Thermal Behavior of Used Alkaline Primary Button Batteries Disposed as General Waste

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***Abstract*—The thermal behavior of new (1.5 V) and used (0 V) primary LR1130 alkaline button batteries was investigated by thermogravimetric differential thermal analysis (TG/DTA). The anode (MnO_2) and cathode (Zn) from the batteries were mixed with paper or plastic (1:1). Cellulose and polyethylene were used to represent paper and plastic, respectively. The thermal behavior of MnO_2, Zn and the separator from both new and used batteries was comparable by TG/DTA using. There was no exo- or endothermic decomposition of Zn and minor exothermic decomposition of MnO_2 from new and used batteries. MnO_2 and Zn were markedly affected by the thermal decomposition of cellulose. However, cellulose mixed with MnO_2 was more of a thermal hazard than when mixed with Zn. Moreover, MnO_2 and Zn from both new and used batteries were also affected considerably by the thermal behavior of polyethylene. Therefore, the accidental disposal of used alkaline button batteries shows high potential to lead to an accident.**

***Index Terms*—LR1130, primary alkaline button battery, thermal characteristics, thermal hazard.**

I. Introduction

A battery consists of one or more electrochemical cells that convert stored chemical energy into electrical energy. A battery contains negative and positive electrode materials, an electrolyte that allows ions to move between the electrodes and terminals that allow current to flow out of the battery to perform work [1]. Batteries operate through the reaction of chemicals contained in the dry cell, such as mercury, manganese, lithium, nickel, cadmium and lead dioxide. If these heavy metals are disposed of in the environment, they could cause ground, water and air pollution and finally enter the food chain and affect humans [2]-[4]. Used batteries should be separated from other waste; however, the behavior of consumers with regards to the disposal of used batteries is poor. Only 7% of batteries are collected and disposed of in designated collecting boxes, while more than 68% are disposed of in normal trash in Thailand [5]. Moreover, 557 battery accidents occurred during 2007–2011 in Japan, with 64 cases involving button batteries [6]. In evaluation of the thermal safety of button batteries, more than 90% of current research has focused on lithium button batteries. Studies have mainly considered the temperature-activated reaction of components in lithium ion cells, such as the positive and negative electrodes and individual electrolytes [7]-[9]. However, research conducted on the thermal safety of used primary alkaline button batteries mixed with other wastes has been limited [10].

In this report, the thermal behavior of used alkaline primary button batteries (LR) mixed with cellulose and polyethylene was investigated by thermogravimetric differential thermal analysis (TG/DTA).

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II. Materials and Methods

A. Materials

Alkaline manganese (LR) batteries (Zn-MnO_2) were purchased from Panasonic. Polyethylene and cellulose (98.0%) were obtained from Tokyo Chemical Industry Co., Ltd.

B. Composition

The composition of the negative (anode) and positive electrode (cathode) materials and electrolyte of new and used mercury-free LR1130 batteries was measured. The structure of a LR1130 battery is shown in Fig. 1.

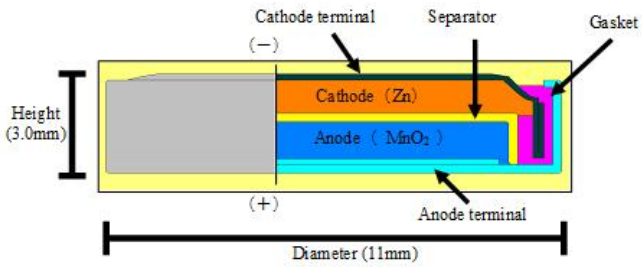

Fig. 1. Structure of LR1130.

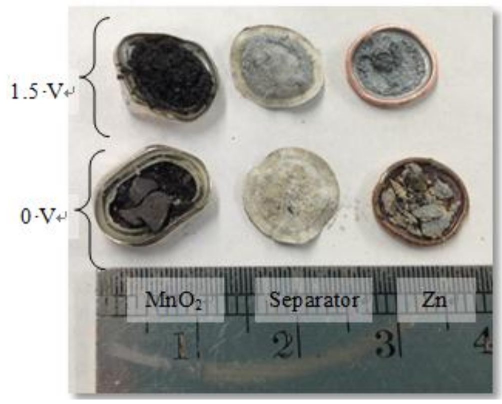

Fig. 2. The removed each internal components of LR1130.

C. Thermal Decomposition

A TG/DTA system (6200 SII Nanotechnology) was used to examine the thermal reactivity of LR1130 primary button batteries. The thermal decomposition of new (1.5 V) and used (0 V) LR1130 batteries was investigated. TG/DTA was

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carried out in a stainless steel cell at a heating rate of 10 K min^{-1} from 30 to 600 ℃ under steady-state air flow using an almost constant sample mass of 1.0 mg.

MnO_2 and Zn from each battery were mixed with paper or plastic with a weight ratio of 1:1 using cellulose and polyethylene to represent paper and plastic, respectively. Fig. 2 shows the MnO_2, Zn and separator that were removed from the new and used LR1130 batteries.

III. Results and Discussion

A. Composition of a Used Hg-Free Button Battery

Fig. 3 shows the mass percentages of components in the LR1130 batteries. The main component of both the new and used batteries is Fe present in the gasket, cathode and anode terminal, and is around 56 wt%. The mass of MnO_2 (anode) in the new battery is 25.5 wt%, while that in the used is 28.8 wt%. Zn (cathode) is 7 wt% of both the new and used batteries. The content of the separator decreased after use. This is because the organic solvent contained in the separator was used to move ions between the electrodes and terminals. When the voltage of LR1130 became 0 V, the H_2O inside the separator was completely used for the current flowing out of the battery process.

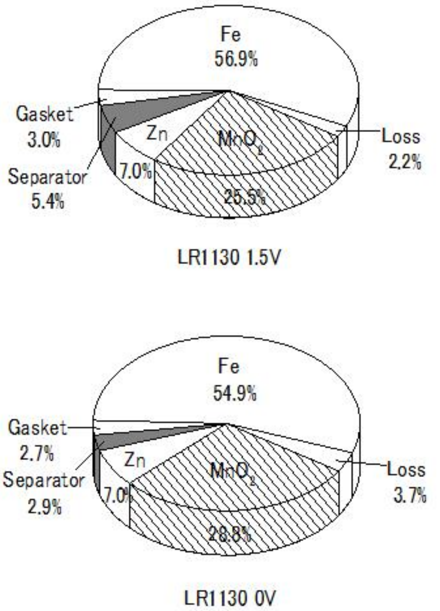

Fig. 3. Compositions of new and used Hg-free LR1130 button batteries.

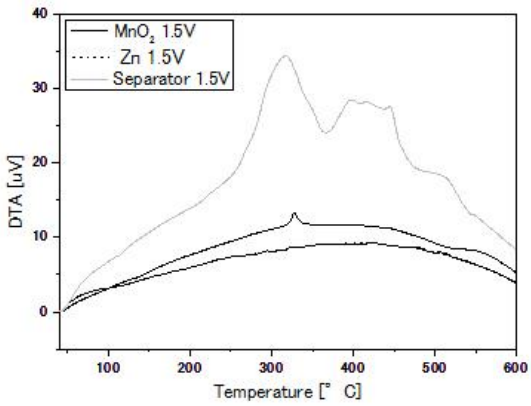

Fig. 4. TG/DTA curves obtained for MnO_2, Zn and the separator of a new battery.

TABLE I: Results of TG/DTA

Sample	Step	Thermal Effect	Temperature [℃]
MnO_2 (1.5 V)	1	Exothermic	315–345
MnO_2 (0 V)	1	Exothermic	310–350
Zn (1.5 V)	N.D.	N.D.	N.D.
Zn (0 V)	N.D.	N.D.	N.D.
Separator (1.5 V)	1 2 3	Exothermic Exothermic Exothermic	250–360 360–470 470–550
Separator (0 V)	1 2 3	Exothermic Exothermic Exothermic	270–370 400–460 460–540
Cellulose	1 2 3	Endothermic Exothermic Exothermic	270–330 345–400 420–565
Cellulose + MnO_2 (1.5 V)	1	Exothermic	275–400
Cellulose + MnO_2 (0 V)	1	Exothermic	275–400
Cellulose + Zn (1.5 V)	1	Exothermic	260–400
Cellulose + Zn (0 V)	1	Exothermic	260–440
Cellulose + MnO_2+Zn (1.5 V)	1 2	Exothermic Exothermic	230–380 380–500
Cellulose + MnO_2+Zn (0 V)	1 2	Exothermic Exothermic	230–380 380–480
Polyethylene	1 2	Endothermic Exothermic	110–150 200–330
Polyethylene + MnO_2 (1.5 V)	1 2 3 4	Endothermic Exothermic Exothermic Exothermic	110–150 210–260 260–400 400–500
Polyethylene + MnO_2 (0 V)	1 2 3 4	Endothermic Exothermic Exothermic Exothermic	110–150 210–260 260–410 410–480
Polyethylene + Zn (1.5 V)	1 2 3 4 5 6 7	Endothermic Exothermic Exothermic Exothermic Exothermic Exothermic Exothermic	110–150 200–300 300–400 400–440 440–470 470–510 510–550
Polyethylene + Zn (0 V)	1 2 3 4 5 6 7	Endothermic Exothermic Exothermic Exothermic Exothermic Exothermic Exothermic	110–150 200–270 270–380 380–430 430–450 450–470 470–505
Polyethylene+ MnO_2+Zn (1.5 V)	1 2 3 4	Endothermic Exothermic Exothermic Exothermic	110–150 200–260 260–400 400–500
Polyethylene+ MnO_2+Zn (0 V)	1 2 3 4	Endothermic Exothermic Exothermic Exothermic	110–150 200–260 260–400 400–480

B. Thermal Behavior

A used mercury-free LR1130 battery was selected to investigate the thermal behavior of a used primary button battery mixed with paper or plastic. This section is divided into three parts. In part 1, the thermal behavior of the anode (MnO_2), cathode (Zn) and separator of new and used batteries is studied. In part 2, the thermal behavior of MnO_2, Zn and the separator of new and used batteries mixed with cellulose is assessed. In part 3, the thermal behavior of MnO_2, Zn and the separator of new and used batteries mixed with polyethylene is examined. The TG/DTA results are summarized in Table I.

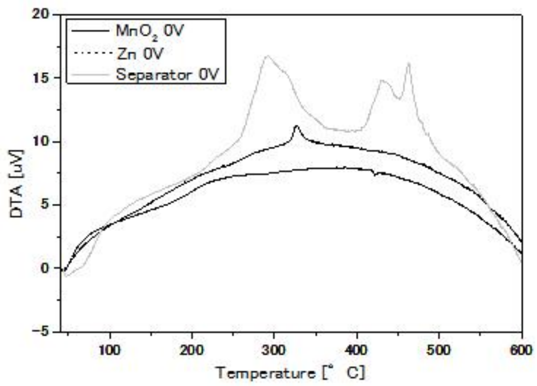

Fig. 5. TG/DTA curves of MnO_2, Zn and the separator of a used battery.

Part 1: Thermal behavior of MnO_2, Zn and the separator of new and used batteries

Fig. 4 and Fig. 5 show the TG/DTA results obtained for MnO_2, Zn and the separator of new and used LR1130 batteries, respectively. From 30–600 ℃ in air, there was no exo- or endothermic decomposition of Zn. In the case of MnO_2, exothermic decomposition only occurred between 310 and 350 ℃ in both the new and used batteries; however, both peaks were very small. The separator showed three similar exothermic peaks for both the new and used batteries. The first peak was between 250 and 310 ℃, the second was between 350 and 470 ℃, and the third between 470 and 550 ℃. The third peak observed for the separator of the used battery was sharper than that of the new one.

Overall, the thermal behavior of MnO_2, Zn and the separator of both the new and used batteries was comparable.

Part 2: Thermal behavior of MnO_2, Zn and separators mixed with cellulose.

1) Thermal behavior of binary mixtures of MnO_2 from new and used batteries with cellulose

Fig. 6 shows the TG/DTA curves obtained for pure MnO_2 from new and used batteries mixed with cellulose. Both mixtures showed a sharp exothermic decomposition peak between 375 and 400 ℃. However, compared with the original TG/DTA curves of MnO_2 (see Fig. 4 and Fig. 5), which had a very small exothermic peak between 315 and 350 ℃ from MnO_2, in the case of the mixtures with cellulose, an endothermic peak was present between 270 and 330 ℃ along with two exothermic peaks. The first exothermic peak of cellulose appeared between 345 and 400 ℃, and the second between 420 and 565 ℃. The second exothermic decomposition peak of cellulose disappeared when it mixed with MnO_2 from both new and used batteries and the first decomposition peak of cellulose between 345 and 400 ℃ was shifted to lower temperature by approximately 100 ℃.

Consequently, the thermal behavior of both MnO_2 and cellulose changed to become more hazardous upon binary mixing.

2) Thermal behavior of binary mixtures of Zn from new and used batteries with cellulose

Fig. 7 shows the TG/DTA curves of pure Zn from new and used batteries with cellulose. A broad exothermic decomposition peak was observed between 260 and 400 ℃ in both cases. This result is similar to that obtained by mixing cellulose with MnO_2, in which the endothermic decomposition peak of cellulose disappeared. Furthermore, the first decomposition peak of cellulose between 345 and 400 ℃ was shifted to lower temperature.

The thermal behavior of the mixture of cellulose and Zn differed from that of Zn or cellulose alone and showed greater thermal hazard. Cellulose mixed with MnO_2 show a sharper exothermic peak than when mixed with Zn.

3) Thermal behavior of ternary mixtures of MnO_2 + Zn + cellulose

Fig. 8 shows TG/DTA curves of cellulose and cellulose + MnO_2 + Zn mixtures using materials from new and used batteries. The endothermic peak of cellulose disappeared in the mixtures. This result is similar to those observed for cellulose + MnO_2 and cellulose + Zn mixtures from new and used batteries. Moreover, comparing the first and second exothermic peaks of cellulose with those of the mixtures of MnO_2 + Zn + cellulose, the first and second peak were shifted to lower temperature by approximately 100 ℃. These results are similar to the case of cellulose mixed with only MnO_2 or Zn from new and used batteries.

These results indicate that both MnO_2 and Zn were markedly affected by the thermal decomposition of cellulose when they were mixed with it. The thermal behavior of MnO_2 was affected more greatly than that of Zn.

Part 3: Thermal behavior of MnO_2, Zn and separators mixed with polyethylene

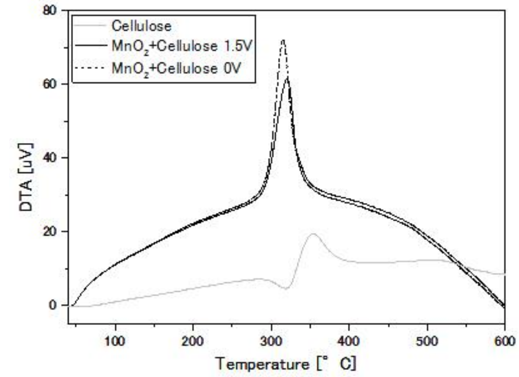

Fig. 6. TG/DTA curves of MnO_2 from new and used batteries with cellulose.

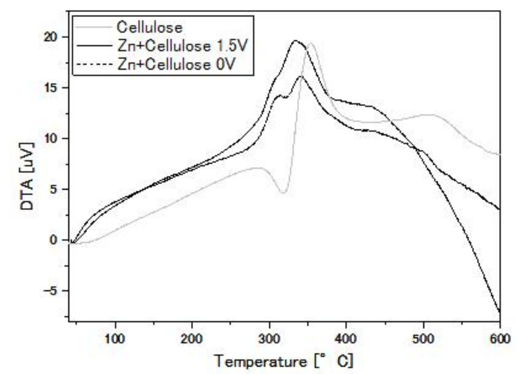

Fig. 7. TG/DTA curves of Zn from new and used batteries with cellulose.

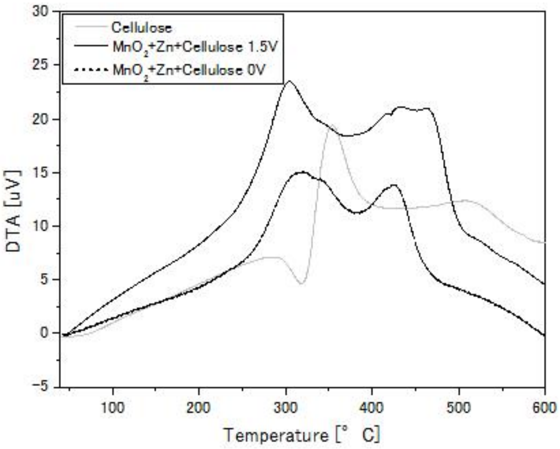

Fig. 8. TG/DTA curves of cellulose and cellulose + MnO_2 + Zn mixtures from new and used batteries.

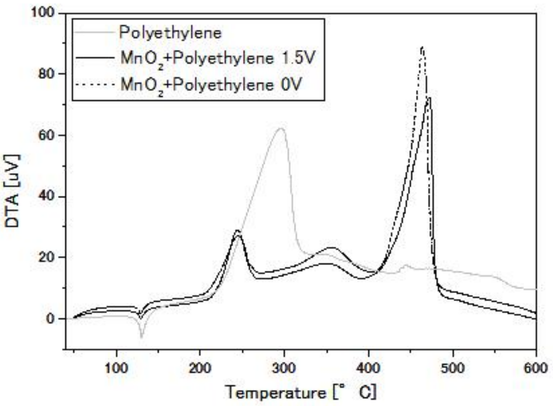

Fig. 9. TG/DTA curves of MnO_2 from new and used batteries mixed with polyethylene.

1) Thermal behavior of binary mixtures of MnO_2 from new and used batteries with polyethylene

Fig. 9 shows TG/DTA curves of pure MnO_2 from new and used batteries with polyethylene. An endothermic peak between 110 and 150 ℃ and three exothermic peaks with the first between 210 and 260 ℃, the second between 260 and 400 ℃, and the third between 400 and 500 ℃, were observed. Not all of these exothermic peaks were observed in the case of MnO_2 and polyethylene alone. Therefore, mixing polyethylene with MnO_2 caused these extra peaks to appear.

2) Thermal behavior of binary mixtures of Zn from new and used batteries with polyethylene

Fig. 10 shows the TG/DTA curves of pure Zn from new and used batteries mixed with polyethylene. There was a sharp exothermic decomposition peak between 470 and 505 ℃. However, this sharp exothermic peak was not seen in the case of Zn or polyethylene alone. An endothermic peak of cellulose remained when it was mixed with Zn from both new and used batteries, similar to the results observed for MnO_2 + polyethylene.

Even though a new exothermic peak was observed for both MnO_2 + polyethylene and Zn + polyethylene mixtures, a sharp exothermic peak was only found in the case of the Zn + polyethylene mixture.

3) Thermal behavior of ternary mixtures of polyethylene + MnO_2 + Zn from new and used batteries

Fig. 11 depicts the TG/DTA curves of polyethylene and polyethylene + MnO_2 + Zn mixtures from new and used batteries. Polyethylene exhibited an endothermic peak between 110 and 150 ℃ and exothermic peak between 200 and 260 ℃. In the case of the ternary mixtures of polyethylene + MnO_2 +Zn from new and used batteries, an endothermic peak from polyethylene was also observed. Moreover, compared with the TG/DTA curve polyethylene alone, the first exothermic peak of polyethylene + MnO_2 +Zn was much smaller in both mixtures. The second peak between 400 and 480 ℃ in the case of the mixtures was a new exothermic peak. These results were similar to those of polyethylene when it was mixed with MnO_2 or Zn from new and used batteries. Therefore, MnO_2 and especially Zn were markedly affected by the thermal behavior of polyethylene.

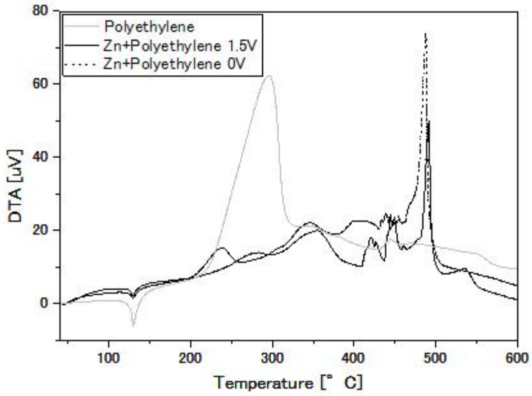

Fig. 10. TG/DTA curves of Zn from new and used batteries with polyethylene.

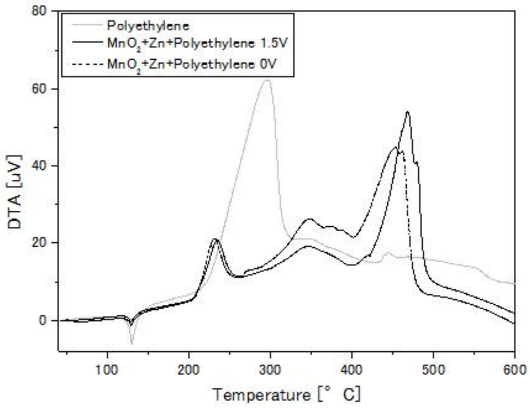

Fig. 11. TG/DTA curves of polyethylene and polyethylene + MnO_2 + Zn mixtures from new and used batteries.

IV. CONCLUSIONS

In this work, the thermal behavior of new and used primary alkaline cells (LR batteries) mixed with paper and plastic were investigated by TG/DTA. The thermal behavior of MnO_2 and especially Zn from new and used batteries was greatly affected by the thermal decomposition of cellulose. Moreover, MnO_2 or Zn alone from both new and used batteries affected the thermal behavior of cellulose more than a mixture of both MnO_2 and Zn. Likewise, new or used MnO_2 or Zn alone influenced the thermal behavior of polyethylene more than a mixture of MnO_2 and Zn. Therefore, the accidental disposal of used alkaline button battery batteries in general waste could lead to an accident.

REFERENCES

[1] G. Hambitzer, K. Pinkwart, C. Ripp, and C. Schiller, "Thermodynamics and Mechanistics," in *Handbook of Battery Materials*, J. O. Besenhatd Ed. Wiley-VCH, 1999. pp 1-17.

[2] J. Pichtel, K. Kuroiwa, and H. T. Sawyerr, “Distribution of Pb, Cd and Ba in soils and plants of two contaminated sites,” *Environmental Pollution*, vol. 100, no. 1, pp. 171-178, 2000.

[3] W. D. Di Marzio, M. Saenz, J. Alberdi, M. Tortorelli, and G. Silvana. “Risk assessment of domestic and industrial effluents unloaded into a freshwater environment,” *Ecotoxicology and Environmental Safety*, vol. 61, no. 3, pp. 380-391, 2005.

[4] R. Parthiban, R. Senthilkumar, and L. Parthiban, “Biosorption of lead with Turbinaria conoides and neuro-fuzzy modelling,” *International Journal of Environmental Sciences*, vol. 1, no. 7, pp. 2037-2047, 2011.

[5] S. Wisitthachaichan. Title of subordinate document in: Consumer Insight. Positioningmag. [Online]. Available: http://www.positioningmag.com/magazine/details.aspx?id=92688.

[6] Product safety center, *To prevent an accident caused by batteries*, Japan National Institute of Technology and Evaluation, 2012

[7] B. K. Mandal, A. K. Padhi, Z. Shi, S. Chakraborty, and R. Filler “Thermal runaway inhibitors for lithium battery electrolytes,” *J. of Power Sources*, vol. 161, no. 2, pp. 1341-1345, 2006.

[8] H. Maleki, G. Deng, A. Anani, and J. Howard, “Thermal stability studies of Li-ion cells and components articles,” *Journal of the Electrochemical Society*, vol. 146, no. 9, pp. 3224-3229, 1999.

[9] H. Yang, H. Bang, K. Amine, and J. Prakasha, “Investigations of the exothermic reactions of natural graphite anode for Li-ion batteries during thermal runaway,” *Journal of the Electrochemical Society*, vol. 152, no. 1, pp. A73-79, 2005.

[10] W. S. Lim, S. R. Li, X. L. Wand, H. Koseki, and O. Hashimoto, “Thermal reactivity of primary lithium coin-cell batteries,” *Science and Technology of Energetic Materials*, vol. 68, no. 4, pp. 120-123, 2007.

Wasana Kowhakul has received her Ph.D. in safety engineering from the University of Tokyo, Japan, 2005. Currently she is an assistant professor at the Department of Chemical Engineering, University of Fukuoka, Fukuoka, Japan. Her research interests are reactive chemical/process safety engineering and dust explosions.