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Evaluation of thermal hazard for commercial 14500 lithium-ion batteries

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Abstract Commercial lithium-ion batteries ranged from different sizes, shapes, capacities, electrolytes, anode and cathode materials, etc. have recently caused many incidents under abusive or normal operating conditions worldwide. Inherently safer designs with active or passive protections have became the captious issues that need more attentions paid to. In this study, the worst scenarios on thermal runaway of four commercial batteries were conducted and compared. A customized-made closed testing instrument was utilized to measure and track thermal behaviors of four brands of cylindrical lithium-ion batteries under maximum open circuit voltage condition. Characteristics on thermal hazards of lithium-ion batteries such as onset temperature, maximum temperature, maximum self-heat rate, maximum pressures, battery mass loss, etc. were measured and evaluated. Results point out that one brand of cells reached the maximum temperature and maximum self-heat rate of 590.9 K and 1,130.4 K min^{-1}, respectively. In conclusion, in case of thermal runaway all the lithium-ion batteries will rupture the cell and catch fire automatically owing to the maximum temperatures over the auto-ignition temperature of electrolytes and the maximum pressure higher than four times of maximum allowable working pressure, respectively. In addition, Lithium-ion battery with cathode material of $LiFePO_4$ was verified to be more stable than the lithium-ion battery with cathode material of $LiMn_2O_4$ or $LiCoO_2$.

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Introduction

Lithium-ion (secondary) battery has become the dominant energy source for consumer electronics, especially, the applications of this kind of battery have expanded in personal or portable devices and have became popular in broad fields of life. It has been widely used as DC power source in various portable 3C products such as mobile phones, notebook computers, video cameras, digital cameras, and LED flashlights, due to its high power density, long life cycle, low self-discharge properties, etc. However, it caught fire and exploded in recent years, and the accidents under normal operation or charging are still happening nowadays. Safety issue in lithium-ion battery is a key aspect of any energy storage device. When considering the electronic equipments using lithium-ion batteries, it is necessary to analyze the characteristics of thermal runaway in lithium-ion batteries under high temperature conditions from the viewpoint of safety [1, 2]. By characterization on these commercial 14500 batteries in relation to the thermal abuses can provide the deep insights into exothermic mechanisms which trigger the thermal runaway under normal operation below 60 °C. In this study, various types of commercial 14500 lithium-ion batteries were dynamically screened to thermal runaway under confined environments. Traces of pressure and temperature before or after thermal runaway were acquired synchronously by respective detector and acquisition system. Normal electrochemical reactions without abuse or abnormal operations were excluding from thermal hazards in lithium-ion batteries. Maximum pressure can be used for explanation of the rupture or explosion of lithium-ion batteries. Discrepancies stressed on the runaway reaction are suspected to be one of the possible reactions of anode with electrolytes, oxidation of cathode with electrolytes, or induced decomposition of polyvinylidene difluoride (PVDF) by LiC_6 in anode compartment. Verifications on the phenomena or results of thermal runaway in lithium-ion batteries or the components of cells are required more advanced studies.

Experimental

Confinement apparatus

To understand thermal behaviors of commercial lithium-ion batteries, customized-made confinement equipment with pseudo-adiabatic condition was established and utilized. The confinement equipment is shown in Fig. 1, including external protective body, test vessel, pressure transducer and temperature detector, graphite furnace, temperature controller, and data acquisition system. Detailed specifications are presented in the following content. The external protective body has the volume of about 5,000 mL, made of SUS316 and can resistant to 100 bars. The internal test vessel has a volume of 100 mL, made of SUS316 with the diameter of 4.8 cm, and can withstand the pressure as high as 40 bars. The pressure transducer with DIN43650 standard electrical interface can measure pressure range from 0 to 60 bars. Full-charged lithium-ion batteries were placed in this specially designed confinement instrument to simulate thermal runaway and measure the corresponding traces of temperature and pressure under pseudo-adiabatic environment.

Commercial 14500 battery samples

Four types of commercial 14500 lithium-ion batteries purchased from different companies are used for confined testing. Standard 14500 battery with cylindrical AA size with the diameter of 1.4 cm and the height of 5.0 cm, has been popularly used in electrical devices of digital electronics. Figure 2 shows the internal structure of UR14500 battery that consists of the positive electrode (cathode), the negative electrode (anode), the separator, a battery can, terminal leads, safety vent, etc. [3]. Table 1 summarizes most common specifications of the cells. The electric capacity, electrolytes, materials of anode and cathode of the four testing samples are somewhat different in their own designs. For instance, the maximum open circuit voltages (OCVs) of US14500, UR14500, and LC14500 are 4.2 V except 3.7 V for IFR14500. The difference in OCV is ascribed to the different cathode material associated with electrochemical reactions under charge and discharge.

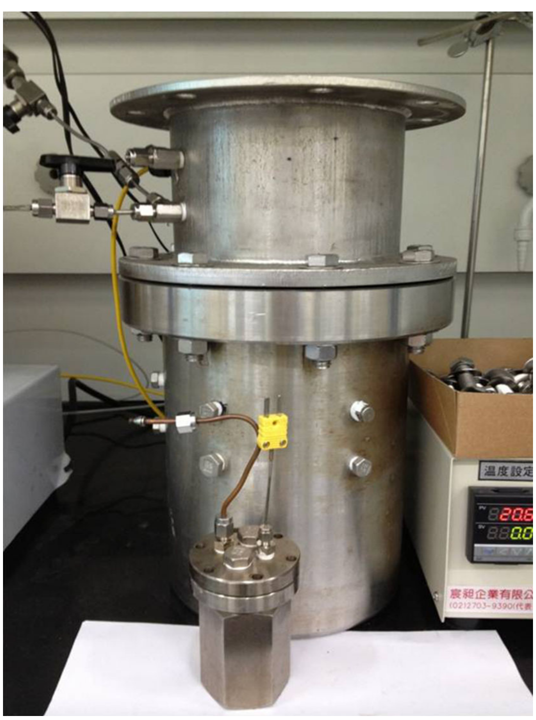

Fig. 1 Diagrammatic sketch of confinement testing instrument

Fig. 2 Side views of UR14500 battery

Table 1 Specifications of the commercial 14500 Li-ion batteries

Battery	Cathode material	Typical capacity/mAh	Open circuit voltage/V	Nominal voltage/V	Total mass/g
US14500	$LiCoO_2$	580	4.2	3.7	19.75
UR14500	$LiCoO_2$	800	4.2	3.7	19.54
LC14500	$LiMn_2O_4$	900	4.2	3.6	19.71
IFR14500	$LiFePO_4$	900	3.7	3.2	17.95

Results and discussion

Safety problems concerning the hazards are attributed to the complexity of reactions inside the batteries and in-depth studies on the reactive hazards of ingredients in lithium-ion batteries are needed. Consequence and probability of thermal runaway occurred in a lithium-ion battery are especially related to the electrolytes, materials of electrodes, and state-of-charge (SOC) [4–6].

Runaway behaviors of UR14500, US14500, and LC14500

Figures 3 and 4 show thermal runaway curves of 14500 Li-ion batteries and Table 2 summarizes experimental results of onset temperature, onset pressure, maximum temperature, maximum pressure, and maximum self-heat rate. All the batteries were observed to follow at least two stepwise runaway behaviors. The first onset temperature (T_{onset1}) is defined as the temperature with corresponding abrupt increase of pressure (P_{onset1}) in the test oven. The second onset temperature (T_{onset2}) is defined as the self-heat rate exceeded the sensitivity (1 °C min^{-1}) in this confinement test. The first step started with relatively lower temperature and was moderate whereas the second step was quite severe and usually caused the cells exploded violently as can be seen in Fig. 5. For UR14500 (Sony company) T_{onset1}, T_{onset2}, maximum temperature, maximum pressure, maximum self-heat rate, and pressure-rising rate were determined to be 157.4 °C (430.4 K), 190.9 °C (463.9 K), 339.8 °C (612.8 K), 33.0 bar, 862.6 °C min^{-1}, and 497.0 bar min^{-1}, respectively. For US14500 (Sanyo company) T_{onset1}, T_{onset2}, maximum temperature, maximum pressure, maximum self-heat rate, and pressure-rising rate were determined to be 171.4 °C (444.4 K), 203.8 °C (476.8 K), 317.9 °C (590.9 K), 31.6 bar, 1,130 °C min^{-1}, and 686.9 bar min^{-1}, respectively. Obviously, less hazardous conditions were observed in LC14500 (Ultra Fire company) with higher T_{onset1}, T_{onset2}, lower maximum temperature, less maximum pressure, lower self-heat rate, and pressure-rising rate of 173.9 °C (446.9 K), 214.9 °C (487.9 K), 286.6 °C (559.6 K), 30.4 bar, 527.9 °C min^{-1},

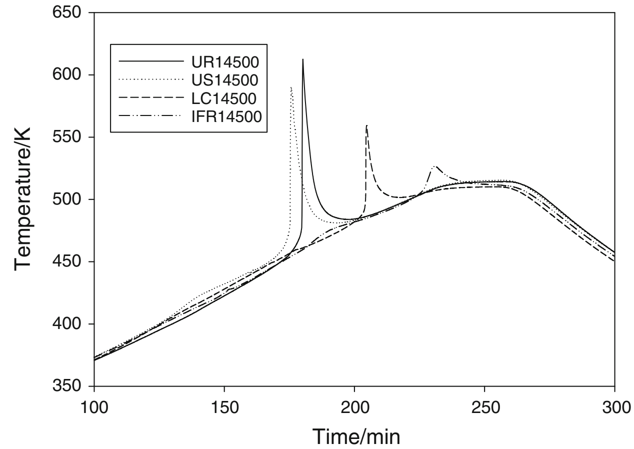

Fig. 3 Thermal runaway temperature profiles of four 14500 batteries

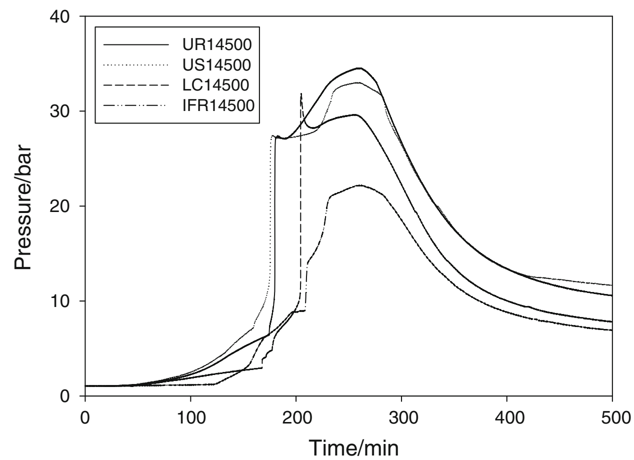

Fig. 4 Thermal runaway pressure profiles of four 14500 batteries

Table 2 Thermal runaway results of four 14500 Li-ion batteries

Li-ion battery	UR14500	US14500	LC14500	IFR14500
T_{onset1}/K	403.5	444.4	448.7	398.2
P_{onset1}/bar	0.27	1.25	0.33	0.27
T_{onset2}/K	463.9	476.8	487.9	478.6
P_{onset2}/bar	7.68	2.65	8.93	7.58
T_{max}/K	618.8	590.9	559.6	526.9
P_{max}/bar	34.5	32.9	31.9	22.2
$(dT/dt)_{max}$/K min^{-1}	862.6	1,130.4	1,024.2	74.0
$(dP/dt)_{max}$/bar min^{-1}	497.0	686.9	424.3	5.78
T_f/K	298.0	298.0	298.0	298.0
P_f/bar	9.1	11.0	6.7	5.7
Mass loss/g	2.59	1.26	4.80	1.63

Fig. 5 Battery severely ruptured after thermal runaway

and 424.3 bar min^{-1}, respectively. From Table 2, the second onset temperature (T_{onset2}) of UR14500 is the lowest whereas the maximum temperature and maximum pressure are the highest one. US14500 possessed the maximum self-heating rate of 1,130 °C min^{-1}. Comparing the onset temperature, maximum temperature, maximum pressure, maximum self-heating rate, etc., less hazardous conditions were observed in IFR14500. Furthermore, at the end of the test the final pressure could not back to atmospheric pressure after cooling down to the ambient temperature, indicating that components of electrolytes were decomposed for these batteries under thermal runaway. In other words, the pressure hazards of these batteries are all quite severe and cannot be neglected.

Runaway behaviors of IFR14500

Thermal runaway curve of IFR14500 lithium-ion battery associated with cathode material of $LiFePO_4$ determined by confinement test is shown in Fig. 3. There is no oblivious thermal and pressure runaway was observed by confinement test until 205.6 °C. This is mainly due to the material of cathode used in IFR14500 lithium-ion battery. Oxidative ability of $LiFePO_4$ is the smallest one in comparison to $LiNiO_2$, $LiNi_{0.8}Co_{0.2}O_2$, $LiCoO_2$, $LiMn_2O_4$, and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_4$. Heat of reaction contributed by the reaction of $LiFePO_4$ and electrolyte has been detected to be one-third compared to that of $LiNiO_2$ or $LiCoO_2$ [7]. The result is similar to Dubaniewicz and DuCarme [8] whom performed an internal short circuit in lithium-ion batteries for studying the intrinsic stability. In their study, a 26650 $LiFePO_4$ cell passed without any ignition of thermal runaway in internal short circuit ten times. However, a severe thermal runaway of the full charged (3.6 V of open circuit voltage) 18650 lithium-ion battery detected by VSP2 was reported by Wen et al. [9] and Jhu et al. [10].

Thermal instabilities of $FePO_4$ with organic carbonates

Cathode material played an important role in the inherent safety and performance of lithium-ion battery. $LiNiO_2$ (lithium nickel oxide), $LiCoO_2$ (lithium cobalt oxide), $LiMn_2O_4$ (lithium manganese oxide), and $LiFePO_4$ (lithium iron phosphate) were with the respective layered, layered, spinel, and olivine-type structures. Their counter parts of de-lithiated transition metal oxides (MO_2 or M_2O_4) have the same crystal structures. In these oxides, only the lithium-ion migrated from cathode to anode then reinserted back into the cathode under charge and discharge processes. Thus, the cathode materials will be unstable under charge/discharge processes and hot environment by the oxidative capabilities to electrolytes or liberation of oxygen to react with electrolytes. Most of the organic solvents in electrolytes decomposed on the surface of cathode materials or reacted with the released O_2 to ignite exothermic runaway which may cause leakage, rupture, explosion, or catch fire in case of thermal abuses. Chen and Richardson have shown that $LiFePO_4$ with electrolyte (PC/DMC) exhibited an exothermic onset temperature at about 260 °C [11]. However, charged $LiFePO_4$ revealed a complex curve which had an onset at about 250 °C and two small peaks appeared at 280 and 315 °C, respectively. For $LiFePO_4$ with DMC and EMC, there was no explicitly exothermic peak found by DSC. For Both $LiFePO_4$ and $FePO_4$ with electrolytes, only very small exothermic peaks could be observed by DSC [11]. Similar results of $LiFePO_4$ and $FePO_4$ reacted with various organic carbonates were also conducted and proposed by Ou et al. [12] and Duh et al. [13]. For $LiFePO_4$ with these carbonates, only the system of $LiFePO_4$ with DEC displayed a distinguishable exothermic behavior. Exothermic onset temperature and heat of reaction were determined to be 403.6 °C and 545.3 J g^{-1}, respectively. For $LiFePO_4$ with EC and PC, exothermic onset temperatures were detected to be 324.0 and 364.3 °C, and heats of reactions were determined to be 48.3 and 106.7 J g^{-1}, respectively [12]. Exothermic onset temperatures of $FePO_4$ with PC, DMC, EC, EMC, and DEC were measured to be 339.8, 344.2, 401.0, 437.6, and 447.1 °C, respectively. Enthalpy changes of $FePO_4$ with DMC, EMC, PC, EC, and DEC were determined to be 57.7, 109.3, 112.6, 182.1, and 189.3 J g^{-1}, respectively [13].

Conclusions

Characteristics on thermal hazards of lithium-ion batteries in onset temperature, maximum temperature, onset pressure, highest pressure, maximum self-heat rate, maximum pressure-rising rate, and mass loss were performed and evaluated. In this study, the maximum temperature and pressure of 14500 lithium-ion battery exceeded auto-ignition temperature (AIT) of electrolytes and four times of maximum allowable working pressure (MAWP), respectively. Results of this study suggest that during the worst thermal runaway case the battery safety devices are unable to control or mitigate under the runaway phenomena and may cause severe explosions of lithium-ion batteries. These results showed that $LiFePO_4$ battery is more thermally stable than $LiMn_2O_4$ and $LiCoO_2$ battery and $LiCoO_2$ battery is the cell with most potential hazard under thermal runaway by the pseudo-adiabatic confinement test. Finally, the customized-made confinement apparatus can provide an alternative way with performing thermal hazard evaluation of the Li-ion battery.

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