Capacity Fade Study of Lithium-ion Battery Cycled at High Discharge Rates

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Submitted as a paper to
Dr. K. C. Dyer, US Regional Editor
Journal of Power Sources
16 Seven Oaks Circle
Madison, New Jersey, 07940-1314

Submission: December 2002

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Abstract

Capacity fade of Sony 18650 Li-ion batteries cycled using different discharge rates was studied at ambient temperature. The capacity losses were estimated after 300 cycles at 2C and 3C discharge rates and were found to be 13.2% and 16.9% of the initial capacity, respectively. At 1C discharge rate the capacity lost was only 9.5%. The cell cycled at high discharge rate (3C) showed the largest internal resistance increase of 27.7% relative to the resistance of the fresh cells. The rate capability losses were proportional with the increase of discharge rates. Half-cell study and material and charge balances were used to quantify the capacity fade due to the losses of primary active material (Li\(^+\)), the secondary active material (LiCoO\(_2\)/C)) and rate capability losses. It was found that carbon with 10.6% capacity loss after 300 cycles dominates the capacity fade of the whole cell at high discharge rates (3C). A mechanism is proposed which explains the capacity fade at high discharge rates.

Keywords: Lithium-ion batteries, Capacity fade, High discharge rates, Solid Electrolyte Interface (SEI).
1. Introduction

It is generally thought that lithium deposition, electrolyte decomposition, active material dissolution, phase transition inside the insertion electrode materials, and further passive film formation on the electrode and current collectors can to different degrees affect the capacity fade of lithium ion batteries[1-5]. Quantifying these degradation processes will not only help to improve the predictive capability of battery models but also help to elucidate the mechanism of this capacity fade.

In this paper, capacity fade of Sony 18650 lithium-ion batteries cycled using 1C, 2C and 3C discharge rates (up to 300 times) at ambient temperature was quantitatively measured. Parameters obtained through fitting EIS spectra and the SEM images taken for the carbon material samples were used to identify the primary cause of the capacity fade of the whole lithium-ion battery.

2. Experimental

The experiments were done on the Sony US18650 (1.4Ah) lithium-ion batteries. The batteries were charged under constant current and constant voltage protocol (CC-CV). The cells were initially charged under 1A constant current until the voltage reached 4.2 V. Next, the voltage was kept constant at 4.2 V until the charge current decayed to 50 mA. To study the effects of the discharge rate, the cells were discharged at 1C (1.4 A), 2C (2.8 A), and 3C (4.2 A) rate. Cycling studies were done on Arbin Battery Test System. The data logging was set up on the basis of differential time and differential voltage during the process of charge or discharge by a computer with Mitspro software. Solartron SI 1255 HF Frequency Response Analyzer and Potentiostat/Galvanostat Model 273A were used for electrochemical characterization of these
cells. For the studies of the capacity fade of whole-cells, cycling would be stopped every 50 cycles so that the batteries would be fully charged (with 1.0 A constant current and 4.2 V constant voltage) and then discharged at constant current (0.7A) between the voltage windows from 4.2 to 2.5 V. The maximum cycle number in our studies was 300.

Internal DC resistance of the whole-cell was determined by intermittently interrupting the discharge current for 5 seconds in the process of discharge and the DC resistance of the whole-cell was calculated using the relationship: \( R_{dc} = \frac{\text{Discharge Voltage} - \text{Open Circuit Voltage (0.1 second after the pulse rest)}}{\text{Discharge Current (1A)}} \)

In order to identify the cause of the capacity fade of the whole-battery, half-cell studies were carried out on both fresh and cycled batteries. Cells under fully discharged state (discharged to cutoff 2.5 V using \( \frac{C}{10} \) discharge rate) were cut open in a glove box filled with pure argon (National Gas and Welder-Class: Regular). Both the LiCoO\(_2\) and Carbon electrodes that were spirally wound together with the separator in between them were carefully taken out. Subsequently the material was cleaned and allowed to dry at ambient temperature for one hour. Small pellets with a diameter of 1.1 cm were punched out of the electrode materials using a sharp steel punch. Since both sides of the current collectors were coated with active materials, the material on one side was scraped to ensure good contact with the steel current collectors of the T-shaped polypropylene Swagelock- type cells. Pellets prepared as mentioned above are the standard samples for all the experiments of the half-cell studies. In the T-shaped cells, pure lithium foil was used as both counter and reference electrodes. Separators were prepared through scissoring the separators in the commercial cells to the size of the pellet. Electrolyte used was 1M LiPF\(_6\) in a 1:1 mixture of Ethylene Carbonate (EC) and Dimethyl Carbonate (DMC).
T-cells/half-cells were charged or discharged with 150 μA to check the capacity. The voltage window is from 4.2 to 2.5 V for the LiCoO₂ half-cell while it is from 2.5 to 0.025 V for the carbon half-cell. EIS measurements were done on the whole-cells cycled up to 300 cycles under both fully charged state and fully discharged state. The batteries were held at least one hour before impedance measurements in order to ensure the stability of the baseline voltage during such a test and in most cases this voltage fluctuation was less than 1 mV. The AC signal for the whole-cell study is a 10 mV sinusoidal voltage covering a frequency range from 1000 Hz to 0.005 Hz. For half-cell impedance studies, different SOC was determined by controlling the charge time. The time interval between the Galvanostatic step and EIS measurement is fixed at 60 minutes. The frequency ranges from 100 kHz to 1 mHz.

3. Results and discussions

3.1. Charge and discharge study of whole battery

Fig.1 shows the capacity fade of batteries as a function of cycle numbers. In order to compare performance of cells cycled at different rates, the capacity was checked with \( \frac{C}{2} \) rate every 50 cycles. If discharge rate has no effect on cell capacity, all batteries should have the similar capacity at any cycle number. However that is not the case in our studies. As can be seen, immediately after the first 50 cycles, capacity fade for batteries cycled at 1C, 2C or 3C shows no big difference. But with cycling, capacity fade diverges. The battery cycled at 3C rate loses almost 16.9% of its initial discharge capacity while the battery cycled at 1C and 2C rate loses 9.5% and 13.2% of its initial capacity after 300 cycles. Further, it’s shown from the slope between 200 cycles and 300 cycles that the rate of capacity fade is faster for 2C-discharge-rate-
cycled or 3C-discharge-rate-cycled battery than for 1C-discharge-rate-cycled batteries. These results indicate the discharge rate plays a strong role in determining the rate of capacity fade of Li-ion cells.

Fig. 2 shows discharge capacity of batteries corresponding to their own discharge rates in the first 50 cycles. In the case of the 1C-discharge-rate-cycled battery, capacity fades almost linearly with cycling. However, in case of 2C-discharge-rate-cycled or 3C-discharge-rate-cycled battery, discharge capacity drops quickly in the first few cycles and then decreases linearly as it does in the case of 1C rate. After 50 cycles, the battery cycled at 1C discharge rate loses only 5% of its initial capacity (corresponding to 1C discharge rate) while batteries cycled at 2C and 3C lose 38% and 45% (corresponding to 2C and 3C discharge rate respectively) of their initial capacity. Although the different discharge rates affect the capacity obtained, the fast drop in capacity in the first few cycles for the battery cycled at high discharge rates indicates that the internal resistance of these cells is large.

Fig. 3 shows the discharge profile of different cells cycled up to 300 times. Discharge current is 0.7 A. Although the basic shape of these plots remained very similar to each other, we can still see that the voltage plateau of the battery cycled at high discharge rate (2C or 3C) is shorter compared with that cycled at low discharge rate (1C). The output voltage of the cell under constant current can be simply represented by Ohm’s law as

\[ V = E_0 - I \times R_t \]  \[1\]

\( E_0 \) is a SOC-dependent (state of charge) equilibrium potential of the cell, \( I \) is the discharge current and \( R_t \) is the total internal resistance of the cell including electrolyte resistance, resistance of cathodic and anodic polarization, contact resistance among particles of electrode
materials and contact resistance between current collector and the electrode materials. It is clear that increasing the internal total resistance will definitely shorten the time for the cell to reach the cutoff voltage (2.5V in our experiment). Discharge capacity is nothing but the product of discharge current and discharge time, so shorter discharge time means lower discharge capacity (provided the discharge current is the same). This indicates that the internal resistance of whole battery cycled at higher discharge rate is larger than that cycled at lower discharge rate.

Fig. 4 presents rate capability studies on fresh Sony US 18650 Cell and cells cycled up to 300 times. All batteries were charged to fully charged state with CC-CV protocol. They were then discharged to 2.5 V at different rates. The performance of the all the cycled batteries was poorer compared with that of the fresh battery. However the batteries cycled at higher discharge rate (3C rate) shows the worst performance. This indicates that the performance of the battery has been hampered by the increase of the internal resistance.

Our next work focused on quantifying the increase of the internal resistance by measuring it as a function of depth of discharge (DOD). This was done by interrupting the discharge current by a 5-second rest pulse intermittently all through the process of discharge and recording the voltage change before and after the interrupting pulse rest. In our experiment, the computer was programmed to log the data 0.1 second after the pulse rest time, which was then used in $R_{dc}$ calculation. Fig. 5 presents the plot of $R_{dc}$ as a function of DOD (depth of discharge). In most cases, the internal resistance of the battery is around 200 mΩ, which is very similar to the results reported by the manufacturer. The $R_{dc}$ corresponding to different DOD remained almost constant except that it increases slightly at the end of discharge. The largest deviation from the average resistance is not more than 3%. The internal resistance of the battery cycled at
1C discharge rate has increased by 12.4% while those cycled at 2C and 3C rate show an internal resistance increase of 18.3% and 27.7%.

3.2. Charge and Discharge Study of Half–Cells

The capacities obtained from the half-cells under 150 μA charge and discharge rate was normalized based on the geometric area of the working electrode of the pellet \((\pi \times 0.55^2 \text{ cm}^2)\), and then this value was multiplied by the total geometric area of the electrode area inside the commercial battery. Twice this value (because of double-side active material loading in this kind of cylinder battery) became the discharge capacity of the negative Carbon electrode or positive LiCoO\(_2\) electrode. Table 1 shows the capacity fade (in percentage) of individual electrode as well as the capacity fade (in percentage) of the whole lithium-ion battery after 300 cycles under 1C, 2C and 3C discharge rates. It is obvious the capacity fade of the negative carbon electrode cycled under high rates contributes more to the fade of the whole battery. One thing that deserves our attention is the total capacity fade of the whole-cell is not as simple as to be equal to the summation of capacity fade of the positive electrode and the negative electrode. In the whole-cells, the mass ratio of positive electrode to negative electrode is well designed according to the theoretical capacity of active electrode materials themselves. On the basis of that ratio, an excess amount of LiCoO\(_2\) was added to compensate for the loss of Li\(^+\) to form surface film over the electrode surface (in the period of formation). Ideally after formation, the rest of Li\(^+\) should be able to shuttle back and forth between positive electrode and negative electrode without any loss. But in reality, a small amount of Li\(^+\) will be continuously consumed due to some unavoidable parasitic reactions (mainly surface film formation reactions). Accordingly, the physical or chemical properties of the surface film will be altered with cycling. So the capacity loss of the whole battery should be directly related to the loss of lithium ions as well as individual
electrode’s ability to intercalate or deintercalate lithium ions. However in case of the half-cell studies, excess amount of lithium salt and solvents were filled into the T-cell, which means the capacity loss in this case is directly related to the loss of electrode material’s ability to intercalate or deintercalate lithium ions. This could arise due to the change in the surface film or due to other causes whose change or whose effects can hamper the electrode’s ability to intercalate or deintercalate. For convenience, we call this capacity loss due to the loss of secondary materials (which is named $Q_2$ later). And this can be measured directly from half-cell studies.

The charge or discharge current used for the half-cell studies were 150 $\mu$A (approximately $\frac{C}{20}$ rate) while discharge current for the whole battery was 0.7 A ($\frac{C}{2}$ rate).

Based on above analysis, the total capacity fade of lithium-ion battery can be divided into three parts and their relationship can be expressed as

$$Q = Q_1 + Q_2 + Q_3 \tag{2}$$

$Q$: total capacity fade of lithium-ion battery ($Q = C_0 - C_{300}$), where $C$ represents the discharge capacity of the Li-ion battery at $\frac{C}{2}$ discharge rate while the subscripts 0 and 300 represent initial and after 300 cycles respectively.

$Q_1$: correction item due to different rate capability ($Q_1 = C_{\frac{C}{2}} - C_{\frac{C}{20}}$), where $C_{\frac{C}{2}}$ represents the capacity of the Li-ion battery at $\frac{C}{20}$ rate while $C_{\frac{C}{2}}$ represents the discharge capacity of the same Li-ion battery at $\frac{C}{2}$ rate.
Q_2: capacity fade due to the loss of carbon electrode or LiCoO_2 electrode:
\( Q_2 = (c_0 - c_{300}) \times \frac{2 \times A_r}{A_p} \), where the lower case c represents the capacity of half-cells, subscripts 0 and 300 represent the capacity initially and after 300 cycles, respectively. \( A_r \) represents the total geometric area of the electrode (The geometric area of positive LiCoO_2 electrode is 46.5 x 5.40 cm² and that of negative carbon electrode is 47.5 x 5.6 cm²), while \( A_p \) represents the geometric area of the punched pellet. (equal to 3.1415 x 0.55² cm²). Q_2 could be due to either LiCoO_2 or carbon, the larger value of which is used in equation [2].

Q_3: capacity fade due to the loss of lithium ions and other reasons. It was indirectly calculated through charge balance.

If above Q, Q_1, Q_2, Q_3 are divided by the initial capacity of the battery, above capacity fade will be expressed in the form of percentage.

\[ Q' = Q'_1 + Q'_2 + Q'_3 \]  \[ [3] \]

It is found from Table 1 that the capacity fade of LiCoO_2 cycled to 300 times under 1C discharge rate (3.98%) outruns that of Carbon (2.77%). This is similar to the result reported by D. Zhang et al. [6], whose conclusion is that the fast increase of the impedance of LiCoO_2 electrode is primarily due to the increase of the surface resistance due to oxidation process and that increase dominates the total resistance of the cell. In the case of the batteries cycled at 2C and 3C discharge rates, the capacity fade of carbon electrode becomes more, namely 8.4% and 10.6% respectively. Increase in the impedance of both cathode and anode of Li-ion cells limit the discharge capacity of the cell or the cycle life of the cell, but the difference reflected in our experimental data is the fast capacity loss due to carbon when the battery was cycled under 2C or 3C rates. It is shown from Table 2 that the Q_1 is very close in all the three cases, which is close to
3%. And Q₂ related to the loss of secondary material (Carbon or LiCoO₂) is still the dominant reason for the total capacity fade of the whole lithium-ion battery, especially when the battery was cycled under high discharge rates. The following studies (EIS measurements) were aimed at explaining the loss of the ability of intercalating or deintercalating Li⁺.

3.3. Electrochemical Impedance Spectroscopy (EIS) study

Fig. 6 (a) and (b) show the Nyquist plots of fresh whole-battery as well as of batteries cycled up to 300 times under different discharge rates. Unlike DC resistance in former sections, AC impedance is a strong function of state of charge (SOC). The impedance of the cell under fully charged state is always smaller than that under fully discharge state. Also, the total impedance of the battery cycled at high discharge rate (2C or 3C) is larger than that of the battery cycled at low discharge rate (1C) at both 0% and 100% SOC. The impedance spectra under fully discharged state (0% SOC) clearly shows a few depressed semi-circles (the one at high frequencies is not as obvious as the other two at middle and low frequencies) with a straight sloping line indicating solid-state diffusion at low frequencies. In the spectra obtained at the fully charged state (100% SOC), it is hard to differentiate the separate regions of semi-circles. To understand the contribution of individual electrode to the performance of the cell, EIS studies on half-cells were done in order to clarify the individual capacity fade of negative or positive electrodes.

Before EIS measurement, the assembled half-cell had been fully charged and fully discharged at 75 μA. The charge /discharge time between fully discharged state and fully charged state of the half-cell in the first cycle has been used as the reference for the calculation of the state of charge (SOC) or depth of discharge (DOD). Suppose the charge time for the half-
cell is T in the first cycle, the SOC is determined by $\frac{\tau}{T}$, where $\tau$ denotes the charge time before the EIS measurement. DOD is calculated the same way. For LiCoO$_2$ half-cells, high SOC corresponds to high potential of the half cell while for carbon half-cells high DOD is correlated to high potential of the half cell. No appreciable capacity fade of the half-cell was found in the first 4-5 cycles.

Numerous papers have been published with regard to the interpretation of the EIS spectra as well as the models to fit the spectra. [1, 2, 7, 8] A modified model of Voigt-FMG model that is basically a combination of Voigt-type analog and the generalized Frumkin and Melik-Gaykazyan impedance was used to interpret lithium intercalation into graphite [2]. The shortcoming with this model is that it doesn’t take into account the electronic resistance of the bulk electrode materials. Based on the shape of observed spectra and results previously used by other groups [1, 2, 5, 7-10], we decided to utilize the Croce's model [5, 12] to analyze our EIS spectra. In this model, the high frequency depressed semi-circle is interpreted as the migration of Li$^+$ through the multi-layered surface films (SEI). The middle frequency semi-circle is related to the charge-transfer resistance across the interface and the low frequency semi-circle is associated with the electric conductivity (or resistance) of the bulk electrode material. At low frequencies, the sloping line (typical characteristics of Warburg diffusion region) accounts for the solid-state diffusion of Li$^+$ in the bulk electrode material. Although this model and interpretation was helpful in our analysis, there should be other models that can similarly interpret this complicated system. Fig. 7 is the equivalent circuit constructed based on above interpretation of the spectra of EIS.

In the equivalent circuit, $R_{\text{elect}}$ represents the resistance of Li$^+$ conduction in liquid electrolyte while the three RC parallel elements in series are related to the passivating surface
layer, charge transfer and electronic resistance of the material respectively. In subsequent data fitting, Q (constant phase element) instead of capacitance has been used to offset the depression of the semi-circle. Apart from those elements, the circuit also takes into account Warburg diffusion impedance ($Z_w$) and the intercalation capacitance ($C_{int}$) that can be reflected only at extremely low frequency. Considering the limited size of the particles, we adopted the finite-length Warburg-type element $Z_w$ [11]. $C_{int}$, the intercalation capacitance, simulates the accumulation and consumption process of Li$^+$ in the bulk material. Based on this model, at the lowest frequency, the EIS spectra measured from these electrodes should be able to reflect the capacitive behavior of the bulk intercalation of the electrode materials with the characteristics of an almost vertical line at the lowest frequency region in Nyquist plots. But such region doesn’t appear in our impedance spectra. It is because the lowest frequency (1 mHz) we applied (due to experimental limit) is not sufficiently low enough to reach that theoretically existing region. However $C_{int}$ can be obtained through fitting model in Fig.7 with the experimental data.

To ensure the accuracy of data fitting for the comparisons among the properties of different-discharge-rate-cycled materials, we only chose the data corresponding to the state of the 10% and 20% DOD.

Fig. 8 shows the change of those parameters of those cycled materials. As can be seen, the resistance of the surface film ($R_f$) is in the range from 2 Ω to 10 Ω. These results are consistent with those published by Croce et al. [5]. Under both 10% DOD and 20% DOD, $R_f$ increases with the increase of discharge rate used in battery cycling. This shows it is likely that products of parasitic reactions deposit on the surface of the carbon material at a faster rate when the battery was cycled under higher discharge rate. As a result, the total thickness of the surface film increases quickly. The electronic resistance of the bulk material ($R_e$) similarly follows the
trend of the resistance of surface film ($R_f$). Since the semicircles in the middle-range frequencies are not clearly defined, we didn’t use $R_{ct}$ values obtained through this fitting method for comparison. As far as the magnitude is concerned, the electronic resistance of the bulk material dominates the total impedance of the carbon half-cell.

The other very important parameter we have indirectly obtained is the ionic chemical diffusion coefficient in the solid-phase carbon materials. [2, 3, 13] Based on SEM study, the average diffusion length $l$ was supposed to be equal to the size of the particle, which is 5 μm for the carbon material. The chemical diffusion coefficient was calculated from $C_{int}$ values that were obtained through fitting experimental data with the model. The value is approximately in the order of $10^{-10}$ cm$^2$/s and it varies little after 300 cycles.

Obviously, the increase in the resistance of the surface film ($R_f$) as well as of the electronic resistance ($R_e$) resulted in the fast capacity fade of carbon half-cell. This also leads to an increase in capacity fade of the whole Li-ion cell cycled under higher discharge rates. One plausible explanation of the fast increase of those physical properties of carbon with cycling is that the surface film formed on carbon electrode may not be as firm or protective as it is expected to be, especially when the battery is cycled at high discharge rate. Continuous small-scale electrolyte or salt reduction on the carbon electrode surface is inevitable due to the instability of the electrolyte to the carbon under cathodic conditions, especially when the surface film formed during early formation is neither fully formed nor solid on the surface of the electrode material [1]. As it is known those reactions will take place when the potential of the carbon electrode is below 1.5 V vs. Li$^+$/Li. The overall electrochemical decomposition of the solvents in the battery such as EC or DMC can be expressed as [14]

$$2\text{Li}^+ + 2e^- + 2(\text{CH}_2\text{O})\text{CO (EC)} \rightarrow \text{CH}_2(\text{OCO}_2\text{Li})\text{CH}_2\text{OCO}_2\text{Li} \downarrow + \text{CH}_3\text{CH}_2 \uparrow [4]$$
\[ 2\text{Li}^+ + 2e^- + (\text{CH}_2\text{O}) \text{ CO (EC) } \rightarrow \text{Li}_2\text{CO}_3 \downarrow + \text{C}_2\text{H}_4 \uparrow \]  
\[ \text{Li}^+ + e^- + \text{CH}_3\text{OCH}_2\text{CH}_3 \text{ (DMC) } \rightarrow \text{CH}_3\text{OCO}_2\text{Li} \downarrow + \text{CH}_3\cdot \]  

[5]  
[6]

The reduction products are primary components of the thickened SEI film on the carbon electrode. It also can be seen from above reaction formula that gaseous products will be formed at the same time. In parallel with those side reactions, the solvent can co-intercalate into the carbon structure to form a ternary graphite intercalation compounds (GIC), as is a direct cause of the exfoliation of the carbon and the expansion of the carbon particles.

For the batteries cycled under high discharge rates, the internal temperature was high. Ohm’s law can easily explain this phenomenon. The heat power generated during discharge can be given by: 
\[ w = I^2 \times R \]  
[7]

More heat is generated per unit time and accordingly the internal pressure during cycling should be higher with high discharge rate. However, the internal temperature couldn’t be easily measured during the cycling because it is almost impossible to put thermal couple into the battery without causing any damage to the battery. Randolph et al. [15] reported that the difference between internal and external temperature of an overcharging cell could be as high as 60°C under high current discharge. The heat generated will not easily dissipate from the battery to the outside environment. The reduction reaction on the surface of carbon electrode will proceed at a faster speed due to high internal temperature and more and more gases will be formed in a short period of time. The buildup of pressure due to those gaseous products and the evaporation of the electrolytes at high temperature during cycling might easily stretch or damage the surface film. As a consequence, Li\(^+\) and electrolyte will go through the enlarged cracks or newly formed cracks and react with the internal lithiated carbon particles. Actually we found more cracks as well as some white color substances (lithium salts) on the surface of the carbon
electrode when we cut open the battery to take out the electrode materials. Fig. 9 shows SEM images of carbon samples cycled at 1C, 2C and 3C discharge rates. It can be seen in Fig. 9-A (1C-discharge-rate-cycled carbon) that the surface of the carbon electrode is smooth and clean, however some white substances are dispersed on the surface in Fig. 9-B (2C-discharge-rate-cycled carbon). When it comes to the carbon samples of 3C in Fig. 9-C and Fig. 9-D, not only more white substances but also more cracks were found on the surface. Based on the impedance analyses and the morphology of the surface of the materials, we believe that the reactions between organic solvents or Li$^+$ and lithiated carbon have never completely stopped because the active species can easily percolate the crevices on the film and reach the lithiated carbon. The products of those side reactions provide enough materials for the formation of new SEI film. So with cycling, the surface film becomes thicker and thicker. Fig. 10 is a schematic of this surface thickening process.

When the battery is cycled under high discharge rate, the internal temperature will rise quickly and the surface film on the carbon particles becomes thicker quickly, so it is easy to understand the increase of $R_f$ which is physically correlated with the migration of Li$^+$ through the SEI film.

4. Conclusion

A systematic capacity fade study was done for Sony US 18650 batteries cycled at normal and high discharge rates. Three major causes including the loss of secondary material, the loss of primary material and the difference of rate capability were quantified. In any case the loss of the secondary material dominates the capacity fade of the whole cell. However unlike in 1C-discharge-rate-cycled battery, the limiting secondary material is in 3C-discharge-rate-cycled cell
is carbon. The capacity loss due to carbon electrode material alone is 10.6% out of 16.9% capacity fade of the whole cell. Such quick capacity fade for the carbon material or the Li-ion battery cycled at high discharge rate is correlated to the increase of the internal resistance. Fitting impedance spectra of carbon half-cell clearly and quantitatively shows that the resistance of surface film and the resistance of bulk carbon material do increase faster for high-rate-discharged cell than for normal-rate-discharged cell. SEM images further demonstrate more substances coming out of side reactions have been deposited on the surface of the high-discharge-rate-cycled carbon. One crucial condition for the parasitic reactions to continue is the protective SEI film cracks under high temperature which results from the high rate discharge with cycling. And the substances will become the components of new film.

Acknowledgements

The authors are thankful for the financial support provided by National Reconnaissance Organization (NRO) under Contract No. NRO-00C-0134.
References


Fig. 1. Capacity Fade of Sony US 18650 batteries under different discharge rates. The discharge capacity was checked at the same discharge rate (1A constant current) once every 50 cycles.
Fig. 2. Discharge capacity of Sony 18650 batteries as a function of cycle number. The discharge capacity corresponds to its own discharge rate (1C, 2C or 3C rate).
Fig. 3 Discharge voltage profile of fresh battery and batteries cycled up to 300 times under different discharge rates. The discharge current used is 0.7A.
Fig. 4. Rate Capability of fresh battery and batteries cycled up to 300 times under different discharge rates. Discharge rates used are \( \frac{1}{10} C, \frac{1}{4} C, \frac{1}{2} C, 1C, 2C \) and 3C.
Fig. 5. DC Resistance $R_{dc}$ as a function of depth of discharge (DOD).
Fig.6 Nyquist plots of fresh battery and batteries cycled up to 300 cycles under 1C, 2C, 3C discharge rates (a) 0% SOC (b) 100% SOC. The geometric area of the LiCoO$_2$ positive electrode in the Li-ion battery is 46.5 x 5.4 cm$^2$ and the geometric area of carbon negative electrode is 47.5 x 5.6 cm$^2$. 
Fig. 7  Equivalent circuit of the EIS spectra
Fig. 8. Comparisons of Parameters (a) $R_f$ resistance of surface film; (b) $R_e$ electronic resistance of the bulk carbon material; Above data were obtained through fitting the model in Fig. 7 with the experimental spectra of EIS of Carbon half-cells (with carbon material cycled at 1C, 2C, and 3C discharge rate)
Fig. 9. SEM (X1000) of Carbon materials cycled at different discharge rates. (A) Carbon cycled at 1C; (B) Carbon cycled at 2C discharge rate; (C) and (D) Carbon cycled at 3C discharge rate.
Fig. 10 Evolution of SEI film on the surface of carbon when the battery is cycled.
Table 1. Half-cell analysis of capacity fade (in percentage) of negative Carbon electrode and positive LiCoO$_2$ electrode

<table>
<thead>
<tr>
<th>Capacity fade</th>
<th>1C Rate Discharge 300cycles</th>
<th>2C Rate Discharge 300cycles</th>
<th>3C Rate Discharge 300cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>2.77%</td>
<td>8.30%</td>
<td>10.59%</td>
</tr>
<tr>
<td>LiCoO$_2$</td>
<td>3.98%</td>
<td>4.38%</td>
<td>5.18%</td>
</tr>
<tr>
<td>Capacity fade of the whole cell (percentage)</td>
<td>9.50%</td>
<td>13.20%</td>
<td>16.90%</td>
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</table>
Table 2. Breakdown of the total capacity fade of the whole lithium-ion battery

<table>
<thead>
<tr>
<th></th>
<th>1C Rate Discharge 300cycles</th>
<th>2C Rate Discharge 300cycles</th>
<th>3C Discharge 300cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity fade of the whole cell (percentage)</td>
<td>9.5%</td>
<td>13.2%</td>
<td>16.9%</td>
</tr>
<tr>
<td>$Q_1'$</td>
<td>3.5%</td>
<td>2.9%</td>
<td>2.8%</td>
</tr>
<tr>
<td>$Q_2'$ (due to carbon)</td>
<td>NA</td>
<td>8.4%</td>
<td>10.6%</td>
</tr>
<tr>
<td>$Q_2'$ (due to LiCoO$_2$)</td>
<td>3.8%</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>$Q_3'$</td>
<td>2.3%</td>
<td>2.0%</td>
<td>3.4%</td>
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