Effect of the Charge Process and Discharge Rate on the Lithium Stripping Process Visibility in LiFePO₄-Graphite Li-ion Cells during Charge-Discharge Cycling at 0°C

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ABSTRACT

Commercially available 18650 LiFePO₄-Graphite Li-ion cells were exposed to charge-discharge cycling at 0°C following two different charge methods: constant current-constant voltage (CC-CV) and constant current (CC), and two different discharge rates: 1 C and 0.2 C. The effect of the charge method and discharge rate on the cell performance was analyzed. The cell exposed to CC charge and 1 C discharge-rate showed a high voltage plateau at the beginning of the discharge voltage, while a high voltage plateau was not observed in the discharge profiles of the cells exposed to a discharge rate of 0.2 C.

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1. Introduction

The degradation of Li-ion cells taking place under low temperature conditions has not been well understood yet compared to high temperature degradation. In particular, lithium plating represents a severe degradation mechanism for Li-ion cells, since its occurrence leads to significant capacity fade and can compromise the safety of battery systems.^{1–7} Lithium plating takes place when metallic lithium is deposited on the negative electrode surface of Li-ion cells during charging, this can occur when the potential of the negative electrode drops below 0 V vs. Li/Li⁺, which makes the deposition of metallic lithium thermodynamically possible.^{2,3} Lithium plating is usually triggered by exposing Li-ion cells to low temperatures and high currents during charging, which promotes the over polarization of the negative electrode. The generation of metallic lithium around the negative active material accelerates the electrolyte reduction, which decreases the amount of lithium inventory, and therefore the cell capacity fades.^{6,7} Furthermore, lithium dendrites can penetrate the cell separator causing internal short circuits with the potential of triggering the cell to go into thermal runaway.^{8,9}

As mentioned above, the occurrence of lithium plating can compromise the reliability and safety of Li-ion cells, consequently, acquiring more knowledge of the occurrence and non-destructive detection of lithium plating is very important. In a previous publication, we compared the performance of fresh and calendar degraded Li-ion cells during charge-discharge cycling at –5°C.¹⁰ We exposed LiFePO₄-Graphite Li-ion cells only to a constant current-constant voltage (CC-CV) process during charging and constant current (CC) process during discharging with a rate of 0.2 C. Lithium plating was identified as the main degradation mechanism. In case of the calendar degraded cell, a high voltage plateau was identified at the beginning of the discharging process,

while in case of the fresh cell this high voltage plateau was not observed despite exhibiting capacity fade. The presence of this high voltage plateau denotes the occurrence of lithium stripping from the negative electroactive material surface taking place at the beginning of the discharging process. It has been stated in the literature that the detection of this high voltage plateau is an effective non-destructive method to identify the occurrence of lithium plating.^{1,3,4,11} However, as mentioned above, there are cases where a high voltage plateau is not observed at the beginning of the discharging process despite charging a Li-ion cell under plating conditions (low temperature and high current). In this investigation, we analyze the visibility of a high voltage plateau at the beginning of the discharge process of fresh LiFePO₄-Graphite Li-ion cells after being charged at plating conditions under a temperature of 0°C. In order to analyze the effect of the charging protocol on the cell performance, the fresh Li-ion cells were exposed to two different charging protocols: CC-CV and CC, and discharged at different C-rates: 1 C and 0.2 C.

2. Experimental

Commercially available 18650 type Li-ion cells with a rated capacity of 1050 mAh were used in this work. The cells use LiFePO₄ and graphite as positive and negative active materials, respectively. All measurements were carried out using a Solartron 1470E battery tester. The cells were placed inside a climate chamber ETAC FL414P to control the temperature during the tests.

Fresh Li-ion cells were exposed to charge-discharge cycling at 0°C. During charge, the cells followed two different protocols: constant current-constant voltage (CC-CV) and constant current (CC) with a rate of 2 C. For the CC-CV protocol, the cells were charge for 2 h. The maximum voltage was 3.6 V. Right after the charge process finished, the cells were discharged until 2.0 V

Figure 1. Voltage (a) and current (b) profiles obtained during charge following a CC-CV protocol with a rate of 2 C. Discharge profiles (c) obtained at 1 C discharge rate. 18650 LiFePO₄-Graphite Li-ion cell. Temperature: 0°C.

following a CC protocol with two different discharge rates: 1 C and 0.2 C. To allow the cell temperature to stabilize after the discharge process, there was a rest time of 40 min.

3. Results

Figure 1 shows the voltage (a) and current (b) profiles during the charge process following a CC-CV protocol with a rate of 2 C at 0°C. Due to the over potential caused by exposing the cell to low temperature and high current, the maximum voltage is reached in the first 17 min, after that the charge process continues in the CV phase. Figure 1c shows the discharge curves obtained with a rate of 1 C right after being charged. After 10 cycles, a capacity fade of 1% was observed. Figure 2 shows the voltage (a) and current (b) profiles during the charge process following a CC protocol with a rate of 2 C at 0°C. The maximum voltage is reached within the first 17 min, and since a CV phase was not included, the charge process ends when a maximum voltage of 3.6 V is reached. Figure 2c shows the discharge curves obtained with a rate of 1 C right after being charged. A voltage plateau is observed at the beginning of the discharge process. This high voltage plateau is a signature of the occurrence of lithium plating during the charge process of a Li-ion cell. After 10 cycles, a capacity fade of 10% is observed.

Figure 3 shows the voltage (a) and current (b) profiles obtained during charge following a CC-CV protocol with a rate of 2 C. As observed in Fig. 1, the maximum charge voltage is reached within the first minutes, and once the maximum voltage is reached the charge process continues in the CV phase. Figure 3c shows the discharge curves obtained with a rate of 1 C right after being charged. A capacity fade of 4% was observed after 10 cycles. Figure 4 shows the voltage (a) and current (b) profiles for a Li-ion cell during charge following a CC protocol with a rate of 2 C at 0°C.

Figure 2. Voltage (a) and current (b) profiles obtained during charge following a CC protocol with a rate of 2 C. Discharge profiles (c) obtained at 1 C discharge rate. 18650 LiFePO₄-Graphite Li-ion cell. Temperature: 0°C.

The charge process ends once a maximum voltage of 3.6 V is reached. Figure 4c shows the discharge curves obtained with a discharge rate of 0.2 C. After 10 cycles, the cell exhibited a capacity fade of 14%.

4. Discussion

When the Li-ion cells were exposed to charge following a CC-CV protocol, the cells exhibited a relatively good performance with a low capacity fade. On the other hand, when the cells were exposed to charge following a CC protocol, a significant capacity fade was observed after 10 cycles. The rated capacity of the cells used in this study is 1050 mAh at room temperature, therefore, it is important to emphasize the observed capacity fade after 10 cycles when the cells are charged following a CC protocol at 0°C, where the capacity fades close to 40% with respect to the rated capacity at room temperature. In addition, a high voltage plateau was detected at the beginning of the discharge process for the cell that was discharged with a rate of 1 C. It has been reported that the detection of a high voltage plateau at the beginning of the discharge process is an effective method to identify the occurrence of lithium plating in the previous charging process.^{1,3,4,10,11} This high voltage plateau denotes the occurrence of lithium stripping from the anode material surface. The over polarization of the negative electrode potential can happen when a Li-ion cell is exposed to low temperatures and high currents during the charge process. When a Li-ion cell is exposed to a CC-CV charge process at plating conditions (low temperature and high current), the generation of metallic lithium happens mainly during the CC phase, where the negative electrode potential over polarizes to negative values. When the charging process switches to the CV phase, the negative electrode potential relaxes to a more positive value and the metallic lithium generated in the previous CC phase

Figure 3. Voltage (a) and current (b) profiles obtained during charge following a CC-CV protocol with a rate of 2 C. Discharge profiles (c) obtained at 0.2 C discharge rate. 18650 LiFePO₄-Graphite Li-ion cell. Temperature: 0°C.

Figure 4. Voltage (a) and current (b) profiles obtained during charge following a CC protocol with a rate of 2 C. Discharge profiles (c) obtained at 0.2 C discharge rate. 18650 LiFePO₄-Graphite Li-ion cell. Temperature: 0°C.

can be diffused and intercalated into the anode active material.¹² Therefore, the inclusion of the CV phase during charging at low temperature and high current contributes to counter the degradation caused by the occurrence of lithium plating.

Furthermore, as mentioned above, the cells that were exposed to a CC charge protocol showed a significant capacity fade. This is mainly caused by the presence of metallic lithium on the negative electrode surface, which accelerates the electrolyte decomposition reducing the amount of lithium ion inventory and therefore the cell capacity decreases. Nevertheless, despite the cells were charged under the same conditions of current and temperature, a high voltage plateau was only detected in the case of the cell that was discharged with a rate of 1 C. These results show that the visibility of the stripping process of metallic lithium from the negative active material surface is sensitive to the cell discharge rate, due to the fact that the stripping rate should be proportional to the discharge rate. When the cell is discharged at 1 C, a large amount of metallic lithium is being stripped from the anode surface, which produces a voltage plateau at the beginning of the discharge process. However, when the cell is discharged at 0.2 C, the stripping rate of metallic lithium is relatively low, which might cause the remaining metallic lithium to dissolve and strip at the same rate, and therefore a voltage plateau is not observed at the beginning of the discharge process.

5. Conclusions

We evaluated the effect of the charge protocol and discharge rate on the lithium stripping process visibility in commercially available LiFePO₄/Graphite Li-ion cell during charge-discharge cycling at 0°C. As a result, the cells that were charged following a CC-CV protocol showed a relatively good performance and a high voltage plateau was not observed during the discharge process. On the other

hand, the cells that were charged following a CC process showed a significant capacity fade. Furthermore, a high voltage plateau was only observed in the cell that was discharge at a rate of 1 C, showing a dependency of the lithium stripping rate on the high voltage plateau visibility.

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