

A consideration of lithium cell safety

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Abstract

The safety characteristics of commercial lithium ion cells are examined in relation to their use as batteries for cellular phones. This report describes a theoretical approach to an understanding of cell safety, example results of safety tests that we performed on lithium ion cells, and also presents our views regarding cell safety. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Lithium ion cells are widely used for cellular phones because of their high energy density. These cells are manufactured by several companies, however, their safety characteristics vary. It is extremely important that the cell user evaluate the safety of such cells before their equipment is marketed. The most important consideration is to ensure that no one using portable equipment is injured should cell trouble occur. To this end, our safety standard makes it unacceptable for a cell to smoke, catch fire or explode during abuse tests replicating potential practical applications.

This report describes how we evaluate the safety of lithium ion cells before practical use and outlines our view regarding their safety. We carried out the safety tests described in this report on commercially available cells. We do not, however, provide detailed information regarding the type of cell or the name of the manufacturer as it would be inappropriate in this context.

2. Basic consideration on cell safety

Lithium ion cells may smoke when abused and can ignite when the abuse is extreme. Thermal stability is a basic problem as regards cell safety. Several exothermic reactions occur inside a cell as its temperature increases. It is generally considered that ‘thermal runaway’ occurs if

heat output exceeds thermal diffusion. The possible exothermic reactions are; (1) the chemical reduction of the electrolyte by the anode, (2) the thermal decomposition of the electrolyte, (3) the oxidation of the electrolyte on the cathode, (4) the thermal decomposition of the anode, and (5) the thermal decomposition of the cathode [1–5]. In this final case, a high voltage metal oxide cathode releases oxygen at elevated temperatures. It should also be noted that, when a separator melts as a result of the temperature exceeding its melting point ($\sim 125^{\circ}\text{C}$ for polyethylene and $\sim 155^{\circ}\text{C}$ for polypropylene), this frequently triggers a large heat output induced by an internal short.

First, we consider the mechanism causing a cell to ignite. Generally, combustion is defined as resulting from a reaction which causes materials to generate heat and light. This reaction is usually oxidation and sometimes halogenation. Fire can be seen if a material is heated to a high temperature and as a result the thermal radiation wave becomes visible. Therefore, a fire is caused by an exothermic reaction which provides a sufficient increase in the temperature of the materials. For combustion to continue, the heat generation and dissipation rates must be equal, as shown in Fig. 1. The expression ‘thermal runaway’ is often used to describe the situation when cells catch fire, however, the expression is unsuitable. If T is higher than T_1 , the materials catch fire. T_1 is called the ignition point, and T_2 the fire point. Therefore, the ignition and fire points are not physical values of the materials but depend on conditions around the materials. A good method for preventing this unsafe situation is to increase T_1 in one of the following two ways: (I) reduce the heat generation rate, or (II) increase the heat dissipation rate. Heat is generated

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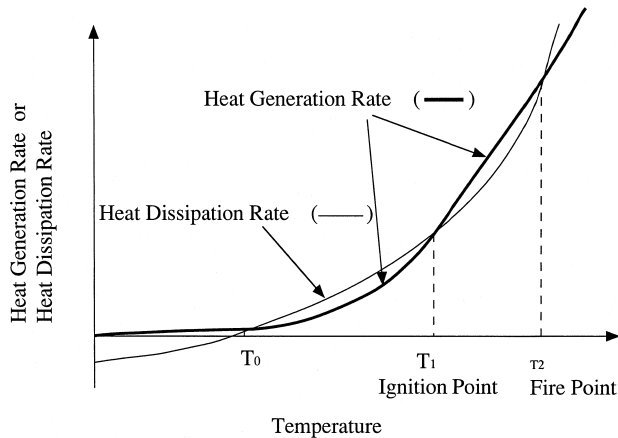


Fig. 1. The balance between heat generation and dissipation rates which describes combustion.

in a cell by the thermal decomposition and/or reaction of materials in the cell. The heat dissipation rate depends strongly on the size and shape of the cell.

3. Abuse tests

Examples of the types of abuse test we use are shown in Table 1. These were established by referring to and modifying the four safety guidelines already published by other organizations. That is, (1) a guideline for the safety evaluation of primary lithium cells for auto-focus cameras (Japan Battery and Appliance Industries Association, 1991), (2) a safety standard for lithium batteries, UL 1642 (Underwriters Laboratories, third edition: 1995), (3) outline of investigation for Household and Commercial Batteries, SU 2054 (Underwriters Laboratories, 1993), and (4) a guideline for the safety evaluation of secondary lithium cells (Japan Battery Association, 1997).

Table 1
Examples of abuse tests

Test items	
Electrical abuse tests	Overcharging
	Forced discharge
	External short circuit
	Abnormal voltage charging
	Abnormal current charging
Mechanical abuse tests	Nail penetration (internal short)
	Crush
	Drop
	Vibration
	Pressure
	Vacuum
Thermal abuse tests	Heating
	High and low temperature cycling
	Fire exposure
	Hot plate
	Oil bath

When cell safety is evaluated, the abuse tests are undertaken on fresh and cycled cells, and on fresh and cycled battery packs, which are handled under the standard cycling conditions specified for their use in each type of portable equipment and its corresponding charger. They are cycled in the middle and at the very end of their cycle lives. The abuse tests are performed on cells and battery packs in which one controlling device is broken and the first protective device works. There are such protective devices in cells, battery packs and chargers. They include a positive temperature coefficient of resistance (thermal and current fuse, PTC), a safety pressure-release vent (safety vent), a thermal fuse, a current fuse, and an electronic circuit for protection against overcharging or a forced discharge. When the safety is reduced after cycling, a more careful investigation is necessary and other tests must be performed.

Below, we provide examples of important abuse tests results.

4. Abuse test results

Before undertaking the abuse tests, we determined the discharge capacity of the cell from the discharge to 3.0 V at a 1 C rate. The cell was charged galvanostatically at a rate of 0.5 C to the voltage recommended by the manufacturers (e.g., 4.13 V), followed by constant voltage charging for 5 h. The cell operation temperature was 21°C unless noted.

4.1. Overcharging

Cells may be overcharged when the cell voltage is incorrectly detected by the charging control system, or when the charger breaks down, or when the wrong charger is used.

Cylindrical cells usually have a current-cut device inside the cell which is generally a thin metal sheet placed between the positive terminal and the jelly roll, and which is operated by an internal pressure build-up. When the cell

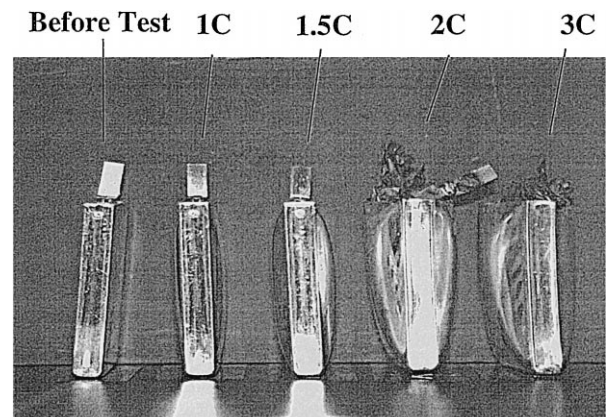


Fig. 2. Prismatic cell with aluminum cell can in overcharging test (10 V).

is overcharged, the current-cut device works just after the electrolyte decomposition starts and the cell temperature rapidly increases. The cell neither smokes nor catches fire, and the cell temperature gradually decreases after the current is cut.

Recently, the cell can of prismatic cells was changed from iron-based materials to aluminum to reduce the cell weight and increase the energy density. Many of these prismatic cells with aluminum cans have no current cut device inside them. A PTC is installed outside the cells. In addition, it is difficult to optimize the safety vent operation because the aluminum is a soft material and deforms easily. The overcharging tests were performed galvanostatically on prismatic cells without a PTC at 1 C, 1.5 C, 2 C and 3 C, and a compliance voltage of 10 V. Fig. 2 shows photographs of an overcharged cell. At 1 C and 1.5 C, the cells swelled but the safety vent did not open or smoke. However, cells overcharged by more than 2 C caught fire after the rapid cell temperature increase caused by electrolyte decomposition. Fig. 3 shows an example of an overcharging test at a charge rate of 2 C for a prismatic cell with an aluminum can. The standard capacity of these test cells is 600 mA h. When the cells are overcharged, the lithium ions remaining in the cathode are removed at approximately 4.5 V and more lithium ions are inserted in the carbon than under standard charging conditions. At this stage, no distinct heat output is observed. If the lithium insertion ability of the carbon anode is small, lithium metal

may be deposited on the carbon, and this causes a drastic reduction in thermal stability. After lithium is removed from the cathode, the electrolyte starts to oxidize since the oxidation potential of the electrolyte is approximately 0.2 V higher than that for complete lithium removal from the cathode. This electrolyte oxidation exhibits a distinct heat output. As the overcharge current increases, the heat output increases greatly because the joule heat output is proportional to i^2R (i :current, R :resistance). At an overcharge of 2 C, the safety vent and the anode cap housing, which is ultrasonically welded, opened simultaneously. This means that the safety vent does not work appropriately and easily explodes. Therefore, since the cell itself cannot withstand overcharging, the practical battery pack and/or charger have a protection system such as mechanical and electronic devices to protect high current and voltage. This system works even if inappropriate chargers, such as those for nickel metal hydride cells or unauthorized poor quality chargers are used.

4.2. Heating test

A heating test to ascertain the thermal stability of a cell is one of the fundamental abuse tests for a rechargeable battery system. Here, no protection is afforded by an electronic device. In the heating tests described by UL-1642, SU-2054 and by the guideline for primary lithium cells for auto-focus cameras, the heating temperatures are

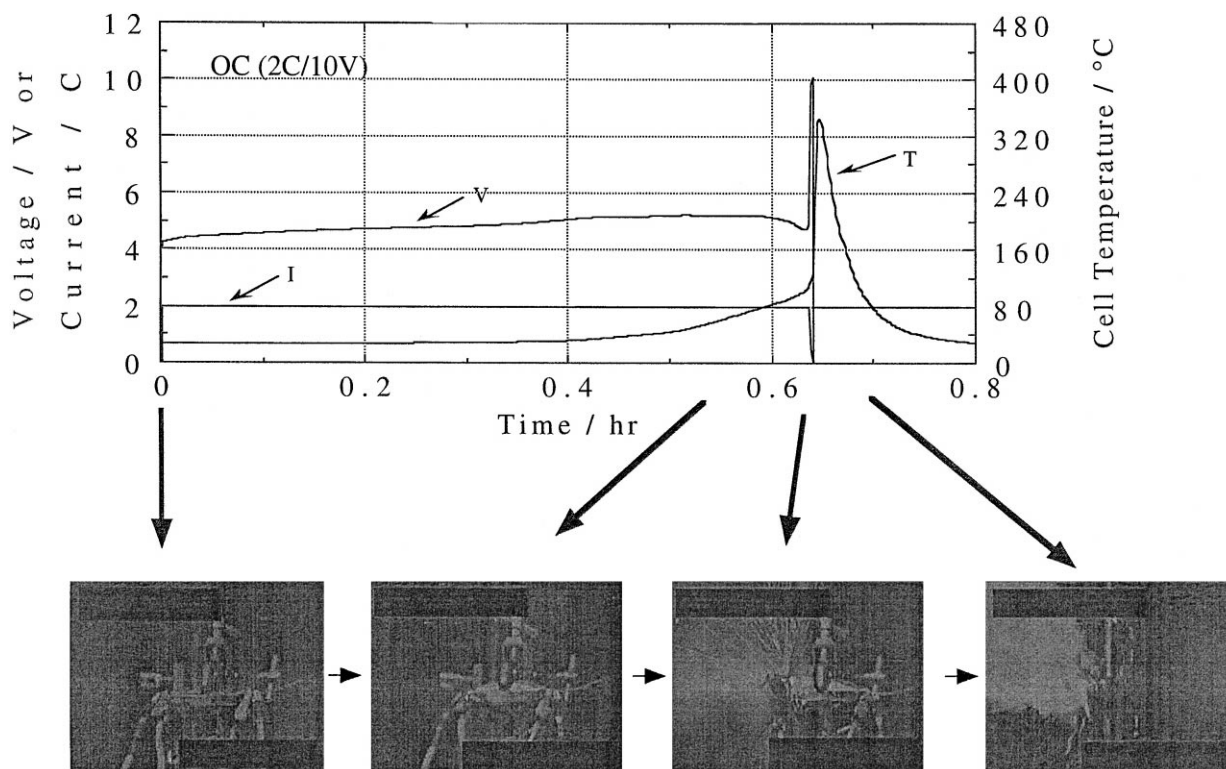


Fig. 3. Overcharging test for prismatic cell with aluminum cell can (2 C rate, 10 V).

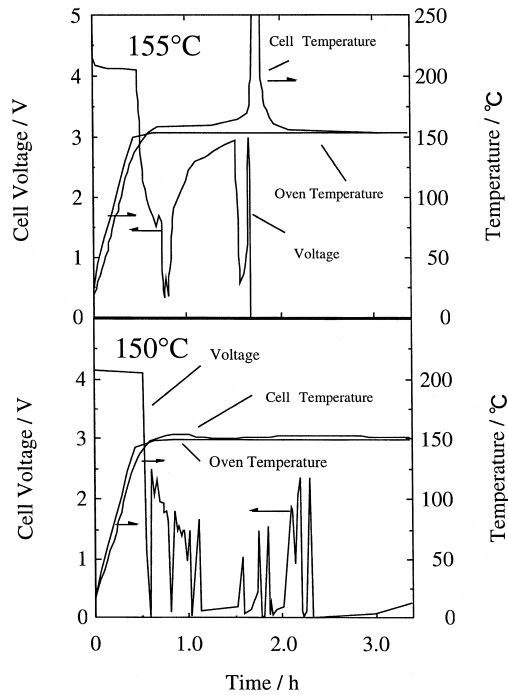


Fig. 4. Heating test results for cylindrical cells.

150°C and 165°C, respectively, and held for 10 min, followed by a temperature increase rate of 5°C/min. from room temperature. In the heating test reported in the guideline for secondary lithium cells, the heating condition is 130°C for 1 h. However, in our heating test, the heating temperature is varied in 5°C steps, and these constant temperatures are held until the cell temperature starts to decrease (a minimum of 30 min). The highest temperature at which the cell does not smoke is determined as the thermal stability limit of the cell. It is very useful to compare the thermal stability limit of different cells. For many commercially available uncycled lithium ion cells, this limit is not lower than 150°C.

Fig. 4 shows examples of heating tests on commercial cylindrical lithium ion cells at 150°C and 155°C, respectively. The cells whose results are shown in Fig. 1 were the same size and made by the same manufacturer. The cells were charged under standard charging conditions and their capacity was 1270 mA h. The cells did not smoke at 150°C but smoked at 155°C. Therefore, we determined the thermal stability limit of these cells to be 150°C. A more careful investigation is necessary when the thermal stability is reduced after cycling.

4.3. Nail penetration

The nail penetration test is very important and is considered to simulate an internal short in a cell. Many actual accidents have occurred involving commercial lithium primary and secondary cells as the result of an internal short. Such internal shorts may be caused by a manufacturing

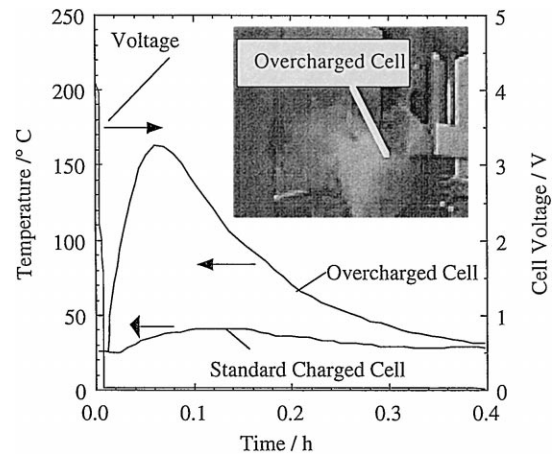


Fig. 5. Nail penetration test result on prismatic cells, overcharged cell is charged 0.03 V higher charge voltage than standard charge voltage.

defect such as a small conductive particle wound in the jelly roll, a wrinkle in the separator, or the poor alignment of a winding. No electronic device can protect against an internal short, therefore, the cell itself should pass this test. When the anode stability decreases, it is possible that the cell may smoke, and lithium insertion, reduces anode stability. In addition, lithium metal deposition on the carbon causes the instability of anodes may be deposited on the carbon. With an increase in cycle numbers with a high rate charge–discharge, or a low temperature charge, or after an extreme overcharge, or a capacity imbalance in anode to cathode (or carbon to lithium) ratio, there is the possibility with some cells of lithium metal deposition on the carbon anode. Furthermore, when the cell is overcharged, the stability of the cathode and electrolyte are reduced.

Fig. 5 shows the results of a nail penetration test in which a 2.5 mm diameter nail was used on commercially available prismatic cells. The cell capacity charged at the standard charge voltage was 835 mA h and that charged at 0.03 V higher than the standard voltage was 863 mA h. The overcharged cell smoked as a result of nail penetration, while cells charged at the standard voltage did not smoke. The stability of this cell is sensitive to overcharging and so the charge voltage should be precisely controlled in this case. Moreover, there must be careful quality

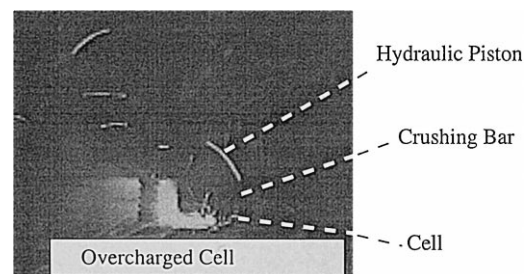


Fig. 6. Crush test result for a 200% overcharged cylindrical cell.

control as regards the anode to cathode ratio during mass production to avoid overcharging.

4.4. Crush

The cell should also be able to survive a crush test because no electronic device can provide protection in this case either. In the UL standard and the safety guideline for lithium secondary cells, the crush test is carried out with a flat plate. However, we recommend a crush test which uses a 10 mm diameter bar. This is a harder test to pass, and the cell is crushed to less than half its original thickness of the cell. Fig. 6 shows a fire caused by a crush test on a commercial cylindrical cell. The nominal capacity of the cell was 720 mA h. Before the crush test, the cell was precharged at a constant 5 V after being precycled 800 times under the standard cycling condition mentioned at the beginning of Section 4. The charge capacity of this overcharged cell was 200% that of a standard-charged cell. The standard-charged cell did not smoke in this crush test. With this overcharging, lithium metal is deposited in fine particles on the anode of this cylindrical cell.

5. Conclusion

The practical use of lithium ion cells is now possible with the help of protective electronic circuits and devices to compensate for their low thermal stability and poor tolerance to overcharging. By making improvements to both the cells and the protection methods to ensure enhanced safety, large practical cells will be realized for electric vehicles and electric power load leveling systems in the near future.

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