Thermal explosion hazards on 18650 lithium ion batteries with a VSP2 adiabatic calorimeter

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ABSTRACT

Thermal abuse behaviors relating to adiabatic runaway reactions in commercial 18650 lithium ion batteries ($LiCoO_2$) are being studied in an adiabatic calorimeter, vent sizing package 2 (VSP2). We select four worldwide battery producers, Sony, Sanyo, Samsung and LG, and tested their Li-ion batteries, which have $LiCoO_2$ cathodes, to determine their thermal instabilities and adiabatic runaway features. The charged (4.2 V) and uncharged (3.7 V) 18650 Li-ion batteries are tested using a VSP2 with a customized stainless steel test can to evaluate their thermal hazard characteristics, such as the initial exothermic temperature (T_0), the self-heating rate (dT/dt), the pressure rise rate (dP/dt), the pressure–temperature profiles and the maximum temperature (T_{max}) and pressure (P_{max}). The T_{max} and P_{max} of the charged Li-ion battery during the runaway reaction reach 903.0 °C and 1565.9 psig (pound-force per square inch gauge), respectively. This result leads to a thermal explosion, and the heat of reaction is 26.2 kJ. The thermokinetic parameters of the reaction of $LiCoO_2$ batteries are also determined using the Arrhenius model. The thermal reaction mechanism of the Li-ion battery (pack) proved to be an important safety concern for energy storage. Additionally, use of the VSP2 to classify the self-reactive ratings of the various Li-ion batteries demonstrates a new application of the adiabatic calorimetric methodology.

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1. Introduction

As society becomes more dependent on hi-tech equipment, the development of capable energy storage systems will be important. The lithium ion (Li-ion) battery is one of the key energy devices that have efficient gravimetric and volumetric energy densities, high power density, long life cycle and low self-discharge properties. Therefore, Li-ion battery applications have attracted wide attention, from small cells in electronic products to large-scale devices in electrical vehicles. However, the thermal instability of Li-ion battery components must also be considered. Among the various Li-ion batteries, those with a lithium cobalt oxide (Li_xCoO_2) cathode have commonly been used as a power source for portable electronics, and lithium manganese dioxide ($Li_xMn_2O_4$) batteries have been used for electronic hand tools because of their capacitance and safety properties [1]. In addition, large-scale application of Li-ion battery packs in electrical vehicles to reduce CO_2 or emission of other pollutants is considered an environmentally green initiative [1,2].

The chemistry, performance, cost and safety characteristics vary among the different commercial Li-ion battery types, which have been common in consumer electronics since 1991. The Li-ion battery is one of the most popular battery types for portable electronics, such as cellular phones, notebook computers (NBs) and camcorders (more than 90% of battery packs use Li-ion cells), and they have one of the best energy-to-weight ratios, no memory effect and a slow loss of charge when not in use [2]. Nevertheless, numerous battery failures or explosions with electronic products have happened worldwide, and faulty Li-ion battery packs may be the reason. Many laptop brands, such as Sony, HP and Dell, have recalled their products to rule out potential explosive hazards, and even Apple Inc. has investigated explosive hazards in its iPhone smartphone. For these reasons, incidents of overheating and of batteries catching fire during device usage have caused safety concerns about Li-ion batteries [3]. The thermal abuses in the electrode–electrolyte reactions of the Li-ion battery occurred at elevated temperatures under conditions of heating, crushing, or short-circuiting. The cathode materials in Li-ion bat-

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teries, such as $LiCoO_2$, $LiMnO_2$, $Li[Ni_xCo_yMn_z]O_2$ and $LiFePO_4$, are thermally unstable and release oxygen at elevated temperatures, which induces an autocatalytic reaction with the electrolytes [4].
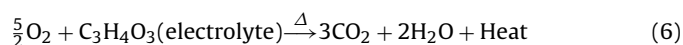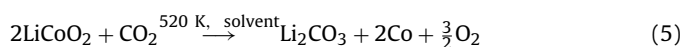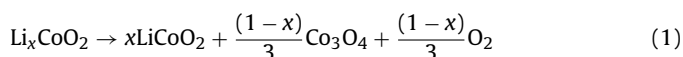
The electrochemical reactions of battery abuse are complex and dependent on the temperature, which can be increased by electrical heating during use, by chemical reactions, and by external thermal effects. Overheating is therefore more likely to be a problem when exothermic chemical reactions reinforce the heat generated by the current flow. Nevertheless, thermal runaway is still possible during the charging of these batteries if they are subjected to overcharging or elevated temperatures. Calorimetry testing standards and quality control mechanisms for Li-ion batteries should be established as a loss prevention program. The main abuse conditions of Li-ion batteries are internal short-circuiting, external overheating, overcharged voltage and charging after over-discharge. However, the damage from thermal abuse in a Li-ion battery is caused by heating, gas eruption, fire, or explosion. The thermal explosion of a Li-ion battery depends on the reactions of the cathode and electrolyte in the battery. Whatever the thermal activation process that leads to the heat buildup in the battery, the exothermic decomposition and accelerated reactions of the battery components result in thermal abuse. Catastrophic failure is due to the thermal runaway reaction of the Li-ion battery's energy release because of the rapid rise of the temperature and the pressure. Safety devices, e.g., positive temperature coefficients (PTCs), current limiting devices, current interrupt devices (CIDs) and scored disk vents, are designed to intervene before a thermal runaway reaction occurs [5]. However, calorimetry studies on batteries and materials could describe the thermal hazards of Li-ion batteries to a greater extent.

2. General overview of Li-ion battery chemistries

A Li-ion battery consists of a positive electrode (cathode) and a negative electrode (anode), both of which are the source of the electrochemical reaction. The cathodes are immersed in an electrolyte medium, which is a solution containing dissociated salts to ensure the ion transfer between the two electrodes. An electrochemical reaction of the active components directly releases electrical energy that can only be extracted if the electrons flow through an external circuit. When the Li-ion battery discharges, the lithium is extracted from the anode and inserted onto the cathode. When the battery charges, the reverse process occurs. Overcharging will supersaturate the lithium cobalt oxide, leading to the production of lithium oxide and often to uncontrolled, highly energetic reactions. The liquid electrolytes in Li-ion batteries typically consist of lithium salts, such as $LiPF_6$, $LiBF_4$ and $LiClO_4$, in an organic solvent that conducts lithium ions, acting as a carrier between the cathode and the anode when the battery passes an electric current through an external circuit [1]. Unfortunately, the organic solvents are easily decomposed on the anodes during charging and are not stable in the presence of high lithium activities. There is also a potential risk of electrolyte decomposition as a result of high temperatures or overcharging. This decomposition is a common problem when using elemental lithium anodes in contact with electrolytes containing organic groups.

A thermal runaway reaction that leads to an explosion is the result of an exothermic reaction of the active materials that causes a temperature increase and gas generation. The reaction rate increases with the rising temperature, which accelerates the self-heating until the process gets dramatically out of control. The exothermic onset temperatures (T_0), the rates of heat production and the rates of pressure development at runaway need to be characterized for inherently hazardous chemicals. The calorimetric methodology is an important and effective measure to analyze the thermal hazards of an unstable substance. The use of adiabatic

systems has the advantage that no heat loss is allowed from the sample, and as a result, its behavior on a real-scale size can be predicted. A high heat of reaction is not on its own sufficient to make an exothermic reaction hazardous. A large quantity of gas released during a fast self-heating process causes the true danger associated with an explosive reaction. In a closed vessel, such as the steel can of a battery, the high pressure generated by the gas evolution can destroy the container. Vent sizing package 2 (VSP2) and the accelerating rate calorimeter (ARC) have been used for the measurement of temperature (T)–pressure (P)–time (t) profiles. The low thermal inertia of the VSP2 is useful for extrapolating beyond the peak temperature of the VSP2 trials. The ARC has been used to measure the thermal stability of Li-ion batteries, such as $Li_{1+x}Mn_{2-x}O_4$ and Li_xCoO_2 [3,4]. The autocatalytic reaction initially proceeds slowly, but it accelerates exponentially as the temperature increases at the start of the runaway reaction. The proposed autocatalytic reaction mechanisms of a Li_xCoO_2 cathode are as follows [6–8]:

$$Li_xCoO_2 \rightarrow xLiCoO_2 + \frac{(1-x)}{3}Co_3O_4 + \frac{(1-x)}{3}O_2 \qquad (1)$$

$$Co_3O_4 \xrightarrow{400\ K,\ solvent} 3CoO + \tfrac{1}{2}O_2 \qquad (2)$$

$$Co_3O_4 + \tfrac{1}{2}C \xrightarrow{400\ K} 3CoO + \tfrac{1}{2}CO_2 \qquad (3)$$

$$CoO \xrightarrow{473\ K,\ solvent} Co + \tfrac{1}{2}O_2 \qquad (4)$$

$$2LiCoO_2 + CO_2 \xrightarrow{520\ K,\ solvent} Li_2CO_3 + 2Co + \tfrac{3}{2}O_2 \qquad (5)$$

$$\tfrac{5}{2}O_2 + C_3H_4O_3(electrolyte) \xrightarrow{\Delta} 3CO_2 + 2H_2O + Heat \qquad (6)$$

A thermal reaction in a solvent predominantly composed of Li_2CO_3 via decomposition of lithium alkyl carbonates is shown in reaction (5), and the combustion of solvent in reaction (6) may generate the heat of the Li-ion battery. Because of the cathode–electrolyte reactions, the generation of heat can be calculated from the battery exposed to a high temperature environment [3,4].

In consideration of the instability of the cathode rechargeability, elemental lithium is used as the negative electrode reactant of rechargeable Li-ion batteries and in a number of electrochemical reactions [1]. The electrolytes used in Li-ion batteries are less stable in the presence of high lithium compositions, which is a common problem when using elemental lithium negative electrodes in contact with electrolytes containing an organic or polymeric cationic group. The calorimetric method has been applied to study the thermal stability of Li-ion batteries, and the calorimeters, such as thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and C80, were used to measure the cathode materials of Li-ion batteries [9]. The calorimetric application of thermal hazards analysis for energetic Li-ion batteries has proven to be a useful alternative technique because of the requirement of temperature measurements. The ARC experimental results of the thermal runaway test showed that the temperature of the exothermic reaction was near 100 °C. As the exothermic reaction progressed beyond temperatures of 150 °C, the reaction rate accelerated, and the battery disintegrated. At this point, the battery components were ejected from the casing, which could lead to burns or even explosions [4,6].

According to the studies reviewed, the porous separator breaks down at temperatures above 120 °C and then induces an internal short circuit [7]. A thermal runaway reaction of lithium ion batteries occurs after the self-generated heating reaches a critical temperature and is usually accompanied by an explosion. Therefore, the safety issues of Li-ion batteries should not be ignored, and their safe use should be ensured. VSP2 has been applied as an apparatus for assessing thermal hazards. The adiabatic condition of the

Table 1
Information on the various commercial 18650 Li-ion batteries.

Producer	Type	Capacitance (mAh)	Charging voltage (V)	Nominal voltage (V)	Mass (g)
Sanyo	UR18650F	2600	4.2 ± 0.05	3.7	45.5
Sony	SE US18650GR	2600	4.2 ± 0.05	3.7	44.5
Samsung	ICR 18650-26D	2600	4.2 ± 0.05	3.7	44.8
LG	LGDB218650	2600	4.2 ± 0.05	3.7	46.5

$LiCoO_2$ is a typical cathode material of a Li-ion battery whose average voltage, gravimetric capacity and gravimetric energy are 3.7 V, 140 mAh g^{-1} and 0.518 kWh kg^{-1}, respectively.

Fig. 1. The broken test can and the exploded 18650 charged Li-ion battery obtained in the VSP2 experiment without a buffer tank to relieve pressure.
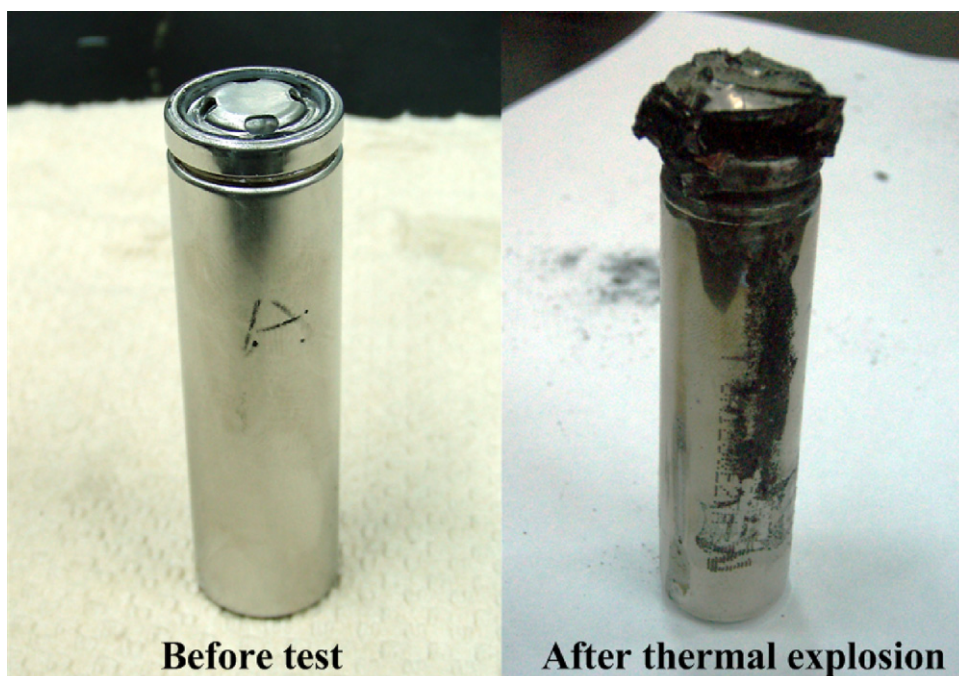

Fig. 2. The features of a Li-ion battery that were changed via the thermal runaway reaction in the VSP2 experiment.
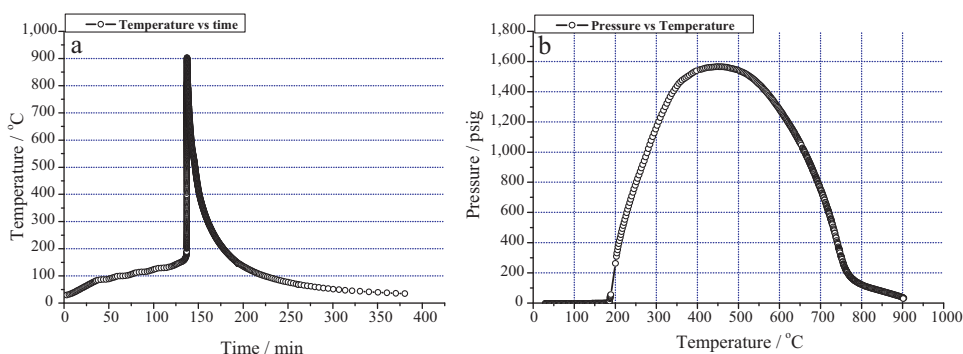
Fig. 3. Temperature–pressure profiles with time of the charged 18650 Sony Li-ion battery by the VSP2 adiabatic tests.

VSP2 with the calorimetric technique is similar to ARC, and the adiabatic characteristic of the calorimeter can be used to obtain related pressure–temperature profile parameters. In past studies, DSC, ARC, TGA, C80, and both thermal ramping and thermal imaging techniques have been employed to evaluate the temperature variations of the batteries with various materials [9–13]. However, none of the researchers used VSP2 to measure the adiabatic thermal hazard and thermal runaway reaction of the Li-ion batteries.

We investigated the initial reaction of commercial 18650 Li-ion batteries under adiabatic conditions by VSP2. The use of the adiabatic system has the advantage that practically no heat loss is allowed from the sample, and therefore, the behavior of a real large-scale substance can be estimated. We obtained the essential parameters of the thermal hazard via VSP2, such as the T_0, self-heating rate (dT/dt), pressure rise rate (dP/dt), maximum temperature (T_{max}) and pressure (P_{max}) [14]. Finally, the self-reactive heats of various 18650 Li-ion batteries were measured via the adiabatic calorimetric methodology to rank the thermal hazards.

3. Experimental setup

3.1. Samples

The Li-ion battery structure consisted of the cathode, anode, electrolyte, separator, steel can, terminals and safety vents. Commercially available 18650 Li-ion battery grade $LiCoO_2$ cathode candidates were purchased from four leading companies, Sanyo, Samsung, LG and Sony, and they had a diameter of 18.0 mm and a length of 65.0 mm, which are broadly used world-wide. The nominal capacity of the Li-ion battery was 2600 mAh. After cycling, the Li-ion batteries had charging voltages of 3.7 V and 4.2 V, and were then used to test the thermal runaway reaction in an adiabatic calorimeter. The information on the commercial Li-ion batteries is listed in Table 1. The batteries were placed in a specially designed test can equipped with a VSP2 to determine the temperature and pressure profiles.

3.2. Vent sizing package 2 (VSP2)

Vent sizing package 2, a commercially available calorimeter manufactured by Fauske & Associates, LLC, is a PC-controlled adiabatic calorimeter with a pressure and temperature system that balances the internal and external pressure and temperature [14]. The VSP2 was developed by the AIChE's Design Institute for Emergency Relief Systems (DIERS) user group to review the application of calorimetric tests of thermally reactive materials and to further contribute to the safe design of process reactors and tanks. Upset scenarios, such as loss of cooling, loss of stirring, mass-loaded upset, batch contamination and fire exposure heating, can be evaluated

[15]. The accurate temperature and reaction system pressure data were received directly from the adiabatic environment, and the temperature, pressure and enthalpy were all measured quantitatively. The adiabatic calorimetric technology for the battery testing, using the VSP2 with a closed test can, essentially ensured that all of the released reaction heat and pressure remained within the Li-ion battery. The stainless steel (SS316) cylindrical test can with an inside volume of 88.0 mL (inside diameter of 4.0 cm and height of 7.0 cm) was designed to be suitable for an 18650 Li-ion battery and to trace the battery's changes of temperature and pressure with time. This test can could be used to assess the experimental data, which can be directly extrapolated from the reactive conditions to real applications.

For the reactive system, overpressure in a vessel was normally due to the heat of the reaction, which obeys the overall energy balance of the materials. Both pressure and temperature equalization techniques were used. The former enables the test can to maintain its integrity at an elevated pressure, and the latter enables the temperature of the sample and outer guard container to remain equal to the usual adiabatic temperature. The pressure developed in the closed test can and was automatically compensated with a pressure of equal magnitude in the enclosed pressure vessel. Fig. 1 displays the Li-ion battery and the original setup of the VSP2 experiment. The experimental heaters, test can and battery burst because of the high energy released and the pressure that rose rapidly. To ensure the normal operation of this apparatus and to avoid bursting the test can, a 150 mL pressure buffer tank was selected for safety in the VSP2 experiments. An approximately 45 g sample of an 18650 Li-ion battery was placed in a test can and surrounded by the heating system. A standard heat-wait-search (HWS) procedure was the
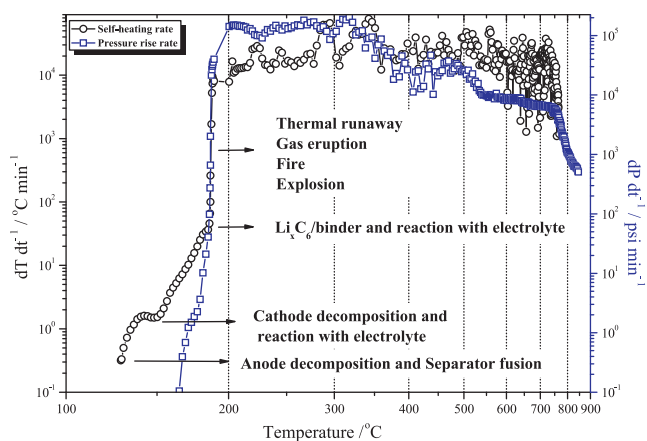

Fig. 4. Self-heating rate and pressure rise rate of the charged 18650 Sony Li-ion battery by a VSP2 adiabatic test is outlining four stages of thermal runaway.

Table 2
VSP2 adiabatic experimental data for the charged 18650 Li-ion batteries.

Sample[a]	Mass (g)	T_0 (°C)	T_{max} (°C)	$(dT/dt)_{max}$ (°C min^{-1})	P_{max} (psig)[d]	$(dP/dt)_{max}$ (psi min^{-1})	m_f[b] (g)	ΔH[c] (kJ)
Sony[e]	46.4	129.1	903.0	77,286.2	1565.9	150,327.8	33.5	26.2
Sony	46.4	125.2	654.3	65,045.6	354.7	23,170.0	35.7	17.9
Sanyo	45.5	131.3	708.7	19,207.0	196.7	7766.2	36.8	19.2
Samsung	44.9	116.5	683.2	33,505.7	262.1	15,596.7	34.9	18.6
LG	46.0	142.5	691.9	51,864.7	229.0	13,453.4	36.2	18.4

[a] Charged to 4.2 V.
[b] The mass of an 18650 battery after the VSP2 experiments.
[c] C_p of the Li-ion battery, which includes the materials in the cell and its can, is approx. 0.73 J g^{-1} K^{-1} [4], and $\Delta T_{ad} = T_{max} - T_0$.
[d] 1 psi = 0.069 bar.
[e] This test was without the blowdown buffer tank. To ensure the normal operation of this apparatus and to prevent the high pressure bursting the test can, a 150 mL pressure buffer tank was deliberately selected for safety in the above experiments.

most common method used to conduct the tests, and it identified and characterized the runaway reaction. The initial temperature range studied was from room temperature to 300 °C. Then, the sample equilibrated in the adiabatic vessel, followed by a 10 min search for the onset self-heating temperature. The detectable sensitivity was 0.20 °C min^{-1}, and the range of the pressure transducer was within 3000 psig. In the specially designed test can, the thermocouple touched the sample to accurately obtain the temperature change in the battery. The runaway reactions occurred under thermal adiabatic conditions to rank the severity of the runaway data, such as the time to maximum rate (TMR), thermal reaction or gas generation of the Li-ion batteries. These adiabatic calorimetric methodologies can be used to estimate the actual self-heating rate of the batteries to determine reliable thermal data, such as T_0, T_{max}, P_{max}, dT/dt, dP/dt and other adiabatic runaway behaviors, either by using a sound adiabatic calorimeter or by calculating them from the chemical kinetic parameters. The VSP2 was used to measure the runaway reaction of the various commercial Li-ion batteries both charged and uncharged. A low thermal mass, temperature and equalized pressure were used via the VSP2 system. Consequently, accurate adiabatic temperature and pressure data were still obtained even with the fastest runaway reactions.

4. Results and discussion

The chemical reactions in a Li-ion battery proceed in tandem at the electrodes, thereby liberating electrons and allowing a current to flow through the resister. Thus, a battery can simply be viewed as an electrochemical device that stores energy in the chemical form and converts it to the electrical form during discharge. Such a system composed of various materials requires a better understanding of its material issues, such as physical characteristics, thermo-chemical stability and system activity [5]. As planned, this study compared the relative thermal instability of various uncharged (3.7 V) and charged (4.2 V) Li-ion batteries under adiabatic conditions for the purpose of runaway reaction screening. Testing 18650 Li-ion batteries using VSP2 is an alternative form of a battery thermal stability evaluation. When the properties of the battery components were evaluated in combination with each other, the reactions were found to be exothermic and to cause local heating because of the electrolytes reacting with the lithium. Additionally, the reactions formed either crystalline or amorphous product lay-

ers on the surface of the electrodes [4]. The experiments using the VSP2 showed the thermally hazardous potential of a rapid reaction as the charged batteries proceeded with the electrochemical reaction. The exothermic formation of the reaction product films also occurred when carbon or alloy electrodes were used, which operate at their potential, and the electrolyte reacted with the lithium. The organic solvents easily decomposed on the anodes and reacted with the lithium during charging. The solid electrolyte interphase (SEI) is electrically insulating yet provides sufficient ionic conductivity [16]. Then, the separators melted, resulting in a short circuit, and the cathode broke down, causing catalytic burning. This process describes the thermal runaway reaction of the Li-ion batteries. However, if their morphology is constant, the surface area does not change substantially, and while this fact can lead to heating, it typically does not lead to a thermal runaway reaction at the negative electrode. The main reason for the combustion or explosion in Li-ion batteries is the exothermic reaction of the positive electrode reacting with the electrolytes shown in reactions (1)–(6).

Tables 2 and 3 also show the results of quantitative tests in the VSP2 trials of the four producers, Sony, Sanyo, Samsung and LG, of the 18650 LiCoO$_2$ batteries, which were charged to 4.2 V and uncharged at 3.7 V. The VSP2 trials of the Li-ion batteries provided T–P–t profiles for the runaway reactions taking place under thermal adiabatic conditions. The results of the various Li-ion batteries were extremely different from each other. A charged Sony Li-ion battery exothermally initiated at approximately 129.1 °C, and between 120 and 160 °C, the heat accumulated and triggered a thermal runaway reaction. Beyond 160 °C, the violently rapid, self-heating reaction resulted in a thermal explosion, and T_{max} and P_{max} reached 903.0 °C and 1569.9 psig (pound-force per square inch gauge), respectively. Our experimental results were different from the ARC tests for the CR2325 coin cell of Li$_x$CoO$_2$ (4.1–4.3 V), in which the maximum temperature and self-heating rate were below 300 °C and 100 °C min^{-1}, respectively [4]. Furthermore, the liquid electrolytes in the Li-ion batteries conducted lithium ions, acting as a carrier between the anodes and cathodes when the battery passed an electrical current through an external circuit. The exothermic temperature range of the commercial electrolyte solutions was determined to be 170–330 °C by the ARC tests [17]. The thermal runaway reaction of the Li-ion battery failure caused a swift rise in the cell temperature and pressure, resulting in an explosion. Fig. 2 displays a commercial Li-ion battery after an explosion from a ther-

Table 3
VSP2 adiabatic experimental data for the uncharged 18650 Li-ion batteries.

Sample[a]	Mass (g)	T_0 (°C)	T_{max} (°C)	$(dT/dt)_{max}$ (°C min^{-1})	P_{max} (psig)	$(dP/dt)_{max}$ (psi min^{-1})	m_f (g)	ΔH (kJ)
Sony	46.6	154.8	517.2	7227.0	45.5	805.4	41.3	12.3
Sanyo	46.0	172.8	402.6	5384.0	51.6	354.7	42.5	7.7
Samsung	46.2	152.8	454.8	4690.0	58.5	805.8	41.6	10.2
LG	45.9	168.0	407.1	5112.3	48.2	749.6	41.5	8.0

[a] Uncharged 3.7 V.

mal runaway reaction during a VSP2 experiment. Figs. 3 and 4 show the dangerous thermal runaway reaction behaviors of the 4.2 V 18650 Sony Li-ion batteries. The thermal responses characterized the dramatically exothermic heat, gas generation with temperature, self-heating rate and pressure rise rate in the schemes. The charged Li-ion batteries caused runaway reactions because of the heat accumulation from the thermal activation process [13,18]. The thermal abuse trajectories can be characterized by the four regimes as illustrated in Fig. 4 [19].

For the safety of the experimental setup and the protection of the apparatus, the maximum pressure reached was 1565.9 psig because the charged Li-ion battery exploded during the runaway reaction. Following the VSP2 trials, we equipped a buffer tank with a pressure detection device to avoid explosive damage to the VSP2 tools or parts. The lowest T_0 was that of the Samsung charged Li-ion battery at 116.5 °C. The Samsung also had the earliest initial self-heating. Furthermore, for the charged Sony, which exhibited the most potential thermal hazards, P_{max}, $(dT/dt)_{max}$ and $(dP/dt)_{max}$ were 354.7 psig, 65,045.6 °C min^{-1} and 23,170 psi min^{-1}, respectively. We also used the VSP2 adiabatic calorimeter to compare the impact of the charge level (3.7 V and 4.2 V) of the 18650 Li-ion batteries during the thermal runaway reactions. Tables 2 and 3 display the adiabatic runaway data of various Li-ion batteries in the two charge level situations. Richard and Dahn [18] used an ARC to determine the thermal abuse behaviors of the battery electrolyte and of Li$_{1+x}$Mn$_{2-x}$O$_4$ in the electrolyte; the self-heating rate was initially detected at 130 °C and 190 °C, respectively. The self-heating at 50 °C increased swiftly after 100 °C for the 18650 Li-ion battery as measured by the ARC tests [3,4,18]. Without sufficient heat removal in a battery, a runaway reaction can occur that may eventually be followed by autocatalytic decomposition or a thermal explosion. If the Li-ion batteries are capable of auto-reactive decomposition at elevated temperatures and if by charging, the battery packs are heated so that the electrodes accelerate toward a runaway reaction, then the energetic substance is an explosive.

In an adiabatic experiment, no heat is lost to the surroundings, and all of the liberated reaction energy is used for the self-heating of the Li-ion battery. The adiabatic thermal explosion is important for practical discussions of safety because it represents the most dangerous case. The self-heating of a Li-ion battery by an exothermic reaction can be described by a heat of reaction (ΔH), total heat capacity (C_p), sample mass (m_{cell}) and adiabatic temperature rise (ΔT_{ad}) of the Li-ion battery [4,15]. These quantities are related as follows:

$$\Delta H = m_{cell} \times C_p \times \Delta T_{ad} \tag{7}$$

The heats of reaction of various Li-ion batteries at different charge levels as determined by Eq. (7) are listed in Tables 2 and 3. The VSP2 adiabatic experiments indicate the dramatic exothermic hazards of charged Li-ion batteries at elevated temperatures. The heat of reaction for the charged Li-ion batteries as determined by VSP2 experiments was 18.55 ± 0.55 kJ, which is much higher than for the uncharged batteries. The potential thermal hazards of Li-ion batteries may cause problems during use.

In a runaway reaction, the overpressure in a vessel is normally due to the heat of reaction, which is released by the runaway of the energetic substances. The adiabatic exothermic behavior was more quantitatively shown in the VSP2 trials, which provided T–P–t profiles for the runaway reactions. A Li-ion battery typically forms materials on the anode, depending upon the ease of decomposition by the electrochemical reactions. Without sufficient heat removal, a runaway reaction can occur, which may eventually be followed by auto-ignition or a thermal explosion. The runaway hazards of a Li-ion battery can be recognized by analyzing the adiabatic trajectories obtained from VSP2 calorimetric trials. When the potential exists for an adiabatic runaway reaction, the temperature and the
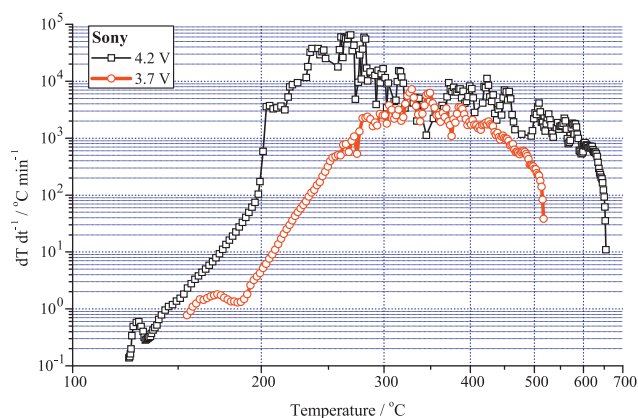

Fig. 5. The self-heating rate for the thermal decomposition of the Sony 18650 charged (4.2 V) and uncharged (3.7 V) Li-ion batteries.

pressure trajectories of the reaction can be used as a proper measure of the magnitude of the thermal hazard of the Li-ion battery using the VSP2 adiabatic calorimetric methodology.

The thermal runaway reaction of a charged 18650 Li-ion battery showed a maximum self-heating rate, a high final temperature, a high final pressure and a high pressure rise rate. Hence, to understand the thermal runaway hazards of the Li-ion battery, we summarized the experimental data to assess the degree of hazard of the various 18650 Li-ion batteries. From the quantitative trials, the characteristic curves of the self-heating rate versus the reciprocal temperature for the four commercial charged and uncharged batteries are shown in Figs. 5–8. The thermal reactive hazards of the charged Li-ion batteries exponentially increased at approximately 200 °C, while the uncharged batteries did not have such a sharp trend. Thus, we determined that with an increasing charge level, there were more battery hazards. The pressure rise rate behavior is shown in Figs. 9–12, and Table 2 presents the change in pressure measured when the various Li-ion batteries were heated from 90 to 300 °C. There was a minor pressure rise at approximately 140 °C, and then a rapid increase was observed near 200 °C, resulting in the explosion of the battery scored disk. The curves of the pressure increase versus the reciprocal temperature profile are shown in Fig. 13. Comparison of the thermal decomposition at the different charge levels shows that the charged Li-ion batteries experienced catastrophic gas generation. Hence, the impact of the charge level on the thermal runaway reaction needs to be taken into account when considering the safety of Li-ion batteries. The time required to reach maximum temperature trajectories is a good measure for
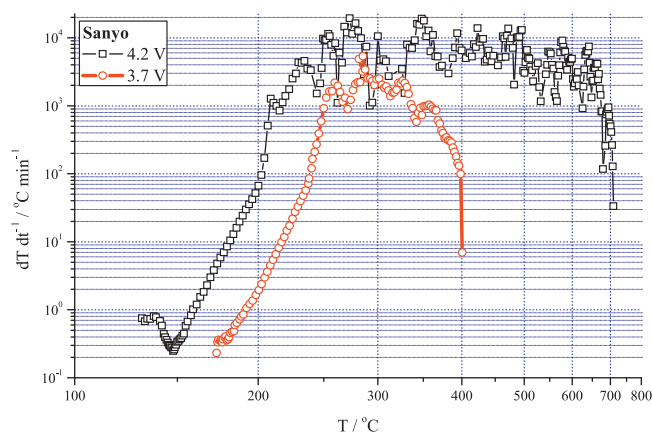

Fig. 6. The self-heating rate for the thermal decomposition of the Sanyo 18650 charged (4.2 V) and uncharged (3.7 V) Li-ion batteries.
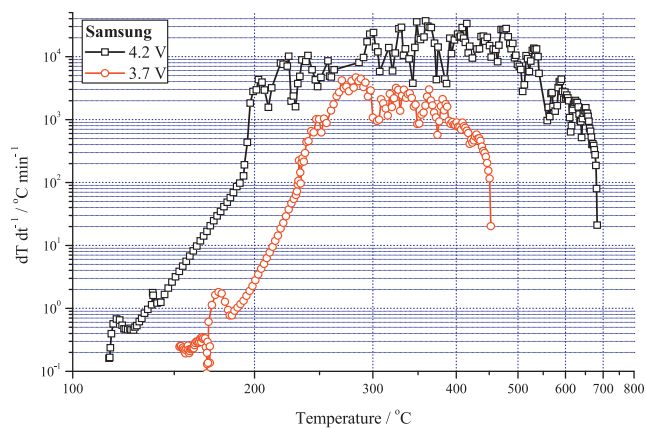
Fig. 7. The self-heating rate for the thermal decomposition of the Samsung 18650 charged (4.2 V) and uncharged (3.7 V) Li-ion batteries.
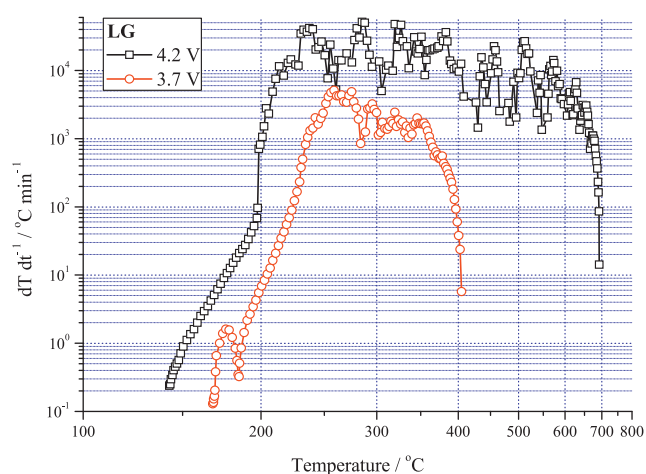

Fig. 8. The self-heating rate for the thermal decomposition of the LG 18650 charged (4.2 V) and uncharged (3.7 V) Li-ion batteries.

comparing the various Li-ion batteries. Fig. 14 presents the time to highest temperature increase for the various brands of Li-ion batteries, which is the time it takes for a thermal runaway reaction to reach its maximum temperature.

The temperature induction and the heat accumulation of the Li-ion batteries mainly resulted in thermal runaway reactions.
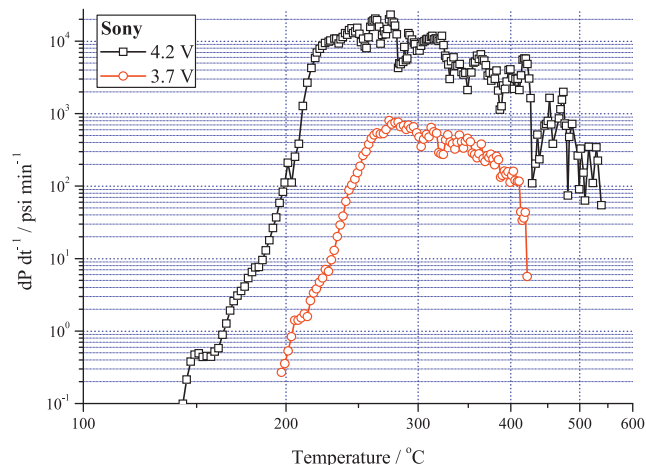
Fig. 9. The pressure rise rate for the thermal decomposition of the Sony 18650 charged (4.2 V) and uncharged (3.7 V) Li-ion batteries.
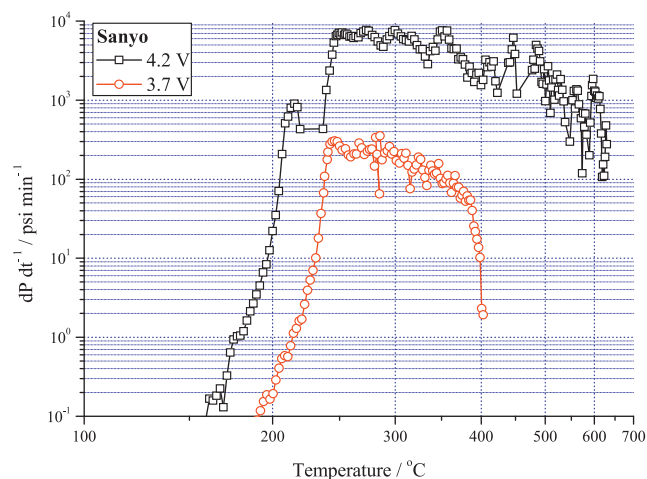

Fig. 10. The pressure rise rate for the thermal decomposition of the Sanyo 18650 charged (4.2 V) and uncharged (3.7 V) Li-ion batteries.
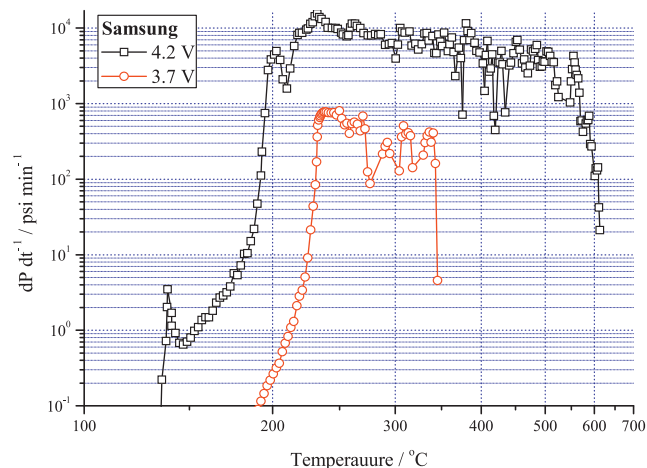

Fig. 11. The pressure rise rate for the thermal decomposition of the Samsung 18650 charged (4.2 V) and uncharged (3.7 V) Li-ion batteries.

When the temperature gradually increased to approximately 120 °C, the lithium batteries experienced solid-electrolyte interphase decomposition. Moreover, the separator diaphragm fused at approximately 130 °C, causing the electrodes to shut down. Then cathode oxidation by the electrolyte of the lithium batteries initiated a self-heating reaction and heat accumulation from 130 °C
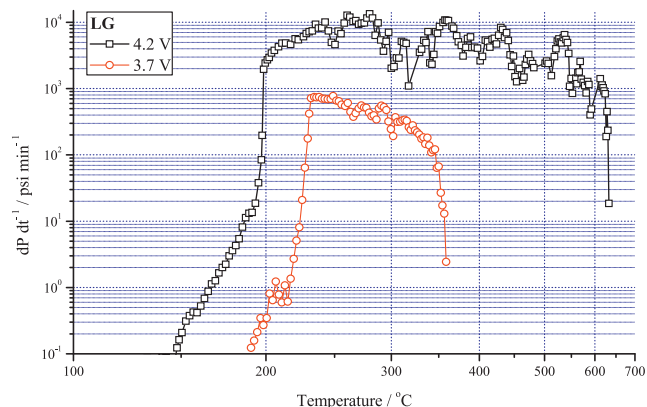

Fig. 12. The pressure rise rate for the thermal decomposition of the LG 18650 charged (4.2 V) and uncharged (3.7 V) Li-ion batteries.
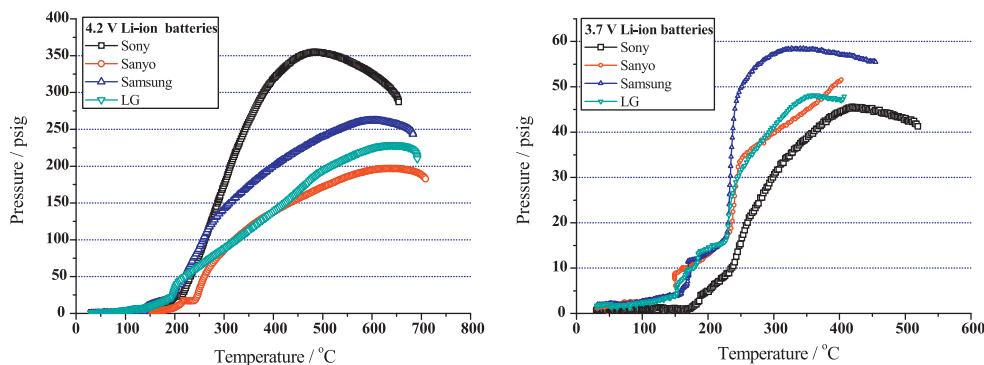
Fig. 13. The temperature–pressure curves for the adiabatic runaway system of the various 18650 Li-ion batteries in a charged (4.2 V) and uncharged (3.7 V) situation.
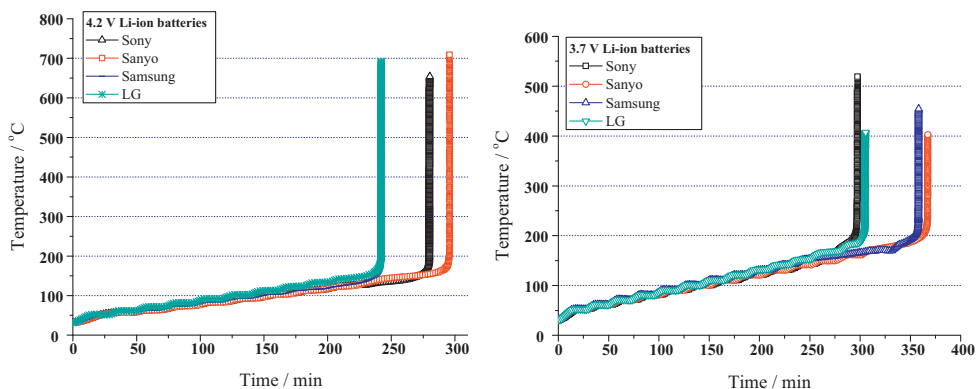

Fig. 14. The temperature–time curves for the adiabatic runaway system of the various 18650 Li-ion batteries in a charged (4.2 V) and uncharged (3.7 V) situation.

to 160 °C in the experimental trials. Finally, the swiftly increasing temperature and pressure resulted in a thermal explosion. The heating rate increased dramatically until the temperature reached above 180 °C, and the sharp exothermic heat generation and gas liberation could cause potential damage to the Li-ion batteries. In our experiments, high temperatures caused the Li-ion batteries to suffer thermal runaway and cell rupture if mistreated. Roth et al. have reviewed the Li-ion battery electrochemical reactions, and they state that SEI typically decomposes at 90–130 °C, intercalated lithium reacts with the electrolyte at 90–290 °C (electrolyte decomposes at 200–300 °C), and positively active materials decompose and react with the solvent at 150–500 °C [19,20].

Finally, We applied the simple analytical equation of self-heating by an exothermic reaction, which for an adiabatic temperature rise can be written as [4,6,9,21]:

$$\frac{dT}{dt} = \Delta T_{ad} A \exp\left(\frac{-E_a}{k_b T}\right) (1 - \mu)^n \tag{8}$$

where k_b is Boltzmann's constant, n is the reaction order and μ is the degree of conversion. By plotting the natural logarithm of the self-heating rate versus the inverse of temperature, the activation energy (E_a) of various Li-ion batteries can be calculated from the slope, and the frequency factor (A) of the Arrhenius equation is determined from the intercept of the fitted line.

$$\ln\frac{dT}{dt} = \ln\Delta T_{ad} + \ln A - \frac{E_a}{k_b T} + \ln(1 - \mu)^n \tag{9}$$

If A is much greater than ΔT_{ad} and $(1 - \mu)^n$, then Eq. (9) can be simplified as [4,9,21]:

$$\ln\frac{dT}{dt} \approx \ln\Delta T_{ad} A - \frac{E_a}{k_b T} \tag{10}$$

It is better to measure the self-heating rate using a VSP2 adiabatic calorimeter. The experimental data can then be used to determine E_a and A with an Arrhenius plot, which is shown in Table 4 and Fig. 15. The fitted lines were used to calculate the kinetic parameters of the thermal explosion for various Li-ion batteries. Our results agree with the values of E_a and A of Li-ion coin cells that were found using ARC tests by MacNeil et al. [4] and Argue et al. [21].

Based on the observations of this study, the self-heating rate of Li-ion batteries increased exponentially with the temperature. The results of the adiabatic runaway reaction experiments agreed with those of the calorimetric methodology. A self-accelerating reaction was identified for 18650 Li-ion batteries, and an accurate technique was proposed to study their thermal decomposition. Violent thermal decomposition and explosions due to runaway reactions pose serious safety hazards that must be considered when using Li-ion batteries.

Table 4
Thermokinetic data from VSP2 adiabatic experimental for the various 18650 Li-ion batteries.

Sample	Voltage (V)	E_a[a] (eV)	A[a] (min^{-1})	Relativity R^2
Sony	4.2	1.3	4.7×10^{13}	0.9752
Sanyo	4.2	1.7	5.5×10^{17}	0.9696
Samsung	4.2	1.3	4.1×10^{13}	0.9737
LG	4.2	1.6	4.2×10^{17}	0.9951
Sony	3.7	1.3	4.5×10^{12}	0.9222
Sanyo	3.7	1.7	3.5×10^{16}	0.9873
Samsung	3.7	1.3	1.1×10^{13}	0.9138
LG	3.7	2.0	4.6×10^{20}	0.998

[a] The activation energy was calculated from the slope, and the frequency factor of the Arrhenius equation was determined from the intercept of the fitted line in Eq. (10). E_a and A were found to be 1.7 eV and 6.6×10^{18} min^{-1} by MacNeil et al. [4] and 1.64 eV and 1.4×10^{18} min^{-1} by Argue et al. [21], respectively.
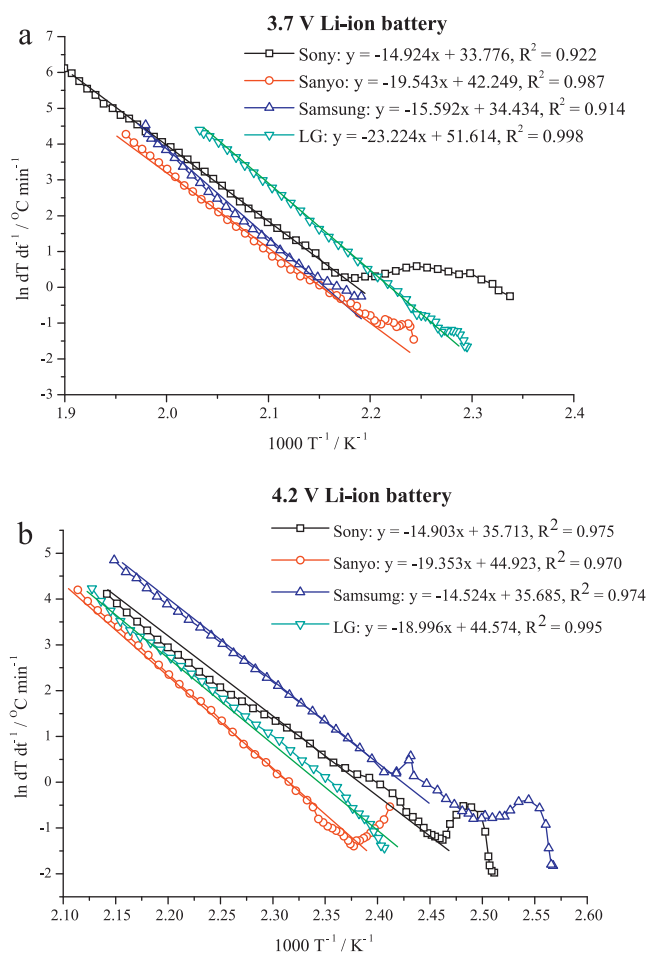
Fig. 15. The plot of $\ln dT/dt$ vs. $1000/T$ for (a) uncharged (3.7 V) and (b) charged (4.2 V) Li-ion batteries, the solid lines were used to estimate the activation energy (E_a) for the thermal runaway reaction.

5. Conclusions

The VSP2 adiabatic calorimeter is the recommended tool for studying the thermal abuse of Li-ion batteries and their materials. The calorimeter is important for determining a battery's inherent electrochemical reactions. Within the field of energy storage applications, the thermal properties of the electrode materials in Li-ion batteries are readily studied using adiabatic calorimeters.

Li-ion batteries convert the energy released by chemical reactions into electrical work. The thermal abuse of 18650 Li-ion batteries with $LiCoO_2$ cathodes was studied using VSP2, and charged batteries were found to be more hazardous than uncharged ones. Thermal runaway reactions caused internal short circuits, resulting in temperature increases, violent fires and explosions. Temperature control of Li-ion batteries is critical in to avoid the occurrence of thermal runaway reactions. The results also demonstrated that applying the adiabatic calorimeter to classify the thermal hazards of a Li-ion battery is an alternative technology for battery safety research. Our future studies include establishing standard tests for batteries and their materials. In summary, the kinetic and thermodynamic parameters of the electrochemical reaction mechanisms have been investigated using an adiabatic calorimetric methodology to determine the crucial factors governing thermal runaway in Li-ion batteries.

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