

Overcharge reaction of lithium-ion batteries

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Abstract

Overcharge reaction was studied in detail using 650 mAh prismatic hermetically sealed lithium-ion batteries with LiCoO₂ cathodes, graphitic carbon anodes and ethylene carbonate/ethyl methyl carbonate (EC/EMC) electrolytes. Several varieties of gases (CO₂, CO, H₂, CH₄, C₂H₆ and C₂H₄) were evolved in the overcharge reaction. The amount of gas increased with the increase in the cell temperature and rose rapidly at the end of the overcharge. In particular, the amount of CO₂ gas produced by the oxidation of the electrolyte at the cathode increased markedly. The exothermic oxidation reaction of the electrolyte was accelerated at the temperature above 60 °C, causing the cell temperature to increase rapidly thereafter. The heating tests of the overcharged anode samples enclosed in cylindrical cell cases with EC/EMC electrolytes resulted in thermal runaways. In contrast, the overcharged cathodes tested in the same manner showed no thermal runaway. The thermal runaway reaction during overcharge was caused by the violent reaction between the overcharged anode (deposited lithium) and the electrolyte solvent at high temperature that was the result of the rapid exothermic reaction of the delithiated cathode and the electrolyte.

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1. Introduction

The safety of lithium-ion batteries is an essential requirement for commercial use. With the increase in the energy of lithium-ion batteries, further advances in safety technology are necessary. There have been reports dealing with the safety and thermal analysis of lithium-ion batteries and their components [1–7]. Overcharge of batteries can sometimes lead to thermal runaways [1]. In order to develop adequate safety measures, it is important to analyze the thermal runaway mechanism in detail. However, there have been few reports on the systematic study of overcharge reaction of lithium-ion batteries [8,9]. This paper details the gas evolution reaction and behaviors of the cathode and anode during the overcharge process and presents the thermal runaway mechanism.

2. Experimental

Prismatic, hermetically sealed 633048-type lithium-ion cells with a nominal capacity of 650 mAh were assembled. The cells were 6.3 mm in thickness, 30 mm in width and 48 mm in height, using LiCoO₂ cathodes, graphitized mesophase-pitch-based carbon fiber (MCF) anodes and polyethylene separator. The graphitized MCF was prepared at Petoca Co. Ltd. The electrolyte was a 1 M solution of LiPF₆ in a mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC). The overcharge test was carried out at a 1 C rate constant current using a 7.5 V power supply. Current limiting or temperature trip safety devices (e.g. PTC) were not used in the experimental cells. An H-shaped glass cell was also used to analyze the gas composition evolved at the cathode and anode, respectively. The cathode (40 mm × 30 mm) and anode (40 mm × 30 mm) were arranged separately in the glass cell, and then overcharge was carried out at 3 mA cm⁻². The internal gas was collected by a micro-syringe, and analyzed by gas chromatography.

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These overcharged cells were disassembled in an argon filled glove box, and the overcharged cathodes and anodes, and the separators were examined by X-ray diffraction analysis, thermal analysis and energy dispersive X-ray fluorescence spectroscopy (EDX). The thermal behaviors of the overcharged cathodes and anodes were investigated in order to understand the thermal runaway mechanism.

3. Results and discussion

3.1. Voltage and temperature change at overcharge

Fig. 1 shows the cell voltage and cell case temperature of a 633048-type lithium-ion cell overcharged at a 1 C rate. The cell voltage increased gradually to a peak of 5.3 V when almost 90% of the lithium was removed from the cathode, and then fell slightly. Finally, the cell voltage rose sharply to the voltage limit of the power supply because of the separator shutdown. In an actual 1 C rate overcharge, all the lithium in the cathode was not removed after 60 min. We analyzed the lithium content of the delithiated cathode. The lithium content (x of Li_xCoO_2) in the cathode was 0.5 at the start of the overcharge, and $x = 0.08$ at the end of overcharge.

The cell case temperature remained low for the first 50 min, and then gradually rose to a maximum temperature of 110 °C with the trip of the voltage before depression. When the overcharge was carried out at a 1 C rate, the cell temperature dropped after the peak point of the temperature as shown in Fig. 1. However, in the case of a 2 C rate overcharge, the cell temperature rise was steep and the cell reached a thermal runaway.

3.2. Gas evolution

These prismatic cells were overcharged to each of stages (A)–(E) (Fig. 1). (A) is the stage where temperature begins to rise, (B) and (C) are the stages in the middle of the temperature rising, (D) is the stage of rapid temperature rising and (E) is the stage where temperature dropped after

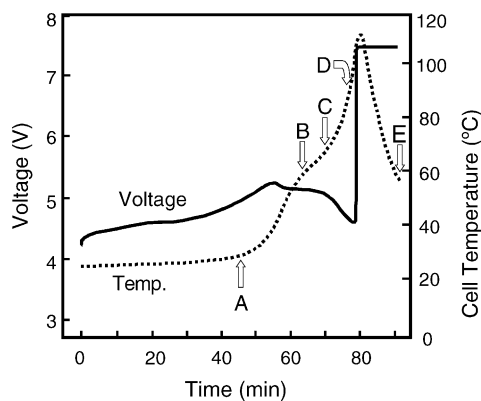


Fig. 1. Voltage and cell temperature profiles of a 633048-type prismatic cell at a 1 C rate overcharge.

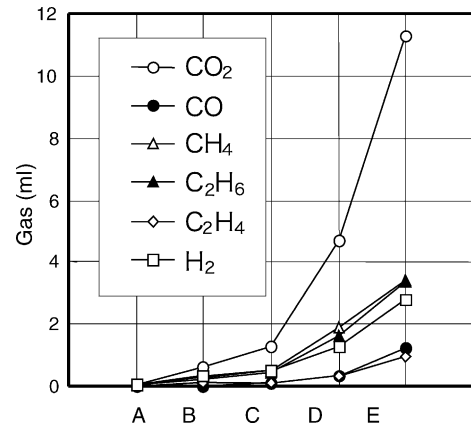


Fig. 2. Gas evolution characteristics of 633048-type prismatic cells at a 1 C rate overcharge.

its maximum. Fig. 2 shows the gas evolution characteristics of the prismatic cells at a 1 C rate overcharge. While the overcharge proceeded, the amount of the evolved gas was very small until the temperature rose. The volume of the evolved gas increased with the increase in the cell temperature and rose rapidly at the end of the overcharge. The evolved gas consisted of carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), ethane (C_2H_6), ethylene (C_2H_4) and hydrogen (H_2). In particular, the amount of CO_2 gas increased along with the rise in the cell temperature, and increased markedly at the end of the overcharge.

3.3. Gas evolution at the cathode and anode (H-type cell)

It is reasonable to consider that the CO_2 gas was generated by the oxidation of the electrolyte at the cathode. To examine it more clearly, we made the H-shaped glass cell. The gas evolved at each of the electrodes was collected separately and analyzed. The result is shown in Fig. 3. Carbon monoxide (CO) gas and carbon dioxide (CO_2) gas were chiefly generated at the cathode. As for the anode, H_2 gas was the main component of the evolved gas, and small amounts of CH_4 , C_2H_4 , C_2H_6 , CO and CO_2 were produced.

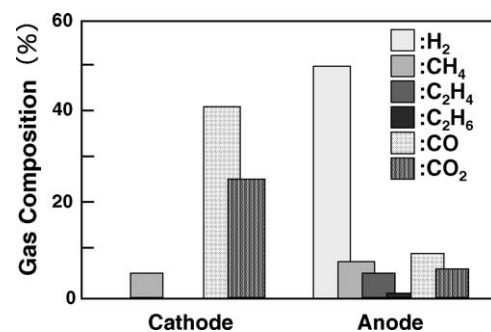


Fig. 3. Gas composition of the H-shaped glass cell overcharged at 3 mA cm^{-2} .

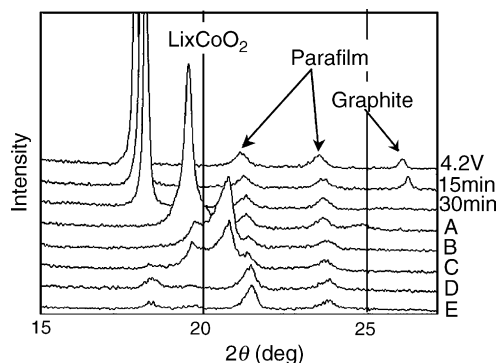


Fig. 4. XRD patterns of the cathode materials overcharged to various stages.

These results confirmed that the CO_2 gas was produced mainly by the oxidation of the electrolyte at the cathode.

3.4. Overcharged cathode

The structural change of the cathode material as a result of the overcharge reaction is shown in Fig. 4. The structure of LiCoO_2 changed from hexagonal to monoclinic form with removal of the lithium from LiCoO_2 . Further overcharge resulted in breakdown of the crystal structure of the cathode material due to the reaction between the electrolyte and the highly oxidized cathode. In order to investigate the gas evolution behavior at the cathode more precisely, the overcharge test was performed while keeping the cell in a water bath at constant temperature.

3.5. Gas evolution behavior of the cells kept in the water bathes at various temperatures

Fig. 5 shows the gas evolution behavior of the cells overcharged in the water bathes kept at constant temperatures from 25 to 95 °C. The overcharge was carried out for 90 min at a 1 C rate. The cell was held in the water bath, and therefore, the heat generated inside the cell was absorbed by the water, and the temperature of the cell case hardly changed. Even if the cell was overcharged in the high temperature condition of 95 °C, the cell did not result in a thermal runaway since all the excessive heat was absorbed by the water. The compositions of the evolved gases were different from one

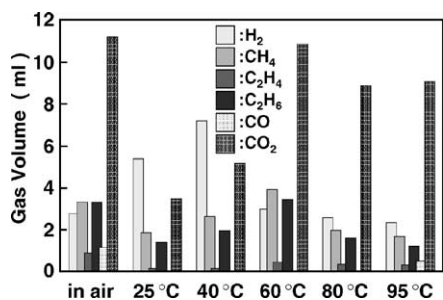


Fig. 5. Gas evolution behaviors for 633048-type prismatic cells overcharged in water bathes kept at various constant temperatures.

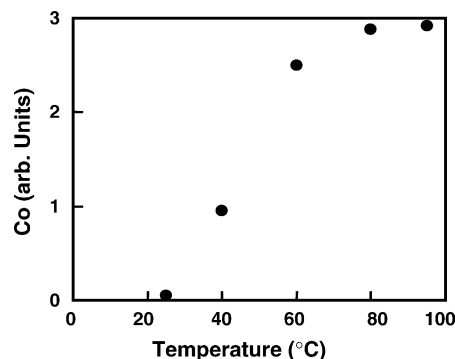


Fig. 6. Analytical data for the cobalt on the separator of overcharged cells.

another depending on the water bath temperature. While H_2 and CO_2 were mainly evolved from the cells overcharged at 25 and 40 °C, the amount of CO_2 was smaller than that of H_2 . The gas composition was different from that of the cell overcharged in air. On the other hand, the gas evolution behaviors in the case of the cells overcharged at 60 °C or higher temperatures differed greatly. A large quantity of CO_2 was generated in the cells overcharged at high temperatures. This behavior was similar to that of the cell overcharged in air. Therefore, it turned out that the reaction between the cathode and the electrolyte accelerated rapidly at over 60 °C.

3.6. Cobalt deposition on the separator

We disassembled the cell in an argon filled glove box after the overcharge, and analyzed the cobalt on a separator by EDX. Fig. 6 shows the amount of cobalt on the separator overcharged at various temperatures. A large quantity of cobalt was detected on the separators of the cells overcharged at 60 °C or higher temperatures. The cathode active material became unstable due to the overcharge dissociated oxygen, and hence, cobalt in LiCoO_2 dissolved in the electrolyte and deposited on the anode. The oxidation reaction of the electrolyte was accelerated at the temperature above 60 °C, causing the cell temperature to increase rapidly thereafter, since the reaction between the overcharged cathode and the electrolyte was exothermic.

3.7. Thermal characteristics of the overcharged anode

In order to investigate the thermal behavior of the overcharged electrode, we disassembled the cells of (A)–(E) in Fig. 1, and took out the overcharged cathodes and anodes. Then, we put each anode and cathode into a cylindrical cell case with a fresh electrolyte, respectively, and crimp sealed the case. These samples were heated from room temperature to 180 °C in an oven. The temperature rising speed was 5 °C min^{-1} . Thermal behaviors for the overcharged anodes with electrolytes are shown in Fig. 7. While the sample with the anode charged to 4.2 V showed no thermal runaway, the samples for (A)–(C) resulted in thermal runaway and cell rupturing. The starting temperature for thermal runaway for

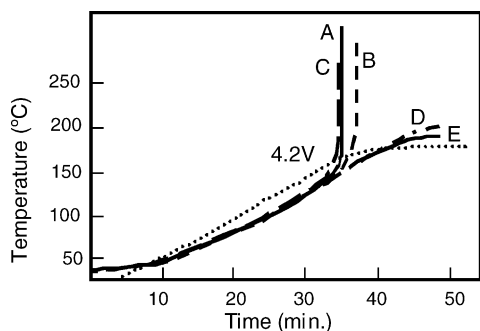


Fig. 7. Thermal behaviors of the overcharged anodes enclosed in cylindrical cell cases with EC/EMC electrolyte.

each of the samples (A)–(C) was near 130 °C. Although overcharged cathodes were tested in the same manner, no thermal runaway reaction was observed with any cathode. The overcharged anode samples for (D) and (E) in which cell temperature exceeded 90 °C showed no rupturing. This was because the negative electrode surface became inactivated with heat during overcharge.

The thermal runaway reaction during overcharge is probably caused by the violent reaction of the overcharged anode and electrolyte at the high temperature that is a result of the exothermic reaction between the delithiated cathode and the electrolyte.

3.8. Overcharge reaction mechanism

From these results, we can complete the picture of overcharge and thermal runaway mechanism by the following (Fig. 8):

- I. Lithium is irreversibly removed from the cathode, and is deposited on the carbon anode. The cell voltage increases gradually with increasing delithiation of the cathode. The cell case temperature remains low and the amount of the evolved gas is very small prior to the temperature rise.
- II. The lithium in the cathode is hardly removed near 100% overcharge; the cell impedance would increase with an increase in the cathode resistance. The cell case temperature rises due to the Joule heat and the heat of electrolyte decomposition.

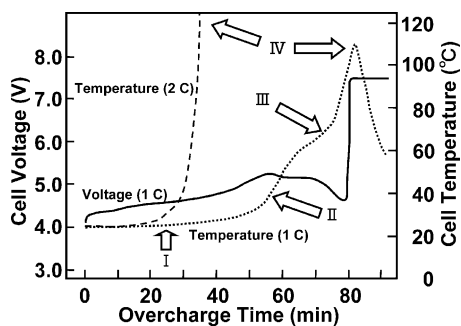


Fig. 8. Overcharge reaction and thermal runaway mechanism of a prismatic lithium-ion battery.

- III. The cell temperature begins to rise more rapidly due to the exothermic reaction between the delithiated cathode and the electrolyte. Above an internal temperature of 60 °C, this reaction is accelerated and a large quantity of CO₂ gas is evolved.
- IV. When the cell internal temperature reaches the shutdown temperature of the polyethylene separator (130–135 °C), the overcharge current drops steeply and the cell temperature falls with no rupturing. On the contrary, the steep rise of the cell temperature in the case of a 2 C rate overcharge leads to the violent reaction of the overcharged anode (deposited lithium) and electrolyte. This reaction causes the thermal runaway with the cell rupturing.

4. Conclusions

Overcharge behavior was studied in detail using prismatic hermetically sealed lithium-ion batteries with LiCoO₂ cathodes, graphitic MCF anodes and EC/EMC electrolytes. Several varieties of gases (CO₂, CO, H₂, CH₄, C₂H₆ and C₂H₄) were evolved in the overcharge reaction. The amount of the gas increased with the increase in the cell temperature and rose rapidly at the end of the overcharge. In particular, the amount of the CO₂ gas produced by the oxidation of the electrolyte at the cathode increased markedly. The exothermic oxidation reaction of the overcharged cathode was accelerated at the temperature above 60 °C, causing the cell temperature to increase rapidly thereafter. The heating tests of the overcharged anode samples for (A)–(C) in Fig. 1 enclosed in cylindrical cell cases with EC/EMC electrolytes resulted in thermal runaways. In contrast, the overcharged cathodes tested in the same manner showed no thermal runaway. Therefore, the thermal runaway reaction during overcharge was caused by the violent reaction of the overcharged anode (deposited lithium) and electrolyte solvent at high temperature that was the result of the rapid exothermic reaction between the delithiated cathode and the electrolyte.

References

- [1] S. Tobishima, J. Yamaki, J. Power Sources 81–82 (1999) 882.
- [2] Ph. Biensan, B. Simon, J.P. Peres, A. de Guibert, M. Broussely, J.M. Bodet, F. Perton, J. Power Sources 81–82 (1999) 906.
- [3] H. Maleki, G. Deng, A. Anani, J. Howard, J. Electrochem. Soc. 146 (9) (1999) 3224.
- [4] Y. Saito, K. Takano, A. Negishi, J. Power Sources 97–98 (2001) 693.
- [5] G.G. Botte, R.E. White, Z. Zhang, J. Power Sources 97–98 (2001) 570.
- [6] D.D. MacNeil, T.D. Hatchard, J.R. Dahn, J. Electrochem. Soc. 148 (7) (2001) 663.
- [7] J. Yamaki, Y. Baba, N. Katayama, H. Takatsuji, M. Egashira, S. Okada, J. Power Sources 119–121 (2003) 789.
- [8] T. Ohsaki, T. Kishi, T. Kuboki, N. Takami, N. Shimura, Y. Sato, M. Sekino, A. Satoh, Proc. 40th Battery Symposium in Japan, 1999, p. 439.
- [9] R.A. Leising, M.J. Palazzo, E.S. Takeuchi, K.J. Takeuchi, J. Electrochem. Soc. 148 (8) (2001) 838.