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A study of the overcharge reaction of lithium-ion batteries

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Abstract

The overcharge behavior of prismatic lithium ion batteries was studied under abusive conditions. Experimental cells were constructed with a systematic variation in cell balance and overcharge tested to the point of failure. This test demonstrated that the point of cell rupture tracked the amount of cathode in the cell, independent of the amount of anode material. The rate of charge was found to be an important parameter, as cells overcharged at low charge rates remained hermetic while high charge rates (C/2 and above) resulted in cell rupture. The internal temperature of the cells monitored during overcharge was found to be as high as 199°C, which was 93°C higher than the external skin temperature of the cell. Coin cell tests identified the cathode as the source of heat produced in the cell, and Rdc measurements identified a large increase in cell resistance past the full delithiation point of Li_xCoO_2.

Keywords: Rechargeable cell; Lithium ion battery; Safety; Overcharge

1. Introduction

The safety of lithium ion batteries, especially under abusive conditions, is a primary concern of battery manufacturers and their customers. In particular, the potentially violent reaction of lithium ion cells at very high temperatures or under extreme overcharge conditions has been documented [1,2]. There have been studies published dealing with the thermal analysis of individual components of lithium ion battery systems [3,4], as well as data generated on safety tests of commercially available lithium ion product [5,6]. However, there has been less reported on the systematic study of overcharged Li-ion cells and the effect of cell parameters on this reaction. This report details the characterization of the overcharge reaction of medium size prismatic Li-ion cells and the effects of rate of overcharge, internal cell temperature, and cell balance (ratio of cathode weight to anode weight).

2. Experimental

Prismatic, hermetically-sealed lithium ion cells enclosed in stainless steel cases with a nominal capacity of 1.5 Ah were assembled using $LiCoO_2$ cathodes, graphite anodes, and polyethylene separator. Cathodes and anodes were coated on aluminum and copper foils, respectively. Both electrodes used PVDF binder, and all of the cells utilized a wound element design and 1 M $LiPF_6$ with carbonate electrolyte. Cells were cycled three times between voltage limits of +4.1 and +2.75 V prior to overcharge testing. All overcharge tests were conducted using constant current charging with a 12 V power supply. Current limiting or temperature trip safety devices were not used in these experimental cells. Coin cells used cathodes 16 mm in diameter, anodes (graphite or Li) 18 mm in diameter, and the same electrolyte and separator as the prismatic cells. Rdc measurements were conducted on coin cells by interrupting the charge current for 5 s intervals every 5 min of the test. Rdc = (charge voltage − OCV after 5 s)/current. Type K thermocouples were used to measure internal and external temperatures during the overcharge reactions. Prismatic cells containing internal thermocouples had the thermocouple inserted into the wound element stack and sealed through the top of the cell with epoxy. All overcharge experiments on prismatic cells were conducted in a specially designed explosion-proof room.

3. Results and discussion

Experimental prismatic lithium ion cells were constructed with a systematic variation in the cell balance (cathode

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Table 1
The results of lithium ion cell overcharge at 1000 mA

Cathode	Anode	Cell balance	Maximum voltage (V)	Maximum temperature (°C)[a]	Charge capacity (Ah)[b]
Low	Fixed	2.3	5.5	112.4	2.8
Middle	Fixed	2.8	5.3	105.0	3.5
High	Fixed	3.3	5.3	107.5	4.1
Fixed	Low	3.3	5.3	104.0	3.4
Fixed	Middle	2.8	5.4	104.3	3.4
Fixed	High	2.4	5.3	105.2	3.3

[a] Temperature measured on external skin of cell prior to rupture.
[b] Total charge capacity prior to rupture of the cell; $x = 0$ for Li_xCoO_2 in each case.

weight/anode weight) in two groups. In the first group, the anodes were held to a constant weight while the cathode weight was varied to produce cell balances of 2.3, 2.8, and 3.3. In the second group, the cathode weight was held constant, while the anode weight was varied for cell balances of 2.4, 2.8 and 3.3. Following formation, these cells were fully charged to +4.1 V and then overcharged using a 1 A constant current at room temperature. The voltage and current were monitored during the test, and the skin temperature of the cell was recorded using a thermocouple attached to the outside case surface. The results for these tests are listed in Table 1, and all of these cells ruptured on overcharge. Notably, the cell rupture point in these tests tracked the amount of cathode material in the cell, occurring near the full delithiation of $LiCoO_2$, independent of the amount of anode material.

The rate of charge was examined in more detail for overcharge of cells with a cell balance of 2.8. Temperature curves are plotted as a function of percentage charge of the cell in Fig. 1, where 100% charge is equivalent to $x = 0$ in Li_xCoO_2. Cells overcharged at 150 (C/10), 300 and 525 mA swelled but remained hermetic, while cells overcharged at 1500 mA (C-rate) ruptured, illustrating the importance of charge rate on the outcome of the overcharge test. Cells overcharged at 525 and 1500 mA were also equipped with internal thermocouples to measure the electrode stack temperature during the overcharge test. The cell charged at 525 mA, which did not rupture, displayed a maximum internal temperature of 148.2°C, while the maximum external temperature was 119.5°C (a 28.7°C difference). In comparison, the cell charged at 1500 mA recorded a maximum internal temperature of 199°C prior to rupture of the cell, and a maximum external temperature of 106.4°C (a 92.6°C difference). From this data, it is clear that internal thermocouples are necessary to accurately characterize the temperature of cell components during overcharge.

Coin cells were assembled using the same electrode composition and thickness as used in the prismatic cells (2.8 cell balance), in configurations of graphite/$LiCoO_2$, Li/$LiCoO_2$ and Li/graphite. These cells were overcharged at a 2C rate and the temperature was monitored by a thermocouple attached to the external positive terminal of the cell. The temperature curves for the cells are displayed in Fig. 2, where the lithium ion and Li/$LiCoO_2$ coin cells displayed nearly identical temperature increases at ~100% charge, while the lithiation of the graphite electrode showed no rise in temperature. The internal resistance of a Li/$LiCoO_2$ coin cell was measured as a function of state of charge by using

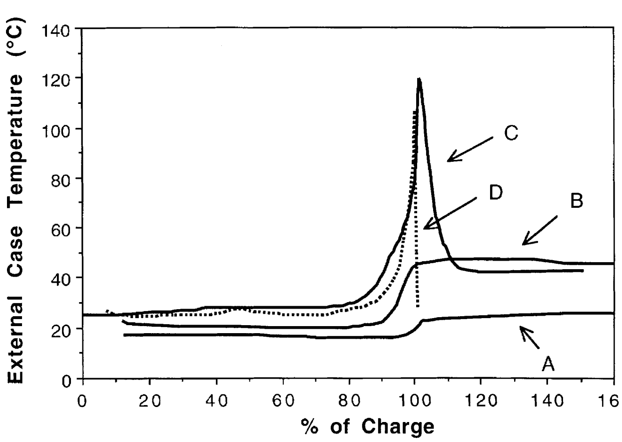

Fig. 1. External skin temperature curves for 1.5 Ah prismatic lithium ion cells overcharged at (A) 150 mA, (B) 300 mA, (C) 525 mA, and (D) 1500 mA with a 12 V power supply at room temperature.

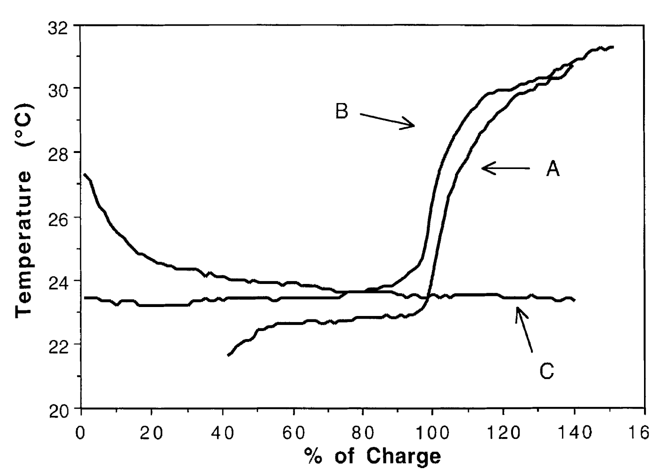

Fig. 2. External skin temperature curves for coin cells overcharged at a 2C rate: (A) graphite/$LiCoO_2$; (B) Li/$LiCoO_2$ and (C) Li/graphite.

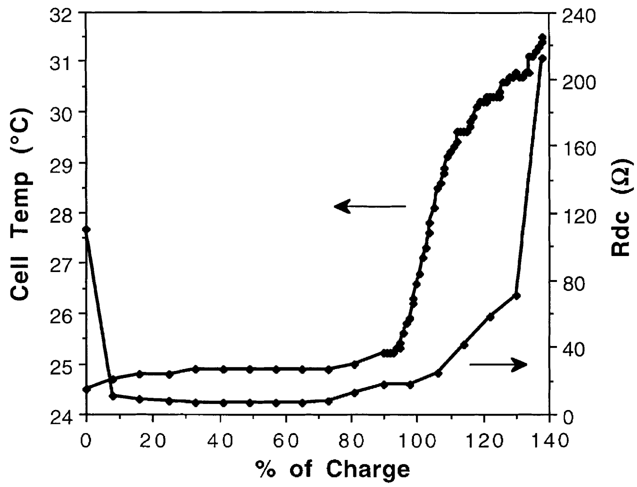

Fig. 3. Cell Rdc and temperature for Li/$LiCoO_2$ coin cell overcharged at a 2C rate.

5 s rest steps (current = 0) during the overcharge test. The Rdc of the coin cell is overlayed with the temperature of the cell as a function of percentage charge in Fig. 3. The internal resistance of the cell is initially very high (>100 Ω) but goes down rapidly with delithiation of the cathode, consistent with reported resistivity measurements on $LiCoO_2$ [7]. After a slight rise in Rdc at 75–90% charge, the Rdc goes up significantly in the range of 105–140% charge. Interestingly, a sharp rise in temperature occurs near 100% charge, prior to the substantial rise in cell Rdc, implying that heat is generated by a chemical reaction at the full delithiation of the cathode in addition to heat caused by increased cell resistance.

4. Conclusions

Overcharge of the lithium ion system sets a complex series of reactions into motion resulting in the build-up of heat and pressure in these cells. The prismatic lithium ion cells of 1.5 Ah with a systematic variation in cell balance showed that a significant voltage increase or rupture point during overcharge correlated with the amount of cathode material in the cell, independent of the amount of anode material in the cell balance range of 2.3–3.3. This result ties the critical overcharge reactions with the full delithiation of the cobalt material. The rate of charge also plays a key role in determining the outcome of the overcharge reaction, based on the size and design of the cell. Moderate currents (C/2 to C-rate) in these cells cause heat build-up during extreme overcharge which can lead to cell rupture. Coin cell tests demonstrated that heat is produced at the cathode during overcharge, which is consistent with exothermic reactivity of Li_xCoO_2 in the presence of electrolyte reported in DSC studies [3]. Internal thermocouples were necessary to accurately characterize the temperature of the cell components during overcharge. A difference of as much as 93°C was observed between the internal and external thermocouple measurements prior to cell rupture. Most notably, a cell with an internal temperature of 148°C did not vent, while another cell with an internal temperature of 199°C did rupture. Above 150°C, an autocatalytic exothermic reaction of Li_xCoO_2 occurs [8], and lithium metal melting takes place at 180°C. Metallic lithium is deposited on the graphite anodes during overcharge at the cell balances used in this study, and the melting of lithium will lead to a strongly exothermic reaction with electrolyte. At the temperature of 199°C achieved in this test, these may be the key factors which result in the rupture of the cell.

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