Experimental analysis on lithium iron phosphate battery over-discharged to failure

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Abstract. In this paper, a series of experiments were performed to investigate the thermal and electrical characteristics of a commercial lithium ion battery (LIB) over-discharged to failure. Specific information including voltage, current, capacity and battery surface temperature were measured and analyzed. According to the results, it is demonstrated that batteries behave obvious temperature rise during the over-discharge process and the temperature rise increase with the increasing charge rate. Besides, the LFP (lithium iron phosphate) exhibits gentler temperature rise than the NMC (nickel manganese cobalt oxide) battery in the over-discharge process. And the discharge rate is found there no huge effect on the lost capacity of battery when it is over-discharged to failure.

1. Introduction
As a result of their excellent performances such as high energy density, less pollution, stable performance and long-life cycle, etc, LIBs have become one of the most promising power sources and widely used for both portable electronics and transportation [1-2]. Meanwhile, one of the major problems remaining to be solved is the safety issue, namely, the failure of LIB under extreme conditions including high temperature, low temperature, overcharge and over-discharge, etc [3-5]. Very often, when a LIB is used in a battery pack, it will experience overcharge or over-discharge to an extent, because there always exist capacity variations among different batteries. It is extremely difficult to control the state of charge (SOC) of each single LIB in a battery pack exactly the same, consequently, a single LIB in a battery pack inevitably experiences overcharge or over-discharge to a certain degree.

Within a variety of LIBs, the cathode materials based on LFP have been proven superior than the traditional materials such as lithium cobaltate (LCO) and lithium manganate (LMO) because of their stable performance and high security [6-8]. Even though, LFP battery is also sensitive to abusive conditions, where, over-discharge is a common abusive condition and has a great influence on the electrochemical performance of LIB including capacity fading, temperature rise and even thermal runaway. Liu et al. [9] found that the temperature variation of over-discharged cell changed significantly with cycle number, and the temperature rise during over-discharge was much faster than that before over-discharge, suggesting that much higher heat generation occurred during the over-discharge stage. It is possible that micro-shorting resulted from the copper dendrite formation and SEI decomposition. Zhang et al. [10] discovered that over-discharge caused the capacity fading of battery capacity and the fading degree would be worse with the increase of over-discharge depth. Besides, to have a better understand on the mechanism of over-discharge destroying battery, Zheng et al. [11] conducted a set of experiments and their results revealed that batteries over-discharged to
0.5-0.0 V experienced serious irreversible capacity losses of 12.56-24.88%, namely, a serious loss of active lithium and anode materials occurred during over-discharge process. Guo et al. [12] investigated the entire over-discharge process and over-discharge-induced internal short circuit of large-format LIBs based on NMC cathode and graphite anode. According to the SEM and XRD results, they found that if the terminal SOC was lower than −12%, then the battery suffered from internal short circuit which was the result of Cu foil dissolution and deposition on electrodes. He et al. [13] systematically investigated the failure of commercial LIBs under different degrees of over-discharge (100-120% DOD). They proposed a possible failure mechanism of LIB during over-discharge process that the Cu was oxidized into Cu cations on the anode side, then, these Cu cations diffused through the separator to reach the surface of the cathode and, finally, these Cu cations were reduced to the Cu metallic form at the cathode. Eventually, the copper bridge formed which caused micro-shorting. However, previous works mainly focus on the slight over-discharge and little research has been done to investigate the characteristics of LIB over-discharged to failure, especially, the effect of discharge rate on the process has not been concerned. In order to fill in this gap, this paper conducted an experimental analysis to investigate the thermal characteristics of a commercial LIB (LFP) over-discharged to failure. Specific information including voltage, current, capacity and battery surface temperature were measured and analyzed to provide necessary basic data for this issue.

2. Experiments

2.1. Batteries
The batteries used in current study were cylindrical SONY 18650 with a diameter of 18 mm, a height of 65 mm and a nominal capacity of 1300 mAh. Its cathode materials were based on LFP and that for anode were graphite. Besides, its cut-off voltages for charge and discharge were 4.2 V and 2.5 V, respectively. Three major components including safety valve, jellyroll and shell casing constituted the batteries. The electrochemical reactions of LFP battery during charge and discharge can be presented as:

\[ \text{LiFePO}_4 + 6C \leftrightarrow \text{Li}_{1-x}\text{FePO}_4 + \text{Li}_x\text{C}_6 \]

2.2 Apparatuses and experimental design
As shown in Fig. 1, experiments were carried out in a well-ventilated cone chamber with a dimension of 1.2 m × 1.2 m × 1.2 m. Batteries were placed upon a supporting mesh made of iron wire in tests. A K-type thermocouple with a diameter of 1 mm was attached to the battery to measure its surface temperature and the temperature was recorded at the data acquisition equipment (NI cDAQ-9174) by a computer. Charging/discharging battery was achieved by a cycle equipment (NEWARE CT-3008) with a diameter of 5 V/6 A. The electrical performances including voltage, current and capacity of batteries were obtained through the cycle equipment. Experiments consisted of 4 discharge rates were carried out to explore the variations including voltage, current, capacity and surface temperature of LIBs during over-discharge to failure. Before tests, each battery was discharged at a 2C rate to 2.5 V, namely, 0% SOC. And then, it was placed still for 24 hours to ensure it remained stable. The experimental configurations are further listed in Table 1, where each configuration was repeated three times under the same condition to guarantee the repetition of results.
3. Results and discussion

The typical curves of surface temperature, voltage and current versus capacity during the over-discharge process for the battery discharged at 2C rate are depicted in Fig. 2. Before experiment, the battery was discharged by a CC (constant current) of 2C rate to 0% SOC. As seen, the over-discharge process can be divided into three stages briefly. At stage (a), the battery was in the state of slight over-discharge. Its surface temperature increased steeply and the voltage decreased rapidly too. At the end of stage (a), the battery achieved the peak temperature of the whole over-discharge process, 30.9 ℃. Then, it entered stage (b) where the surface temperature and voltage declined gradually, while the current kept stable. With the processing of over-discharge, the discharge current began to descend at a rapid speed, while the drop rate of voltage became slower at stage (c). It was the result of the serious over-discharge of battery so that the CC discharge could not be retained. When the over-discharge process approached the end, the voltage and current declined to 0.22 V and 0 mA respectively. After the over-discharge treatment, the battery could not be charged over 80% SOC again, the failure threshold for LIB [14], which implies that the battery failed. It is induced by the excessive loss of lithium ions from the anode which resulted in the damage of graphite structure and then lithium ions could not deposit into the anode efficiently any more [15].
Further, Fig. 3 presents the battery surface temperature histories during over-discharge process where the over-discharge treatment was carried out at a CC of 1C, 2C, 3C and 4C, respectively. It can be found that with the increasing discharge rate, the peak temperature ($T_p$) of battery during over-discharge increased and possessed a peak temperature of 29.1, 30.9, 32.0 and 32.4 °C, respectively. Besides, the time to peak temperature ($t_p$) for the four batteries were 452, 412 378 and 346 s separately, namely, it was earlier to get to the peak temperature for the battery with a larger discharge rate. It implies that the battery over-discharged by a larger rate exhibited severer temperature rise and it was prone to heat up.

Combined by the results of previous experiments, Fig. 4 displays the peak temperatures of two commercial LIBs (LFP and NMC) during over-discharge process under different rates. As shown, the peak temperatures of LFP batteries during the over-discharge process were lower than that of NMC batteries especially for the high rate condition. Namely, the NMC exists severer temperature rise than the LFP in the over-discharge process and this finding corresponds to the result of our paper published before [16], which also confirmed that the LFP has higher security compared to the NMC in some extent.

When battery was over-discharged to failure, its capacity would decrease in comparison with the original state. Fig. 5 shows the lost capacities of LFP and NMC batteries when they were over-discharged to failure under different rates. It is interesting to find that their lost capacities floated around 0.16 Ah, in other words, the -12.3% SOC. This finding is identical to the result of Guo et al. [8] and it indicates that when battery is over-discharged over a critic, it will suffer irretrievable damage even failure. The discharge rate does not have huge effect on the critic, and their critics are similar for LFP and NMC.
Fig. 3. Typical curves of surface temperatures of batteries and air temperature vs time during over-discharge

Fig. 4. The peak temperatures of LFP and NMC batteries in over-discharge
4. Conclusion

An experimental analysis was conducted to investigate the thermal and electrical characteristics of the LFP batteries over-discharged to failure. Results show that batteries have obvious temperature rise during the over-discharge process and the temperature rise will be worse and quicker with the increase of discharge rate. After comparing, it is demonstrated that the NMC battery presents severer temperature rise than that of the LFP in over-discharge process. In addition, discharge rate is found there no huge effect on the lost capacity of battery when it is over-discharged to failure.

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