

Thermal runaway features of 18650 lithium-ion batteries for LiFePO₄ cathode material by DSC and VSP2

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Abstract In view of availability, accountability, and applicability, LiFePO₄ cathode material has been confirmed to be better than LiCoO₂ cathode material. Nevertheless, few related researches were conducted for thermal runaway reaction of the LiFePO₄ batteries. In this study, vent sizing package 2 (VSP2) and differential scanning calorimetry were employed to observe the thermal hazard of 18650 lithium-ion batteries and their content—LiFePO₄ cathode material, which were manufactured by Commercial Battery, Inc. Two states of the batteries were investigated, which was charged to 3.6 V (fully charged) and 4.2 V (overcharged), respectively, and important parameters were obtained, such as self-heating rate ($dT \text{ dt}^{-1}$), pressure-rise rate ($dP \text{ dt}^{-1}$), and exothermic onset temperature (T_0). The results showed that T_0 for fully charged is about 199.94 °C and T_{\max} is about 243.23 °C. The entire

battery for LiFePO₄ cathode material is more stable than other lithium-ion batteries, and an entire battery is more dangerous than a single cathode material. For process loss prevention, the data of battery of VSP2 test were applied as reference for design of safer devices.

Keywords LiFePO₄ · 18650 lithium-ion batteries · Pressure-rise rate · Process loss prevention · Thermal runaway · Vent sizing package 2 (VSP2)

List of symbols

T_0	Initial exothermic temperature (°C)
$dT \text{ dt}^{-1}$	Self-heating rate (°C min ⁻¹)
$dP \text{ dt}^{-1}$	Pressure-rise rate (bar min ⁻¹)
P_{\max}	Reaction maximum pressure (bar)
T_{\max}	Reaction maximum temperature (°C)
ΔH_d	Decomposition of heat (J g ⁻¹)
V	Voltage (V)
CC	Constant current (A)
CV	Constant voltage (V)
A	Ampere (A)
Mass	Mass of sample before VSP2 experiment (g)

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Introduction

In recent years, the implementation of green and substitute energy has been advocated globally due to the escalating energy crisis. The development of a highly efficient system of energy stored devices is needed imminently. The lithium-ion battery is one of the alternative power sources, which possesses high power, high voltage, long cycle life, and low self-discharged performance [1]. Accordingly, its

applications in electric vehicles have attracted much attention with booming development [1, 2].

All kinds of lithium-ion batteries have been developed over the past decade. The universal chemical formula of the cathode material of a lithium-ion battery is LiM_xO_x or LiM_xPO_4 , where M can be any metal ion, such as Fe, Co, Mn, and Ni [3]. Most cathode materials are unstable at high temperature which decompose and release a certain amount of oxygen. Then the oxygen reacts with organic solvents, which generates a large amount of heat in the battery. This is an extremely dangerous state, and it may lead to fire or explosion when the heat cannot be adequately removed [4–6]. Therefore, the application of the cathode material safety of lithium-ion battery is important for development of electric vehicles especially under abnormal situations.

Numerous reports have indicated that lithium iron phosphate batteries (LiFePO_4 batteries) are more stable and safer than other batteries because they have Olivine-type [3]. However, relative to the efficiency of LiCoO_2 , LiMnO_2 , and $\text{Li}[\text{Ni}_x\text{Co}_y\text{Mn}_z]\text{O}_2$ batteries with regard to the application of electric products, LiFePO_4 batteries are not enough. Hence, the small cells of LiCoO_2 , LiMnO_2 , and $\text{Li}[\text{Ni}_x\text{Co}_y\text{Mn}_z]\text{O}_2$ batteries in electronic products have been commonly used. The LiFePO_4 batteries are applied to large-scale devices in electric vehicles due to the better and safer property [7, 8].

Although the LiFePO_4 batteries have been claimed to be highly safe, fires and explosions have sporadically occurred in electric vehicles for a variety of reasons. In June, 2010, an electric scooter incurred a fire during charging [9]. In 2011 and 2012, serious fire accidents for electric vehicles keep occurring in China [10, 11]. From these events the thermal hazards and runaway nature of LiFePO_4 batteries were established urgently. For this reason, we investigated the initial reaction of 18650 LiFePO_4 battery under adiabatic condition by vent sizing package 2 (VSP2) calorimeter.

Safety issues of thermal abuse as well as development for high capacity batteries are being taken into consideration and are attracting more concern. VSP2 is one of the alternative methodologies for obtaining self-reactive behaviors of lithium-ion batteries [12, 13]. Many studies have reported that the majority of lithium-ion batteries undergo thermal runaway due to overheat or abuse [14–16]. Thermal runaway reactions in lithium-ion batteries are sensitive to various cathode materials. For LiFePO_4 cathode material, many literatures have shown that it has remarkable thermal stability [17]. However, the research of an entire battery like LiFePO_4 18650 cell type regarding thermal runaway reaction has been relatively few [17, 18]. The thermal hazard of an entire battery is more dangerous than for a single material. Therefore, the loss prevention development of the lithium-ion battery should obtain more details about the performance of individual batteries.

Experimental

Sample

The LiFePO_4 battery is a rechargeable battery and the element of lithium iron phosphate is used as cathode material. Compared with the LiCoO_x and LiMn_xO_y battery, the LiFePO_4 battery is cost-effective and non-toxic, with high abundance of iron, decent thermal stability, security characters, and sound electrochemical performance. The cathode material of LiFePO_4 can be employed broadly in small and large capability batteries in the future. Table 1 shows the recommended method of commercial 18650 LiFePO_4 battery [19]. We focused on the commercial 18650 charge–discharge electrical lithium-ion battery which charges to 3.6 and 4.2 V. The preliminary experiment explored the variation of temperature and pressure with respect to time under the two voltages. According to recommendations from Table 1, we used a charge–discharge electrical device to perform charge or discharge action. The batteries were charged to 3.6 and 4.2 V, individually, and were tested to observe their thermal runaway reaction. Table 2 displays the test condition of the two samples. The fully charged lithium battery was sample A, and overcharged was sample B.

Differential scanning calorimetry (DSC)

Dynamic scanning experiments were conducted on a Mettler TA8000 system coupled with a DSC 821^e measuring test cell (Mettler ME-26732). DSC is considered

Table 1 Commercial 18650 LiFePO_4 batteries of safety recommendations [19]

Recommendation	Method
Nominal capacity and voltage	1.1 Ah, 3.3 V
Recommended stand charge method	1.5 A to 3.6 V CCCV, 45 min
Recommended fast charge current	5 A to 3.6 V CCCV, 15 min
Maximum continuous discharge	30 A
Recommended charge and cut-off V at 25 °C	3.6–2 V
Recommended charge and cut-off V below 0 °C	4.2–0.5 V

Table 2 Commercial 18650 LiFePO_4 batteries

Sample	Type	Voltage/V	Mass/g
Sample A	Commercial 18650 LiFePO_4 batteries	3.6	38.11
Sample B	Commercial 18650 LiFePO_4 batteries	4.2	38.35

Table 3 Heat flow versus temperature for thermal decomposition of the anode and cathode of commercial 18650 LiFePO₄ batteries under heating rates ($\beta = 4 \text{ }^{\circ}\text{C min}^{-1}$) by DSC

LiFeO ₄ Li-ion battery	Voltage/V	Mass/mg	$T_0^{\text{a}}/{}^{\circ}\text{C}$	2nd $T_0^{\text{b}}/{}^{\circ}\text{C}$	2nd $T_{\max}^{\text{c}}/{}^{\circ}\text{C}$	$\Delta H_d/\text{J g}^{-1}$
Cathode material	3.6	23.7	100.13	197.27	270.14	71.08
Anode material	3.6	6.5	—	—	—	—

^a The initial exothermic temperature of SEI decomposition

^b The initial exothermic temperature of the second peak

^c The peak temperature of the second peak

to be a useful tool for assessing the decomposition mechanism of the thermal hazards of reactive chemicals [20]. The range of temperature rise was set from 30 to 550 °C for each experiment. The heating rates (β) were chosen as 4 °C min⁻¹ for the sake of better thermal equilibrium [21]. Before the experiment, a commercial LiFePO₄ battery was disassembled into a high-pressure gold crucible in the nitrogen-filled glove box. The appearance of first exothermic excursion in cathode and anode materials of a LiFePO₄ battery was confirmed. The results of commercial 18650 LiFePO₄ batteries under heating rates ($\beta = 4 \text{ }^{\circ}\text{C min}^{-1}$) by DSC shown in Table 3.

Vent sizing package 2 (VSP2)

VSP2 is a computer-controlled adiabatic calorimeter system manufactured by Fauske & Associates, LLC [22]. The test data of a sample such as self-heating rate; control reaction of temperature, pressure, and time and reaching maximum heating temperature and pressure; and other related data were obtained by VSP2. In addition, the runaway process was acquired for test items as a reference of safe design which prevents a thermal disaster. The most significant feature for VSP2 is the heat-wait-search (H-W-S) function, which can acquire initial self-heating reaction. The sample is heated to set temperature, and then stopped to search for samples with or without self-heating exothermic decomposition. When self-heating reaction of the sample is detected by thermocouple, the main heater is closed. Only the guard heater is operated to keep the adiabatic environment until the thermal runaway reaction of sample is complete [23–27]. In this study, the test temperature range was from 40 to 300 °C, and the detection sensitivity was 0.15 °C min⁻¹. An 18650 battery was encased in a customized stainless steel test can. Furthermore, the thermocouple which can obtain accurate temperature was connected with the battery in the test can.

Results and discussion

The thermal hazard of the anode and cathode was evaluated according to the application of the scanning rate of

4 °C min⁻¹, as illustrated in Fig. 1. DSC detected thermal curves of decomposition of the anode and cathode, such as exothermic onset temperature (T_0), the maximum exothermic temperature (T_{\max}), the heat of decomposition (ΔH_d), and other parameters (see Table 1). From the experimental results, the thermal decomposition traits of LiFePO₄ battery rated voltage of 3.6 V, shown in Fig. 1, were acquired. Figure 1 shows three exothermic peaks. The first exothermic reaction peak appeared at 100.13 °C which mean thermal cracking of the SEI film. As the main exothermic stage, T_0 of the second peak is at 197.27 °C. From the second peak, we guess the cathode material with slight electrolyte of the exothermic reaction after the SEI film pyrolysis [4]. The T_{\max} was 270.14 °C, and the ΔH_d for cathode material with slight electrolyte was 71.08 J g⁻¹ by DSC ($\beta = 4 \text{ }^{\circ}\text{C min}^{-1}$). The anode material within the electrolyte did not undergo exothermic reaction in our experiments.

DSC was used to determine the main exothermic material in the lithium-ion battery. Figures 2, 3, 4, 5, and 6 depict the decomposition curve of LiFePO₄ batteries with 3.6 and 4.2 V under VSP2 tests. The results of the VSP2 test regarding runaway reaction under adiabatic conditions,

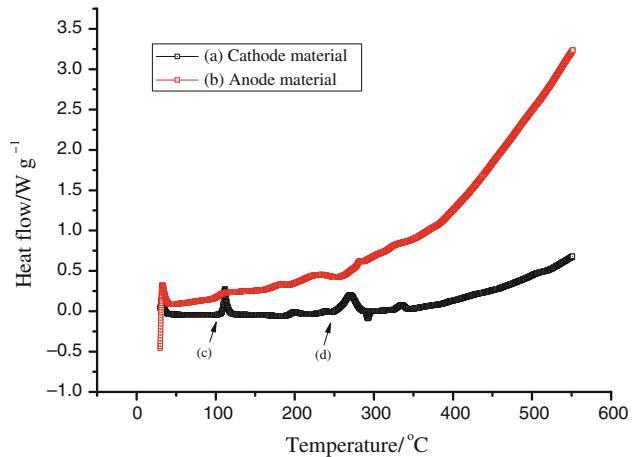


Fig. 1 DSC curves of *a* cathode material wetted within electrolyte, *b* anode material within electrolyte, *c* the initial exothermic temperature of SEI decomposition, and *d* the initial exothermic temperature of the second peak

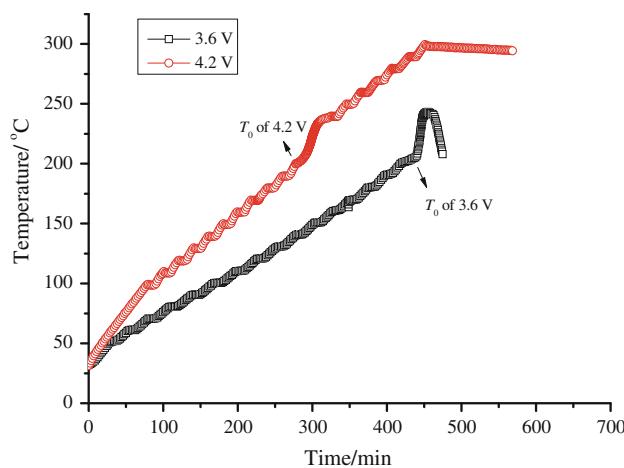


Fig. 2 Temperature versus time for thermal decomposition of LiFePO₄ batteries of 3.6 and 4.2 V by VSP2

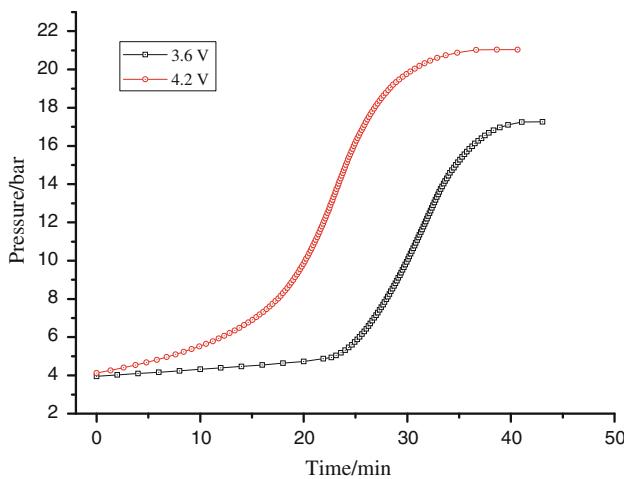


Fig. 3 Pressure versus time plots for thermal decomposition of LiFePO₄ batteries of 3.6 and 4.2 V by VSP2

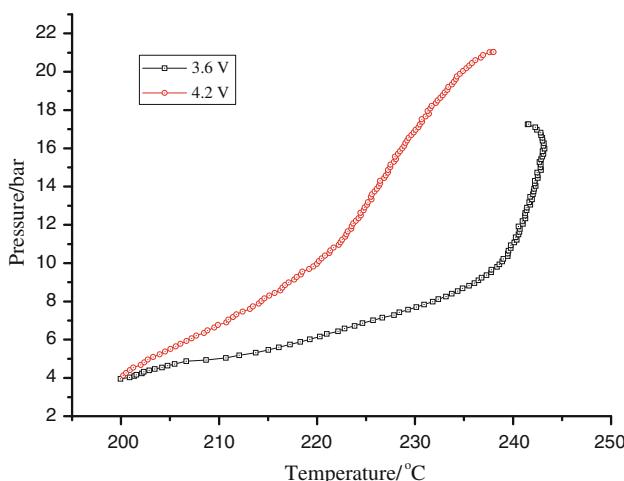


Fig. 4 Temperature versus pressure plots for thermal decomposition of LiFePO₄ batteries of 3.6 and 4.2 V by VSP2

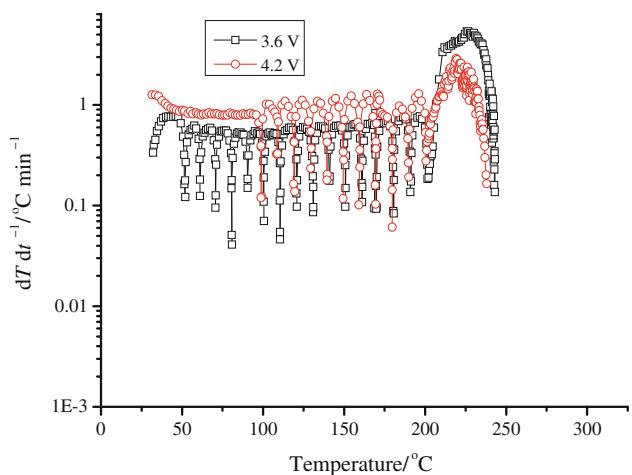


Fig. 5 Dependence of self-heating rate on temperature from VSP2 experimental data for LiFePO₄ batteries with 3.6 and 4.2 V

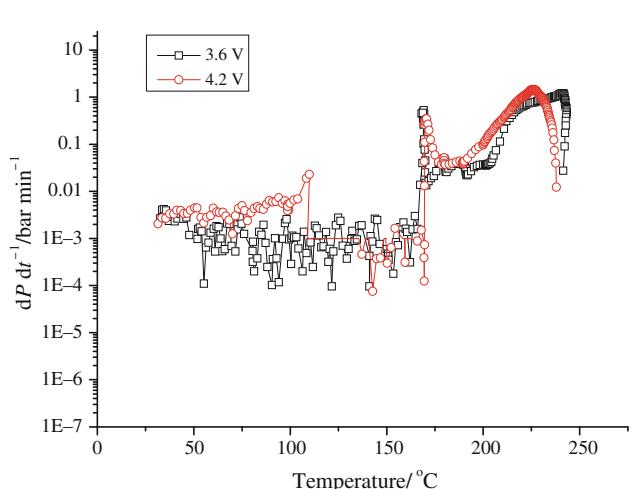


Fig. 6 Dependence of pressure-rise rate on temperature from VSP2 experimental data for LiFePO₄ batteries with 3.6 and 4.2 V

such as temperature (T), pressure (P), time (t), initial exothermic temperature (T_0), self-heating rate (dT/dt^{-1}), maximum reaction pressure (P_{\max}), pressure-rise rate (dP/dt^{-1}), and thermokinetic parameters of LiFePO₄ batteries were acquired, which can help us understand the uncontrolled thermal behaviors of LiFePO₄ batteries during elevated temperature exposure. VSP2 can facilitate the design of the lithium-ion battery—cooling system temperature and alerting for disconnection system.

The internal content in the battery possesses a spontaneous chemical material that can cause a self-chemical reaction. The thermal runaway reaction of LiFePO₄ battery was measured by VSP2. Figure 1 shows temperature versus time for thermal decomposition of the battery of 3.6 and 4.2 V by VSP2. The results indicate that the exothermic temperature of 3.6 V battery was higher than that for the 4.2 V battery. Here, T_0 is 199.94 °C and the maximum

Table 4 Thermal runaway reaction of experimental data for LiFePO₄ 18650 batteries by VSP2 test

Sample	Mass/g	T ₀ /°C	T _{max} /°C	P _{max} /bar	(dT dt ⁻¹) _{max} /°C min ⁻¹	(dP dt ⁻¹) _{max} /bar min ⁻¹
Sample A ^a	32.41	200.24	238.36	21.03	2.90	1.46
Sample B ^b	32.84	199.94	243.23	17.27	5.39	1.21

^a Charge level was 4.2 V

^b Charge level was 3.6 V

temperature is 243.23 °C for charging to 4.2 V. We detected the T₀ for the entire battery of LiFePO₄, which was lower than that for a single material [3]. Figure 2 shows the pressure versus time plots for thermal runaway reaction of LiFePO₄ batteries of 3.6 and 4.2 V by VSP2. The maximum pressure for the 4.2 V battery was higher than that for the 3.6 V batteries. The self-heating reaction for 4.2 V battery appeared at 200.24 °C by H–W–S method test. Table 4 and Fig. 2 show that the difference in temperature between 3.6 and 4.2 V battery is inconspicuous. However, the maximum pressure for 4.2 V was very distinct at about 3.7 bar in Fig. 3. This study employed lithium iron phosphate for cathode material conductivity, cyclic voltammetry, materials modification, and other issues in the past. This part of the pressure may be due to larger 4.2 V Li-ion battery powers and oxygen in the air caused by thermal stress.

The change in the self-heating rate and pressure-rise rate with temperature are revealed in Figs. 4 and 5. The (dT dt⁻¹)_{max} and (dP dt⁻¹)_{max} of the rated voltage commercial 18650 LiFePO₄ batteries were about 5.39 °C min⁻¹ and 1.21 bar min⁻¹. DSC provided a prior scanning test of the T₀ on the rated voltage, which is the same as that determined on the VSP2; the above test provided another measurement of pressure to confirm the capability of VSP2. These results show that abnormal applications for high temperature condition may induce a runaway reaction. This is a crucial matter, because it further illustrates that the phosphate lithium iron salts could maintain the system under thermal stability, even in the most adverse conditions, and could avoid any heat accumulation. Therefore, we used a self-test cell in VSP2 instrument applications; it can become an alternative measure to investigate thermal runaway for LiFePO₄ battery.

Conclusions

With the development of high energy density batteries, the primary concern is consumer safety, and the secondary concern is the development of more advanced loss prevention technology. The exothermic behavior and thermal stability of LiFePO₄ were observed for the batteries by VSP2; to ensure the future applications in lithium-ion

battery for electric vehicles, the overall design should shoot for the smallest cell with an inherently safer approach. The internal material in the battery causes a spontaneous chemical reaction that may be attributed to an internal short circuit, which may incur a follow-up fire and explosion. Although the maximum temperature for a single 18650 battery appeared at ca. 230–250 °C, this temperature may also have significant detrimental effects when many 18650 batteries are connected as a series–parallel pack. An entire battery is more dangerous than a single cathode material. Therefore, the thermal safety considerations are required imminently. Finally, the results proved that the thermal hazard assessment by the calorimetric method VSP2 is an alternative to assess lithium-ion battery technology.

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