



## Deterioration of lithium iron phosphate/graphite power batteries under high-rate discharge cycling



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### ABSTRACT

In this study, the deterioration of lithium iron phosphate (LiFePO<sub>4</sub>)/graphite batteries during cycling at different discharge rates and temperatures is examined, and the degradation under high-rate discharge (10C) cycling is extensively investigated using full batteries combining with post-mortem analysis. The results show that high discharge current results in an instability of electrode/electrolyte interface and unstable solid electrolyte interphase (SEI) layers are expected to form on the newly exposed graphite anode surface, which cause sustainable consumption of active lithium and further lead to the performance degradation of active materials. For LiFePO<sub>4</sub> cathode, the initial capacity is largely recovered under low rate (0.1–0.2C), whereas a decline in the capability is observed at higher rates (0.5–3.0C). For graphite anode, half-cell study shows that considerable capacity loss occurs even at low rates. A small amount of Fe deposition is observed on graphite anode after cycling under 10C discharge at 55 °C. X-ray photoelectron spectroscopy (XPS) analysis confirms that a layer composed of lithium compounds is formed on the surface of anode, which can not participate in the reversible electrochemical reaction again. In addition, electrochemical impedance spectrum (EIS) measurements of half-cell indicate that the increased resistance of the positive electrode is suggested to be the root cause of power fading under high-rate discharge cycling, especially at high temperature.

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## 1. Introduction

Lithium iron phosphate (LiFePO<sub>4</sub>) is one of the most significant and promising cathode materials with high theoretical capacity (170 mAh·g<sup>-1</sup>), high thermal stability, low cost, environmental benignity and cycling stability [1–5]. The graphite anode has a theoretical capacity of 372 mAh·g<sup>-1</sup>, good electrical conductivity, high crystallinity and stability of layered structure, which make it as a major commercial battery anode material [6,7]. The advantages of LiFePO<sub>4</sub> cathode and graphite anode promote a wide application of LiFePO<sub>4</sub>/graphite batteries as power sources for hybrid electric vehicles (HEVs) and energy storage systems (ESSs). It is believed that the LiFePO<sub>4</sub>/graphite power batteries will play a significant role in the future low carbon life.

Although LiFePO<sub>4</sub> has a very stable structure, it has been indicated that the LiFePO<sub>4</sub>/graphite batteries still suffer from life and power decay during long time cycling [8–11]. Therefore, aging of this type of battery remains one of the biggest concerns of automakers and end customers. Understanding the degradation mechanism clearly is favorable to improve the battery performance. It is worth noting that the properties of batteries at high discharge rate become the most important factor for their applications in the HEVs and ESSs, which affects the output power of energy storage power system. ESSs used in HEVs are required to supply and store electric energy at comparably high power rates within a limited state-of-charge (SOC) range, typically 30–60%. For heavy-duty commercial vehicles, very high power is expected with a very high usage rate of 10–20 h/day. Therefore, the research on decay mechanism under high-rate discharge current of LiFePO<sub>4</sub>/graphite batteries is urgently necessary.

Some efforts have already been carried out to illustrate the reason of capacity loss of LiFePO<sub>4</sub>/graphite batteries during cycling tests [12–21]. Generally, the performance degradation during cycling can be attributed to several factors, such as: (a) loss of

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active material (material dissolution, structural degradation, particle isolation, and electrode delamination), (b) loss of cyclable lithium (SEI growth at carbon anode due to electrolyte decomposition), and (c) resistance increase (passive films at the active particle surface, loss of electrical contact within the porous electrode). Safari et al. investigated the aging behavior of LiFePO<sub>4</sub>/graphite cell during both cycling and storage at 25 or 45 °C by non-destructive electrochemical techniques. They proposed that the loss of cyclable lithium is identified as the main source of capacity fading in all cases [20]. Zhang et al. investigated the cycling degradation of LiFePO<sub>4</sub>/graphite batteries at 50 °C using electrochemical impedance spectroscopy as well as capacity and power fading characterization at different test temperatures (45, 25, 0 and –10 °C). They also proposed that the primary mechanism for capacity fading is loss of cyclable lithium in the cell resulting from lithium-consuming solid electrolyte interphase (SEI) layer growth and side reactions [21].

It is well-known that the capacity decrease and power fading are affected by various factors such as working temperature, depth of discharge, charge/discharge current, etc [22–28]. In previous work, most studies focused on investigating the effects of temperature on the aging of this type of battery, whereas, unfortunately, the influence of current on the degradation of battery during cycling is still unclear, especially at high discharge rate. Generally, the batteries display relatively poor cycling performance at high discharge rate. Further studies remain necessary for quantifying the effects of current on capacity and power fading in detail, especially during high-rate discharge.

In this paper, the degradation of LiFePO<sub>4</sub>/graphite batteries under different discharge rates and temperatures was investigated using 18650-type battery combining with post-mortem analysis. Both structure deterioration and capacity loss of positive and negative electrodes of batteries after 600 cycles at 25 and 55 °C were analyzed. Electrode surface and microstructure change of cathode and anode materials were also detailed examined and their effects on the electrochemical performance decay were extensively analyzed.

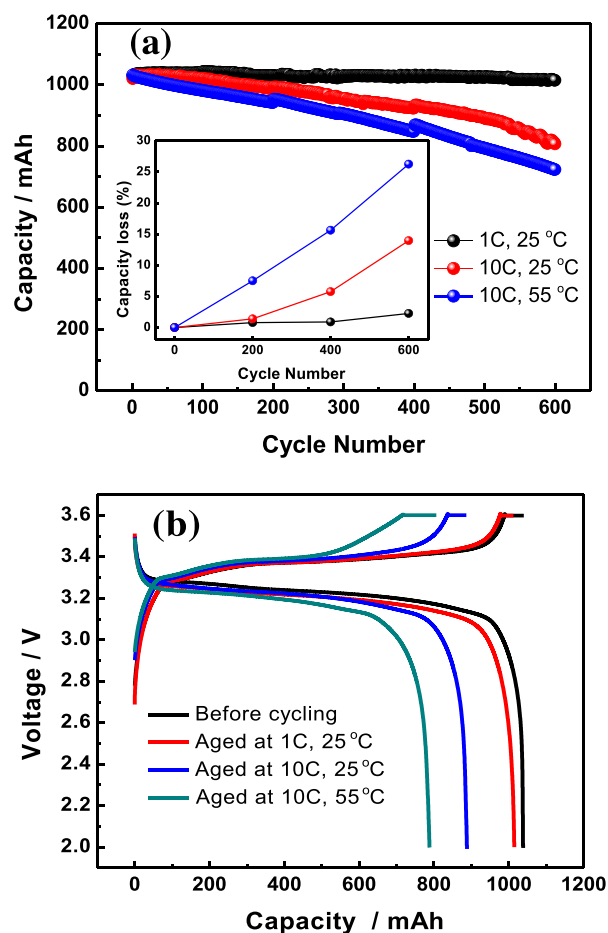
## 2. Experimental

The 18650-type commercial LiFePO<sub>4</sub>/graphite batteries were used as the candidate for the investigation, which were obtained from Tianjin Lishen Battery Joint-Stock Co., Ltd. The designed nominal capacity of the batteries under 1C-rate is 1.06 Ah. The cycling performance of batteries were examined between 2.0 and 3.6 V under 1C charge rate and different discharge rates (1C, 10C) and temperatures (25, 55 °C). Two cells were tested at each of the conditions. Before the cycling tests, the capacities of all cells were determined by a 1C charge/discharge current at 25 °C. All the cells were firstly charged to 3.6 V and kept at 3.6 V until the current dropped to 0.02C (22 mA), then the cells were discharged to 2.0 V. During the cycling tests, the real capacity of each cell was verified every 200 cycles by using the procedures described above. The electrochemical working station (IM6eX, Germany) was used to measure the electrochemical impedance spectrum (EIS) of 18650 LiFePO<sub>4</sub>/graphite batteries and coin cells before and after cycling tests. The impedance was measured by applying a 5 mV of ac oscillation with the frequency ranging from 100 kHz to 0.01 Hz. The EIS measurement of 18650 LiFePO<sub>4</sub>/graphite batteries before and after cycling was carried out in the state of 60% SOC at 25 °C.

The capacity and cycling performance tests of batteries were performed using Neware CT-4008 Battery Tester. The Espec Environmental Chamber was adopted to provide constant temperature environment for all the tests. The fully discharged high power batteries before and after cycling tests were transferred to a glove box and then disassembled. Before

disassembly, the batteries were discharged to 2 V at 1C, and then hold the constant voltage of 2 V until the discharge current lower than 0.05C. The LiFePO<sub>4</sub> and graphite electrodes were washed by dimethyl carbonate (DMC) to remove the electrolyte from the cathode and anode surface. LiFePO<sub>4</sub> and graphite disc electrodes with 15 mm diameter were then punched out and coin cells were assembled with a lithium metal foil as counter electrode. A constant current protocol between 2.5 and 4.2 V for the LiFePO<sub>4</sub> coin cells and between 0.0 and 2.0 V for the graphite coin cells was used. The coin cells were tested by Land CT2001A Battery Test System. The capacities of LiFePO<sub>4</sub> and graphite electrodes at 0.1C were obtained. EIS was carried out in the fully discharged state for the coin cells after 4 cycles.

X-ray diffraction (XRD) patterns of the LiFePO<sub>4</sub> samples before and after cycling tests were obtained by a Rigaku D/max 2500/PC diffract meter (Rigaku Corp., Japan) using Cu K $\alpha$  radiation in an angular range of 10–90° (2 $\theta$ ) with a 0.02° (2 $\theta$ ) step. The surface morphology and microstructure analysis were observed using a field emission scanning electron microscope (FE-SEM, HITACH S4800, Japan) with energy dispersive X-ray spectroscopy (EDS) and transmission electron microscopy (TEM, JOEL JEM-2100F, Japan). X-ray photoelectron spectroscopy (XPS) measurements were conducted on a physical Electronics PHI5802 instrument using an X-rays magnesium anode (monochromatic Ka X-rays at 1253.6 eV) as the source.



**Fig. 1.** Cycling performance of 18650 LiFePO<sub>4</sub>/graphite batteries using charge rate of 1C and different discharge rates and temperatures: (a) cycling performance and capacity loss at 1C/1C during cycling; (b) voltage profiles at 1C/1C for each batteries under the three different conditions before and after 600 cycles.

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