

Thermal reactivity of primary lithium coin-cell batteries

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Abstract

Coin type primary lithium batteries were used to analyze their thermal hazard by a modified closed pressure vessel test (MCPVT) and a C80 at different conditions such as being damaged, accidentally mixed with water or with other wastes when disposed of. As a result, such handlings lead to heat generation in the systems and increase the risk during the usage or disposal of lithium cell.

Keywords: Coin type primary lithium battery, Thermal reactivity, Waste, Hazard.

1. Introduction

A battery is a complex device which delivers electrical energy by transforming chemical energy. The thermal reactivity of lithium battery results from its containing combustible materials such as lithium metal and organic solvent. Improper handling can lead to heat generation, bursting or fire. With more and more application especially in the IT development, safety problems on lithium batteries have gained much more attentions. Primary lithium and secondary lithium ion batteries were developed from 1990s, while the safety concerns of the latter are more focused. Compared to accident occurrences in secondary lithium ion batteries during their recharging, problem in primary lithium batteries arises when abuse use, or with large amount of storage. One reported accident of primary lithium coin-cell batteries was that in 1994, a fire happened in a cardboard box, in which 2,000 cells were packed¹⁾.

On the other hand, unlike reusable lithium ion batteries, risk of primary lithium coin-cell batteries increases when they are disposed to the environment after used once. Usually used batteries are separated from other wastes and then crushed in the processing facility. To evaluate the thermal safety of lithium batteries, at present most research (about 90 %) is focused on the temperature acti-

vated reactions of the components, mainly in lithium ion cells^{2), 3)}, such as positive electrode, negative electrode, and electrolytes individually. However, the safety of the battery cells themselves and the disposed ones should be enhanced, especially when the batteries are mixed into other wastes⁴⁾. This paper studied the risk coming from primary lithium cell and other various possibilities of its handling: such as mixed with other wastes and water, danger during its crushing process, abuse use, and near heating place. Here RPF (= Refuse paper & plastic fuel) was used as representative of various wastes, which is mixture of plastics, paper and wood.

2. Experimental

A C80 and a modified closed pressure vessel tester (MCPVT) were used to examine the thermal reactivity of primary lithium coin-cell batteries. Details of both test methods are shown in our previous papers^{5), 6)}. In the C80, heat flux was measured from the room temperature to 100°C at a heating rate 0.1 K min⁻¹, for the purpose of observing the thermal behavior of lithium battery within the handling temperatures below 100°C. In the MCPVT, pressure was measured in a wider temperature range of the room temperature to 350°C at a heating rate of 2.5 K

Table 1 Energy of batteries.

Battery	Voltage, V	Energy, Wh kg ⁻¹
Lithium primary cell	3	380 ~ 450
Lithium-ion secondary cell	3.6	100
Polymer cell	2.7	150
Alkaline dry cell	1.5	80
Lead-acid battery	2.0	30
Nickel-cadmium battery	1.2	60
Nickel hydrogen battery	1.2	70

Table 2 Properties of RPF⁷⁾.

Component, %	carbon: 65.9, hydrogen: 7.6, oxygen: 23.6, sulfur: 0.04, water: 0.67
Heat of combustion (JIS M 8814) measured by a bomb heat flux meter, MJ kg ⁻¹	26.4 ~ 16.8
Flash point (Cleveland open cup) (Seta open tester), °C	>180 314
Ignition point measured by a high pressure DTA, °C	155 ~ 185

min⁻¹, to examine the onset temperature of a visible reaction in the battery and the intensity of the reaction.

Since volume and energy of general batteries are too large to be fitted for laboratory thermal analysis apparatus, a small coin battery (cell), CR1220 ($\phi 12 \times 2$ mm, weight: 0.8 g) was used as sample for the measurements. Several conditions were considered to be accompanied with the lithium cell usage and disposal process: new (3 V) and used (0.5 V left) cells, crushed, mixed with water (by 1:1), mixed with the RPF waste (refused plastic/paper fuel, by 1:1).

The energies of batteries are compared in Table 1. The primary lithium battery shows a much higher energy amongst the other commercial ones. Being a combustible material, the properties of RPF which was used in this study are listed in Table 2.

3. Results and discussion

Figure 1 shows the experimental results of the lithium cell in the C80. The heat flow of the lithium cell increased to a maximum immediately after the start of measurement, then decreased a little and gradually increased again from 2.7 mW at 25°C to 5.6 mW at 100°C. In the case of a crushed cell, the heat flow underwent the same tendency, but with much higher heat release, that is, it increased from 24 mW at 38°C to 25 mW at 68°C. These results imply that at a temperature elevated condition in the C80, some of the energy of lithium cell is released by a gradual slope way with the temperature.

In the case of a crushed cell, this kind of energy is released significantly with inside components leaking and becomes more dangerous. Its successive (2nd and 3rd) measurements showed that there was not much energy left in the cell after the first run measurement.

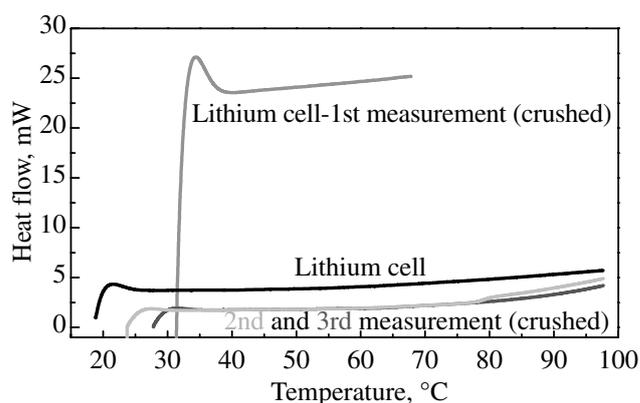


Fig. 1 Results in the C80.

Figures 2 and 3 show the MCPVT results of primary lithium cell, CR1120, in different conditions which may be accompanied with the lithium cell. The reason of large difference of the onset temperature between the MCPVT and the C80 is the difference of sensibility of both measurements. The MCPVT has low sensibility and has been proposed as a screen test method for energetic materials⁶⁾.

As seen in Fig. 3, the pressure rise of all samples started from about 100°C. The pressure of lithium cell gradually reached a maximum of 42 kgf cm⁻² at about 329°C. When the battery is destroyed to some extent, the pressure of the system is higher than the original one – the maximum pressure of the crushed one was 51 kgf cm⁻² at about 285°C. This shows that the reactions taking place in the destroyed system is more violent and complete. When the batteries contacted with water, the pressure of the system becomes higher. This shows that some components of the battery may react with water. The pressure of the used bat-

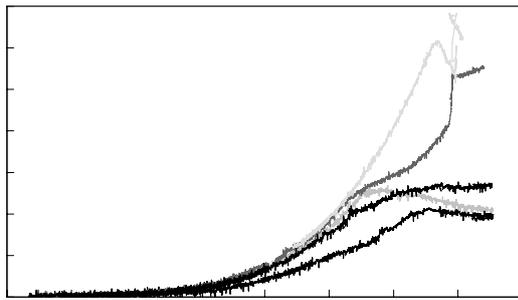


Fig. 2 Pressure vs. temperature curves of the lithium cells and mixture with water in the MCPVT.

tery system was lower than the new one because the active materials, metal lithium, which changes to ion lithium or others, have reduced. In a lithium cell, a manganese dioxide compound is used as the active material for the positive electrode (cathode). Lithium is used for the negative electrode (anode) to produce a cell with high voltage and high energy density. In addition an organic electrolyte is employed to which lithium batteries are added. The discharge reaction is as follows⁸⁾.

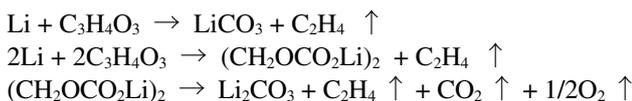
Anode reaction: $\text{Li} \rightarrow \text{Li}^+ + \text{e}^-$

Cathode reaction: $\text{Mn}^{\text{IV}}\text{O}_2 + \text{Li}^+ + \text{e}^- \rightarrow \text{Mn}^{\text{III}}\text{O}_2 (\text{Li}^+)$

Overall battery reaction: $\text{Mn}^{\text{IV}}\text{O}_2 + \text{Li} \rightarrow \text{Mn}^{\text{III}}\text{O}_2 (\text{Li}^+)$

An extreme case in Fig. 2 was that when the crushed cell contacted with water, the pressure increased very rapidly and the maximum pressure was three times as much as that of the lithium cell.

In Fig. 3, when the battery was added into the RPF, compared to the individual lithium cell or RPF, the pressure of the mixture of the cell and RPF did not change much. However, when the three materials - the crushed cell, RPF and water were mixed together, the pressure became the highest among the other samples. The pressure of this sample attained 170 kgf cm⁻² at about 330°C. This implies when disposed cell meets with other waste or water, it would be very dangerous. Thermal activation of chemical reactions introduces a self-heating of the cell which may bring it up to the point of no return thermal runaway. Some reaction paths of lithium cell are considered as the following, in which lithium reacts with solvent when separators leaks:



On the other hand, in the presence of water, some components may react with water and produce hydrogen besides the above reactions:

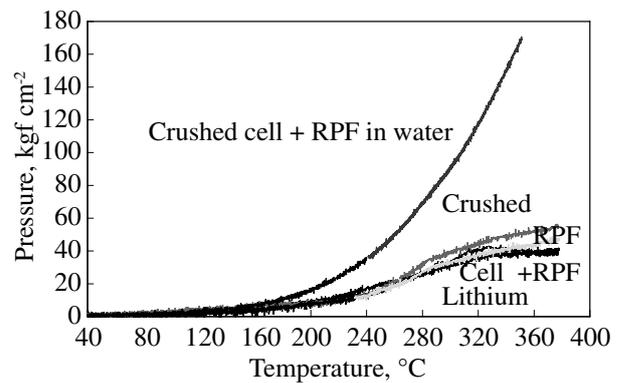
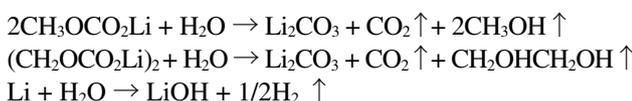


Fig. 3 Pressure vs. temperature curves of the lithium cells mixing with RPF in the MCPVT.

The reaction mechanism of the lithium mixing with RPF is still not so clear. However since both contain combustible components, when they are mixed, the reactions are promoted by each other in the presence of water.

4. Conclusion

Study on the batteries themselves and the safety of the disposed ones should be enhanced, especially when the batteries are mixed into other wastes. As a result, when the battery is cut or crushed to some extent, both heat flow and pressure of the system are higher than the original one. This shows that the reactions taking place in the destroyed system are more violent and complete. When the batteries contact with water, the pressure of the system becomes higher. In this case some components of the battery may react with water. The pressure of the used battery system is lower than the new one because the active materials have reduced.

When crushed lithium batteries are mixed with plastic and paper waste like to RPF, the reaction becomes much more vigorous. The reactivity of lithium cell mixed with other wastes should be also investigated.

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コイン型リチウム一次電池の熱反応性

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コイン型リチウム一次電池の熱反応性について熱量計 (MCPVT, C80) を使って調べた。最近廃棄物処理施設でコイン型リチウム一次電池による事故が多いことからその反応性について廃棄物や水分の存在の影響を調べた。RPFを廃棄物の代表として使った。廃棄物や水の存在でより低温から急激に反応が始まることが明らかになった。

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