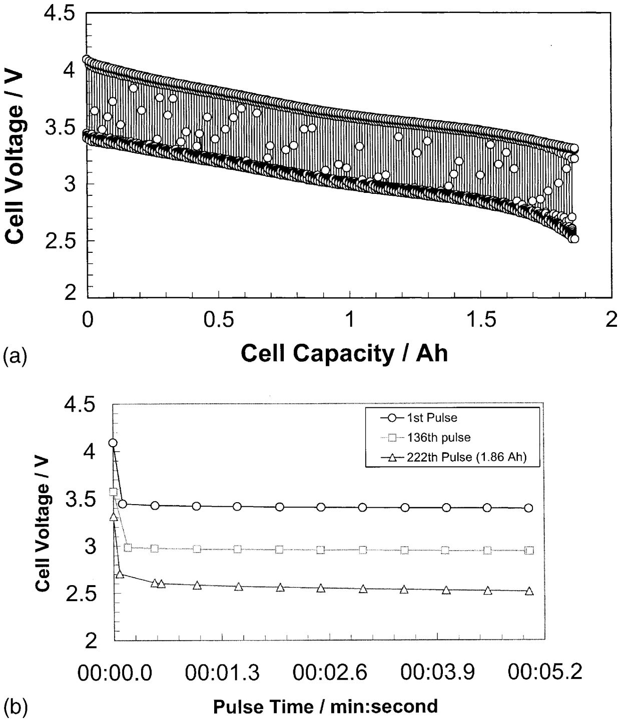

Fig. 3. (a) The typical cell discharging voltage-capacity profiles during the 6 A pulse for the cell charged to 4.1 V for 2 h at 0.8 C, and (b) some examples of the individual pulse discharging voltage profiles during the pulse test. The pulse is 5 s on (6 A) and 25 s off (zero current).

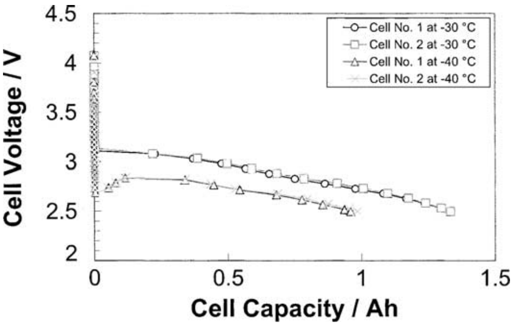

Fig. 4. The typical cell discharging voltage profiles at −30 and −40 °C and at 0.67 A for the cells charged to 4.1 V for 2 h at 0.8 C.

Table 1
Cell capacity before and after 50 C storage for one week at 4.1 V

Cell ID	Capacity before the storage (Ah)	First discharge capacity after the storage (capacity retention) (Ah)	Capacity after the storage (Ah)
No. 1	2.0348	1.941	2.0253
No. 2	2.0466	1.951	2.0116
No. 3	2.0353	1.950	2.0043

3.4. Cell cycle life

Fig. 5 shows the cell capacity versus the cycle number for two cells according to MIL-PRF-320521 and the GP accelerated cycling condition. The low capacity spike in Fig. 5 is due to the cell being charged at 0.5 C to 4.1 V for 2 h. The cell lost about 8% after 224 cycles according to the military condition while it lost about 13% after 300 cycles according to the GP cycling condition. The capacity of the cell cycled according to the GP condition is higher than that obtained according to the military condition during the whole cycle life test even though the capacity fading rate is slightly higher with the GP accelerated cycling condition than with the military condition.

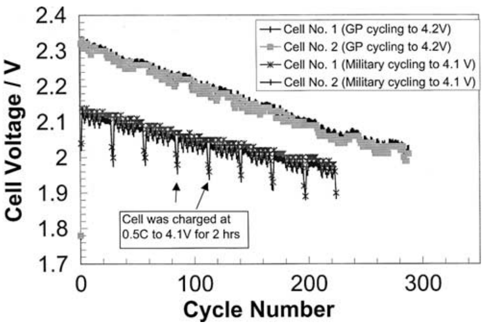

Fig. 5. The cell capacity in relation to the cycle number for the cells cycled according to the military and GP accelerated cycling protocol.

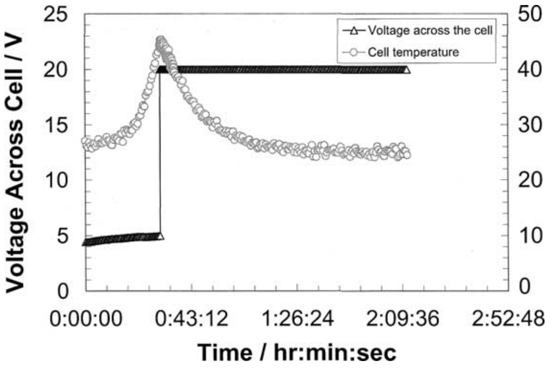

Fig. 6. The typical cell voltage and temperature profiles during the 20 V overcharge test at 0.5 C.

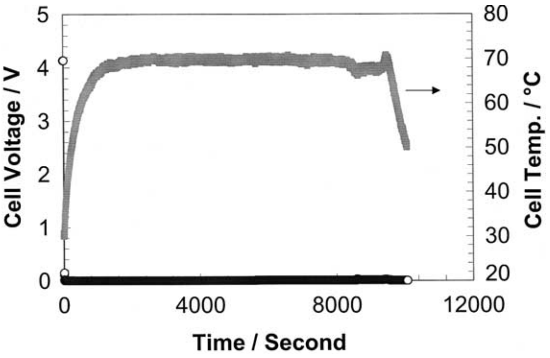

Fig. 8. The typical cell voltage and temperature profiles during the external short. It can be seen that the cell temperature increased to the maximum value in 1000 s.

3.5. *Cell abuse tolerance*

Fig. 6 shows the typical cell voltage and temperature profiles during the 0.5 C–20 V overcharging test. The cell maximum temperature is about 50 °C. The cell became open circuit at around 28 min during the overcharging. There was no leakage, fire, explosion or sparks.

Fig. 7 shows the typical cell temperature profile during the forced discharging. The maximum cell temperature is about 62 °C. There was no leakage, fire, explosion or sparks.

Fig. 8 shows the cell temperature profile during the external short. The maximum cell temperature is about 70 °C. There was no leakage, fire, explosion or sparks.

4. Discussion

4.1. *Cell capacity and specific energy*

It is clear from Fig. 1 that the cell capacity with the military charging protocol is lower than that obtained with a typical general commercial charging protocol. For instance, the military charging at 0.8 C to 4.1 V leads to about 6.5% (=(2.3 − 2.15)/2.3) lower in the cell capacity than the general commercial charging condition 0.8 C to 4.2 V. This observation means that the designed capacity of the general commercial lithium-ion cell is not fully used under the military charging voltage 4.1 V. The cell capacity is further limited significantly by the military charging protocol 0.5 C to 4.1 V for 2 h since the discharge capacity of the cell charged at 0.5 C for 2 h to 4.1 V is only about 95% (=(2150 − 2040)/2150) of that obtained from the cell charged at 0.8 C for 2 h to 4.1 V. This is understandable because it requires 2 h to fully charge the cell at 0.5 C rate without any voltage limit. With the charging limit 4.1 V, the charging current will decrease when the cell voltage hits the limit during the charge. As a result, the cell will not be fully charged at 0.5 C for 2 h. In view of the above discussion, both 4.1 V charging voltage limit and 2 h–0.5 C charging to 4.1 V led to a significant decrease in the cell capacity. To fully take advantage of commercial lithium-ion cell for this particular military application, either the military changes their specification to 4.2 V or the lithium-ion manufacturer redesigns their cells according to 4.1 V for this military application.

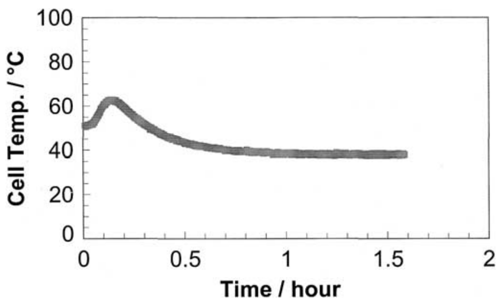

Fig. 7. The typical cell temperature profile during the forced discharging. Some data was lost in the beginning of the test.

Table 2 lists the cell specific energy calculated according to Fig. 1 and the cell weight ∼41 g. Similar to the cell capacity, the specific energy of the cell is about 8% (=100% × (201 − 184)/201) lower with 2 h–0.8 C military charging and about 14% (=100% × (201 − 173)/201) lower with 2 h–0.5 C military charging compared with that obtained according to the general commercial condition. It is not surprising to see that the difference is larger than that in the cell capacity discussed above. The cell specific energy depends on both the cell capacity and the discharging voltage. As mentioned in the result section, the subsequent discharging voltage is relatively low with these military charging protocols (see Fig. 1). Again, the incentive is significant for the military to adopt the general commercial standard 4.2 V since the cell specific energy can be enhanced immediately by 8 or 14% depending on the charging rate. The military FY-07 goal >200 Wh/kg can be met sooner in view of 201 Wh/kg obtained here according to the general commercial standard.

4.2. *Cell rate capability at room temperature*

4.2.1. *High rate discharging*

Table 3 lists the cell performance shown in Figs. 1–8 according to the various kinds of military conditions. For

Table 2
The specific energy of the cells under the different charging protocols

Charging condition	Specific energy (Wh/kg)	Comments
0.8 C to 4.2 V for 2.5 h	201	0.2 C (0.46 A) discharging to 2.8 V (general commercial condition)
0.8 C to 4.1 V for 2 h	184	0.67 A discharging to 2.5 V (military condition)
0.5 C to 4.1 V for 2 h	173	0.67 A discharging to 2.5 V (military condition)

Table 3
The military requirements and the information shown in Figs. 1–8

Test	Current (A)	Requirement	Studied GP 18650
Full discharge capacity	0.67	2 Ah	∼2.04 Ah
High rate discharge	3.33	1.36 Ah	∼2.05 Ah
Pulse discharge (5 s on 25 s off)	6	1.34 Ah	∼1.86 Ah
Discharge at −30 °C	0.67	1.33 Ah	∼1.34 Ah
Retention of charge after seven days at 50 °C	1.15	1.8 Ah or 94% retention	∼1.95 Ah or ∼95% (=1.95/2.04)
Cycle life, 224 cycles	0.67	1.8 Ah in the end	∼1.97 Ah
Cell overcharge	1.15	No fire; no explosion; no spark	No fire; no explosion; no spark
Cell short circuit		No fire; no explosion; no spark	No fire; no explosion; no spark
Cell forced discharge		No fire; no explosion; no spark	No fire; no explosion; no spark

comparison, the military requirements are also included in Table 3. It is noted that the studied GP lithium ion cell delivers 2.05 Ah (or 95% (=2.05/2.15)), which exceeds the requirements by 51% (=100% × ((2.05 − 1.36)/1.36) at 3.33 A or 1.43 C (=3.33/2.3) rate, and is much better than those reported previously [1]. George et al. [1] reported that the battery made with the commercial 18650 cells (2 Ah) can only deliver ∼67% (=100% × 4.7/5.6) of their low-rate capacity at such high rate. Further, the studied GP lithium-ion cell can deliver about 7% (=100% × (2.2 − 2.05)/2.2) more capacity if the cell charging voltage can be increased to 4.2 V in view of 2.2 Ah capacity obtained with the cell charged to 4.2 V at 0.8 C for 2.5 h.

4.2.2. High pulse discharging

Table 3 shows that the cell can deliver about 86% (=100 × 1.86/2.15) of the expected capacity with 5 s–6 A (or 2.6 C rate (=6/2.3)) pulses, which exceeds the requirement by 39% (=100% × (1.86 − 1.34)/1.34)). This result indicates that the positive temperature coefficient (or PTC) will not interfere with this high current pulse discharging if the PTC is selected properly and the cell rate capability is good like the studied cell. The PTC will have an effect in less than 5 s if the current is too high. In view of the individual pulse voltage profile shown in Fig. 3b, the major voltage drop is due to the ohmic resistance. Therefore, the cell performance can be improved further by decreasing the cell ohmic resistance. This can be done with more conductive electrolyte, composite electrodes, and more efficient current collection.

4.3. Discharge capability at low temperatures

Table 3 indicates that the studied GP cell not only meets the military requirement at −30 °C but also delivers about 47% of the expected capacity 2.15 Ah at 0.67 A or C/3.4 (=0.67/2.3). This result means that the operation temperature of lithium ion cell can be extended to −40 °C, which may become a requirement in 2004 [2].

4.4. High temperature stability

Tables 2 and 3 show that the cells still retained ∼1.95 Ah (or 95%) after one week at 50 °C and 4.1 V, which exceeds the requirement 1.8 Ah by about 8% (=(100% × (1.95 − 1.8)/1.8)). Further, the irreversible loss is only about 1.6%, which is similar to the past report in the literature [1].

4.5. Cycle life

The cell only lost ∼8% and still retained about 1.97 Ah at 0.8 C charging rate and about 1.9 Ah at 0.5 C charging rate after 224 cycles with the military cycling protocol. The studied cells exceed the requirement 1.8 Ah by 9% (=100% × (1.97 − 1.8)/1.8)) at 0.8 C charging rate and 5.6% (=100% × (1.9 − 1.8)/1.8) at 0.5 C charging rate. For comparison, the cell lost about 9.6% and still retained about 2.08 Ah (see Fig. 5) after 224 cycles according to the GP accelerated cycling condition. Clearly, the capacity loss is more when the cell is cycled to 4.2 V. However, as indicated in the result section, the cell capacity during the whole cycle life test with the 4.2 V limit or the GP cycling condition is much higher than that obtained according to the military cycling conditions (see Fig. 5). Therefore, the cycle life should not be a concern if the military changes their specification to 4.2 V from 4.1 V.

As the last point in the cycle life study, the cell rate capability does not degrade seriously after 224 cycles. Fig. 9 shows the discharging voltage profiles during the cycle life test according to the military conditions. It can be seen that

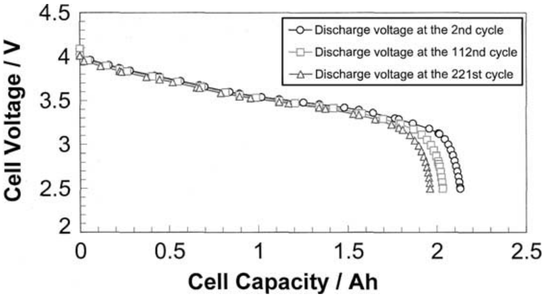

Fig. 9. The discharging voltage profiles at 0.67 A during the cycle life test according to the military cycling test protocol.

there is little decrease in the cell discharge voltage at 0.67 A with the increase in the cycle number.

4.6. *Abuse tolerance*

All tested cells passed the tests nicely. The cell temperature during the tests ranged from 62 to 70 °C, which means that the studied cells behave much better than some commercial cells reported previously [1]. For instance, Au et al. [1] reports that some commercial cells failed the military overcharge test violently. Further, there is no leakage in these abuse tests, which is a nice feature since the leaked electrolyte may cause a short and possibly a fire in the electronic controlling board used in battery packs [9].

5. Conclusions

GP 18650 cylindrical cells made with doped $LiNiO_2$ positive perform well under military conditions. The studied cells can deliver about 184 Wh/kg according to the military specification MIL-PRF-320521 while it delivers about 201 Wh/kg under the general commercial standard. The studied GP cells exceed all major military requirements including a high rate discharging, high current pulse discharging, low temperature discharging, cycle life, high temperature storage, and abuse tolerance such as overcharging, forced discharging, and external short. The cell capacity exceeds the requirement by 51% at the high discharge rate (3.3 A) and by 39% with the high current (6 A) pulse. The cell delivers not only ∼62% of the expected capacity at −30 °C but also ∼47% at −40 °C and at 0.67 A. The cell still retained 1.97 Ah (or 92%) after 224 cycles, which exceeds the requirement by ∼9%. The cell retained 1.95 Ah (or 95%) after one-week storage at 50 °C and at 4.1 V, which exceeds the requirement by 8%. The abuse tolerance is also very high. The maximum cell temperature ranged only from 62 to 70 °C during the overcharging, external short, and forced discharging, which is better than the some commercial cells reported in the literature [1]. Finally, it should be pointed out that, to take full advantage of the commercial lithium-ion cell, either the military increases the voltage limit to 4.2 V from 4.1 V or the cell manufacturers redesign their cells according to the 4.1 V charging voltage limit.

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