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Journal of Power Sources 146 (2005) 97–100

JOURNAL OF POWER SOURCES

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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 $LiCoO_2$ cathodes, graphitic carbon anodes and ethylene carbonate/ethyl methyl carbonate (EC/EMC) electrolytes. Several varieties of gases (CO_2, CO, H_2, CH_4, C_2H_6 and C_2H_4) 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 CO_2 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.

Keywords: Overcharge; Safety; Thermal runaway; Lithium-ion battery; Rechargeable cell

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 $LiCoO_2$ 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 $LiPF_6$ 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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doi:10.1016/j.jpowsour.2005.03.105

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 runway.

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 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.

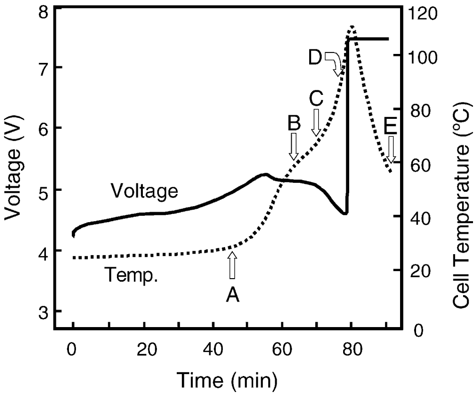

Fig. 1. Voltage and cell temperature profiles of a 633048-type prismatic cell at a 1 C rate overcharge.

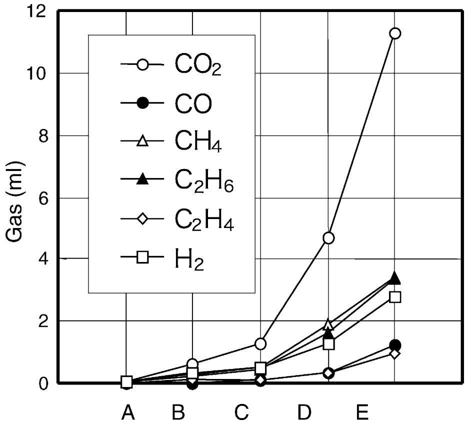

Fig. 2. Gas evolution characteristics of 633048-type prismatic cells at a 1 C rate overcharge.

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.

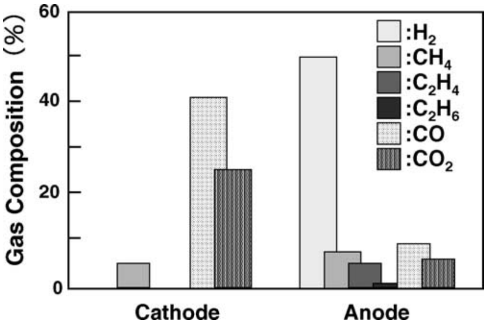

Fig. 3. Gas composition of the H-shaped glass cell overcharged at $3\,mA\,cm^{-2}$.