

Lithium ion cell safety

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Abstract

The safety characteristics of recent commercial lithium ion cells are examined in relation to their use for cellular phones. These are prismatic cells with an aluminum cell housing (can) and a 500–600 mA h capacity. They have one of two types of 4-V class cathodes, lithium cobalt oxide (LiCoO₂) or lithium manganese oxide (LiMn₂O₄). This report provides results of the safety tests that we performed on lithium ion cells and outlines our views regarding their safety. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Lithium ion cells are widely used for cellular phones and personal computers (PC) because of their high voltage and high-energy density. In 1998, approximately 300 million units of such cells were sold. However, the safety margin of these cells is still small for practical use [1]. Several accidents involving lithium ion cells have been reported in newspapers and via the Internet. In 1996, a battery pack consisting of two series 18650 type cylindrical lithium ion cells for cellular phone use exploded when they were crushed by a bus. Also in 1996, a PC battery pack ignited during an extremely high voltage charge (over 10 V) by poor quality charger prior to its commercialization. In 1997, a battery pack containing lithium ion cells with gel-electrolyte for a notebook PC burned, supposedly as a result of a short in the battery. PC battery packs consisting of two series and three parallel 18650 type cells were recalled in 1998 because of the possibility of temperature increase leading to an explosion as a result of electronic circuit shorting induced by electrolyte leakage from the cells.

It is extremely important that cell manufacturers evaluate the safety of such cells before their equipment is

marketed. The most important consideration is to ensure that no portable equipment consumer is injured, even if cell trouble occurs. To this end, our safety standards make it unacceptable for a cell to emit smoke, catch fire or explode during abuse tests that replicate potential practical applications.

In a previous report [1], we described how we evaluate the safety of lithium ion cells before practical use. As a result, we found that the safety margin of lithium ion cells is small for their practical use. Cell safety must be ensured by installing an electronic protection circuit even if the battery pack employs only one cell. The battery pack safety is determined by the total effect of the electrodes, electrolyte and separator materials of the cells, the cell structure and the protection systems. We think that the best way at present to evaluate the cell safety is to carry out the abuse tests on the bare cells without protection systems. The abuse tests on the cells are not an academic approach. However, we believe that these results provide very valuable information. This report provides the results of safety tests on prismatic cells that were recently developed for cellular phones. These cells have an aluminum cell housing (can) and a capacity of 500–600 mA h. They use one of two types of 4-V class cathodes, lithium cobalt oxide (LiCoO₂) or lithium manganese oxide (LiMn₂O₄). They have liquid organic electrolytes and carbon anodes. We carried out the safety tests on commercially available cells. We do not, however, provide detailed information regard-

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ing the type of cell or the name of the manufacturer as it would be inappropriate in this context.

2. Current status of lithium ion cells for cellular phones in Japan

The cellular phones recently developed by NTT DoCoMo of Japan normally employ battery packs consisting of one prismatic lithium ion cell with an average discharge voltage of 3.6 or 3.7 V, an electronic protection circuit and device, and a plastic battery case, because these phones have an operating voltage of 3.0–3.2 V. The battery pack structure is shown in Fig. 1. The required capacity is 500–600 mA h, which allows the cellular phone to operate for 300 h in a waiting mode or for 2 h in talking mode. Consumer demand has meant that the weight of the lithium ion cells has been decreasing year by year. The first step in the weight reduction process was to change the cell housing from iron-based material to aluminum followed by attempts to reduce its thickness. For example, in 1998, 580 mA h cells with an outer thickness of 6.2-mm cell for use in cellular phones achieved an energy density of 121 W h/kg (264 W h/l) with an aluminum housing thickness of 0.30 mm compared with a value of 110 W h/kg (240 W h/l) for a cell with a 0.45-mm thick housing.

3. Basic cell safety considerations

Lithium ion cells may emit smoke when abused and can ignite when the abuse is extreme, which makes thermal stability a basic problem as regards cell safety. Several exothermic reactions occur inside a cell as its temperature increases. Many factors can be possible triggers of cell heating: external shorts, dropping or crushing the cells and cell internal shorts. 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, (5) the thermal decomposition of binder for coated electrodes, and (6) the thermal decomposition of the cathode [2–7]. 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.

4. Abuse tests and results

Our previous abuse test results [1] showed that the safety margin of the lithium ion cells was still small for their practical use and that they had two fundamental weak points: (1) they have insufficient tolerance to overcharging and (2) poor thermal stability. When overcharging and heating occur simultaneously, cell safety is drastically reduced.

In this study, we carried out abuse tests on aluminum-cased prismatic cells with a 500–600 mA h capacity designed for cellular phone use, and compared the difference between LiCoO_2 and LiMn_2O_4 as cathode materials with special attention to heating and overcharging. Before undertaking the abuse tests, we determined the discharge capacity of the cell from its discharge to 3.0 V at a 1C rate (approximately 600 mA). The cell was charged galvanostatically at a rate of 0.5C (approximately 300 mA) 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 otherwise noted.

4.1. 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 “A safety standard for lithium batteries” (UL-1642, Underwriters Laboratories, 3rd edn., 1995), and “A guideline for the safety evaluation of primary lithium cells for auto-focus cameras” (Japan Battery and Appliance Industries Association, 1991), the heating temperatures are 150°C and 165°C , respectively, and held for 10 min, followed by a temperature increase rate of $5^\circ\text{C}/\text{min}$ from room temperature. In the heating test reported in “A guideline for the safety evaluation of secondary lithium cells” (Japan Battery Association, 1997), the heating condition is 130°C for 1 h. The heating tests must be carried out at a temperature higher than the melting point of the separator to induce an internal short in the cell, namely a direct reaction between the cathode and anode. In our heating test, the heating temperature is changed in 5°C steps, and these constant temperatures are held until the cell temperature starts to

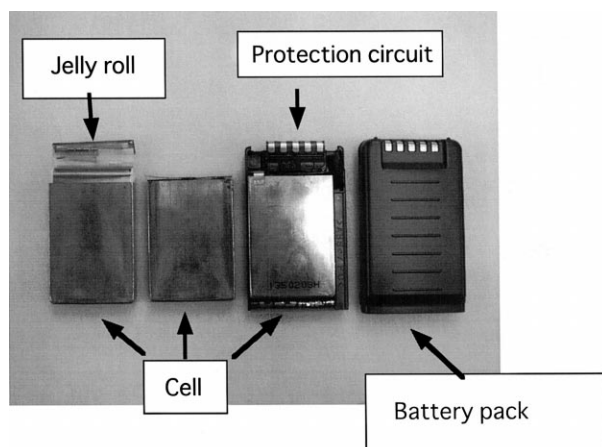


Fig. 1. Structure of a battery pack for cellular phones.

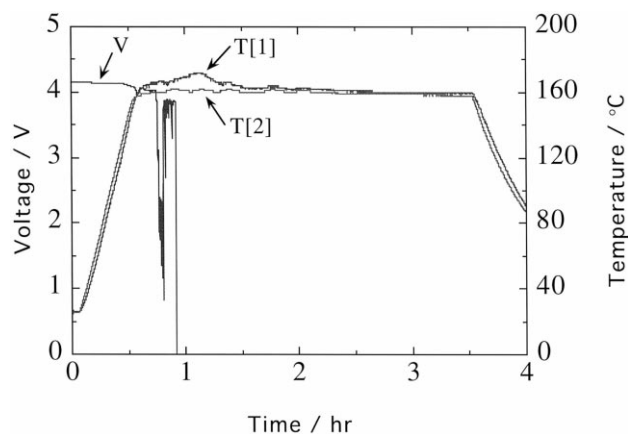


Fig. 2. Heating test on LiCoO₂ cell (cell A) at 160°C. T[1]: cell skin temperature, T[2]: oven temperature.

decrease. We hold the temperatures for a standard duration of 3 h. Then, we carried out the heating tests separately with different heating temperature, and we have to carry out the heating tests many times. When the room temperature is 25°C and a holding temperature is 160°C, the heating time to 160°C is 27 min because the heating rate is 5°C/min. The highest temperature at which the cell does not go up in smoke is defined as the thermal stability limit of the cell.

Figs. 2 and 3 show examples of heating test results on commercial prismatic lithium ion cells with LiCoO₂ cathodes manufactured by “manufacturer A” (cell A) at 160°C and 165°C, respectively. The cells were charged under standard charging conditions to 4.13 V and their capacity was 570 mA h. As shown in Figs. 2 and 3, the cell voltages suddenly dropped to 0 V. This is because internal shorting occurred as a result of the heating temperature exceeding the melting point of the separator. The cells did not emit smoke at 160°C but emitted smoke at 165°C after a rapid temperature increase with a maximum cell skin

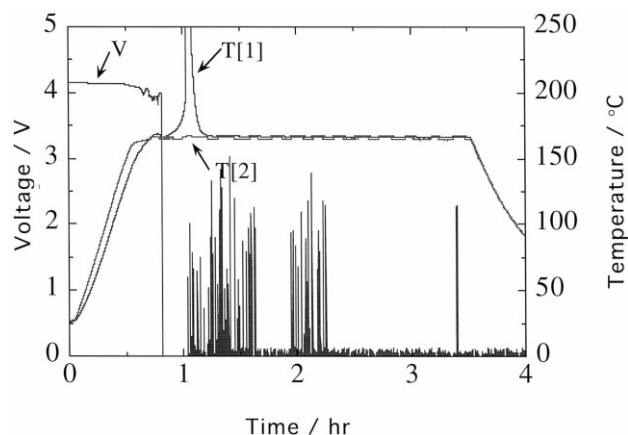


Fig. 3. Heating test on LiCoO₂ cell (cell A) at 165°C. T[1]: cell skin temperature, T[2]: oven temperature.

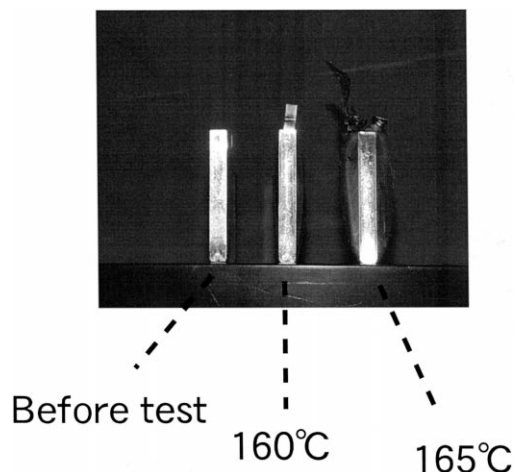


Fig. 4. LiCoO₂ cells (cell A) before and after heating test.

temperature above 200°C. We determined the thermal stability limit of these cells to be 160°C. Fig. 4 shows a photograph of these cells before and after the heating tests. The laser-sealed anode cap exploded and some of the electrode material (powder) was expelled from the cell in the 165°C heating, although the cell swelled without the pressure vent opening at 160°C.

Fig. 5 shows another example of a heating test on commercially available prismatic lithium ion cells with a LiCoO₂ cathode manufactured by “manufacturer B” (cell B) at 160°C. The cell capacity was 580 mA h for 4.15 V charging. The cells did not emit smoke at 155°C but sent out smoke at 160°C. The thermal stability limit of these cells was, therefore, 155°C, which is 5°C lower than cell A. Fig. 6 shows a photograph of these cells before and after the heating tests. The results were very similar to those shown in Fig. 4 except for the heating temperatures.

Figs. 7 and 8 show examples of heating tests on commercially available prismatic lithium ion cells with a LiMn₂O₄ cathode manufactured by “manufacturer C”

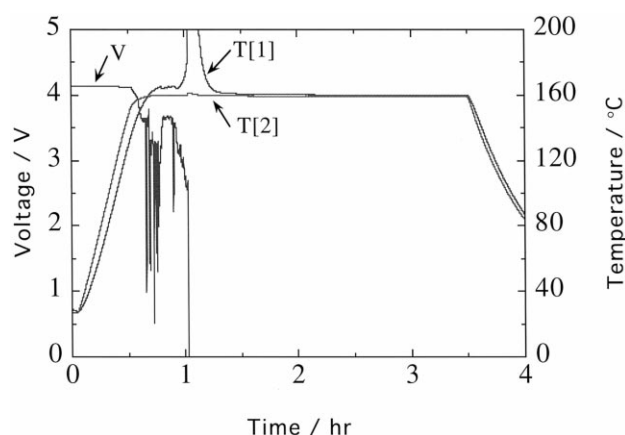


Fig. 5. Heating test on LiCoO₂ cell (cell B) at 160°C. T[1]: cell skin temperature, T[2]: oven temperature.

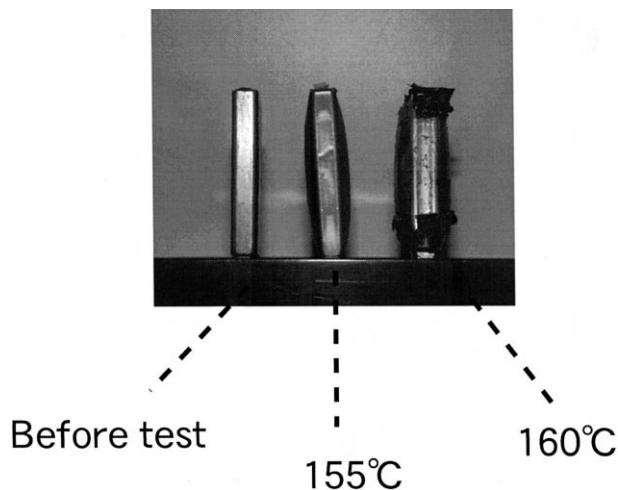


Fig. 6. LiCoO₂ cells (cell B) before and after heating test.

(cell C) at 170°C. Their capacity was 560 mA h for 4.25 V charging. The cells did not emit smoke at 170°C, although this temperature exceeded the melting point of the separator and the cell voltage was 0 V. A photograph of these cells before and after the heating tests was shown in Fig. 8. The cell swelled but the safety vent did not open. This means that the cells with LiMn₂O₄ cathodes are more thermally stable than the cells with LiCoO₂ cathodes. One important reason is the difference between the thermal stabilities of the cathode materials. LiCoO₂, LiNiO₂ and LiMn₂O₄ are well known as 4-V class cathodes. When these compounds are heated, they decompose rather than melt, releasing oxygen and subsequently exhibit exothermic reactions. Based on the accelerated reaction calorimeter (ARC) measurement, results for these cathodes reported by Fouchard et al. [6], the temperature starting the exothermic reaction is in the order LiNiO₂ (ca. 180°C) < LiCoO₂ (ca. 200°C) < LiMn₂O₄ (ca. 220°C). Furthermore, the heat output rate is in the order LiNiO₂ > LiCoO₂ > LiMn₂O₄ [6]. This indicates that the thermal stability is in the order of LiNiO₂ < LiCoO₂ < LiMn₂O₄. So, the difference be-

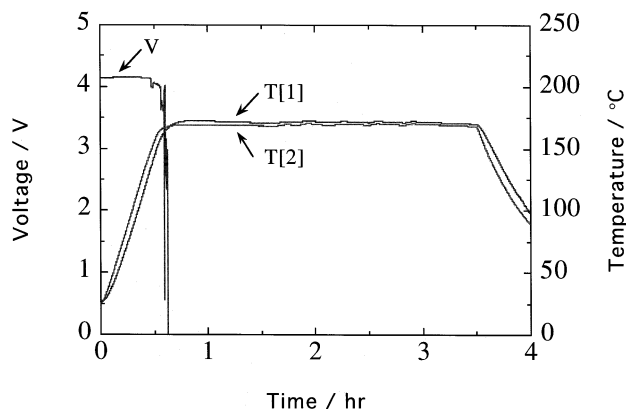


Fig. 7. Heating test on LiMn₂O₄ cell (cell C) at 170°C. T[1]: cell skin temperature, T[2]: oven temperature.

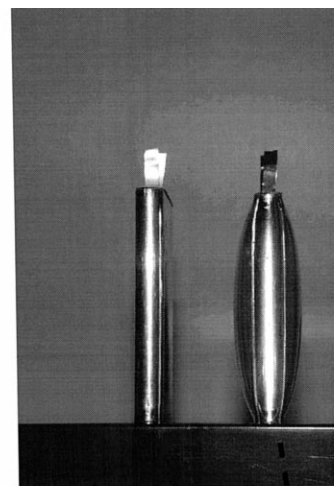
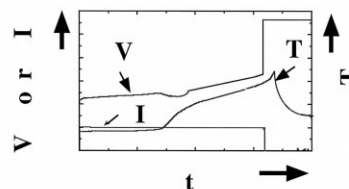


Fig. 8. LiMn₂O₄ cells (cell C) before and after heating test.

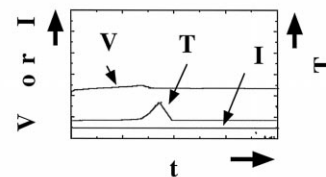
tween the heating test results for LiCoO₂ and LiMn₂O₄ cells arises mainly from the thermal stability of the cathodes.

4.2. Overcharging

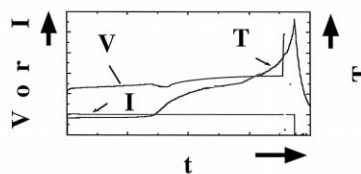
Cells may be overcharged when the cell voltage is incorrectly detected by the charging control system, or



(A) Separator shut down or electrolyte decomposition



(B) Lithium dendrite soft short (shunting)



(C) Thermal runaway

Fig. 9. Possible overcharging patterns; *t*: charging time, *T*: cell skin temperature, *V*: cell voltage, *I*: charging current.

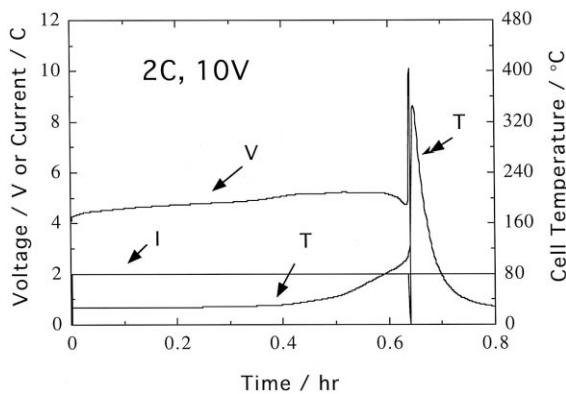


Fig. 10. Overcharging result for LiCoO₂ cell (cell A).

when the charger breaks down, or when the wrong charger is used. Many of the prismatic cells with aluminum cans have no current cut device inside them. A positive temperature coefficient resistance (PTC, thermal and electrical fuse) is provided outside the cells.

There are three possible voltage–temperature patterns (imagination figures based on our experience) when a lithium ion cell is overcharged as shown in Fig. 9 when a high compliance voltage, such as 10 V, is applied to the cells. When the cells are overcharged, the lithium ions remaining in the cathode are removed at approximately 4.5 V and more lithium ions are supplied to 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 serious reduction in thermal stability. After lithium has been removed from the cathode, the electrolyte starts to be oxidized. This electrolyte oxidation results in a distinct heat output. With an increase in cell temperature, the electrolyte reduction by the anode may occur simultaneously. When the overcharge current is low or the cells are thermally stable, there is a good balance between the heat generation and dissipation rates, the cell does not smoke as a result of the

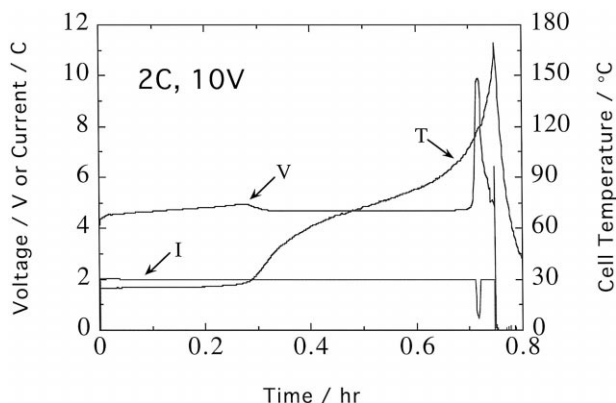


Fig. 11. Overcharging result for LiCoO₂ cell (cell B).

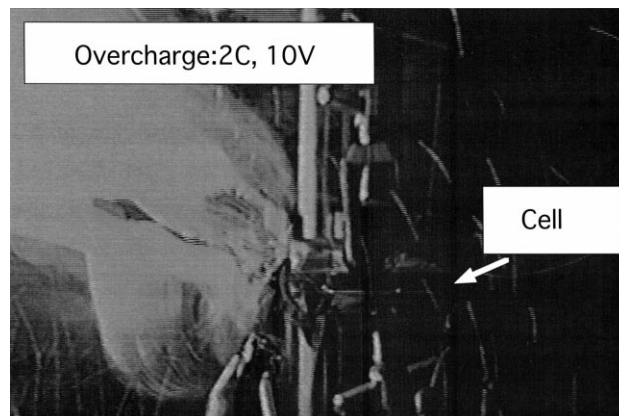


Fig. 12. Overcharging result for LiCoO₂ cell (cell A).

increase in impedance caused by electrolyte decomposition or separator shut down (Fig. 9(A)). When the excess lithium deposition is large and the dendritic lithium causes a soft short, current flows only through a resistance showing a constant cell voltage in subsequent overcharging (Fig. 9(B)). In this case, the cell temperature does not increase and the cell may die without incident. This may happen with LiCoO₂ cells. A severe case of cell overcharging occurs when a high rate overcharging current is applied, such as 2C, or the cell thermal stability is extremely low. In this case, the cell may smoke, ignite or explode (Fig. 9(C)).

We performed overcharging tests galvanostatically on prismatic cells without a PTC at 2C and a compliance voltage of 10 V to investigate the overcharge tolerance of the cell itself. Figs. 10 and 11 show examples of overcharging tests for prismatic cells with LiCoO₂ cathodes (cells A and B). Figs. 12 and 13 show photographs of overcharged cells. Both cells with LiCoO₂ cathodes ignited after the rapid cell temperature increase caused by electrolyte decomposition. The safety vent and the laser-sealed anode cap housing opened simultaneously, and the jelly rolls were expelled completely from the cell housings.

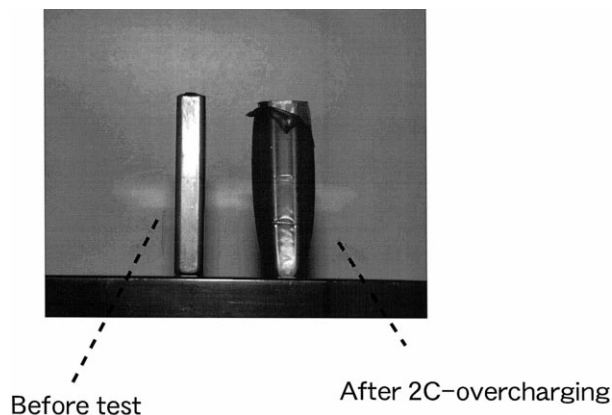


Fig. 13. LiCoO₂ cells (cell B) before and after heating test.

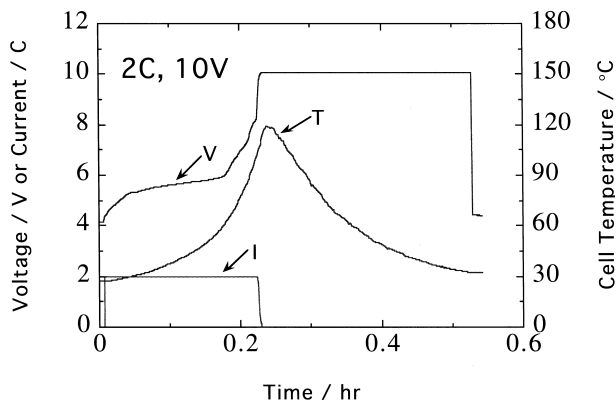
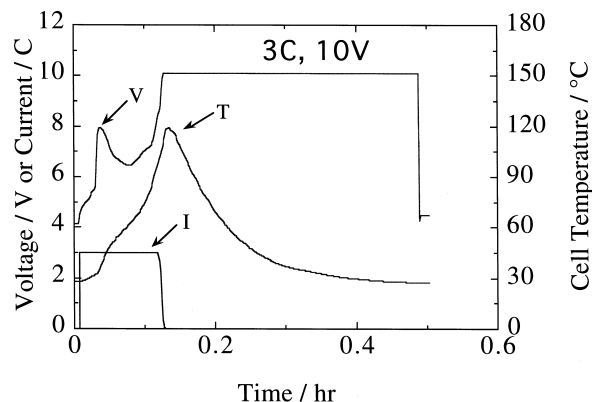
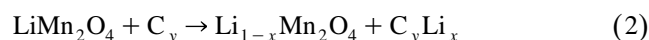
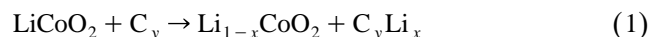
Fig. 14. Overcharging result for LiMn₂O₄ cell (cell C).Fig. 16. Overcharging result of LiMn₂O₄ cell (cell C).

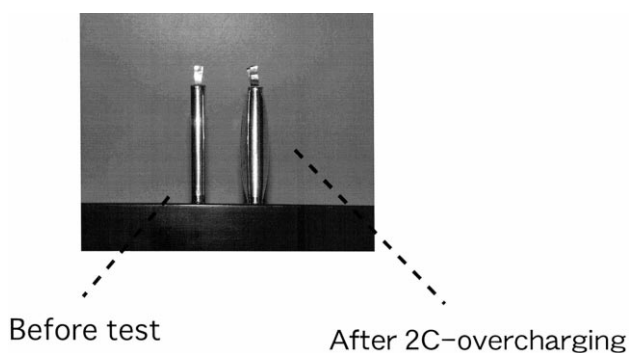
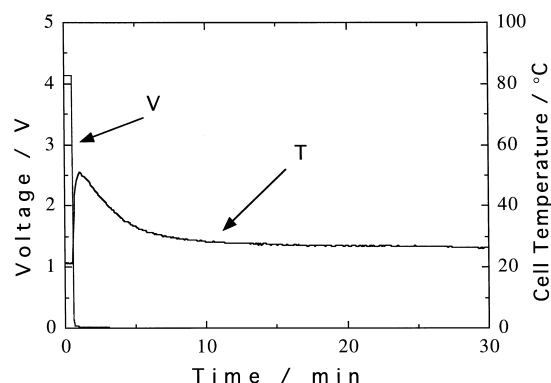
Fig. 14 shows the overcharging result for a cell with the LiMn₂O₄ cathode (cell C) and Fig. 15 shows the photograph of the cell after the test. The cell with the LiMn₂O₄ cathode swelled because of the gas produced by the electrolyte decomposition but the safety vent did not open or emit smoke. In the overcharging of the LiMn₂O₄ cell, after small amounts of lithium had been removed from the cathode, the cell temperature increased as a result of the electrolyte decomposition. However, the charging current suddenly stopped flowing when the cell skin temperature exceeded 120°C by the separator shut down. That means, the LiMn₂O₄ cell has a margin of thermal stability that can wait for separator shut down, while the LiCoO₂ cells cannot because of their poorer thermal stability. The LiMn₂O₄ cell still did not smoke even at 3C overcharging (Fig. 16). One reason for this difference between the overcharging test results for the LiCoO₂ and LiMn₂O₄ cells (in addition to the thermal stability of the cathode) is the stability of the anode of the overcharged cell. We explain this in more detail below. The cell reaction of LiCoO₂ and LiMn₂O₄ for the standard full charging is shown in Eqs. (1) and (2). x is around 0.5 for LiCoO₂ and around 0.9 for LiMn₂O₄. When the LiCoO₂ cell is overcharged, approximately the same capacity of lithium as that of the standard full charging is supplied to the anode from LiCoO₂. The thermal stability limit of the lithium metal cell (e.g., 100°C) is reported to be much lower than

that of ion cells [2–5]. Otherwise, when the LiMn₂O₄ cell is overcharged, lithium ions accounting for 10% of the standard full charge capacity are supplied from the cathode to the anode. Then, in overcharge tests on the lithium ion cells with different cathodes, the cathode affects the stability of the anode. One important point must be noted to avoid misunderstanding. The cells with LiMn₂O₄ cathodes are relatively more stable than those with LiCoO₂ cathodes as regards overcharging. However, this is insufficient to allow the removal of the overcharge protection circuit from the battery pack, because the LiMn₂O₄ cells have similar anodes and electrolytes to LiCoO₂ cells, and thermal stability is certainly greatly reduced when the overcharge cycling is repeated. For example, LiMn₂O₄ cells that had undergone 200 cycles at 1C discharging to 3.0 V and 1C charging at a constant 4.5 V, smoked at far below 170°C in heating tests. In these cycling tests, the practical charger DC output is assumed to be 4.5 V.



4.3. Nail penetration

The nail penetration test is very important and is considered to simulate an internal short in a cell. Many actual

Fig. 15. LiMn₂O₄ cells (cell C) before and after heating test.Fig. 17. Nail penetration test on LiCoO₂ cell (cell A).

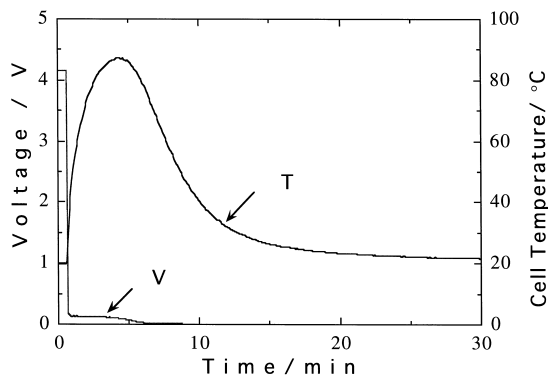


Fig. 18. Nail penetration test on LiMn_2O_4 cell (cell C).

accidents have occurred involving commercial lithium primary and secondary cells as a result of an internal short. Such internal shorts may be caused by a manufacturing 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.

Figs. 17 and 18 show the results of a nail penetration test in which a 2.5-mm diameter nail was used on prismatic cells with a LiCoO_2 cathode (cell A) and with a LiMn_2O_4 cathode (cell C). The cells were fully charged under the standard charging conditions. Neither cell emitted smoke. There were no distinct differences between these cathodes. However, if the cells are overcharged before nail penetration, the probability of smoking increases with LiCoO_2 cells because their stability is sensitive to overcharging as described in a previous report [1].

4.4. Forced discharge

Figs. 19 and 20 show the forced discharge test results for the LiCoO_2 and LiMn_2O_4 cells, respectively. The cells were fully charged before the forced discharge. The discharge current was 600 mA (approximately 1C rate) and the compliance voltage was -10 V. The tests were carried out until the discharge capacity reached 250%, that is, the

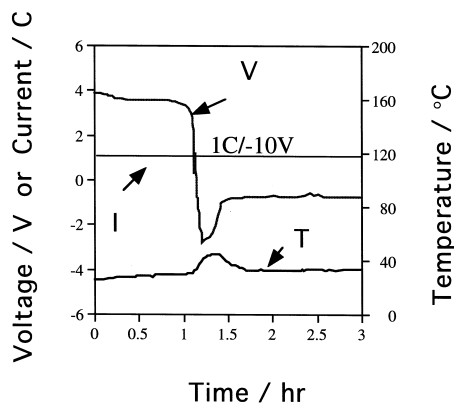


Fig. 19. Forced discharge result for LiCoO_2 cell (cell A).

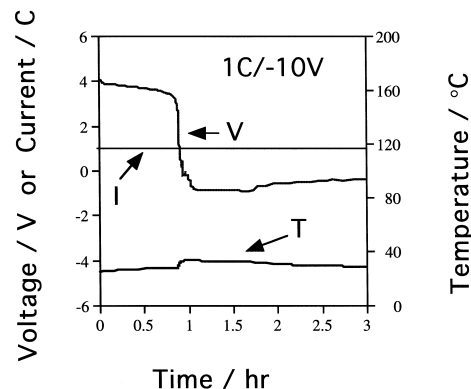


Fig. 20. Forced discharge result for LiMn_2O_4 cell (cell C).

forced discharge capacity was 150% from the standard complete discharge. The forced discharge results for the LiCoO_2 and LiMn_2O_4 cells are similar. That is, the forced discharge proceeds as described below. First, almost all the lithium ions in the carbon anode disappear at the standard full discharge. Second, there is a slight electrolyte reduction with a small heat output between 1.0 and 2.0 V. Then, the copper (Cu) of the anode substrate starts to dissolve (discharge) electrochemically from approximately 0.7 V and suddenly the voltage dropped. At that time, Cu is deposited on the cathode. The lithium ion cells turn into Cu anode/Cu cathode cells, whose OCV is 0 V, and exhibit a discharge voltage of below 0 V because of the IR drop. At this stage, no distinct temperature increase is observed and nothing dangerous occurs. If the forced discharge continues further, Cu dendrite soft-shortening could occur and the cell should die without incident.

5. Conclusion

In terms of the 600 mA h class, commercially available prismatic cells examined here, LiMn_2O_4 cells are safer than LiCoO_2 cells. However, 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. The next step is to improve the safety even further to realize cells with a much higher energy density or large practical cells for electric vehicles and electrically powered load leveling systems.

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