doi: 10.3969/j. issn. 1001-8352. 2013. 05. 001

A Study on Hazard of Lithium and Lithium-ion Batteries*

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[ABSTRACT]　With increasing application, lithium and lithium-ion batteries show hazards during usage, storage, disposal and waste. To evaluate the thermal stability of lithium and lithium-ion batteries, their electrolytes were assessed by Chemical Thermodynamic and Energy Release (CHETAH) and measured by a Differential Scanning Calorimeter (DSC), since they sometimes caused fires and accidents. Moreover, thermal reactivity of lithium, silver oxide and alkaline batteries were analyzed by using a modified closed pressure vessel test (MCPVT). As a result, lithium battery is more hazardous than the other batteries. The sensitiveness to mechanical stimuli, such as a fall hammer, of lithium battery was also much higher than other batteries. The explosive power, which was evaluated by a ballistic mortar, of lithium coin battery was higher than those of other batteries.

[KEY WORDS]　lithium battery, lithium-ion battery, thermal reactivity, MCPVT, mechanical stimuli, explosive power

[CLASSIFICATION CODE]　X932

Introduction

Battery is a high energy density device which delivers electrical energy by transforming chemical energy[1]. Batteries come in different configurations, sizes and voltages. Conventional batteries contain heavy metals such as mercury, lead, cadmium and nickel. Lithium battery types, on the other hand, include lithium-manganese dioxide, lithium-sulfur dioxide and lithium-thionyl chloride. The anode is composed of lithium and the cathode is composed of manganese dioxide (or sulfur dioxide, or thionyl chloride). The electrolyte of the lithium-manganese dioxide battery is composed of an organic solvent (propylene carbonate and 1,2 dimethoxyethane) solution of lithium perchlorate. In the case of lithium-sulfur dioxide, the electrolyte is also an organic solvent (acetonitrile) solution with lithium bromide. The thermal reactivity of battery results from its containing electrolyte as combustible materials, which lead to heat generation, bursting or fire if it is improperly handled. With more and more widely application since 1990s in various portable consumer electronic devices, such as cameras, electronic notes and electronic calculators, safety problem in lithium batteries arises when abuse, discard or with large amount of storage. One reported accident of primary lithium coin-cell bateries was that in 1994, a fire happened in a cardboard box, in which 2,000 cells were packed[2-3]. Lithium-ion battery made accidents and fires[4], with sizes generally larger than that of lithium battery. The study of the hazard of lithium battery is very limited, and more studies were concerned with the electrolyte of lithium-ion batteries[5-6]. This paper studied the risk of primary lithium battery and lithium-ion battery compared with other types of batteries. Considering the electrolyte is a combustible material, the hazard was evaluated by the

* 收稿日期: 2013-05-30

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Chemical Thermodynamic and Energy Release (CHETAH) program[7] and a Differential Scanning Calorimeter(DSC). Then, a modified closed pressure vessel tester (MCPVT)[8] was used to measure their thermal reactivity in terms of pressure and temperature histories during heating. The measurements were also performed on an alkaline and a silver oxide batery. Their sensitiveness to mechanical stimuli, such as a fall hammer, was also examined by a drop hammer test[9]. The explosive power of battery was evaluated by a ballistic mortar[9].

1 Evaluation of hazard of electrolytes by CHETAH

The thermal reactivity of battery results from its containing electrolyte as combustible materials. The program CHETAH 7.2, the ASTM computer program for chemical thermodynamic and energy release evaluation, was used for classifying the electrolyte of lithium battery for their ability to decompose with violence and for estimating heat of reaction or combustion by terms of the maximum heat of decomposition, the fuel value-heat of decomposition, the oxygen balance and the CHETAH ERE Criterion, y, defined as:

$$y = 10(M^2 W/n)$$

where M is the maximum heat of decomposition, W is the weight of the composition in gram and n is the number of moles of atoms in the composition.

Two electrolytes for lithium primary and one for lithium-ion battery were calculated:

1) Lithium perchlorate 10% + propylene carbonate (in lithium primary battery);

2) Lithium perchlorate 10% + γButyrolactone (in lithium primary battery);

3) Ethylene carbonate (in lithium-ion battery).

The results are given in Table 1, and both electrolytes for primary rated as medium energy hazard potential and the electrolyte for ion battery is lower.

2 Experimental

2.1 Thermal analysis

The Differential Scanning Calorimeter (DSC) test was conducted for two electrolytes with 5% and 10% (wt) of lithium perchlorate ($LiClO_4$) in propylene carbonate, and 13% (wt) of lithium hexafluorophosphate ($LiPF_6$) in ethylene carbonate ($C_3H_4O_3$). In the measurements, sample of 1.8-1.9 mg in a sealed SUS cell was heated at 5 K/min from room temperature to 400℃ and heat flux was measured during the entire process.

A modified closed pressure vessel tester[8] (MCPVT, heating rate, 2 K/min) was used to examine the thermal reactivity of primary lithium coin-cell batteries. Lithium-ion battery is too large to be measured by MCPVT. Samples were a small coin battery (cell), CR1220 (Ø12.4 × 2.0 mm, weight: 0.88 g) or CR1226 (made in Germany, Ø12.4 × 1.6 mm, weight: 0.98 g), alkaline LR44 (Ø11.5 × 5.1 mm, weight: 1.96 g) and silver oxide SR44 (Ø11.5 × 5.2 mm, weight: 2.19 g) batteries.

Comparison of summary of DSC and MCPVT is shown in Table 2.

Tab.2 Summary of DSC and MCPVT

name	DSC	MCPVT
Sample	Electrolyte, 1.8-1.9 mg	Entire coin battery, ca. 1-2 g
Heating rate/ (K·min^{-1})	5	2
Temperature	Room temp. -400℃	Room temp. -ca. 400℃
Measurement	Heat of reaction	Temperature and pressure

2.2 Drop hammer test

The drop hammer test, based on JIS-K4810, was used to measure the sensitiveness of batteries to drop weight impact. A 5.0 kg steel anvil was used at fall heights from 0.5 m to 1.0 m, in steps until the limiting impact energy was determined. Most samples were

Tab.1 Results of hazards evaluation by CHETAH 7.2

Electrolyte	Maximum heat of decomposition /(kJ·g^{-1})	Fuel value-Heat of decomposition/(kJ·g^{-1})	Oxygen balance/ %	y
1	−1.834 (Medium)	−13.394 (Medium)	−106.810 (High)	15.949 (Low)
2	−1.955 (Medium)	−18.083 (Medium)	−144.510 (Medium)	16.624 (Low)
3	−1.725 (Medium)	−1.118 (Medium)	−90.841 (High)	14.984 (Low)

new one. However discharged and sheared lithium batteries were also tested. Lithium-ion battery, Casio NP-20 which was used for digital camera, was added to the test samples. Sample was about 70 % charged.

2.3 Ballistic mortar Mk. IIID test

The Ballistic mortar Mk. IIID test was used to measure the explosive power of batteries. A detonator was initiated in the battery whilst the battery was confined in the bore of a mortar. The recoil of mortar was measured and, after allowing for the effect of the detonator, the power was calculated as a percentage equivalence of TNT and picric acid, the explosive standards.

3 Experimental results and discussion

3.1 Thermal analysis

The results of three eletrolytes in the DSC are shown in Figure 1. It is seen that with increasing the concentration of $LiClO_4$, the heat of reaction increased. Comparing with standard materials, such as 80% BPO (benzoyl peroxide) and 70% DNT (dinitrotoluene) according to the evaluation method of Japanese Service Law, they are lower than the standard line which was obtained from the results of standard materials, and less dangerous than standard materials. However, the positions of the lithium electrolytes are close to the standard line, whereas the lithium ion electrolyte (13% $LiPF_6$ in $C_3H_4O_3$) is much lower.

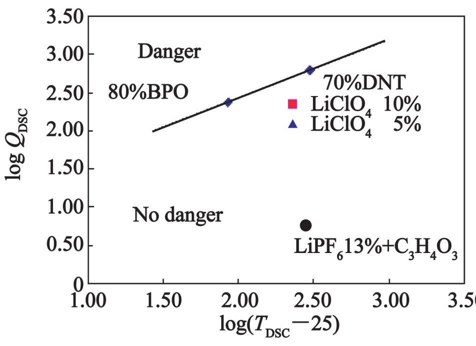


Fig. 1　Evaluation of the electrolytes

(T_{DSC}—onset temperature, Q_{DSC}—heat of reaction)

Pressure vs. temperature curves of lithium battery in the MCPVT was compared with two other batteries, silver oxide and alkaline cells, in Figure 2. It is seen that no reaction occurred for silver oxide and alkaline cells up to 350℃. In contrast, lithium cell was quite reactive. The pressure rise started at about 100℃. The pressure of lithium cell gradually reached a maximum of 42 kgf/cm^2 at about 329℃.

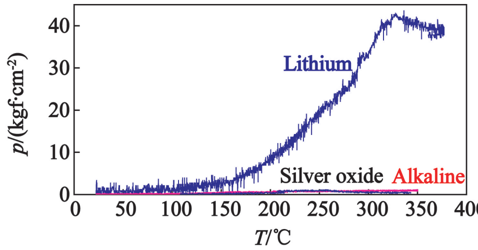
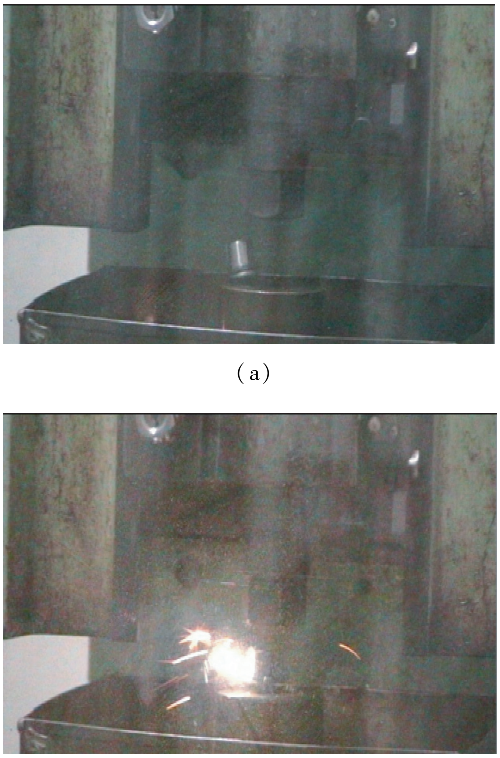


Fig. 2　Pressure vs. temperature curves of lithium, silver oxide and alkaline cells in MCPVT

3.2 Drop hammer test

Sensitiveness of batteries to mechanical stimuli was assessed on the basis of whether an explosion occurs at particular impact energy by dropping a 5.0 kg hammer. The impact energy, characterising the impact sensitiveness, is calculated from the mass of the drop weight and the fall height. The results are shown in Table 3 and Figure 3. It implies that explosive did not occur for alkaline and silver oxide batteries even at much larger impact energy, 50 J (Figure 3a). In contrast, explosive occurred in lithium battery and a discharged one at lower impact energy, 30 J (Figure 3b). For a sheared one, impact energy at which explosion occurred was 25 J for lithium-ion battery gave no explosion, but it increased its temperature to about 120 ℃ after three minutes from the test, which was surface temperature measured with thermal paper and 0.1 mm



(a)

(b)

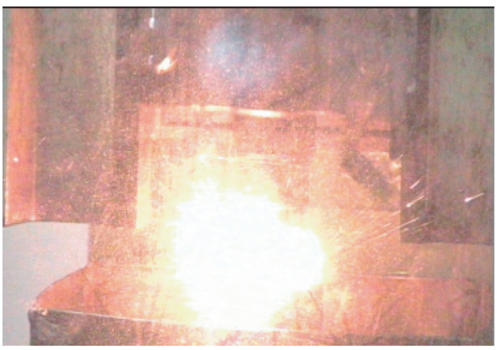
Tab. 3 Results of drop hammer test

Sample	CR1220	CR1220 used	CR1220 sheared	LR44	SR44	Li-ion *
Fall height/m	0.6/1.0	0.6	0.5	1.0	1.0	1.0
Explosion **	+	+	+	–	–	–
impact energy/J	30, >50	30	25	>50	50	50

*: Electrolyte and Casio NP-20; **: + stands for explosion, – does no explosion.

Tab. 4 Results of ballistic mortar Mk. IIID test

Sample	CR1216	CR1220	CR2025	LR44	Electrolyte 1 Li battery	Electrolyte 3 Li-ion battery
Weight/g	2.6,5.1	3.5	4.6	3.9	5.0	5.0
Mean of TNT/%	7.8	3.9	16.7	3.9	2.3	1.6



(c)

(a) LR44, SR44, Height = 1 m; (b) Li-battery (CR1220), Height = 0.6 m; (c) Li-battery (CR1220), Height = 1.0 m

Fig. 3 Results of drop hammer test

diameter K-type thermocouples. Impact from 1.0 m high gave much vigorous result (Figure 3c).

3.3 Ballistic mortar Mk. IIID test

The explosive power was calculated as a percentage of the value given by TNT in the ballistic mortar Mk. IIID test. In Table 4, lithium batteries CR2025 and CR1216 presented medium explosive power. Whereas the explosive powers of CR1220, alkaline LR44 and electrolytes were low. Electrolytes were also tested, and they gave lower values than those of coin type batteries. Among the results, electrolyte of lithium-ion battery gave the smallest value.

4 Conclusion

In order to understand hazard of lithium battery and lithium-ion battery, CHETAH calculation and various evaluation tests were conducted. Based on the results lithium coin battery was most hazard.

1) The reactivity of the electrolytes of lithium battery and lithium ion battery was predicted by the CHETAH program. Lithium electrolytes presented medium hazard by CHETAH, whereas the electrolyte of lithium-ion battery was lower.

2) The electrolytes of these batteries were measured by the DSC. The hazard of lithium battery electrolytes was lower than those of BPO and DNT, but higher than that of lithium ion battery.

3) The entire cells were measured by the MCPVT. As a result, the reactivity of lithium coin battery was much higher than those of silver oxide and alkaline batteries. Lithium-ion battery was too large to be tested by the MCPVT.

4) The drop hammer test resulted that lithium coin battery gave high sensitiveness. And the explosive power of lithium coin battery, which was evaluated by the ballistic mortar, was higher than those of other types of batteries.

Acknowledgements

This work was partly supported by a research fund from the Ministry of the Environment.

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锂电池和锂离子电池的危险性研究

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[摘　要] 随着锂和锂离子电池应用的不断增加,在其使用、储存、处理和废弃过程中也呈现出越来越多的危险性。锂和锂离子电池的电解质是可燃物质,会引起火灾,其热稳定性分别由 CHETAH 和 DSC 评估和测定。另外,锂电池、氧化银电池和碱性电池的热稳定性通过在一个改性的密闭压力容器中测定(MCPVT)。结果表明锂电池比其它电池的危险性更大。锂电池对力学冲击(如落锤试验)的敏感度高于其它电池。其爆炸威力(如对弹道冲击)也高于其它电池。

[关键词] 锂电池　锂离子电池　热反应性　改性密闭压力容器试验　力学冲击　爆炸威力

文　　摘

1　适用于爆破药包和煤矿装药的工业炸药

俄罗斯专利,RU2159757,2000 年 10 月 27 日(俄文)

这种炸药为 5 级工业炸药,适用于作为煤矿爆破药包,不会引爆煤矿地区空气中的甲烷和煤尘。这种炸药含有硝酸酯、氯化铵、硝酸钾、羧甲基纤维素钠、硬脂酸锌、胶态棉、苏打灰和聚氯乙烯。这种炸药具有低的摩擦感度、易于处理和高的贮存安定性。

2　防水粒状炸药组成

日本专利,JP2002,29877,2002 年 1 月 29 日,共 5 页(日文)

这种防水粒状炸药由多孔粒状硝酸铵和燃料油组成。多孔粒状硝酸铵用聚合物包覆,聚加物在热熔后为液态或乳状液状态,并在包覆后凝固。所用聚合物有丙烯酸树脂、苯乙烯—丁二烯聚合物、聚氨酯、苯乙烯—丁二烯共聚橡胶、丙烯腈—丁二烯共聚橡胶或它们的混合物。这种炸药在使用上,对松密度、流动性和抗水性方面与铵油炸药(ANFO)有相同的特性。

3　2′,4′-二硝基苯基-1,2,4-三唑酮-5 的合成

《火工品》,2001(2),36-37,44(中文)

题称的化合物是由草酸、氨基脲和 2,4-二硝基氟苯合成的,并通过熔点、^{1}H-核磁共振和元素分析对它作出鉴定。

4　防水粒状炸药组成

日本专利,JP2002,47088,2002 年 2 月 12 日,共 5 页(日文)

这种防水粒状炸药是由粉状硝酸铵包覆、然后再用固体聚合物包覆的多孔粒状硝酸铵组成的。粉状硝酸铵在包覆多孔粒状硝酸铵以前可先与增粘剂、粘合剂和天然聚合物相混合。这种炸药也像铵油炸药(ANFO)一样,具有良好的处理特性和高的抗水性。

5　防水粒状炸药组成

日本专利,JP 2002 47089,2002 年 2 月 12 日,共 5 页(日文)

这种防水粒状炸药是由微球(microballon)和固体聚合物包覆的多孔粒状硝酸铵组成的。多孔粒状硝酸铵的油吸收量为 5.0% ~20.0%,含有微球的多孔粒状硝酸铵的装填密度为 0.55 ~0.78g/cm^3。这种炸药也像铵油炸药(ANFO)一样,具有良好的处理特性和高的抗水性。

钟一鹏译自美国《化学文摘》

Vol. 136,No. 7,9-11(2002)