

On the discharge capability and its limiting factors of commercial 18650 Li-ion cell at low temperatures

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Abstract

We here study the discharge capability of commercial 18650 cylindrical lithium-ion cells at low temperatures. The discharge capacity at $-20\text{ }^{\circ}\text{C}$ ranges from 67 to 88% of the rated capacity at 0.2C rate, which is good. However, the cell discharge capacity varies substantially at -30 and $-40\text{ }^{\circ}\text{C}$ among the studied cells. It ranges from 2 to 70% of the rated capacity at $-30\text{ }^{\circ}\text{C}$, and 0 to 30% at $-40\text{ }^{\circ}\text{C}$ at 0.2C rate. The cell impedance at 1 kHz increases very little from room temperature down to -20 or $-30\text{ }^{\circ}\text{C}$ in general, which does not correlate with the cell discharge capability. However, the dc impedance is increased by a factor of about ten at $-30\text{ }^{\circ}\text{C}$ and about twenty at $-40\text{ }^{\circ}\text{C}$ from room temperature. The discharge capability at low temperature correlates well with the dc resistance at both room and low temperatures. The limiting factors in the discharge capability at low temperatures and the direction for the future improvement are discussed according to the cell discharge capability, the electrode geometric area, the cell impedance at 1 kHz, and the dc impedance at various temperatures. It appears that the ionic conductivity of the electrolyte and lithium solid diffusion in the electrode do not limit the cell discharge capability, while the lithium diffusion in the SEI layer on the positive surface may be the limiting factor. Cell discharge capability at low temperature does not correlate with cycle life at room temperature.

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Keywords: Discharge capability; Limiting factor; Li-ion cell

1. Introduction

The low temperature performance of a lithium-ion cell has been actively studied in the last 7 years. The effort is mainly in two directions: the development of a novel electrolyte and an understanding of the limiting factors in low temperature performance. In the early days, electrolyte development was the major effort. In 1997, Ein-Eli et al. [1] tried to develop an electrolyte for lithium-ion cells at low temperatures. Searching for a new electrolyte is still an on going effort [2]. In recent years, understanding the low temperature performance has started to attract significant attention. For instance, Ding et al. [3] recently studied extensively the phase diagrams of the conventional binary carbonates and clearly defined the limits of the mixtures in terms of the liquid phase stability at low temperature. Fan et al. [4] studied the electrochemical impedance spectroscopy (EIS) of lithium-ion cells and concluded that a significant increase in the impedance associated with the positive electrode is the main cause of poor performance at low temperatures, and that the ionic conductivity of

the electrolyte does not limit the low temperature performance. Huang et al. [6] considered that lithium diffusion in the carbon negative is the limiting factor. But their conclusion which excluded the effect of the SEI layer on the cell low temperature performance conflicts with previous [4,5] and recent studies [2,7]. Wang et al. [7] considered that the SEI layer impedance is the limiting factor at $-30\text{ }^{\circ}\text{C}$ even though they confirmed a beneficial effect [6] from the non-graphitized carbon on the low temperature discharge capability. Clearly, the limiting factors are still not defined well probably because of some serious limitations in the studies. The major limitation comes from the fact that most of these studies were done at very low rates such as C/10 or C/20 or even lower [2,6,7] probably because of (i) the cell type used (e.g. a coin cell which is a low rate cell because of its low stacking pressure inside) and (ii) a formulation that is not optimized to the cell rate capability. A non-optimized cell may obscure some real-limiting factors in the cell rate capability in view of the past studies showing that the cell rate capability can be strongly influenced by factors like separator porosity [8a], electrode active surface area [8b], electrode density [8b,9], and electrode loading [11]. Therefore, studies on the low temperature performance of a commercial 18650 cell is more

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appropriate and may offer some very instructive insights in understanding the limiting factors in the Li-ion cell performance at low temperatures because most commercial 18650 cells have been optimized to for the $C/5$ or $C/2$ rate.

The requirement of commercial 18650 cells in terms of low temperature performance is different from that in the military, aerospace and electric vehicle applications where a low temperature performance down to $-40\text{ }^{\circ}\text{C}$ is required [1]. The widely accepted industry standard for the lithium-ion cell in general electronic appliances is 80% of the rated capacity at the $0.2C$ rate at $-20\text{ }^{\circ}\text{C}$. This industry standard is met generally by most of the major lithium-ion manufacturers around the world. The acceptability of this low temperature performance is partially the reason why it has not improved as fast as the cell capacity at room temperature. The limited discharge capability at $-30\text{ }^{\circ}\text{C}$ is highlighted by the observations of Au et al. [10]. It was noted that the battery BB-2590 voltage profile in the initial discharge stage was a “V” shape and the minimum voltage was 20.8 V, which corresponds to 2.6 V (20.8/8) per cell since BB-2590 was made with three parallel groups of eight 18650 cells in series. If a typical cell discharge cut-off voltage like 2.7 or 2.8 V were used or the heat dissipation were better inside the battery, the battery BB-2590 would not deliver any significant capacity at the $0.33C$ rate at $-30\text{ }^{\circ}\text{C}$.

However, the situation has changed recently after cell capacity has advanced by more than 100% of that of the Sony cell introduced in 1990 and has started to approach the practical limit ~ 2.5 Ah predicted by Fan and Magnuson [11] through a computer simulation. A significant amount of attention has now been shifted to some other improvements including the cell discharge capability at low temperatures. We have characterized the discharge capability of recently commercially available 18650 cells at low temperatures to establish a new reference point for this unique product (the cell charge capability at low temperature will be addressed in future work because it is a different issue compared with the discharge capability [7]). Subsequently, we shed some light on the limiting factors on the discharge capability at low temperature by studying the cell rate capability at room temperature, the ac and dc cell impedance at various temperatures, and the effects of cell design properties such as the electrode geometric area. We hope that our studies provide some directions for future improvements in cell discharge capability at low temperatures. Finally, we check the cycle life at room temperature to see whether there is any correlation between low temperature performance and cycle life.

2. Experimental

All cells were obtained from the commercial market. The rated capacity is usually 2 Ah according to the cell manufacturer except the cell from manufacturer E. For the cells from the manufacturer E, the rated capacity is 2.2 Ah.

Typically, two or three cells from each brand were tested in every measurement.

For the discharge test at low temperatures, each cell was charged at $0.8C$ rate for 2.5 h at room temperature first and then cooled down to and kept at the target temperature in a controlled low temperature chamber for 4 h before the cell was discharged. The 4 h at the low temperature ensured that the electrolyte was not in the super cooled state [12] and the result truly reflects the cell discharge capacity at the target low temperature. Typically, the test sequence was room temperature, -20 , $-30\text{ }^{\circ}\text{C}$, and finally $-40\text{ }^{\circ}\text{C}$.

The discharge capability test at room temperature was done in an open tray using Maccor BTS-4000 with the following procedure: (1) charge the cell to 4.2 V for 2.5 h at $0.8C$, (2) rest for 5 min, (3) discharge at $0.2C$ rate to 2.8 V, (4) rest for 20 min, (5) charge the cell to 4.2 V for 2.5 h at $0.8C$, (6) rest for 5 min, (7) discharge at $0.5C$ rate to 2.8 V, (8) rest for 20 min, (9) charge the cell to 4.2 V for 2.5 h at $0.8C$, (10) rest for 5 min, (11) discharge at $1C$ rate to 2.8 V, (12) rest for 20 min, (13) charge the cell to 4.2 V for 2.5 h at $0.8C$, (14) rest for 5 min, (15) discharge at $2C$ rate to 2.8 V, and (16) end. A thermocouple was attached to the middle of the outside can wall with an electronic insulating black tape for monitoring the cell temperature simultaneously during the test.

The cycling test was carried out in an open tray at room temperature using Firing Circuit BRT 2000 with the accelerated cycle life testing procedure including the following steps: (1) charge the cell to 4.2 V for 2.5 h at $0.8C$, (2) rest for 5 min, (3) discharge at $1C$ rate to 2.8 V, (4) rest for 5 min, (5) discharge at $0.2C$ rate to 2.8 V, (6) rest for 20 min, and repeat steps (1–6) for 300 cycles or until the cell capacity at $1C$ rate was decreased by 20%.

3. Results

3.1. Discharge capability at low temperatures

Fig. 1 shows the discharge capacity of lithium-ion 18650 cells at $-20\text{ }^{\circ}\text{C}$ at the $0.2C$ rate (0.4 A) from two major Japanese manufacturers (A and B), and four major non-Japanese manufacturers (C, D, E, and GP). All cells except from the C cell (~ 1.35 Ah) can deliver over 1.6 Ah at $0.2C$ rate and $-20\text{ }^{\circ}\text{C}$. The B and GP cells can deliver about 1.75 Ah, which is the best. Further, the GP cell can deliver ~ 1.5 Ah at $0.5C$ rate (or 1 A).

Fig. 2 shows the discharge capacity at $-30\text{ }^{\circ}\text{C}$ at the $0.2C$ rate. Unlike the small difference in the discharge capacity at $-20\text{ }^{\circ}\text{C}$, the variation at $-30\text{ }^{\circ}\text{C}$ was quite substantial. The GP and B cells can deliver ~ 1.4 Ah at $0.2C$ rate, which again was the best. The D and E cells can deliver ~ 1.2 and ~ 0.77 Ah, respectively, at $0.2C$. However, the A and C cells can only discharge 0.04 and 0.08 Ah, respectively, at $0.2C$ rate. Further, the GP cell can deliver 1 Ah at the $0.5C$ rate even though this discharge capacity may be effected to some

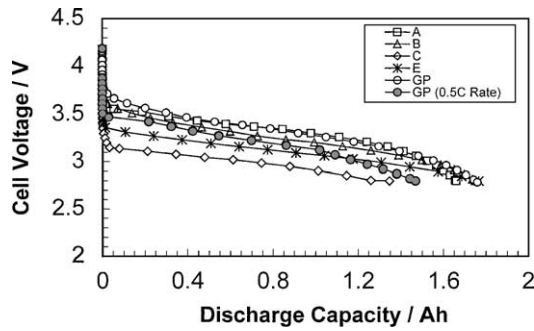


Fig. 1. The discharge voltage vs. the cell capacity at $-20\text{ }^{\circ}\text{C}$ and $0.2C$ or 0.4 A rate with the cut-off voltage 2.8 V for the cells made by two major Japanese manufacturers A and B, and three non-Japanese manufacturers C, E, and GP. For a comparison, the discharge capacity of GP cell at $0.5C$ rate was also included. The cells were charged at $0.8C$ for 2.5 h at room temperature before the discharge at $-20\text{ }^{\circ}\text{C}$.

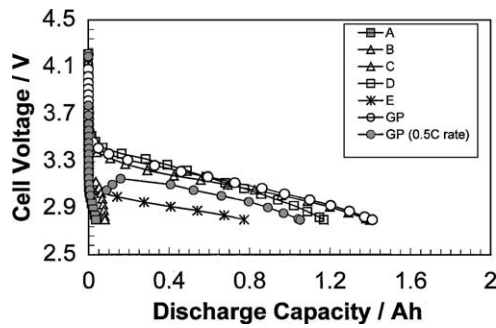


Fig. 2. The discharge voltage vs. the cell capacity at $-30\text{ }^{\circ}\text{C}$ and $0.2C$ or 0.4 A rate with the cut-off voltage 2.8 V for the cells made by two major Japanese manufacturers A and B, and four non-Japanese manufacturers C, D, E, and GP. For a comparison, the discharge capacity of GP cell at $0.5C$ rate was also included. The cells were charged at $0.8C$ for 2.5 h at room temperature before the discharge at $-30\text{ }^{\circ}\text{C}$.

degree by the cell self heating manifested by the “V” shape of the discharge voltage profile at the beginning of the discharging process.

Fig. 3 shows the discharge capacity at $-40\text{ }^{\circ}\text{C}$ at the $0.2C$ rate. The performance gap is even larger compared with the

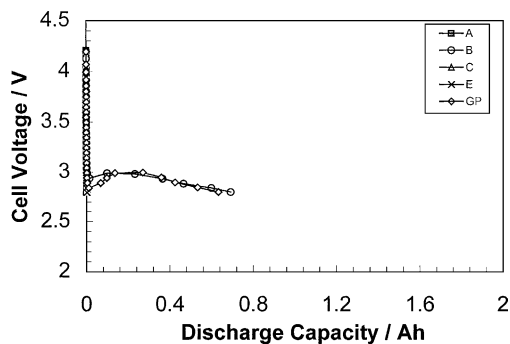


Fig. 3. The discharge voltage vs. the cell capacity at $-40\text{ }^{\circ}\text{C}$ and $0.2C$ or 0.4 A rate with the cut-off voltage 2.8 V for the cells made by two major Japanese manufacturers A and B, and three non-Japanese manufacturers C, E, and GP. The cells were charged at $0.8C$ for 2.5 h at room temperature before the discharge at $-40\text{ }^{\circ}\text{C}$.

results obtained at $-30\text{ }^{\circ}\text{C}$. The B and GP cells can still deliver about 0.7 Ah at $0.2C$ rate. However, the A, C, and E cells cannot perform at $-40\text{ }^{\circ}\text{C}$ and at $0.2C$ rate at all.

3.2. Rate capability at room temperature

Fig. 4a–f show the discharge capacities at nominal room temperature ($\sim 21\text{ }^{\circ}\text{C}$) and their corresponding temperature profiles at 0.2 , 0.5 , 1 , and $2C$ rates for the cells made by different manufacturers: (a) A, (b) B, (c) C, (d) D, (e) E, and (f) GP. Four observations can be made. First of all, the cells usually meet their claimed capacity, 2 or 2.2 Ah at $0.2C$ rate except the A cell, which is very surprising since manufacturer A is the industry leader. Secondly, there is no significant difference in the cell capacity at $1C$ or lower C rates among all tested cells. Thirdly, the cell capacity at $2C$ rate varies substantially from 0.6 Ah to about 2 Ah among the tested cells. Fourthly, the cell self heating is significant especially in the high C rate discharging. It is noted that the cell temperature is increased dramatically with increase in the discharge rates. The cell temperature at the $2C$ rate goes up almost linearly and approaches up to $\sim 50\text{ }^{\circ}\text{C}$ for some cells like the E cell. The B cell shows the lowest temperature rise to $\sim 43\text{ }^{\circ}\text{C}$ during $2C$ rate discharging. The C cell shows the fastest increase in the cell temperature during $2C$ rate discharging. Within 9 min , the C cell temperature increases from 21 to $44\text{ }^{\circ}\text{C}$.

3.3. Electrode geometric area

The electrode geometric area has been measured from the open cell, and is listed in Table 1. The electrode thickness data are neglected because it is difficult to obtain accurate electrode thicknesses from the opened cells due to electrode expansion caused by electrolyte absorption, lithium intercalation and de-intercalation.

3.4. Cell impedance at 1 kHz and dc impedance at various temperatures

Table 2 lists the cell impedances at 1 kHz . The cell impedance was increased only by about $23\text{ m}\Omega$ for the 30% charged B cell and $10\text{ m}\Omega$ for the 30% charged E cells from room temperature to $-30\text{ }^{\circ}\text{C}$. For the fully charged A,

Table 1
Electrode geometric area (cm^2) for the cells made by different manufacturers

Manufacturer	Negative	Positive
A	644	602
B	700	637
C	654	600
D	638	611
E	670	652
GP	613	578

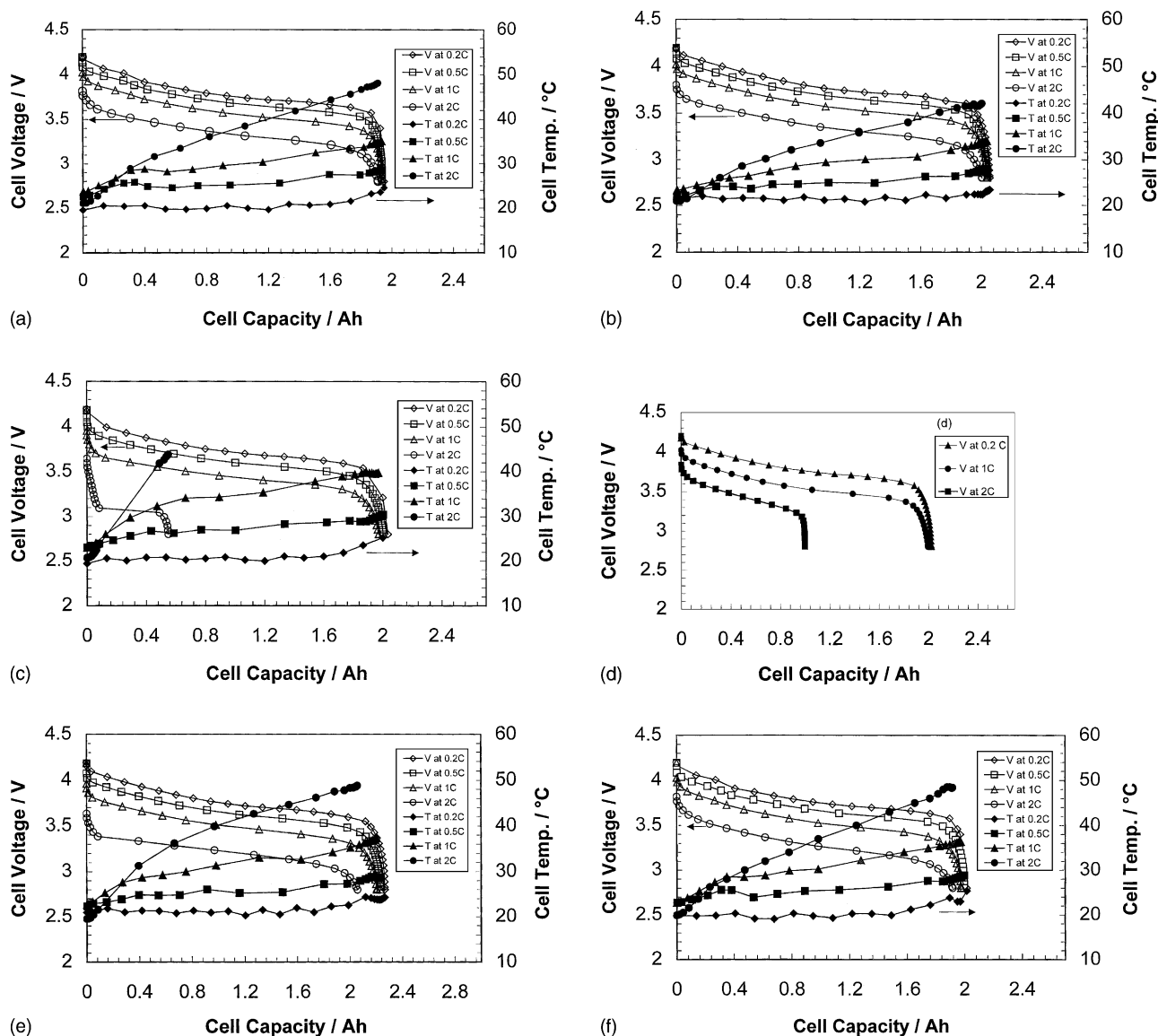


Fig. 4. The discharge capacity voltage profiles and their corresponding temperature profiles at 0.2C (0.4 A), 0.5C (1 A), 1C (2 A) and 2C (4 A) rates and room temperature for the cells made by (a) A, (b) B, (c) C, (d) D, (e) E, and (f) GP. The cell was placed in an open tray without temperature controlling. The cell temperature at 0.2C rate increased very little, which means that the cell was optimized according to 0.2C rate.

C, and GP cells, the impedance was increased by about 50 mΩ from room temperature to −30 °C. The relatively large increase in the cell impedance at 1 kHz for the fully charged cells is probably due to the changes in the origins of the cell impedance at 1 kHz. It is highly likely that the

charged cell impedance at 1 kHz at −30 and −40 °C contains more contributions from the electrode interface. Fig. 5 shows the temperature dependence of the cell impedances at 1 kHz. It is noted that the temperature dependence is not a linear or Arrhenius behavior, which suggests the origin of the charged cell impedance at 1 kHz is changed when the temperature is decreased to −30 or −40 °C from room temperature.

Table 2
The cell impedance (mΩ) at 1 kHz at different temperatures

Manufacturer	State of charge (%) ^a	23 °C	0 °C	−20 °C	−30 °C
A	100 (4.19)	63	67	78	112
B	30 (3.8)	58	59	68	81
C	100 (4.19)	70	80	90	120
E	30 (3.8)	68	68	70	78
GP	100 (4.19)	66	71	88	108

^a The values given within parenthesis are in volts.

Table 3 lists the dc impedances obtained from the A, B, C, D, E, and GP cells. The voltage drop extrapolated to zero capacity (or time) of the polarization at the 0.2C rate is used to estimate the dc impedance (see the insert in Fig. 6). The intention of this data treatment is to have a more generic dc impedance for a better comparison among the different temperatures and cells from the different manufacturers. Fig. 6 shows the temperature dependence of the dc impedance for

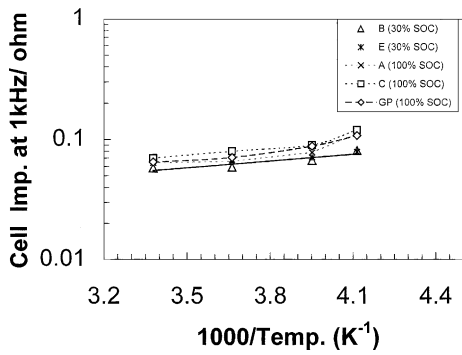


Fig. 5. The temperature dependence of the impedance at 1 kHz for the cells made by A, B, C, E, and GP. For the B and E cells, the cells were in 30% state of charge. For the A, C, and GP cells, the cells were in 100% state of charge.

Table 3
The dc impedance (Ω) at various temperatures

Manufacturer	23 °C	0 °C	−20 °C	−30 °C	−40 °C
A	0.18		1.5	3.0	
B	0.17		1.4	1.9	3.2
C	0.37		2.5	3.0	
D	0.20	0.41		2.1	
E	0.31		2.1	2.9	
GP	0.17		1.3	1.9	3.4

the cells from the different manufacturers. It is noted that the temperature dependence is linear in the Arrhenius plot except the A cell, which will be discussed later. It is also noted that the dc impedance is increased substantially when the cell temperature is decreased from room temperature to low temperatures like -30 or -40 °C. For instance, the cell dc impedance from the B cell is 0.170Ω at room temperature and 3.2Ω at -40 °C. The highest dc impedance was seen with the C and E cells. Their dc impedance are 0.37 and 0.31Ω at room temperature, and 3 and 2.9Ω , respectively, at -30 °C.

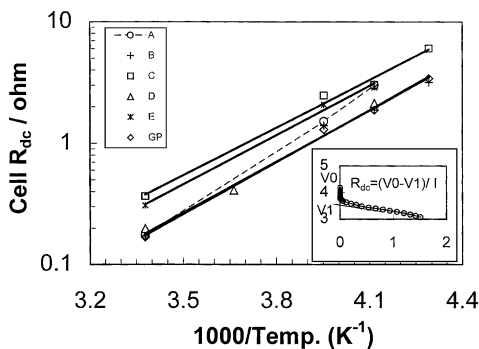


Fig. 6. The temperature dependence of the dc impedance for the cells made by A, B, C, D, E, and GP. It is striking to note that the slope is very similar for most of the cells except the A cell.

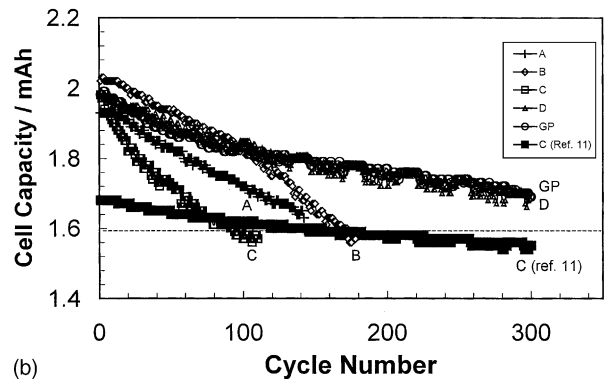
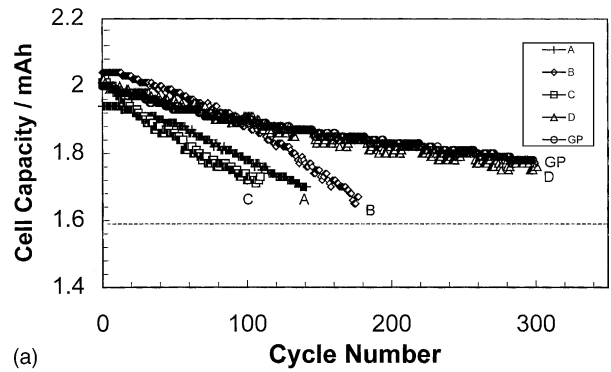


Fig. 7. The cell capacity vs. the cycle number at room temperature and at (a) $0.2C$ ($0.4 A$) rate, and (b) $1C$ ($2 A$) rate, for the cells made by A, B, C, D, and GP using the accelerated test procedure described in Section 2. For a comparison, the cycle life of the 1.6 Ah cell from the manufacturer C was also included. The cells were placed in an open tray without any temperature control. The cell temperature was typically 25 – 28 °C in the $0.2C$ rate discharging, and 35 – 40 °C in $1C$ discharging during the cycling test.

3.5. Cycle life at room temperature

Fig. 7a and b shows the cycle life at (a) $0.2C$ rate and (b) $1C$ rate for the cells made by A, B, C, D, and GP. At the $0.2C$ rate, the cycle life for a 20% loss of the rated capacity is: GP \sim D (>300 cycles) $>$ B (~ 200 cycles) \sim A (~ 200 cycles) $>$ C (~ 170 cycles). At the $1C$ rate, the cycle life for a 20% loss of the rated capacity is GP \sim D (>300 cycles) $>$ B (~ 170 cycles) $>$ A (~ 150 cycles) $>$ C (~ 94 cycles). It is noted that the cycle life at the $1C$ rate is poorer in general than that obtained at $0.2C$ rate, especially for the C cell.

4. Discussion

4.1. Discharge capability at low temperatures

As can be seen from Fig. 1, the cells perform well and meet the widely accepted standard 80% of the rated capacity at -20 °C at the $0.2C$ rate except the C cell. The C cell can deliver about 67% of the rated capacity at -20 °C and the $0.2C$ rate. The order of the discharge capability normalized

according to the 0.2C capacity at room temperature is B (88%) ~ GP (88%) > A (85%) > E (80%) > C (67%) at -20°C .

In view of Fig. 2, the discharge capability at -30°C varies in a wide range from 2% of the rated capacity for the A cell to 70% of the rated capacity for the B and GP cells. The order of the discharge capability normalized according to the 0.2C capacity at room temperature is B (70%) ~ GP (70%) > D (58%) > E (35%) > C (4%) > A (2%) at -30°C . The conflicting order for the A cell at -20 and -30°C is probably due to the electrolyte in the A cell being frozen to a large degree between -20 and -30°C , which is also suggested by the non-linear behavior in the dc impedance (see the later section for the detail).

The discharge capability at -30°C from the GP and B cells is better than that from an AA prototype reported in [2] and a 25 Ah aerospace battery reported in [16]. Smart et al. [2] reported that their AA prototype lithium-ion cell could deliver ~70% of the rated capacity at -30°C and C/20 rate. Marsh et al. [16] showed that their 25 Ah aerospace battery could deliver 36% at 0.2C rate and -30°C . For the performance at -40°C , only B and GP cells can discharge a significant capacity at 0.2C rate, which signifies a milestone development in the low temperature performance of the commercial 18650 cells. This low temperature performance is a new reference point for the 18650 cells and may become a new industry standard in the future.

4.2. Discharge capability at room temperature and its relation to the low temperature discharge capability

As can be seen from Fig. 4a–f and Table 4 (Table 4 lists the normalized capacity at the various rates), there is no significant difference in the discharge capacity at 1C or low C rates. The ratio of 1C capacity to 0.2C capacity only varies from 99 to 97%. This observation is due to the effect from the cell self heating in the test. However, the difference in the cell rate capability at room temperature can still be inferred from the cell capacity at 2C rate and the cell temperature during the 1C or 2C discharging processes. The ratio of the 2C capacity to the 0.2C capacity is only 27% for the C cell but 98% for the A and B cells. The C cell gets the worst discharge capability at room temperature in view of its lowest discharge capacity at 2C rate and the fastest temperature increase during the 2C discharge mentioned in the result section. In fact, the rate of

the C cell is so poor that the cell self-heating trips its PTC so as to limit the cell discharge capacity. The PTC effect can also be seen in the D cell probably because of the low rated PTC used in view of its decent rate capability at room and low temperatures. The B cell gets the best rate capability at room temperature in view of its highest 2C discharge capacity and the lowest cell temperature during the discharging processes at 1C and 2C rates. The discharge capability of B and C cells at room temperature correlate well with their discharge capability at low temperatures. This correlation suggests that the limiting factors in discharge capability at room temperature are similar to those at low temperatures if there is no phase change in the electrolyte like the cell A.

4.3. Limiting factors in the discharge capability at low temperatures

4.3.1. Effect from the electrode geometric area

It is common knowledge that a relatively large electrode geometric area or a relatively thin electrode allows a higher cell discharge capability. The question is to what degree in the presently studied cases. As the first step, the positive electrode geometric area in Table 2 is normalized according to the electrode area of GP cell. The positive is considered because the positive area controls the cell capacity. It is noted that the order of the normalized electrode geometric area is:

$$E (1.13) > B (1.10) > A (1.04) \sim C (1.04) > GP \quad (1)$$

In view of the low temperature discharge capability shown in Figs. 1–3, clearly there is only a weak correlation, if any, between the electrode area and the discharge capability at the low temperatures since the E cell shows the second poorest discharge capability at low temperatures even though its electrode area (or thickness) is the largest (or lowest). (Please note that the largest electrode area corresponds to the thinnest electrode because the inside 18650 can volume is fixed.) In other words, the effect from the electrode geometric area or thickness on the cell discharge capability is very limited in the studied cases. The only possible conclusions we can make are (i) that the second largest electrode area in the B cell may be partially responsible for the over all best rate capability of the B cell, and (ii) that the relatively large electrode area may contribute the difference between the C and E cells in the discharge capability.

Table 4

The normalized cell capacity and the temperature increase during the discharging at the various C rates

Manufacturer	1C cap/0.2C cap (%)	2C cap/0.2C cap (%)	ΔT at 0.2C ($^{\circ}\text{C}$)	ΔT at 0.5C ($^{\circ}\text{C}$)	ΔT at 1C ($^{\circ}\text{C}$)	ΔT at 2C ($^{\circ}\text{C}$)
A	99	98	5	6	11	27
B	99	97	1	6	11	21
C	97	27	7	7	17	23
D	99	50				
E	97	91	4	6	14	30
GP	98	96	5	6	13	28

4.3.2. Effect from the ionic conductivity of the electrolyte

It has been found in previous studies [4,21] that there was no correlation between the cell discharge capability at low temperature and the ionic conductivity of the electrolyte. For instance, the ionic conductivity at $-20\text{ }^{\circ}\text{C}$ is $\sim 1.9\text{ mS/cm}$ for both 1 M LiPF_6 in 30% EC + 70% DEC and 1 M LiPF_6 in 30% EC + 70% DMC electrolytes, but the cell using 1 M LiPF_6 in 30% EC + 70% DEC can deliver 90% more than that using 1 M LiPF_6 in 30% EC + 70% DMC does at the same rate [21]. It appears that our observation of the cell impedance at 1 kHz confirms that the electrolyte ionic conductivity does not limit the cell discharge capability at low temperature.

Let us look at the cell impedance for the 30% charged cells at 1 kHz only because the cell impedance at 1 kHz for the fully charged cells is complicated as mentioned in Section 4.3.1. As can be seen in Table 2, there is only about 2–10 m Ω increase (5–15% increase) in the cell impedance at 1 kHz from room temperature to $-20\text{ }^{\circ}\text{C}$. This very small increase agrees well with Nagasubramanian et al. [13] observation in which the ohmic impedance of the Sony 18650 cells remains nearly constant to $-20\text{ }^{\circ}\text{C}$. This extremely weak temperature dependence of the cell impedance at 1 kHz indicates that the cell ohmic resistance must be dominated by the electronic resistance of the electrodes and the cell header. The cell impedance at 1 kHz is mainly the cell ohmic resistance that is the summation of the electronic and ionic resistance. The electronic resistance has negligible temperature dependence in the studied temperature range. The cell impedance would be increased by about 100% from room temperature down to $-20\text{ }^{\circ}\text{C}$ and about 200% down to $-30\text{ }^{\circ}\text{C}$ if the ionic resistance of the electrolyte dominates the cell impedance at 1 kHz in view of $\sim 100\%$ decrease at $-20\text{ }^{\circ}\text{C}$ [4] and $\sim 200\%$ decrease at $-30\text{ }^{\circ}\text{C}$ [19] in the electrolyte ionic conductivity.

Further, the electrolyte ionic resistance in the cell should be 2–10 m Ω at room temperature and 4–20 m Ω at $-20\text{ }^{\circ}\text{C}$ because the cell electrolyte ionic resistance should be equal to the increase in the cell impedance increase in view of the 100% decrease in the electrolyte conductivity from room temperature to $-20\text{ }^{\circ}\text{C}$ [4] as mentioned above. The voltage drop caused by the cell ionic resistance at 0.2C rate (0.4 A) will be only 4 mV ($0.4 \times 10\text{ m}\Omega$) at room temperature and 8 mV ($0.4 \times 20\text{ m}\Omega$) at $-20\text{ }^{\circ}\text{C}$. Obviously, unless there is a recrystallization (or solidification) in the electrolyte, the electrolyte conductivity should not be among the limiting factors in the cell discharge capability at room temperature as well as at low temperatures.

4.3.3. Effect from the SEI layer on the electrode surfaces

It is generally considered that the SEI layer on either positive or negative can affect the cell rate capability greatly [2,5,7]. We examine this issue through the cell dc impedance.

Unlike the cell impedance at 1 kHz, the cell dc resistance or impedance is increased by a factor of around 10 to $-30\text{ }^{\circ}\text{C}$ and about 20 to $-40\text{ }^{\circ}\text{C}$ from room temperature, which can be seen clearly in Table 3. This cell dc impedance is a good

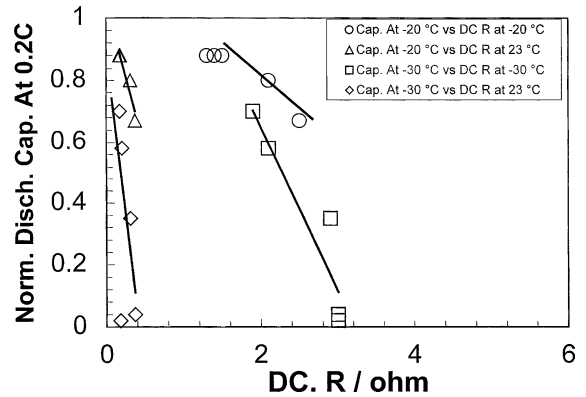


Fig. 8. Shows the dc resistance at various temperatures vs. 0.2C normalized discharge capacities at $-20\text{ }^{\circ}\text{C}$ and $-30\text{ }^{\circ}\text{C}$ according to 0.2C capacity at room temperature for A, B, C, D, E, and GP cells. The 0.2C normalized discharge capacity is equal to the discharge capacity at 0.2C rate and low temperature like $-20\text{ }^{\circ}\text{C}$ divided by the discharge capacity at 0.2C rate and room temperature. The discharge capacity at low temperatures is inversely and linearly proportional to the dc resistance at both room and low temperatures.

measure of the cell rate capability at both low and room temperatures. There is a correlation between the dc impedance and the low temperature discharge capability. For instance, the C cell gets the highest dc impedance at both low and room temperatures, which correlates with the poorest discharge capability at both room and low temperatures. The B cell gets the lowest dc impedance at both low and room temperatures, which correlates with the best over-all discharge capability at room and low temperature like $-40\text{ }^{\circ}\text{C}$. Further, it appears that this correlation is approximately linear, which can be seen in Fig. 8. Fig. 8 shows 0.2C normalized discharge capacities at -20 and $-30\text{ }^{\circ}\text{C}$ according to 0.2C capacity at room temperature in relation to the dc resistance at either room temperature or low temperatures. The discharge capacity at low temperatures is inversely and linearly proportional to the dc resistance at both room and low temperatures. This observation is significant in a sense that the discharge capability at low temperature can be predicted from the dc resistance at room temperature. This is not surprising since, as suggested above, the rate-limiting factor in the discharge capability does not change when the temperature is decreased from room temperature to $-30\text{ }^{\circ}\text{C}$ for most of the studied cases except A cell. Please note that no change in the rate-limiting factors in the discharge capability is further supported by the fact that the temperature dependencies of the dc impedances are linear for all the cells except the A cell. For the A cell, as mentioned above, it is highly likely that most of the electrolyte is frozen between -20 and $-30\text{ }^{\circ}\text{C}$ so that the temperature dependence is not linear beyond $-30\text{ }^{\circ}\text{C}$. This scenario justifies the effort in searching for a new electrolyte with a relatively low freezing point.

No change in the rate-limiting factors seems to conflict with previous work [4]. It was thought that the different factors like the electrolyte conductivity and SEI layer

impedance may have a very different temperature dependence, therefore, the rate-limiting factors may change when the temperature changes from room temperature to low temperatures like -20 or -30 °C. However, the conflict disappears if the factor with the weak temperature dependence like the electrolyte conductivity is not considered among the limiting factors at room temperature. In other words, the conflict will not be there if the cross over point is pushed to above room temperature, and only factors with relatively strong temperature dependence are considered as among the limiting factors in the cell discharge capability at both room and the studied low temperatures. In view of this point, the scope of the limiting factors in the cell discharge capability will narrow down to the charge transfer reaction on the electrode surface and lithium solid diffusions in the carbon, positive active particles, and the SEI layers on the surface of either positive or negative electrodes or both. The charge transfer reaction and the solid diffusion usually depend on the temperature more strongly than the diffusion in the liquid phase [4,14,15,20] because the activation energy is usually higher for the charge transfer reaction and solid diffusion than for the liquid diffusion. For instance, lithium diffusion in coke is decreased by a factor of about 200 from 1.14×10^{-9} to 3.04×10^{-11} cm^2/s when the temperature decreases from room temperature to -40 °C [20], which is well above the decrease in the electrolyte conductivity as mentioned above [4].

The SEI layer on the carbon surface and the lithium diffusion in the carbon have been considered as two of the limiting factors [2,6,7] in the cell discharge capability at low temperatures. The increase in the charge transfer resistance on the positive surface has been thought as the major cause in the cell rate degradation in the cell aging and cycling [22]. However, as will be discussed below, the lithium diffusion in the SEI layer on the surface of LiCoO_2 particles may be the most important rate-limiting factor in the studied cases.

As can be concluded, all studied cells were made with LiCoO_2 positives and the highly graphitized carbon negative in view of the flat voltage profiles at $0.2C$ rate seen in Fig. 4a–f. The voltage profile at $0.2C$ rate is very close to the cell OCV and hence can be used to identify the kinds of the electrode actives used. In terms of lithium diffusion in the carbon particles, these highly graphitized negatives should behave similarly and not cause any significant difference in the dc impedance. This is because only non-graphitized coke gets a higher lithium diffusion in the carbon particles than that in the highly graphitized MCMB due to the high slope open circuit voltage (OCV) profile of the non-graphitized carbon according to the reports [6,7]. Further, it is likely that the lithium diffusion in the LiCoO_2 particle may not be the rate-limiting factor also in view of (i) a smaller particle size for a typical commercial LiCoO_2 particle compared with that for a typical commercial graphite particle and (ii) the similar lithium diffusion coefficient in LiCoO_2 (10^{-9} to 10^{-12} m^2/s at room temperature) reported in the literature

[25–28] compared with reported value (10^{-9} to 10^{-12} m^2/s at room temperature) [23,24] in the graphitized carbon. Furthermore, the effect from the impedance of the negative SEI layer should not be as significant as from that of the positive in view of the positive being the major contribution to the ac impedance of lithium-ion cells in mid or low frequencies including the commercial 18650 cells at both room temperature and low temperatures [4,9,13,17]. It is understandable for the positive to dominate the cell impedance because (i) the chemical composition of the SEI layer should be similar on positive and negative electrode surfaces [22] and (ii) the surface area of the commercial LiCoO_2 [29] is normally only a fraction of the commercial MCMB or natural graphite [30]. On the basis of above discussion, the SEI layer on the positive surface should be the most important factor among the rate-limiting factors for all studied cells. The similar apparent activation energies of the cell dc resistance for most of studied cells support the view that the discharge capability of all studied cells is controlled by the SEI layer on the positive (the apparent activation energies are 25 kJ/mol for C cell, 26 kJ/mol for E cell, and 27 kJ/mol for B and GP cells). The effect from the charge transfer resistance on the surface of the positive is not considered because of many convincing previous studies on the effect of the SEI layers [2,5,7,31] on either positive or negative. The relatively high dc resistances of C and E cells compared with these of B, D and GP cells is likely due to the effect from the SEI layer on the surface of positive. Specifically, the SEI layer on the positive surface of C and E cells is more resistive than that on the positive surface of B, D, and GP cells. The exact cause for a highly resistive of the positive SEI layer in the C and E cells is subject to further studies.

However, it should be pointed out that the positive being limiting may be overcome considering the fact that an exceptional high rate capability of the LiCoO_2 positive can be obtained from a LiCoO_2 with a high surface area [8]. Specifically, the low temperature performance of the commercial 18650 cells may be improved further with a better-engineered formulation, electrode design, electrolyte, and a proper selection in the electrode material.

4.3.4. Cycle life and its relation to cell discharge capability at low temperatures

It appears that the cycle life has degraded significantly for the cells made by some manufacturers compared with the previous study [18]. The manufacturers like A, B, and C have increased their cell capacity at the expense of the cell cycle life since they used to make better cells in the past [11,18]. The cycle life of the D and GP cells are the best in this study.

There is no good correlation between the cycle life and the discharge capability at low temperature. The C cell has both poor cycle life and discharge capability at low temperature. However, the B cell with the best rate capability does not yield a good cycle life. It appears that the cycle life and the discharge capability can be optimized separately.

5. Conclusions

All of studied commercial 18650 cells perform well at $-20\text{ }^{\circ}\text{C}$ and a $0.2C$ rate. However, there is a large variation in the cell discharge capacity at or below $-30\text{ }^{\circ}\text{C}$. The cell discharge capacity ranges from 2 to 70% of the rated capacity at $-30\text{ }^{\circ}\text{C}$ and 0–30% at $-40\text{ }^{\circ}\text{C}$. There is no significant increase in the cell impedance at 1 kHz, but the dc impedance increased by a factor of twenty when the cell temperature decreases from room temperature to $-40\text{ }^{\circ}\text{C}$ for some cases like B and GP cells. It appears that the electrolyte ionic resistance does not limit the cell discharge capability at room and low temperatures. Further, it appears that the rate-limiting factors at room temperature are the same as those at low temperatures. Furthermore, the positive or most likely the SEI layer on the positive surface may be the most important rate-limiting factor in the cell discharge capability at both room temperature and low temperature in these studied cells. A better discharge capability may be obtained with a thin electrode, fine active material, and a better-engineered electrode formulation.

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