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Self-reactive rating of thermal runaway hazards on 18650 lithium-ion batteries

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Abstract Vent sizing package 2 (VSP2) was used to measure the thermal hazard and runaway characteristics of 18650 lithium-ion batteries, which were manufactured by Sanyo Electric Co., Ltd. Runaway reaction behaviors of these batteries were obtained: 50% state of charge (SOC), and 100% SOC. The tests evaluated the thermal hazard characteristics, such as initial exothermic temperature (T_0), self-heating rate ($\mathrm{d}T\ \mathrm{d}t^{-1}$), pressure-rise rate ($\mathrm{d}P\ \mathrm{d}t^{-1}$), pressure temperature profiles, maximum temperature, and pressure which were observed by adiabatic calorimetric methodology via VSP2 using customized test cells. The safety assessment of lithium-ion cells proved to be an important subject. The maximum self-heating rate $(\mathrm{d}T\ \mathrm{d}t^{-1})_{\max}$ and the largest pressure-rise rate $(\mathrm{d}P\ \mathrm{d}t^{-1})_{\max}$ of Sanyo 18650 lithium-ion battery of 100% SOC were measured to be 37,468.8 °C min^{-1} and 10,845.6 psi min^{-1}, respectively, and the maximum temperature was 733.1 °C. Therefore, a runaway reaction is extremely serious when a lithium-ion battery is exothermic at 100% SOC. This result also demonstrated that the thermal VSP2 is an alternative method of thermal hazard assessment for battery safety research. Finally, self-reactive ratings on thermal hazards of 18650 lithium-ion batteries were studied and elucidated to a deeper extent.

Keywords Adiabatic calorimetric methodology · 18650 lithium-ion batteries · Runaway characteristics · Thermal hazard · Vent sizing package 2 (VSP2)

List of symbols

T_0	Initial exothermic temperature (°C)
$\mathrm{d}T\ \mathrm{d}t^{-1}$	Self-heating rate (°C min^{-1})
$\mathrm{d}P\ \mathrm{d}t^{-1}$	Pressure-rise rate (psi min^{-1})
$\triangle T_{\mathrm{ad}}$	Adiabatic temperature rise (°C)
$\triangle P_{\mathrm{ad}}$	Adiabatic pressure-rise (psig)
$P_{\max}$	Reaction maximum pressure (psig)
$T_{\max}$	Reaction maximum temperature (°C)
$\triangle H$	Heat of reaction (J, kJ)
W	Power (J s^{-1}, kJ s^{-1})
C_{total}	Total specific heat capacity (J g^{-1} K^{-1})
C_{can}	Specific heat of the 18650 stainless steel can (J g^{-1} K^{-1})
C_{cell}	Specific heat of the materials of the lithium-ion batteries (J g^{-1} K^{-1})
m_{total}	Total mass of the 18650 lithium-ion (g)
m_{can}	Mass of the 18650 stainless steel can (g)
m_{cell}	Mass of the materials of the lithium-ion batteries (g)
M_{f}	Mass of the lithium-ion batteries after experiment (g)

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Introduction

As our lives become more dependent on electricity, the development of systems capable of storing the energy form will be important and indispensable. The lithium-ion battery is one of the key energy devices with high-energy, high-voltage, long life cycle, and low self-discharge properties. The application of lithium-ion batteries has attracted world wide attention in the 3C electronic industry and electrical vehicles [1]. However, large amounts of thermal energy can be released because of thermal abuse behavior that results in high temperature and high pressure, leading to a fire or explosion [2].

Numerous severe explosion accidents with fire caused by lithium-ion batteries, which supply the power in the 3C, have occurred over the previous years [3]. Lithium-ion batteries are exposed at high temperature holding in a period of time, and higher energy density of electrode materials for lithium-ion batteries could result in thermal runaway reaction [4]. Tobishima et al., indicate that thermal runaway reaction occurs because the heat output exceeds thermal diffusion [5]. Certain studies have indicated that porous separators incur breakdown at temperature above 120 °C and then induce an internal short circuit [6, 7], leading to continued rise of thermal hazard. Thermal runaway reactions of lithium-ion batteries have occurred after self-generated heating reaches a critical temperature, and usually accompanies explosion [8]. Therefore, safety issues of lithium-ion batteries cannot be ignored. In addition, it is critically important that safe use of lithium-ion batteries be ensured.

The adiabatic condition of vent sizing package 2 (VSP2) with calorimetry technique is similar to the accelerating rate calorimeter (ARC), and the characteristics of the adiabatic calorimeter can obtain pressure related parameters, such as pressure-rise rate ($dP\ dt^{-1}$) and maximum pressure (P_{max}). In previous studies, differential scanning calorimetry (DSC), ARC, thermogravimetric analysis (TGA), thermal ramp, and thermal image techniques have been used to evaluate the temperature variation of the batteries with various materials [9, 10]. However, fewer researches have used VSP2 to measure the thermal hazard and thermal runaway reactions of lithium-ion batteries in the open literature. Safety tests and standards of lithium-ion batteries have been mainly performed for product evaluation, such as Underwriters Laboratories (UL), United Nations (UN) for transportation, and Japan Battery and Appliance Industries Association [11]. Thus, this study proposes a new technique that measures various commercial 18650 lithium-ion batteries.

We investigated the initial reaction of commercial Sanyo 18650 lithium-ion batteries under adiabatic condition by VSP2 calorimeter method and obtained the essential parameters of thermal hazard via VSP2, such as initial exothermic temperature (T_0), self-heating rate ($dT\ dt^{-1}$), $dP\ dt^{-1}$, pressure–temperature profiles, adiabatic temperature rise (ΔT_{ad}), and pressure-rise (ΔP_{ad}) [12–15].

Experimental setup

Battery conditions

Commercial 18650 lithium-ion batteries are widely employed worldwide, including by Sony, Samsung, LG, and Sanyo. In this study, commercial Sanyo 18650 lithium-ion battery was chosen because its output represents the greatest quantity in the whole world. Table 1 shows information on the commercial Sanyo 18650 lithium-ion battery. Two types of lithium-ion batteries were experimented within a specially designed test cell by adiabatic calorimeter, 50% SOC and 100% SOC, respectively. The stainless steel cell was designated as suitable for the 18650 battery in order to trace temperature and pressure with time.

Vent sizing package 2 (VSP2)

Vent sizing package 2 (VSP2) has been applied as thermal hazard assessable apparatus. Manufactured by Fauske & Associates, Inc., it is an adiabatic calorimeter system [15]. Upset scenarios such as batch contamination, loss of cooling, loss of stirring, mass-loaded upset, and fire exposure heating can be simulated [16]. Data of accurate temperature and reacting system pressure are obtained directly in an adiabatic environment [17–19]. A standard heat-wait-search (HWS) procedure is the most characteristic and prevalent way that determines the onset temperature of self-heating. Temperature range is detected from room temperature to 350 °C, and maximum detectable sensitivity is 0.15 °C min^{-1}. The range of pressure transducer was investigated within 2,000 psig. In a specially designed test cell, a thermocouple was contacted with a battery in order to obtain accurate temperature. VSP2 could be used for measuring the runaway reaction of various commercial lithium-ion batteries of charged and discharged. A patented low thermal mass, temperature, and pressure equalization was applied by VSP2. Consequently,

Table 1 Information of commercial Sanyo 18650 lithium-ion batteries

Sample	Type	SOC/%	Voltage/V	Mass/g
Sample A	UR18650FM	50	3.77	45.42
Sample B	UR18650FM	100	4.20	44.71

accurate adiabatic temperature and pressure rate data can be still acquired at the fastest runaway reactions.

Estimate of the heat of reaction

The thermodynamic estimate was executed by Eqs. (1), (2), and (3), which can determine the heat of reaction ($\triangle H$) and power (W). Total mass of the 18650 lithium-ion (m_{total}) was about 45 g, and the mass of the cell can (m_{can}) was about 10 g. Mass of its material (m_{cell}) was about 35 g, and its specific heat (C_{cell}) was 0.8 J g^{-1} K^{-1}. Specific heat of the 18650 stainless steel can (C_{can}) was ca. 0.5 J g^{-1} K^{-1}. The total specific heat (C_{total}) was 0.73 J g^{-1} K^{-1} as obtained from Eq. (1):

$$C_{\mathrm{total}} = \frac{(C_{\mathrm{cell}}\, m_{\mathrm{cell}} + C_{\mathrm{can}}\, m_{\mathrm{can}})}{(m_{\mathrm{cell}} + m_{\mathrm{can}})} \tag{1}$$

The $\triangle H$ can be calculated after the C_{total} is obtained from Eq. (2):

$$\Delta H = C_{\mathrm{total}}\, m_{\mathrm{total}} \Delta T_{\mathrm{ad}} \tag{2}$$

The W can be calculated from Eq. (3):

$$W = C_{\mathrm{total}}\, m_{\mathrm{total}} \left(\frac{\mathrm{d}T}{\mathrm{d}t}\right) \tag{3}$$

where $\triangle H$ and W are the keys of thermal hazard assessment in this study.

Results and discussion

These adiabatic exothermic behaviors are much more quantitative in VSP2 trials which provide time (t), temperature (T), pressure (P) profiles for runaway reactions taking place under thermal adiabatic condition. The thermal abuse effects of the 18650 lithium-ion battery were extremely hazardous in initial exothermic temperature (T_0), self-heating rate (dT dt^{-1}), reaction maximum pressure (P_{max}) and temperature (T_{max}), pressure-rise rate (dP dt^{-1}), and so on, of adiabatic runaway behaviors.

Thermal accumulation was evaluated continuously because of exothermic reaction of internal materials of the batteries by electrochemical reactions. Without sufficient heat removal, a runaway reaction could inevitably occur, which may eventually be followed by auto-ignition, a thermal explosion or bursting release. Runaway hazards of lithium-ion battery can be recognized from the adiabatic trajectories obtained from VSP2 calorimetric trials. In the cases here the potential exists for an adiabatic runaway reaction, the temperature and pressure trajectories of the reaction could be recognized as one suitable measure of the magnitude of the thermal hazard of lithium-ion battery via VSP2 adiabatic calorimetric methodology.

Thermal runaway of the 18650 lithium-ion battery had the maximum self-heating rate, the highest final temperature, maximum pressure, and the largest pressure-rise rate, as listed in Table 2. Table 3 summarizes the thermokinetic data given by Eqs. (2) and (3). Figure 1 shows that the battery of 100% SOC was more dangerous because of T_0 being about 144.3 °C and T_{max} reaching 733.1 °C. The maximum self-heating rate (dT dt^{-1})$_{\mathrm{max}}$ and the largest pressure-rise rate (dP dt^{-1})$_{\mathrm{max}}$ of a Sanyo 18650 lithium-ion battery of 100% SOC were measured to be 37,468.8 °C min^{-1} and 10,845.6 psi min^{-1}, respectively. In Figs. 3 and 4, sample B is more dangerous than A. Hence, for providing the needs of understanding the thermal runaway hazard of the lithium-ion battery, we summarized the experimental data to assess the hazard degree of a Sanyo 18650 lithium-ion battery. From both trials, the characteristic curves of self-heating rate and pressure-rise rate behaviors versus reciprocal temperature for two samples are recorded in Figs. 3 and 4, and the curves of pressure increasing versus reciprocal time profile are recorded in Fig. 2. Thus, a cell can simply be viewed as an electrochemical device that stores energy in chemical form and converts it into electrical form during discharge. Such a composite material characteristic requires a better understanding of its material issues, such as physical characteristics, thermochemical stability, and system activity. A cell testing using VSP2 is an alternative way of battery thermal stability test. Experiments using a VSP2 have shown the thermally hazardous concern of the dramatically reaction as charged cells are initiating an electrochemical reaction.

Through VSP2 adiabatic experiments, a charged Sanyo lithium-ion cell exothermally initiated and accumulated heat from 140 to 200 °C to trigger a thermal runaway reaction. After 200 °C, a dramatically self-heating reaction will result in a thermal explosion. From open literature, the ARC tests for the sample of 4.2 V Li$_x$CoO$_2$, which was

Table 2 VSP2 adiabatic experimental data on Sanyo lithium-ion batteries

Sample	$M_{\mathrm{f}}^{\mathrm{a}}$/g	T_0/°C	T_{max}/°C	P_{max}/psig	(dT dt^{-1})$_{\mathrm{max}}$/°C min^{-1}	(dP dt^{-1})$_{\mathrm{max}}$/psig min^{-1}
Sample A	41.9030	179.3	403.6	54.0	5,147.7	891.7
Sample B	35.7659	144.3	733.1	175.9	37,468.8	10,845.6

[a] After VSP2 experiments

Table 3 Estimates of the heat of reaction for samples A and B

Sample	$\triangle T_{ad}$/°C	$\triangle H$/kJ	W/kJ s^{-1}
Sample A	224.3	7.4	2.8
Sample B	588.8	19.2	20.4

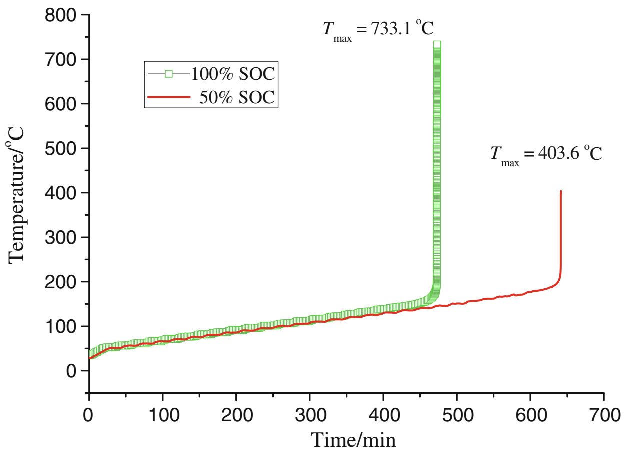

Fig. 1 Temperature versus time for thermal decomposition of lithium-ion batteries of 50 and 100% SOC by VSP2

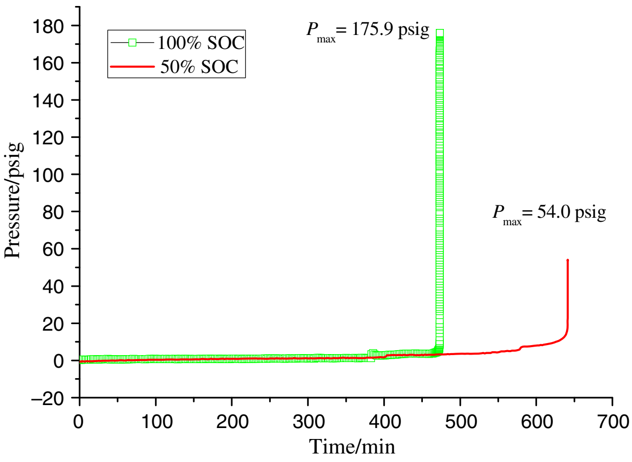

Fig. 2 Pressure versus time plots for thermal decomposition of lithium-ion batteries of 50% and 100% SOC by VSP2

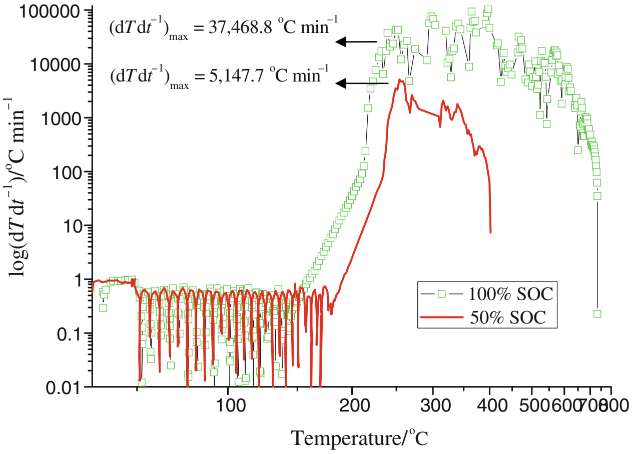

Fig. 3 Dependence of rate of temperature rise on temperature from VSP2 experimental data for lithium-ion batteries with SOC of 50% and 100%

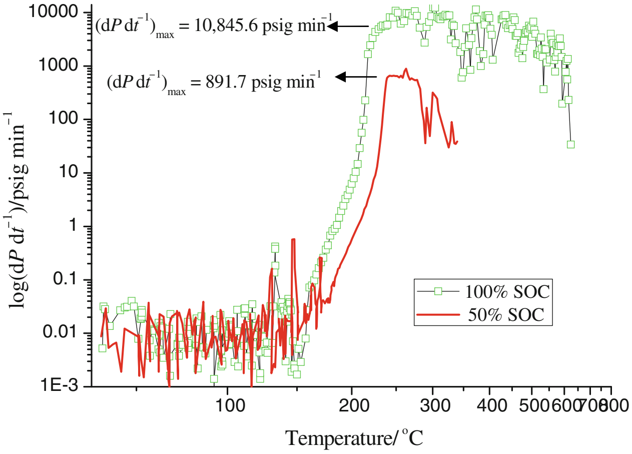

Fig. 4 Dependence of rate of pressure-rise on temperature from VSP2 experimental data for lithium-ion batteries with SOC of 50% and 100%

prepared in a 2325 coin cell, exothermic onset at 150 °C and the self-heating rate were lower than our results [20, 21]. The thermal abuse behaviors of the batteries have been determined on small samples by ARC, the temperature of self-heating rate initially being detected at 130 °C [22]. The temperatures were terminated below 250 °C by ARC trials [8, 21, 22]. However, thermal runaway reaction of the charged batteries were concluded until the temperature was above 700 °C, and variation of pressures which were changed along with temperature increasing was also found by VSP2 in Fig. 5. Thermal runaway of the lithium-ion batteries was due to the rapidly rising temperature and pressure, a resulting in catastrophic explosion.

It is well recognized that the self-heating rate of Sanyo 18650 lithium-ion battery increases exponentially with temperature, and the results of the adiabatic runaway reaction experiment agreed with those obtained by calorimetric methodology, for which the lithium-ion battery for the self-accelerating reaction was identified; and its technique was proposed to study thermal decomposition characteristics. We can be fairly certain that a lithium-ion battery can experience intense thermal decomposition and violent explosion in a runaway reaction. Caution should be paid to ensure safe use of this kind of battery.

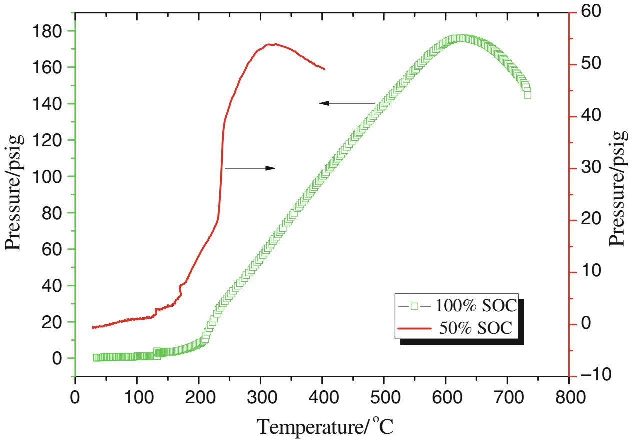

Fig. 5 Temperature versus pressure plots for thermal decomposition of lithium-ion batteries of 50 and 100% SOC by VSP2

Conclusions

Lithium-ion batteries convert the energy released by spontaneous chemical reactions to electrical work. The thermal stability of a charged 18650 lithium-ion battery, $LiCoO_2$, was studied using VSP2. A charged lithium-ion battery showed much higher hazard than an uncharged one. An internal short circuit could lead to high temperature and violent fire and explosion because of a thermal runaway reaction. Temperature control of lithium-ion batteries is important to avoid the occurrence of such reactions. This result also demonstrated that applying calorimetric methodology to classify the thermal hazards of lithium-ion battery is an alternative technology for battery safety research.

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