Effect of the Charge Process on the Performance of Li-ion Cells during Charge-Discharge Cycling at 0°C

Omar Samuel MENDOZA-HERNANDEZ, Eiji HOSONO, Daisuke ASAKURA, Hirofumi MATSUDA, Andreas PFRAK, Akos KRISTON, Minoru UMEDA, and Yoshitsugu SONE

ABSTRACT

Commercially available 18650 Li-ion cells were exposed to charge-discharge cycling at 0°C using two different charging protocols: constant current-constant voltage (CC-CV) and constant current (CC). The effect of the charge process protocol on the Li-ion cell performance is shown and analyzed. After exposing the cells to low temperature charging, a high voltage plateau appeared at the beginning of the discharge. This high voltage plateau is related to the occurrence of lithium plating during the charging process. Interestingly, the intensity of the observed high voltage plateau decreased with cycling. In addition, the Li-ion cells that were charged using a CC protocol exhibited a larger capacity fade in comparison to those that were charged using a CC-CV protocol. Furthermore, electrochemical impedance spectroscopy (EIS) measurements were carried out during cycling. It was shown that the internal impedance of the cells increased with charge-discharge cycling, indicating the formation of an interphase layer during low temperature cycling.

1. Introduction

Li-ion cells have become the first choice to provide power in a wide range of applications such as satellites, spacecraft, electric buses, all electric and hybrid electric vehicles and these applications demand a high reliability, level of safety and performance. In order to meet these demands, it is very important to acquire more knowledge about the factors that contribute to the degradation of Li-ion cells. Many efforts have been carried out to understand and analyze the degradation mechanisms of Li-ion cells and it is well known that degradation can be accelerated by certain operating and environmental conditions.1-5 It has been reported that factors such as temperature, state of charge (SoC), as well as negative and positive electroactive materials and electrolyte have an impact on the degradation mechanisms of Li-ion cells.6-9 Lithium plating is a severe degradation process for Li-ion cells which can reduce their lifetime drastically and compromise the safety of battery systems.10-14 Lithium plating occurs when the potential of the negative electrode drops below 0 V Li/Li+, which makes the deposition of metallic lithium on the negative electrode thermodynamically possible.9 This metallic lithium deposited on the anode material surface can grow dendritically and these dendrites can penetrate the Li-ion cell separator creating internal short circuits which can cause a battery system to go into thermal runaway.15,16 It has been identified that the combination of low temperature and high current rates during charging favors the occurrence of lithium plating, since these conditions promote the over polarization of the anode potential.17,18 Furthermore, it has been stated in the literature that a reliable non-destructive method to detect lithium plating resulting from a previous charging is the appearance of a high voltage plateau at the beginning of the discharge process.10,12,17 This voltage plateau is a signature of metallic lithium that is being stripped from the anode active material surface. Since lithium plating represents a serious concern for the reliability and safety of Li-ion cells, it is very important to gather more information about this degradation mechanism.

In this investigation, in order to elucidate the impact of the charge protocol on the degradation of Li-ion cells during continuous charge-discharge cycling at low temperature, we evaluate the performance of fresh Li-ion cells exposed to two different charge protocols: constant current-constant voltage (CC-CV) and constant current (CC) and two different discharge rates: 1C and 0.2C. Commercially available 18650 Li-ion cells with Lithium Nickel Cobalt Aluminium Oxide (LiNiCoAlO2) as positive active material and graphite as negative active material were used in this study. The cells were exposed to charge-discharge cycling at 0°C. Furthermore, electrochemical impedance spectroscopy measurements were carried out during breaks in the charge-discharge cycling.

2. Experimental

Commercially available 18650 type Li-ion cells with a rated capacity of 2900 mAh were used in this work. These Li-ion cells use LiNiCoAlO2 as the positive active material and graphite as the negative active material. All electrochemical measurements were carried out using a battery tester (Solartron 1470E, voltage and current accuracy of ±0.1% of range) interconnected with a
frequency response analyzer (Solartron SI 1250). To control the environmental temperature during the measurements, the cells were placed inside a climate chamber (ETAC FL414P, temperature deviation ±0.3°C). Thermocouples (type k, accuracy ±1.5°C) were attached on the center of the cells to monitor their surface temperature. In order to check reproducibility, two Li-ion cells were tested at the same conditions. There were no significant differences in the results of the two cells tested under the same conditions.

2.1 Charge-discharge cycling

Fresh Li-ion cells were exposed to charge-discharge cycling at 0°C following two different charging protocols: constant current-constant voltage (CC-CV) with a tapering current cut-off of 59 mA, and constant-current (CC). The maximum voltage and charge-rate were 4.2 V and 0.7 C, respectively. During discharge, a CC protocol with two different discharge-rates was used: 0.2 C and 1 C. The discharge cut-off voltage was 2.5 V. To assure that the cells were charged at a cell temperature of 0°C, there was a rest time of 40 min after each discharge to allow the cell temperature to stabilize. No rest period was applied after charging. The cells were cycled 20 times.

2.2 Electrochemical impedance spectroscopy (EIS) measurements

EIS was carried out at 0°C and 50% state of charge (SoC) interrupting the charge process. The cells were allowed to rest for 1 h at open circuit voltage before carrying out the EIS measurements. Measurement was performed by applying an AC voltage of 5 mV within a frequency range of 10 kHz–0.01 Hz. Impedance spectra were obtained in the following cycles: 0, 1, 3, 5, 10 and 20. Impedance spectra fittings were carried out using Zview 2 software (Scribner Associates Inc.).

3. Results and Discussion

Figure 1 shows the discharge curves of the Li-ion cells directly after being charged following a CC-CV (Fig. 1a) and CC (Fig. 1b) protocols with a charge-rate of 0.7 C at 0°C. The cells were discharged with a rate of 1 C. A high voltage plateau is observed at the beginning of the discharge process for low cycle numbers. This voltage plateau is related to the stripping process of metallic lithium, which is a consequence of lithium plating generated during the charge process at 0°C.10,12 Also, it can be observed that occurrence of the high voltage plateau decreases with cycling until it disappears. After 20 cycles, the cells charged with a CC-CV protocol exhibited a capacity fade of 16%, while the cells charged with a CC protocol showed 32%. Low temperature and high charge rates promote the high polarization of the negative electrode potential, which facilitates lithium plating. The contact of metallic lithium with the electrolyte enhances lithium decomposition, reducing the amount of lithium inventory and therefore the cell loses capacity. In the case of the cell charged using a CC protocol, the observed capacity fade after 20 cycles was 32%, which is two times larger than that of the cell charged using a CC-CV protocol. This indicates that the inclusion of CV phase during the charge process at low temperature has a positive impact on the cell capacity fade. At low temperatures, the lithium ion intercalation kinetics is hindered during the CC charge process, enhancing the occurrence of lithium plating, and then the inclusion of CV phase allows the accumulated metallic lithium to intercalate and diffuse into the negative active material.

Figure 2 shows electrochemical impedance spectra of the cells exposed to CC-CV (Fig. 2a) and CC (Fig. 2b) charge protocols and discharge with 1 C. The spectra were obtained at 50% SoC and 0°C interrupting the charge process. These impedance spectra were fitted according to the equivalent circuit shown in Fig. 2c following a nonlinear least square fitting method. In the high frequency region of the spectra, an inductance element L and an electrolyte resistance element R_e are identified. In the middle frequency region, the elements R_{SEI} and R_{ct} are identified. R_{SEI} corresponds to the solid electrolyte interphase resistance and R_{ct} corresponds to the charge transfer resistance. In the low frequency region, a Warburg element Z_W is identified. This Warburg element represents the Li-ion diffusion. Chi-squared (χ²) values within the range of 10⁻²–10⁻⁴ were obtained from the fittings. Figure 3 shows the R_e, R_{SEI} and R_{ct} resistance values obtained from the impedance spectra fittings for the cells that were charged using CC-CV (Fig. 3a) and CC (Fig. 3b) protocols and discharged with a rate of 1 C. It can be seen that R_e slightly decreases in the first cycle and then remains almost constant and slightly increases in the cycle number 20. On the other hand, R_{SEI} increases with the number of cycles. This is likely due to the formation of an interphase during low temperature cycling, which is the result of electrolyte decomposition due to the presence of metallic lithium.18 Furthermore, in case of the cell exposed to CC-CV charge protocol R_e tends to decrease within the first cycles and then slightly increases, while in case of the cell exposed to CC charge protocol R_e decreases with cycles and after 20 cycles a
drastic decrease is observed. A drastic decrease in $R_{ct}$ would indicate that the activation energy related to the interfacial charge transfer reaction also would decrease, suggesting that $R_{ct}$ kinetics improved after degradation which is not likely to occur. Since the cell overall resistances are relatively small, this observed difference might be related to a fitting discrepancy between $R_{SEI}$ and $R_{ct}$. The observed change in charge transfer resistance is likely due to a shift in the capacity of the negative and positive active materials to compensate a loss of lithium ion inventory related to electrolyte decomposition generated by the occurrence of lithium plating.

Figure 4 shows the discharge curves of the Li-ion cells after being charged following a CC-CV (Fig. 4a) and CC (Fig. 4b) charge protocols and discharged with a rate of 0.2C. A high voltage plateau, related to the occurrence of lithium plating during charge, is observed at the beginning of the discharge process. As in the case of discharge at 1C (Fig. 1), the intensity of this high voltage plateau tends to disappear through cycling. This is due to a shift in the capacity of the electroactive materials caused by lithium plating which affects the difference in potential between lithium stripping and lithium intercalation. After 20 cycles, the cells that were charged following a CC-CV protocol showed a capacity fade of 18%, while the cells exposed to a CC charge protocol exhibited 31%. A similar tendency was observed in the case of the cells that were charged under the same conditions but discharge with a rate of 1C (Fig. 1).

Figure 5 shows electrochemical impedance spectra of the cells exposed to CC-CV (Fig. 5a) and CC (Fig. 5b) charge protocols and discharged with a rate of 0.2C. The impedance spectra were fitted according to the equivalent circuit shown in Fig. 2c. Chi-squared ($\chi^2$) values within the range of $10^{-5}$–$10^{-3}$ were obtained from the fittings. Figure 6 shows the $R_e$, $R_{SEI}$ and $R_{ct}$ of the cells charged using CC-CV (Fig. 6a) and CC (Fig. 6b) charge protocols and discharge with a rate of 0.2C. It can be observed that $R_e$ remains almost constant from cycle number 1 to 10 and slightly increases in cycle number 20. Moreover, $R_{SEI}$ tends to increase with cycling while $R_{ct}$ decreases. A similar behavior for $R_e$, $R_{SEI}$ and $R_{ct}$ was also observed in the case of the cells that were discharged with a rate of 1C (Fig. 3).

Figure 7 shows the charge and discharge capacities obtained through cycling at 0°C for the cells that were charged using a CC-CV and CC protocols and discharged with a rate of 1C (Fig. 7a and
b), and the cells that were charged using a CC-CV and CC protocols but discharged with a rate of 0.2C (Fig. 7c and d). As expected, the charge capacity exceeds the discharge capacity. However, in the case of the cell that was charged following a CC protocol and discharged with a rate of 0.2C (Fig. 7d) the discharge capacity was slightly larger than that of the charge. This was observed from the cycle number 1 to 13. X.-G. Yang et al. developed a physics-based model with the incorporation of lithium plating and stripping, focusing on the internal Li-ion cell characteristics and the key parameters that affect the rate of lithium stripping. It is reported that at the beginning of the discharge process, after charging at plating conditions, lithium ion intercalation into graphite still occurs. This is due to the fact that at the beginning of discharge, the part of the negative electrode near the separator has a high local current density of lithium stripping which exceeds the limiting current density of lithium ion intercalation. Then the deposited lithium near the separator is removed first, while the remaining lithium can intercalate into graphite as long as the lithium stripping reaction can sustain the discharge current. This atypical phenomenon is more likely to occur in the case of Li-ion cells exposed to CC charge. However, a positive difference between the discharge and charge capacities was only observed in the cell that was discharged with 0.2C (Fig. 7d). Since high discharge rates lead to high stripping rates, this difference in the discharge capacity is not observed in the cell discharged with 1C. In the case of cells being charged using a CC-CV protocol at plating conditions, a positive difference between the discharge and charge capacities might not occur, since the inclusion of CV phase allows the diffusion and intercalation of some amount of the metallic lithium generated around the negative electrode during the CC phase, decreasing the amount of remaining lithium to be removed in the discharge process. In addition, in case of the cells that were cycled and discharged with a rate of 1C (Fig. 7a and b), it is observed that the charge capacity is recovered in the cycles where the impedance was measured. This indicates that metallic lithium generated through cycling can be dissolved when a Li-ion cell is allowed to rest for a long period of time after being charged at plating conditions.

In a recent publication we reported the performance of fresh and calendar degraded LiFePO₄/graphite 18650 Li-ion cells during cycling at −5°C. Lithium plating was identified as the main degradation mechanism. We found that calendar degraded cells exhibited a large capacity fade after 20 cycles, while fresh cells presented a relatively good performance. This difference in performance was mainly due to a difference in the internal impedance between fresh and calendar degraded cells. Compared to the cells used in this study, the LiFePO₄/graphite configuration presented a better performance during cycling at low temperature. Since graphite is commonly used in both LiFePO₄ and LiNiCoAlO₂ Li-ion cells, the variation in performance can be related to the redox

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**Figure 3.** Li-ion cell electrolyte ($R_\text{e}$), solid electrolyte interphase ($R_{\text{SEI}}$) and charge transfer ($R_{\text{ct}}$) resistance values derived from impedance spectra fitting for the Li-ion cells exposed to CC-CV (a) and CC (b) charge protocols and discharged with a rate of 1C.

**Figure 4.** Discharge curves of the Li-ion cells obtained after being charged following a CC-CV (a) and CC (b) protocols and discharged with a rate of 0.2C at 0°C.
potential of the positive active materials. Because the redox potential of LiNiCoAlO₂ is higher than that of LiFePO₄, a lower electrode potential for graphite is achieved when a LiNiCoAlO₂/graphite cell is charged to high SoCs, which increases the risk of reaching negative potential values at which lithium plating can occur. Furthermore, cell internal impedance rise is sensitive to the concentration of Al in LiNiCoAlO₂ active material, and high internal impedance can lead the polarization of the negative electrode to lithium plating levels during charging. In addition, other factors such as electrolyte composition, difference in the microstructures of active materials and cell engineering have an impact on the variation in cell performance under low temperature environments.

4. Conclusions

We evaluated and compared the performance of fresh Li-ion LiNiCoAlO₂/graphite 18650 cells exposed to charge-discharge cycling at 0°C using two different charge protocols: CC-CV and CC, and discharged with two different rates: 1C and 0.2C. After 20 cycles, the cells that were exposed to a CC charge protocol exhibited a capacity fade 2 times larger than that of the cells charged following a CC-CV protocol. These results showed that the inclusion of a constant-voltage phase can prolong the life of Li-ion cells during cycling at low temperatures. Furthermore, a high voltage plateau, observed at the beginning of the discharge process as a consequence of the occurrence of lithium plating tended to disappear through charge-discharge cycling. This is due to a shift in the capacity of the cell electroactive materials to compensate a loss of lithium inventory in the electrolyte caused by lithium plating. Additionally, EIS measurements showed that size of spectra increased through charge-discharge cycling, indicating the formation of an interphase.
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References

1. B. Markovsky, A. Rodkin, Y. S. Cohen, O. Palchik, E. Levi, D. Aurbach, H.-J. Kim, and M. Schmidt, J. Power Sources, 119–121, 504 (2002).
2. P. Keil and A. Jossen, J. Electrochem. Soc., 164(13), A3081 (2017).
3. D. Li, H. Li, D. Danilov, L. Gao, J. Zhou, R. A. Eichel, Y. Yang, and P. H. L. Notten, J. Power Sources, 396, 444 (2018).
4. A. J. Smith, H. M. Dahn, J. C. Burns, and J. R. Dahn, J. Electrochem. Soc., 159(6), A705 (2012).
5. T. Waldmann, M. Wilka, M. Kasper, M. Fleischhammer, and M. Wohlfahrt-Mehrens, J. Power Sources, 262, 129 (2014).
6. N. N. Sinha, A. J. Smith, J. C. Burns, G. Jain, K. W. Eberman, E. Scott, J. P. Gardner, and J. R. Dahn, J. Electrochem. Soc., 158(11), A1194 (2011).
7. E. R. Logan, E. M. Tonita, K. L. Gering, J. Li, X. Ma, L. Y. Beaulieu, and J. Dahn, J. Electrochem. Soc., 165(2), A21 (2018).
8. Q. Q. Liu, R. Petibon, C. Y. Du, and J. R. Dahn, J. Electrochem. Soc., 164(6), A1173 (2017).
9. S.-P. Kim, A. C. T. van Duin, and V. B. Shenoy, J. Power Sources, 196, 8590 (2011).
10. M. Petzl and M. Danzer, J. Power Sources, 254, 80 (2014).
11. M. Petzl, M. Kasper, and M. A. Danzer, J. Power Sources, 275, 799 (2015).
12. T. Waldmann, B.-I. Hogg, and M. Wohlfahrt-Mehrens, J. Power Sources, 384, 107 (2018).
13. T. Rauhala, K. Jalkanen, T. Romann, E. Lust, N. Omar, and T. Kallio, J. Energy Storage, 20, 344 (2018).
14. P. Arora, R. E. White, and M. Doyle, J. Electrochem. Soc., 145(10), 3647 (1998).
15. C. Monroe and J. Newman, J. Electrochem. Soc., 150(10), A1377 (2003).
16. S. Santhanagopalan, P. Ramadass, and J. Z. Zhang, J. Power Sources, 194(1), 550 (2009).
17. X.-G. Yang, S. Ge, T. Liu, Y. Leng, and C.-Y. Wang, J. Power Sources, 395, 251 (2018).
18. B. P. Matadi, S. Genies, A. Delaille, C. Chabrol, E. de Vito, M. Bardet, J.-F. Martin, L. Daniel, and Y. Butel, J. Electrochem. Soc., 164(12), A2374 (2017).
19. O. S. Mendoza-Hernandez, E. Hosono, D. Asakura, H. Matsuda, S. Shironita, M. Uneda, and Y. Some, J. Electrochem. Soc., 166(15), A3525 (2019).
20. P. Keil, S. F. Schuster, J. Wilhelm, J. Travi, A. Hauser, R. C. Karl, and A. Jossen, J. Electrochem. Soc., 163(9), A1872 (2016).
21. I. Bloom, S. A. Jones, V. S. Battaglia, G. L. Henrikson, J. P. Christopherson, R. B. Wright, C. D. Ho, J. R. Belt, and C. G. Motloch, J. Power Sources, 124, 538 (2003).

Figure 7. Charge and discharge capacities obtained through cycling at 0°C for the Li-ion cells that were exposed to CC-CV and CC charge protocols and discharged with a rate of 1C (a and b), and the Li-ion cells that were exposed to CC-CV and CC charge protocols and discharged with a rate of 0.2C (c and d).