



Overcharge failure investigation of lithium-ion batteries



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ABSTRACT

Safety behaviors of a 32 Ah prismatic lithium-ion battery are investigated under abusive charge conditions by monitoring the internal and external cell temperature variation. Results show that the cell internal temperature can reach 235 °C before firing, which is almost 140 °C higher than the cell external temperature. Although the cell resistance increases abruptly due to electrolyte oxidization when the cell is firstly overcharged to its maximum voltage (5.10 V), the cell internal temperature keeps a low temperature of 50 °C without notable temperature rise. However, the cathode/electrolyte interface becomes highly reactive as the cell is further overcharged. Cell internal temperature goes up to more than 200 °C accompanied with massively gas production when the cell is overcharged to 180% SoC. Post-overcharge analysis on both cathode and anode indicates that lithium plating during overcharge is the major cause responsible for thermal runaway because the observed cell temperature is well above the melting point of lithium metal.

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1. Introduction

Rechargeable lithium-ion batteries (LIB) have been widely used as the power source for portable electronic devices including mobile phones, bluetooth, notebook computers, and (hybrid) electric vehicles due to their high energy density, long cycle life and other unique properties. However, improvements on both battery materials and battery management system are necessary to address the safety concerns before LIBs can be used to power electric vehicles. Because of the co-presence of combustible materials and oxidizing agents in LIBs, runaway reaction occurs when the battery is used under abusive conditions and leads to severe hazardous consequences like firing and explosion. Therefore, understanding of battery safety behavior under abusive conditions is very important for the development of a safe LIB that can be used for electric or hybrid electric vehicles. Among all different kinds of abuses, overcharge is one of the most important common abuses for LIB, and thus investigation of battery behavior during overcharge can give a comprehensive clue of improvement of battery safety. A lot of studies that inspired by such a thought can

be found in literature. Thermal analysis of individual components on the overcharge was performed by Zhang et al. [1] and Richard et al. [2], and the data were collected from commercially available lithium ion products [3]. Electrode material thermal stability was tested by accelerated rate calorimetry (ARC) and differential scanning calorimetry (DSC) [4]. Experiment results also reveal that functional additives can be an effective mean to improve the overcharge performance [5–7]. Detailed overcharging testing procedures for lithium-ion battery were provided by different research groups [8–10] and results from independent tests suggest that the lithium concentration in the cathode material is one of the key factors for the battery thermal runaway.

It is mentionable that these previous works were mainly focused on the evaluation of material thermal stability or the impact of charge current density under overcharge on small size batteries, and few reports on the failure behavior monitoring of large battery can be found. In this study, a full cell (32 Ah prismatic cell) is used and the overcharge behaviors are investigated by closely monitoring of internal/external cell temperature during the whole charge process. Benefited from the online monitoring on internal cell temperature and gas generation, correlation between battery overcharge safety and the state of charge (SoC) was identified. Moreover, analysis on cathode and anode after overcharge reveals that lithium plating is one of the major causes responsible for thermal runaway during overcharge.

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2. Experimental

A prismatic, hermetically-sealed lithium ion cells with a nominal capacity of 32 Ah (provided by Ningde Amperex Electronics Technology Co. Ltd. (ATL)) was enclosed in an Al can. The cathode consists of $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ as an active material (95.0 wt%), carbon black as a conductive additive (2.0 wt%), and polyvinylidene fluoride (PVDF) as a binder (3.0 wt%). Carbonaceous microsphere (CMS) as the active material with 2.0 wt% Sodium salt of Carboxy Methyl Cellulose (CMC), 3.0 wt% Styrene-Butadiene Rubber (SBR), and 3.0 wt% conductive carbon was used as an anode. Porous polypropylene film (20 μm thickness) was used as the separator, and 1.0 mol cm^{-3} LiPF_6 dissolved in EC:DEC:EMC (1:1:1, by volume) was used as the electrolyte. Capacity design is limited by the ratio of cathode side and the negative capacity vs. Positive capacity ratio (N/P) was 1.18. Cells were cycled three times in the potential range between 4.1 V and 2.8 V before overcharge testing. All overcharge tests were conducted using constant current charge protocol with a 12 V power supply. Current limiting or temperature trip safety devices were not used in these experimental cells.

K-type thermocouples were inserted into the middle part of wound jelly-roll to monitor their internal temperatures. The down-leads of the thermocouple were sealed during the jelly-roll assembly before the electrolyte injection. Another thermocouple was fixed at the center of the upper surface of the cell to monitor its external temperature. The overcharge testing was conducted on Arbin BT-2000 battery tester at $25 \pm 3^\circ\text{C}$. The potential upper limit of 4.1 V was preset before the overcharge test was carried out.

2032 coin cell was constructed by using $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ as working electrode, and experimental details could be found in another published paper [11]. Cyclic voltammograms (CVs) was performed by using computer-controlled Solartron 1480 electrochemical workstation at a system at a current density of 10 mA g^{-1} cycled between the limitations of 3.0 and 3.5–5.0 V, respectively.

For the convenience of discussion, the nominal cell capacity (32 Ah) is defined as 100% SoC, and different SoC will be defined accordingly based upon capacity obtained during charge. Internal charge resistance (R_{cc}) measurements were conducted by interrupting the charge current for 5 s intervals every 10% SoC after overcharge test started, and R_{cc} can be expressed as $R_{cc} = (\text{charge voltage} - \text{OCV (Open Circuit Voltage) after 5 s standby}) / \text{current}$.

$$\text{SoC} = \frac{\text{Total charge capacity}}{\text{Capacity between 2.8 and 4.1 V}} \times 100\%$$

Cell volume change during overcharge test was examined by pouch cell, which had the identical chemistry from the prismatic cell. The 2.0 Ah cell had a dimension of 4.0 mm \times 60 mm \times 130 mm (Thickness \times Width \times Length). Cell volume change was examined by a water drainage method described as following: cell with different SoC was connected with a rigid wire which was fixed to a specially designed jigs; submerged the cell into a beaker filled with de-ion water fluid (not touch the beaker bottom) and keep the system in static equilibrium; the weight changes of the beaker at different SoC were monitored by high precision balance (accuracy of 0.001 g). Finally, the cell volume changes with different SoC can be calculated according to Archimedes principle ($\Delta V = \Delta m / \rho_{\text{liq}}$). Here, the cell volume variation was monitored at by 10% SoC increasing interval. Meanwhile, gas component during overcharge test was analyzed by Gas Chromatograph–Mass Spectrometer (GC–MS). The overcharged cell with various SoC can be well controlled by cell initial capacity calculation and charging time. The batteries were carefully dismantled in a dry room with controlled dew point (-53°C) to avoid short circuit. After the dissection of the jelly-roll,

the cathode and anode electrode, separator and electrolyte were examined. DSC and X-ray diffraction (XRD) were used to characterize the thermal stability and crystal structure of the cathode materials at different SoC. The samples for DSC analysis were obtained by scraping off the electrode materials from the current collector in an argon-filled glove box with water and oxygen contents in the range of 0.1–3 and 1–5 ppm, respectively. After full cell disassembly, cathode electrode after washing was directly used for XRD test. Inductively coupled plasma (ICP) test was carried out in order to confirm the Li content in the cathode material at different overcharge state.

3. Results and Discussion

The full cell capacity is about 32 Ah full, and the vent in the top cap begins to work when the inner pressure is higher than 1.0 MPa. The capacity of the full cell before overcharge test was determined by 1C rate charge/discharge between 2.8 and 4.1 V under $25 \pm 3^\circ\text{C}$. 1C is defined as that the cell is galvanostatically charged to 100% SoC or discharged to 100% depth of discharge (DoD) in one hour and then the cell was further charged for predetermined periods to reach different SoC (i.e. 6 min charging corresponds to 10% SoC increase). If the cell voltage reaches 12 V or constant current charge exceeds 4 h, the cell will automatically turn to potentiostatically charge mode.

As shown in Fig. 1, the cell is delivers a charge capacity of 32 Ah with negligible irreversible capacity loss in the range of 2.8–4.1 V during the first charge/discharge. All the cells were pre-charged to 100% SoC before 1C/12 V overcharge test. As shown in Fig. 2, the cell voltage increases with time and then drops gradually after the cell reaches to the highest voltage (5.10 V) at 180% SoC. Combining with the Li^+ content analysis shown in Table 1, this phenomenon should be attributed to the insufficient Li^+ extraction from the cathode crystal lattice to sustain the constant current charge after 5.10 V, which results in tempestuous electrolyte decomposition, leading to cell voltage drop. Cell internal and external temperature profiles during overcharge were monitored as shown in Fig. 2. The internal and external temperature rising trend is quite similar and the value is almost the same as that of 25°C before cell reaches 160% SoC. However around 200% SoC, the cell skin temperature rises up quickly and then cell thermal runaway occurs at around 200% SoC. To our great surprise, our results show that cell internal temperature is only 45°C even at the highest OCV (OCV = 5.10 V) although it has been reported that electrolyte oxidation followed by gassing issue occurs when OCV is higher than 4.6 V [12–14]. Based on the temperature increase rate, three main temperature segments can be identified from the temperature profile. In the first segment (from A to B), the temperature keeps around 25°C from 100% SoC to 160% SoC. Temperature rise can be detected in the

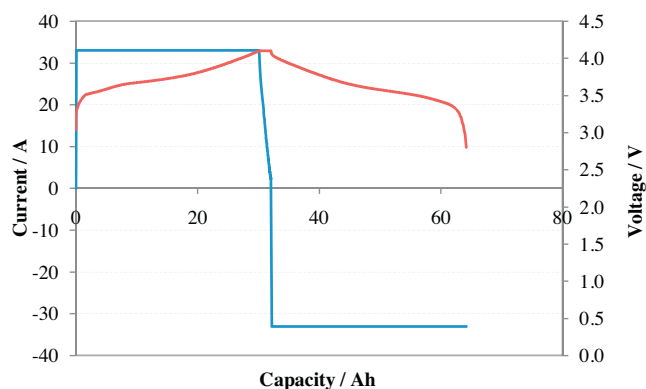


Fig. 1. Charge–discharge profiles of a 32 Ah lithium-ion cell.

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