Applied Energy 100 (2012) 127–131

Contents lists available at SciVerse ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

Thermal runaway potential of $LiCoO_2$ and $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ batteries determined with adiabatic calorimetry methodology

Can-Yong Jhu [a], Yih-Wen Wang [b,*], Chia-Yuan Wen [c], Chi-Min Shu [a,c]

[a] Doctoral Program, Graduate School of Engineering Science and Technology, National Yunlin University of Science and Technology (YunTech), 123, University Rd., Sec. 3, Douliou, Yunlin 64002, Taiwan
[b] Department of Occupational Safety and Health, Jen-Teh Junior College of Medicine, Nursing and Management, 1, Jen-Teh Rd., Houlong, Miaoli 35664, Taiwan
[c] Process Safety and Disaster Prevention Laboratory, Department of Safety, Health, and Environmental Engineering, YunTech, 123, University Rd., Sec. 3, Douliou, Yunlin 64002, Taiwan

HIGHLIGHTS

- Thermal analysis is employed to classify hazardous rating for Li-ion cell cathodes.
- The thermal hazards of the $LiCoO_2$ cathode at elevated temperatures is significant.
- VSP2 is an alternative measurement of a battery thermal stability evaluation.
- Calorimetry method provide the safety design considerations of Li-ion batteries.

ARTICLE INFO

Article history:
Received 20 February 2012
Received in revised form 19 May 2012
Accepted 31 May 2012
Available online 15 July 2012

Keywords:
Thermal runaway hazards
18650 Li-ion battery
Vent sizing package 2 (VSP2)
Thermal abuse trials
Adiabatic calorimetry methodology

ABSTRACT

Thermal runaway hazards related to adiabatic runaway reactions in various 18650 Li-ion batteries were studied in an adiabatic calorimeter with vent sizing package 2 (VSP2). We selected two cathode types, $LiCoO_2$ and $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$, and tested Li-ion batteries to determine the thermal runaway features. The charged 18650 Li-ion batteries were tested to evaluate the thermal hazard characteristics, such as the initial exothermic temperature (T_0), self-heating rate (dT/dt), pressure rise rate (dP/dt), pressure–temperature profiles, maximum temperature (T_{max}) and pressure (P_{max}), which are measured by VSP2 with a customized stainless steel test can. The thermal reaction behaviors of the Li-ion battery packs were shown to be an important safety concern for energy storage systems for power supply applications. The thermal abuse trials of the adiabatic calorimetry methodology used to classify the self-reactive ratings of the various cathodes for Li-ion batteries provided the safety design considerations.

1. Introduction

The Li-ion battery is a highly useful energy device. It has an efficient energy density (gravimetric and volumetric), a high power density, a long life cycle and low self-discharge properties, which can be useful for power storage systems. Therefore, Li-ion battery applications, from small cells in electronic products to large-scale devices in electrical vehicles, have attracted much attention [1,2]. The use of Li-ion battery packs in portable electronics and electrical vehicles to reduce CO_2 emissions or the emission of other pollutants is considered an environmentally green system [2,3].

To improve the performance of Li-ion batteries, it is necessary to understand the cell chemistry. The thermal and electrical abuses in the electrode–electrolyte reactions of the Li-ion cell occur at a high temperature under conditions of heating, crushing, or short-circuit. Efforts have been made to identify candidate cathode materials and a stable electrolyte and to understand the cell electrochemistry [4]. The cathode materials in the Li-ion batteries, such as $LiCoO_2$, $LiMnO_2$, $Li[Ni_xCo_yMn_z]O_2$ (LiMnCoNi) and $LiFePO_4$, are thermally unstable and release oxygen at elevated temperatures to induce an autocatalytic reaction with the electrolytes [4–6]. Many studies reported that the majority of Li-ion batteries underwent thermal runaway due to overheating or abuse because the components are toxic or flammable [7–9]. Thermal runaway reactions in Li-ion batteries are sensitive to the various charging levels; the higher the charged voltage, the lower the onset temperature and exponential heating rate. The 18650 cell type and the relatively low melting point of lithium (180.5 °C) indicate that batteries must be prevented from reaching high internal temperatures [2,4]. Therefore, the battery manufacturers should take the safety concerns surrounding Li-ion batteries seriously and obtain more details about the performance of individual batteries.

* Corresponding author. Tel.: +886 37 720 903; fax: +886 37 726 979.
E-mail address: g9410825@yuntech.edu.tw (Y.-W. Wang).

0306-2619/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.apenergy.2012.05.064

Safety issues involving thermal abuse and development for high-capacity batteries are taken into consideration. Thermal analysis is one of the alternative methodologies used to classify the hazardous rating for Li-ion batteries, which is caused by flammable electrolytes, thermally unstable cathodes, overcharging, overheating and short-circuits. The thermal stability of Li_xCoO_2 cathode material is determined by calorimeters, and the results show that the exothermic reaction increases with higher charging voltages [7,10]. Knowledge about the potential hazards of an Li-ion battery and its internal components, such as lithium metal and flammable solutions, are needed to characterize the physicochemical data.

In our previous studies, we described the thermal runaway characteristic for 18650 Li-ion batteries with various charging levels as determined by the adiabatic calorimetry methodology. The thermal abuse trajectories of an $LiCoO_2$ battery can be characterized by the following regimes [5,9,10]:

(1) The obvious onset temperature of anode decomposition begins at approximately 125 °C. The fusion of the separator leads to reaction of the electrolyte at the negative electrode.
(2) Exothermic decomposition of the cathode with the electrolyte as the temperature rises over 140 °C is accompanied by gas generation caused by thermal effects. The cathode materials in the Li-ion batteries are thermally unstable and release oxygen at elevated temperatures to induce an exothermic reaction with the electrolytes.
(3) A rapid temperature rise and overpressure occur due to a runaway reaction of the decomposing cathode and the electrolyte, which consists of lithium salts. The heating rate increased violently until the temperature was above 180 °C, and the rapid exothermic heat generation and gas liberation could cause potential damage to the cell.

The thermal runaway reaction initially proceeds slowly, but it accelerates exponentially as the temperature increases because of the start of the runaway reaction. Due to the cathode–electrolyte reactions, the local heat of generation from a battery exposed to a high-temperature environment or under external fire could cause the battery pack thermal runaway or explosion [4]. The unstable growth is a major problem with large-scale battery packs and requires a safety recommendation for the development of commercial Li-ion batteries. Experiments using adiabatic calorimetry methodology to classify the Li-ion battery types, electrode materials, thermal electrochemistry, and so on, are our proposed safety features. We investigated the thermal runaway characteristics of commercial 18650 Li-ion batteries using adiabatic calorimetry methodology [10,11]. The use of the calorimeter has the advantage that it is practical to estimate the behavior of a real-scale battery. We obtained the essential parameters of the thermal hazard via VSP2 to compare Li-ion batteries that have different electrodes: $LiCoO_2$ and $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ (LiMnCoNi). The thermal profiles of both 18650 Li-ion batteries were measured via adiabatic calorimetry methodology to compare the thermal hazards.

2. Experimental

2.1. Samples

The commercial-grade 18650 Li-ion battery cathode candidates $LiCoO_2$ and $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ were selected, both of which are widely used in special custom battery packs. The specifications were a 4.2 V charge voltage and a mass of 45.5 g. The information is shown in Table 1.

Table 1
The information for $LiCoO_2$ and LiMnCoNi battery.

Sample	Cathode material	Capacitance (mAh)	Voltage (V)	Mass (g)
A	$LiCoO_2$	2600	4.2 ± 0.05	44.9
B	LiMnCoNi	2000	4.2 ± 0.05	41.7

2.2. Vent sizing package 2 (VSP2) [12]

The adiabatic calorimetry technology of the battery testing, which used the VSP2 with a closed test can, essentially ensured that all of the released reaction heat and pressure remained within the Li-ion battery [11]. 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 to trace the changes of temperature and pressure with time. This test can be used to evaluate the experimental data, which can be directly extrapolated from the reactive conditions to real applications.

2.3. Adiabatic calorimetry methodology

A standard heat-wait-search (HWS) procedure was the most common way to conduct the tests, and it was used to determine and elucidate the runaway reaction. The temperature range initially detected 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, and the range of the pressure transducer was within 3000 psig. In a specially designed test can, the thermocouple touched the battery can to accurately obtain the temperature change in the battery. The runaway reactions take place 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 calorimetry methodologies may be used to estimate the actual self-heating rate of the batteries to obtain reliable thermal data, such as T_0, T_{max}, P_{max}, dT/dt, dP/dt and other adiabatic runaway behaviors, using a sound adiabatic calorimeter or calculated from the thermokinetic parameters. The VSP2 was used to measure the runaway reaction of the various commercial Li-ion batteries, both charged and uncharged. A patented low thermal mass, temperature, and equalized pressure were used via the VSP2 system. Consequently, accurate adiabatic temperature and pressure data were still achieved with the fastest runaway reactions.

In an adiabatic calorimetric experiment, no heat is lost to the surroundings, and all of the liberated reaction energy is used for self-heating of the Li-ion battery. The adiabatic reaction enthalpy is important for practical discussions of safety because it represents the thermal runaway profile for the Li-ion battery. The simple thermal analytical equations describing the reaction heat of an Li-ion battery as determined by VSP2 trials, which are characterized by a heat of reaction (ΔH_{cell}, kJ), the total heat capacity of full cells (C_p, J/g/K), the sample mass (m_{cell}, g), and the adiabatic temperature rise (ΔT_{ad}, K) of the Li-ion battery, can be expressed as: [8,10]

$$\Delta H_{cell} = m_{cell} \times C_p \times \Delta T_{ad} \quad (1)$$

We consider a simplified calculation of the self-heating rate ($(dT/dt)_{cell}$, K/min) of the Li-ion battery to characterize the consequence of a runaway reaction that is dependent on the exothermic trajectories of Li-ion battery thermal abuse conditions. We proposed a simplified equation for calculating the thermokinetic parameters [8,10]:

$$\ln\left(\frac{dT}{dt}\right)_{cell} \approx \ln \Delta T_{ad} A - \frac{E_a}{k_b T} \quad (2)$$

where k_b is Boltzmann's constant, A (1/min) is the frequency factor, T (K) is the adiabatic temperature change and E_a (eV) is the activation energy. The thermal analysis of the battery runaway type often implies suggestions for the safe operation of the battery packs.

3. Results and discussion

The 18650 Li-ion battery testing using VSP2 is an alternative measurement of a battery thermal stability evaluation. The contribution of both cathodes, $LiCoO_2$ and LiMnCoNi, to the full cell thermal runaway profile as seen by VSP2 can be determined by measuring the battery components' thermal stability under similar conditions. 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 [7,8,13]. 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 heat due to the electrolytes reacting with the lithium, and they formed either crystalline or amorphous product layers on the surface of the electrodes [4,14,15].

The experiments using the VSP2 have shown the thermally hazardous potential of the dramatic reaction as the charged cells proceed with the electrochemical reaction at an elevated temperature [10,11]. Fig. 1 shows the failed Li-ion battery with the $LiCoO_2$ cathode that generated a blast pressure to destroy the cell cylinder can under a thermal explosion in the VSP2 experiment. The safeguards of the battery pack may not be sufficient if they are not designed for the energy release and gas evolution that occur in a worst-case scenario. Figs. 2 and 3 delineate the temperature–pressure profiles as a function of time for the $LiCoO_2$ and LiMnCoNi cathode materials. Fig. 2 shows that $LiCoO_2$ and LiMnCoNi cathode materials underwent exothermic reactions beginning as low as 131.5 and 175.4 °C, respectively, and the TMR via adiabatic calorimeter of the $LiCoO_2$ (ca. 23 min) is shorter than that of the LiMnCoNi (ca. 75 min). The magnitudes of the $LiCoO_2$ cathode reaction initial temperature and gas generation were significantly greater than those of the LiMnCoNi. This result is in agreement with those of a study showing that the 18650 LiMnCoNi/graphite high-power batteries do not explode during an oven test at 150 °C, showing good safety performance [16,17].

The main reason for combustion or explosions in Li-ion batteries is the exothermic reaction of the cathode materials with the electrolytes. Table 2 lists the results of quantitative tests of both cathodes in the VSP2 trials of the 18650 Li-ion batteries, which were charged to 4.2 V. The VSP2 trials of the Li-ion batteries provided time (t)-temperature (T)-pressure (P) profiles for the runaway reactions taking place under thermal adiabatic conditions. The results of both Li-ion batteries were extremely different from each other in terms of the T_0, dT/dt, P_{max}, T_{max}, dP/dt, and other adiabatic runaway behaviors. The characteristic curves of the self-heating rate versus the reciprocal temperature and pressure for the various cathodes from commercial charged batteries are shown in Figs. 3–5. The mechanism of this difference in reaction rates is not clearly understood at this time but may relate to the differences in anode particle morphology shown previously or may be due to different levels of gas generation, which can affect the apparent heat generation rate [18,19]. The pressure–temperature diagrams of both cathodes shown in Figs. 4 and 5 display dramatic thermal runaway behaviors. The thermal explosions for $LiCoO_2$ and LiMnCoNi cathodes at ca. 180 and 250 °C, respectively, would generate a sharply increasing rate of pressure rise. Accordingly, the curve for Li-ion batteries has the steepest ascent shortly after the beginning of the exothermic runaway reaction [10,11].

Finally, the VSP2 data were used to calculate the Arrhenius parameters. By plotting the natural logarithm of the self-heating rate versus the inverse of temperature, the heat of reaction, activation energy and frequency factor of $LiCoO_2$ and LiMnCoNi batteries can be calculated from Eqs. (1) and (2) [7]. The experimental data from the VSP2 test can be used to obtain E_a and A with an Arrhenius plot, which is shown in Table 3 and Fig. 5. The activation energy values of $LiCoO_2$ and LiMnCoNi are 1.4 and 1.3 eV,

Fig. 1. The $LiCoO_2$ material battery was destroyed by VSP2 trials.

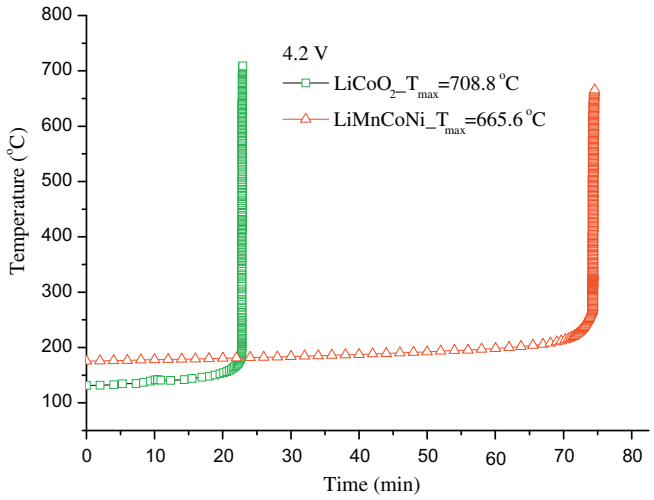

Fig. 2. Temperature–time profiles of 4.2 V Li-ion batteries ($LiCoO_2$ and LiMnCoNi) by VSP2 adiabatic tests.

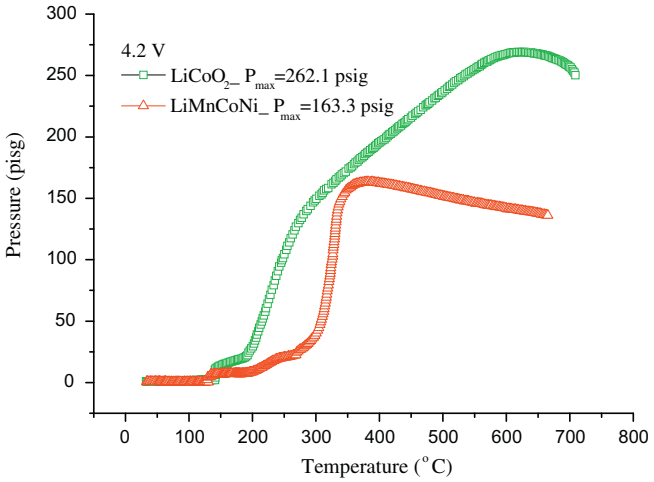

Fig. 3. Temperature–pressure profiles of 4.2 V Li-ion batteries ($LiCoO_2$ and LiMnCoNi) by the VSP2 adiabatic tests.

Table 2
Comparison on $LiCoO_2$ and LiMnCoNi cathodes of 4.2 V 18650 Li-ion batteries by VSP2 trails.

Sample[a]	T_0 (°C)	T_{max} (°C)	$(dT/dt)_{max}$ (°C/min)	P_{max} (psig)	$(dP/dt)_{max}$ (psi/min)	ΔH[b] (kJ)	m_f[c] (g)
$LiCoO_2$[d]	131.5	708.8	54,090.7	269.2	15,122.5	18.9	34.8
LiMnCoNi[e]	175.4	665.6	15,213.4	163.3	6,331.8	14.9	34.2

[a] Charge levels is 4.2 V.
[b] C_p of the Li-ion battery, which include the materials in the cell and its can, is ca. 0.73 J/g/K [4].
[c] Mass of sample after VSP2 experiment.
[d] Lithium cobalt battery.
[e] Lithium transition-metal oxides ($Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$) battery.

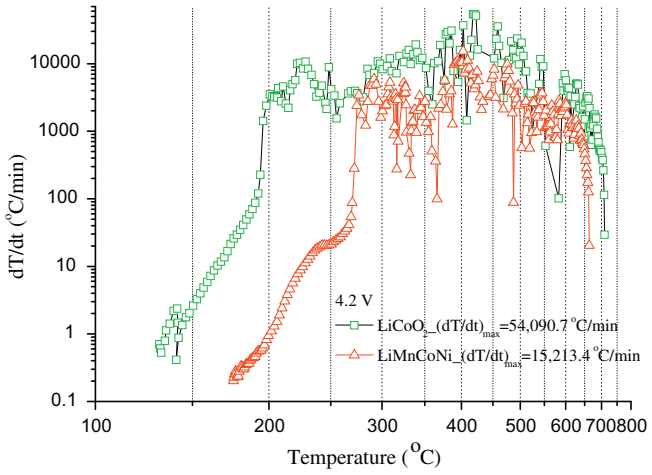

Fig. 4. The self-heating rate for the thermal decomposition of 4.2 V Li-ion batteries ($LiCoO_2$ and LiMnCoNi).

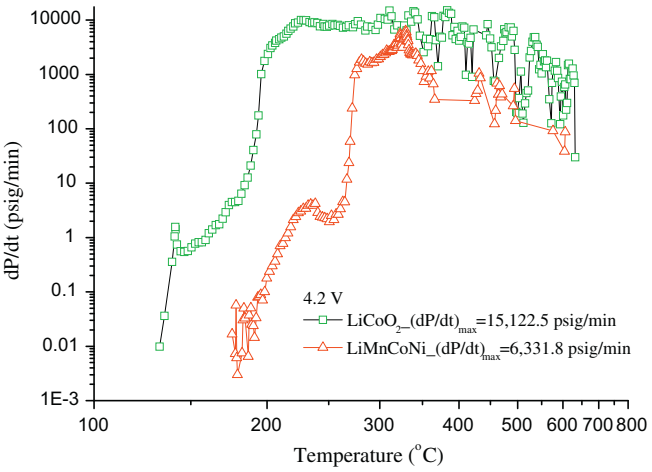

Fig. 5. The pressure rise rate for the thermal decomposition of 4.2 V Li-ion batteries ($LiCoO_2$ and LiMnCoNi).

respectively. These results are shown in Fig. 5. The $LiCoO_2$ activation energy was slightly higher than the LiMnCoNi activation energy (see Fig. 6). The lowest value of the activation energy for both cathodes was observed at the charged 4.2 V level. The self-heating rate can be increased by increases in frequency factor [4].

Among various cathode materials, $LiCoO_2$ is most used owing to its acceptable specific capacity performance. However, LiMnCoNi is an alternative cathode for Li-ion batteries because of its higher reversible capacity and small cobalt content, which is different from $LiCoO_2$ the relatively high cost of Co and concerns about toxicity and thermal safety [20]. Based on the observations from this study, the self-heating rate of $LiCoO_2$ and LiMnCoNi batteries

Table 3
Thermokinetic data from VSP2 adiabatic experimental for 4.2 V Li-ion batteries ($LiCoO_2$ and LiMnCoNi).

Sample	Voltage (V)	E_a (eV)	A (1/min)	Coefficient of determination, R^2
$LiCoO_2$	4.2	1.4	3.3×10^{14}	0.9666
LiMnCoNi	4.2	1.3	1.1×10^{12}	0.9806

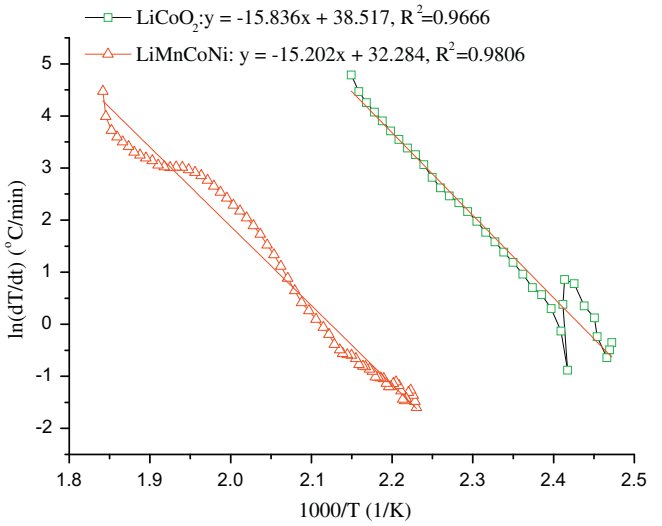

Fig. 6. The plot of $\ln(dT/dt)$ *v.s.* $1{,}000/T$ for 4.2 V Li-ion batteries ($LiCoO_2$ and LiMnCoNi).

increased exponentially with the temperature. It is evident that the $LiCoO_2$ batteries are more hazardous in terms of thermal runaway excursion potential. The full thermal response of the battery depends on the cathode materials in the cell. These reaction profiles suggest that the cathodes were contributing significantly to the magnitude of the cell heat generation, while both cell components contributed to the different thermal hazards during the explosive decomposition of the various batteries [21–23].

4. Conclusions

Li-ion batteries convert the energy released by chemical reactions to electrical work. The thermal stabilities of charged 18650 Li-ion batteries with $LiCoO_2$ and LiMnCoNi, were characterized via VSP2. The $LiCoO_2$ battery proved to be more hazardous than the LiMnCoNi battery. The thermal accumulation could cause a temperature rise and explosion because of the thermal runaway reactions. The temperature control of Li-ion batteries is critical to

avoid the occurrence of thermal runaway reactions. The results also demonstrated that using adiabatic calorimetry methodology to classify the thermal hazards of a Li-ion battery is an alternative technology for battery safety research. In summary, the kinetic and thermodynamic properties of the electrochemical reaction mechanisms that need to be understood to determine the crucial factors for thermal runaway can be investigated with adiabatic calorimetry methodology.

This problem is common when using elemental cathodes in contact with electrolytes containing organic cationic groups. These reactions are exothermic and cause local heating. Various cathode contributions to battery thermal runaway occur at different temperatures and lead to different exothermal behaviors. Calorimetric experiments have shown that this problem increases dramatically as batteries are charged at high levels and for various cathodes. The results of the adiabatic runaway reaction experiments agreed with those acquired by the adiabatic calorimetry methodology. The Li-ion battery for the self-accelerating reaction was identified, and an accurate technique was proposed to study the thermal decomposition. We can be fairly certain of the damage that a Li-ion battery can caused from the violent thermal decomposition and explosion in a runaway reaction, and we must pay attention to the safe use of this type of Li-ion battery. The calorimeter is important for the determination of a battery's inherent electrochemical reactions. The thermal properties of the electrode materials of a Li-ion battery, within the field of energy storage applications, can be readily studied with adiabatic calorimeters.

Acknowledgement

The authors wish to express their appreciation to the National Science Council of Taiwan, ROC (NSC 100-2221-E-407-001), for the financial support of this study.

References

[1] Hu C, Youn BD, Chung J. A multiscale framework with extended Kalman filter for lithium-ion battery SOC and capacity estimation. Appl Energy 2012;92:694–704.
[2] Julien C. Design considerations for lithium batteries. In: Julien C, Stoynov Z, editors. Materials for lithium-ion batteries. Netherlands: Kluwer Academic Publishers; 2000. p. 1–20.
[3] The Electropadeia: battery and energy technologies, <http://www.mpoweruk.com/protection.htm>.
[4] Huggins RA. Binary electrodes under equilibrium or near-equilibrium conditions. In: Julien C, Stoynov Z, editors. Materials for lithium-ion batteries. Netherlands: Kluwer Academic Publishers; 2000. p. 47–74.
[5] He H, Xiong R, Guo H. Online estimation of model parameters and state-of-charge of $LiFePO_4$ batteries. Appl Energy 2012;89:413–20.
[6] Adams S. Ultrafast lithium migration in surface modified $LiFePO_4$ by heterogeneous doping. Appl Energy 2012;90:323–8.
[7] Ottaway M. Lithium batteries, highly energetic materials: the varied use of adiabatic calorimetry to aid safety and battery development. In: 37th North American thermal analysis society (NATAS) annual conference, USA; 2009.
[8] MacNeil DD, Christensen L, Landuect J, Paulsen JM, Dahn JR. An autocatalytic mechanism for the reaction of Li_xCoO_2 in electrolyte at elevated temperature. J Electrochem Soc 2000;147:970–9.
[9] Sun F, Xiong R, He H, Li W, Aussems JEE. Model-based dynamic multi-parameter method for peak power estimation of lithium–ion batteries. Appl Energy 2012;96:378–86.
[10] Jhu CY, Wang YW, Shu CM, Chang JC, Wu HC. Thermal explosion hazards on 18650 lithium ion batteries with a VSP2 adiabatic calorimeter. J Hazard Mater 2011;192:99–107.
[11] Jhu CY, Wang YW, Wen CY, Chiang CC, Shu CM. Self-reactive rating of thermal runaway hazards on 18650 lithium-ion batteries. J Therm Anal Calorim 2011;106:159–63.
[12] FAI. VSP2 manual and methodology. Fauske & Associates, LLC: Burr Ridge, Illinois, USA; 2002.
[13] Roth EP, Doughty DH. Thermal abuse performance of high-power 18650 Li-ion cells. J Power Sources 2004;128:308–18.
[14] Veluchamy A, Doha CH, Kima DH, Lee JH, Shina HM, Jin BS, et al. Thermal analysis of Li_xCoO_2 cathode material of lithium ion battery. J Power Sources 2009;189:855–8.
[15] Dai H, Wei X, Sun Z, Wang J, Gu W. Online cell SOC estimation of Li-ion battery packs using a dual time-scale. Appl Energy 2012;95:227–37.
[16] He YB, Ning F, Yang QH, Song QS, Li B, Su F, et al. Structural and thermal stabilities of layered $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ materials in 18650 high power batteries. J Power Sources 2011;196:10322–7.
[17] Jiang J, Dahn JR. ARC studies of the thermal stability of three different cathode materials: $LiCoO_2$; $Li[Ni_{0.1}Co_{0.8}Mn_{0.1}]O_2$; and $LiFePO_4$, in $LiPF_6$ and LiBoB EC/DEC electrolytes. Electrochem Commun 2004;6:39–43.
[18] Gnanaraj JS, Zinigrad E, Asraf L, Gottlieb HE, Sprecher M, Aurbach D, et al. The use of accelerating rate calorimetry (ARC) for the study of the thermal reactions of Li-ion battery electrolyte solutions. J Power Sources 2003;119:794–8.
[19] Wang Q, Sun J, Yao X, Chen C. Micro-calorimeter study on the thermal stability of lithium-ion battery electrolytes. J Loss Prev Process Ind 2006;19:561–9.
[20] Ozawa K. Lithium ion rechargeable batteries. Germany: Wiley-Vch; 2009. p. 39–52.
[21] Zhang Z, Fouchard D, Rea JR. Differential scanning calorimetry material studies: implications for the safety of lithium-ion cells. J Power Sources 1998;70:16–20.
[22] Al Hallaj S, Prakash J, Selman JR. Characterization of commercial Li-ion batteries using electrochemical–calorimetric measurements. J Power Sources 2000;87:186–97.
[23] Ishikawa H, Mendoza O, Sone Y, Umeda M. Study of thermal deterioration of lithium-ion secondary cell using an accelerated rate calorimeter (ARC) and AC impedance method. J Power Sources 2012;198:236–42.