

Overcharge investigation of lithium-ion polymer batteries

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Abstract

The overcharge performances of lithium-ion polymer batteries (LIPB) have been studied by monitoring their temperature variation and analyzing the generated heat during overcharge. The critical concentration of lithium in the cathode material is determined for the thermal runaway of the battery. Solutions against the thermal runaway are proposed based on these results.

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1. Introduction

Rechargeable lithium-ion batteries (LIB) have been popularly accepted in a wide variety of applications including mobile phones, blue teeth, notebook computers, (hybrid) electric vehicles, etc. due to their high energy density, long cycle life and other unique properties. The lately developed lithium-ion polymer batteries (LIPB), because of their higher energy density and safety than the traditional lithium-ion batteries with liquid electrolyte, are expected to share more of the battery market. In spite of the great success in development and market, battery safety remains the main concern of the consumers and the fabricators. This concern becomes more severe when the battery works at high temperatures, high-rate charge and discharge, extreme overcharge and other abusive operations [1]. The more energy is stored, the more hazardous will be the energy storage system potentially.

Overcharge performance is an important feature of a battery. Some thermal analyses of LIB materials have been carried out in order to understand the overcharge mechanism [2–4]. Some authors used accelerated rate calorimetry (ARC) while others applied differential scanning calorimetry (DSC), trying to learn more about the reasons for the thermal runaway [5–7]. Tobishima and Yamaki [1,8] reported the overcharge reaction while Leising et al. conducted systematic studies on the over-

charge of LIB cells [9,10]. Most of these studies are emphasizing the importance of the overcharge performances of the battery materials.

Systematic investigations are rare on the overcharge performances and solutions to the overcharge-induced failure for the newly born lithium-ion polymer batteries. This paper will investigate the thermal performances of Bellcore-type lithium-ion polymer batteries during overcharge and propose some solutions to the thermal runaway from the point of views of battery designing and operation.

2. Experimental

The stacked lithium-ion polymer batteries with a capacity of 650 mAh were products of Dongguan Amperex Electronics Technology Co., Ltd. (ATL). Cathode films were prepared by mixing LiCoO_2 and carbon black in a solution of poly(vinyl difluoride)-hexafluoropropylene (PVDF-HFP) binder and dibutyl phthalate (DBP) plasticizer dissolved in acetone. The mixture was cast on a Mylar film to prepare the cathode film. Then the cathode film and Al grid were stacked together by hot lamination to prepare the cathode electrode. The Mylar film was removed meanwhile. Analogously were the anodes made with carbonaceous microsphere (CMS) as the active material but hot laminated onto a piece of Cu grid. PVDF-HFP treated porous polypropylene film (25 μm thick) was used as the separator. One mole per liter of LiPF_6 dissolved in EC:DEC:EMC (1:1:1, v/v/v) was used as the electrolyte. Another hot lamination completed the construction of a bi-cell. Seven bi-cells were

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hermetically sealed in a pocket to form a 650 mAh LIPB package.

K-type thermocouples were built inside the LIPB or sandwiched between the bi-cells to monitor their internal temperatures. The down-leads of the thermocouple were sealed on one side of the pocket before the electrolyte was filled in. Another thermocouple was fixed at the center of the upper surface of the cell to monitor its external temperature. The testing was conducted on Arbin BT-2000 battery tester at $23 \pm 3^\circ\text{C}$. All batteries were at first charged to 4.2 V and then discharged to 3.0 V before the overcharge test was carried out.

For the convenience of discussion, the nominal cell balance (CB) of the capacity of the anode to the cathode is defined as

$$\text{CB} = \frac{\text{CMS weight at unit area} \times 300}{\text{LiCoO}_2 \text{ weight at unit area} \times 137}$$

The 300 and 137 mAh g^{-1} are the available capacities of CMS and LiCoO_2 , respectively. The CB for all the cells is 1.05 unless specified in this paper.

In order to understand the overcharge mechanism, both the charger's voltage (U) and battery's voltage (E) were recorded. The U was measured after the battery was charged for 2 min, while the E was obtained after the battery stood by for 10 min, following the 2-min galvanostatic charge.

3. Results and discussion

The theoretical specific capacity of LiCoO_2 is 274 mAh g^{-1} . The coulombic efficiency in the first cycle of an LIPB is ca. 92%. This means that the capacity loss of LiCoO_2 is roughly 11 mAh g^{-1} considering that the actually available (reversible) capacity of LiCoO_2 is 137 mAh g^{-1} when the battery is charged to 4.2 V. Therefore, the actual value of x in Li_xCoO_2 at full discharge (3.0 V) after the initial charge is $((137 \times 0.92 + 137)/274) = 0.96$. As the coulombic efficiencies for most commercial cells and laboratory test cells are over 99% in the second and subsequent cycles, it is reasonable to suppose that the coulombic efficiency was 100% if the battery is cycled between 3.0 and 4.2 V. Then it is calculated that the theoretical value of x at full charge (4.2 V) is $(x = 0.96 - 0.5) = 0.46$. Now we further presume that the amount of Li ions extracted from the cathode is proportional to the galvanostatic overcharge time before $x = 0$ in Li_xCoO_2 . Considering the polarization effect of the battery and the decomposition of the electrolyte, this might be not reasonable. However, such a presumption will help estimate the Li concentration in the overcharged cathode materials and obtain some interesting information as shown in the following.

Fig. 1 presents the voltage and current profiles of a 650 mAh LIPB with the 2C/12V overcharge mode. "2C/12V" means that the battery is galvanostatically charged to 4.2 V in half an hour. Then it is further charged at the same current density for some predetermined time (4 h in total, for example). If the voltage of the cell reaches 12 V within this period, the cell will automatically turn to be potentiostatically charged. It is seen that the voltage of the cell increases with time until the highest value (5.1 V) is reached at $t = 57.5$ min. Then it drops

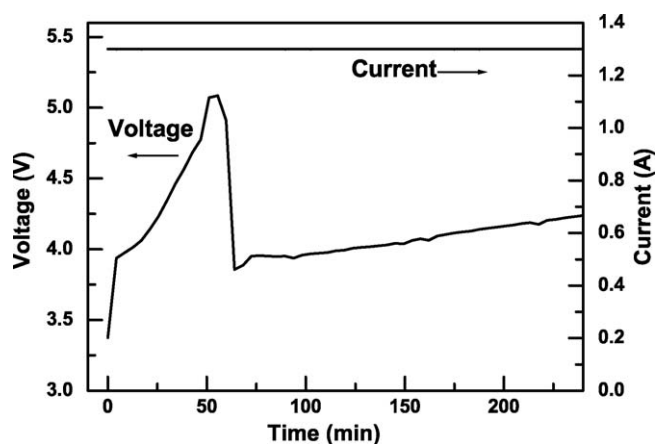


Fig. 1. Plots of the voltage and current of a 650 mAh LIPB with the 2C/12V overcharge mode.

sharply to 3.9 V. After that, the voltage becomes stable at around 4.0 V.

Fig. 2 shows the internal and external temperature profiles of this battery in the above overcharge test. The variation of its internal temperature is quite similar to that of its external temperature. Both temperatures are just a little over the room temperature until about $t = 52.0$ min. Then both of them increase sharply with time. The internal temperature reaches its maximum, 167°C , at $t = 65.5$ min while the external temperature reaches its summit, 112°C , at $t = 67$ min. The time interval between these two peak values is clearly due to the heat conduction of the battery materials. As the battery is further charged, both the internal and external temperatures drop quickly and then keep unchanged at around 105 and 80°C , respectively.

The same type of cells are charged with 1C/12V and 3C/10V overcharge modes, respectively, to find out the influence of charge rate on their overcharge performances. For the convenience of comparison, the voltage and the internal temperature of the battery have been shown in Figs. 3 and 4, respectively. The internal temperature rises obviously after ca. 31 min and reaches the maximum at $t = 37$ min in the 1C/12V overcharge

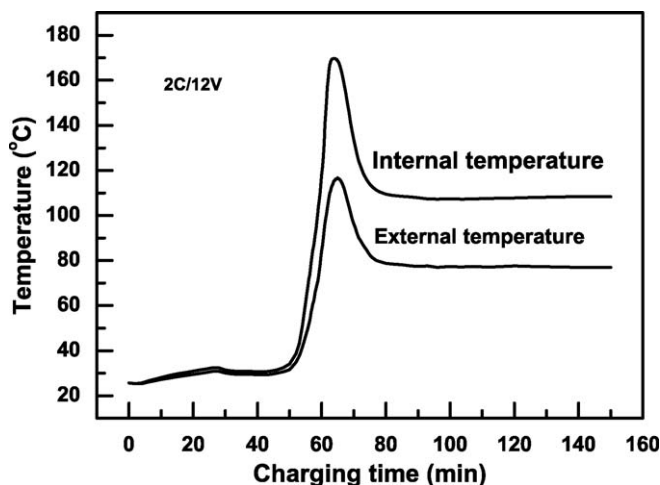


Fig. 2. The time-dependent internal and external temperature plots of the same 650 mAh LIPB (as in Fig. 1) with the 2C/12V overcharge mode.

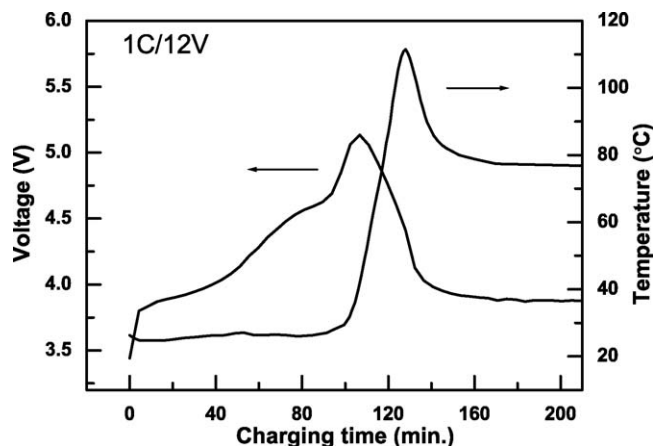


Fig. 3. Comparison of voltage and internal temperature of a 650 mAh LIPB in the overcharge mode of 1 C/12 V (current = 650 mA).

test. However, the same type of battery fails to pass the 3 C/10 V test. Figs. 2–4 show clearly that the maximum internal temperature increases with increasing charge rate, implying that charge rate is an important factor responsible for the thermal runaway of an overcharged battery.

Cell balance (CB) has been considered another factor that might influence the safety of an overcharged battery because the extra lithium extracted from the cathode material might be plated on the surface of the anode if the CB value is not sufficiently high. Therefore, 650 mAh LIPBs with CB as high as 2 are assembled and charged with 1 C/12 V, 2 C/12 V and 3 C/10 V overcharge modes, respectively, in order to evaluate the impact of the CB on their overcharge performances. In comparison with batteries with CB = 1.05, these batteries demonstrate no obvious differences in their overcharge performances: their temperatures rise sharply after ca. $x = 0.16$ and reach their summits short after $x = 0$. Meanwhile the voltages reach the peak value at ca. $x = 0$. In addition, 3 C/10 V overcharge also leads to fire short after $x = 0$. The temperature is about 190 °C before fire. This indicates that increasing the CB value cannot prevent the thermal runaway of the battery in a rather wide range above its normal value. That

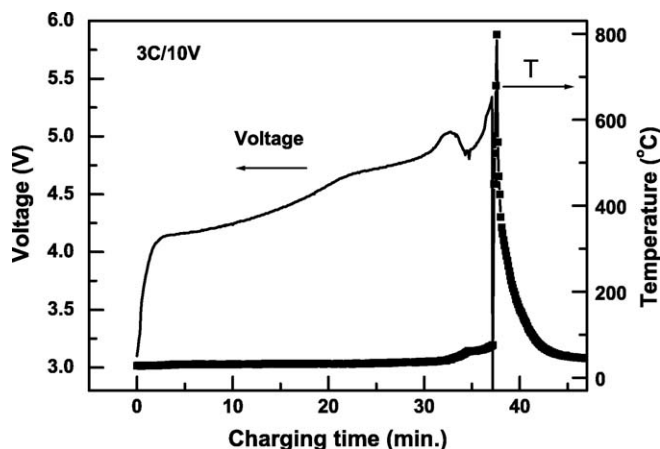


Fig. 4. Variation of voltage and internal temperature of a 650 mAh LIPB with charge time at 3 C rate (3 C/10 V/4 h overcharge mode).

Table 1

The temperature, charge time, calculated Li concentration x in Li_xCoO_2 and battery voltage at some critical points during overcharge

Rate	Items	Onset temperature	Maximum voltage	Maximum internal temperature
1 C	Temperature (°C)	28.5	41.8	111.5
	Charge time (min)	95.6	106.7	127.9
	Calculated x in Li_xCoO_2	0.16	0.07	^a
	Voltage (V)	4.799	5.136	4.414
2 C	Temperature (°C)	32.7	46.8	169.6
	Charge time (min)	47.9	53.5	63.9
	Calculated x in Li_xCoO_2	0.16	0.07	^a
	Voltage (V)	4.856	5.086	3.856
3 C	Temperature (°C)	39.9	43.4	797.9
	Charge time (min)	31.9	32.7	37.6
	Calculated x in Li_xCoO_2	0.16	0.14	0.02
	Voltage (V)	5.000	5.042	^b

The coulombic efficiency of the battery is supposed to be 100% before $x = 0$ in Li_xCoO_2 in the overcharge test.

^a The calculated x value is negative at this point.

^b The battery catches fire at this point and the corresponding voltage is not available.

is, lithium deposition on the anode surface does not occur or is not the reason for the thermal runaway of the battery with CB = 1.05.

LIPB cells with smaller (200 mAh) and larger (2000 mAh) capacities were also fabricated with the same materials and overcharged with the same modes. The overcharge performances of both cells are similar to and consistent with that of the above batteries. However, the 2000 mAh battery caught fire even at 1 C/12 V overcharge while the 200 mAh cell passed the 3 C/10 V overcharge test.

Summarizing the relationship between the calculated Li concentration in Li_xCoO_2 and the internal temperature of the battery, it is interesting to find that the temperature of the battery does not obviously increase before ca. $x = 0.16$ and the maximum temperature arrives later than that of the voltage. Table 1 lists the temperature, charge time, calculated Li concentration in Li_xCoO_2 and the battery voltage at some critical points during overcharge. It shows that the temperature at which the temperature begins to rise sharply (onset temperature) and the maximum temperature of the battery all depend strongly on and increase with the charge rate. However, the influence of the charge rate is slight on the maximum voltage that the battery can reach. In addition, the voltages at which the sharp temperature rise begins increases with the charge rate, probably because of the polarization effect of the battery materials.

It is interesting that the onset temperature of the cells with different overcharge modes is at $x = 0.16$ although the calculated Li concentration at the maximum voltage and temperature of the cell departs from the reasonable value, independent of the charge rate. This implies that the calculated x value indeed reflects the actual x value in Li_xCoO_2 before any thermal runaway takes place. Therefore, $x = 0.16$ is an important reference point for solutions to the thermal runaway of the battery.

The above results may be summarized as follows:

- (i) $x=0.16$ in Li_xCoO_2 is the critical point for the beginning of sharp rise of temperature and voltage during galvanostatic overcharge. Both the temperature and the voltage reach their maximum at ca. $x=0$.
- (ii) Increasing the CB value cannot prevent the thermal runaway in a wide range above the normal value.
- (iii) Charge rate is an important factor that influences the overcharge performance of the cell, especially those with high capacities.
- (iv) Battery capacity, or more exactly, the ratio of surface area to the battery capacity is another important factor that impacts the safety of the battery.

Clearly the quick temperature rise and the firing of the cell are all related to the heat generated during 1 C/12 V overcharge and the heat generation process is related to the exothermic reactions in the overcharged cell [1–11]. Therefore, the above findings actually point to one point: the rate of heat generation (related to charge rate and exothermic reaction rate) and the rate of heat dissipation (related to the size and shape as well as the materials) of the cell are responsible for the battery safety. This means that the heat generation and heat dissipation is a pair of discrepancy. If the heat generation and dissipation are in balance, the temperature of the cell will be under control. This occurs only in low-capacity cells or cells operated with low current density. If this balance is broken but the rate of heat generation is not very high, the temperature of the cell will rise and a new balance is built at a higher level. This is the case for most practical cells. However, if the balance is broken and the temperature overrides a critical point before the new balance is built, the cell will catch fire or be exploded. In this case, the cell fails to pass the overcharge test.

In order to understand the above thermal performances of the cell, analysis to the heat generation during the charge process is necessary. The heat balance of any thermodynamic system can be written as

$$\sum_i \rho_i C_{pi} \frac{\partial T}{\partial t} = \nabla^2(kT) + \sum_i Q_{gi} \quad (1)$$

At the boundary of a cell

$$\left(\frac{\partial T}{\partial n}\right)_{\text{surface}} = -\frac{h}{k}(T_{\text{surface}} - T_{\text{room}}) \quad (2)$$

where ρ represents the mass density of a component in the system, T for the equilibrium temperature of the system, t for time, C_p for the specific heat capacity of a component, k for the heat conduction coefficient, Q for the heat generation rate and h for the film coefficient between the cell pocket and air, n for the normal direction of the battery surface.

Dahn and co-workers [11] used the dimensionless Biot number (defined as $Bi = h(V/A)/k$) as a criteria of heat flow rate within a body when compared to heat flow at the surface (V for volume and A for surface area of the cell) and to evaluate if their cylindrical (18650 model) battery can be regarded as a lumped

mass with uniform temperature. It has been popularly accepted that the temperature of a system can be regarded uniform [12] if its $Bi \leq 0.1$. For our 650 mAh LIPBs, $h = 13.5 \text{ W m}^{-2} \text{ K}^{-1}$, $k = 20.06 \text{ W m}^{-1} \text{ K}^{-1}$, $V = 4.52 \times 10^{-6} \text{ m}^3$, $A = 4.04 \times 10^{-3} \text{ m}^2$. Therefore, the Biot number is calculated to be 0.0754. This means that a lumped mass approach is a good approximation for the solid LIPB. That is, our LIPB can be simplified as a lumped mass with homogeneous temperature during cycling. Based on this, Eq. (1) can be simplified as

$$mC_p \frac{dT}{dt} = -hA(T - T_{\text{room}}) + Q_{\text{in}} \quad (3)$$

where $C_p = 1280 \text{ J kg}^{-1} \text{ K}^{-1}$ [13] and Q_{in} is the input electric power.

The heat generation rate Q_g can be classified into two parts during charging, due to physical processes (Q_p) and due to chemical reactions (Q_c , including entropy variation and reaction between the active material and the electrolyte, etc.). That is,

$$Q_g = Q_p + Q_c \quad (4)$$

According to Eq. (3), the generated heat can be calculated if the temperature T is known. Q_p can be written as

$$Q_p = I(U - E) \quad (5)$$

Thus Q_c can be deduced by $Q_c = Q - Q_p$. The generated heat will lead to temperature rise. Clearly temperature rise is easier to probe than the heat generation. Therefore, temperature variation rather than the generated heat will be used in the following discussion. Supposing that all the input energy is converted to heat, Eq. (3) can be used to estimate how much the temperature will rise. Fig. 5 compares the actual (measured) and virtual (calculated) temperature curves of the cell overcharged with the 2 C/12 V mode.

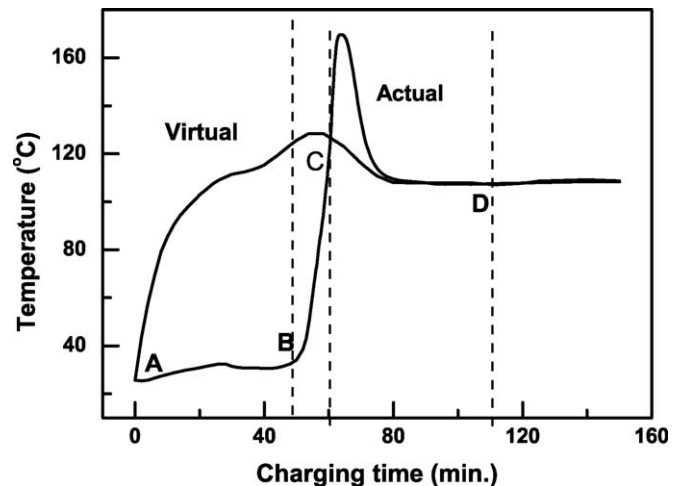
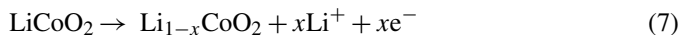


Fig. 5. Comparison of the virtual (calculated) and actual (measured) temperatures of the battery overcharged with the 2 C/12 V mode. The virtual temperature is calculated by supposing that all the input electric energy is converted to heat (Eq. (3)). The measured temperature represents the actual internal temperature of the battery during overcharge.

The electric energy input into a battery will be converted into chemical energy and heat. For an LIPB in charge, the following reactions are expected. On the anode



On the cathode



During the charge process, the chemical energy is stored in the anode and cathode. Take the 2C/12V overcharge mode for example, the charge process may be divided into four periods (Fig. 5):

- (i) Between A and B, the cell temperature rises very little. This is the normal charge process for most batteries. Most of the input energy is converted to chemical energy and stored in the cell between $x = 0.96$ and 0.16 .
- (ii) Between B ($x = 0.16$) and C ($x = 0$), the calculated temperature rises at first and then turns to drop but the cell temperature keeps rising sharply. In this period, most of the input energy is converted to heat.
- (iii) Between C and D (after $x = 0$), the output heat becomes more than the input electric energy. That means that an exothermic chemical reaction occurs in this period. By subtracting the total output heat from the total input energy, it is seen that the released chemical energy is only a small portion of the total input energy.
- (iv) Far beyond $x = 0$ (after D), the calculated temperature is roughly equal to the actual temperature of the cell, indicating that our supposition for Fig. 5 (most of the input energy is converted to heat) is reasonable.

Fig. 6 presents the contributions of Q_g , Q_p and Q_c to the temperature rise of the battery during overcharge. It is seen that the contributions of both the physical and chemical heats before $t = 45$ min are very little. The battery temperature rises very little in this period. Between $t = 45$ and 75 min, the chemical heat

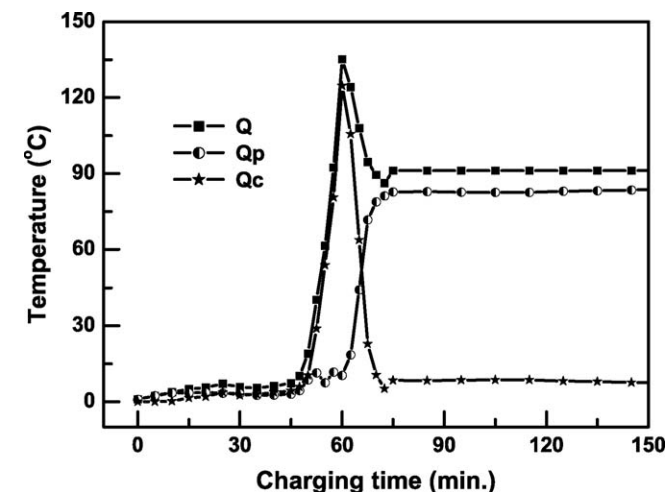
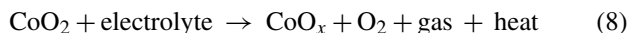


Fig. 6. Contributions of the chemical (Q_c) and physical (Q_p) heats to the temperature rise of the battery with 2C/12V mode.

is responsible for the sharp increase and the maximum of the battery temperature. After the summit of the battery temperature the chemical heat contribution decreases quickly to about zero while the physical heat begins to take its part at this point. The physical heat works to keep the battery temperature at a higher level of balance after $t = 75$ min.

The cells that passed the 3C/12V/4h overcharge test were disassembled after the overcharge test. Inspection of each part of the battery shows that

- (i) Very little gas is produced, most of which is CO_2 . Therefore, electrolyte decomposition is not the main reason for the fire of the cell.
- (ii) No obvious changes are observed on the Al and Cu current collectors.
- (iii) The anode material is golden to reddish when the cell is disassembled in the glove box. It becomes white after exposed to air for a few seconds. The white species is LiOH due to the violent reaction of LiC_6 and water (moisture) in air. Violent reaction takes place and a lot of gas is given off when the anode is put into water. Therefore the material on the anode after overcharge must be LiC_6 and deposited Li. These indicate that the chemical energy stored in the anode during charge is not released or that the anode does not contribute to the above temperature increase of the battery.
- (iv) The cathode material becomes gray after overcharge. It was reported that the end member of $LiCoO_2$ at deep charge is highly oxidative CoO_2 [14]. Therefore, the cathode material will oxidize the electrolyte and get itself reduced. During this process, CoO_2 is reduced to CoO_x and much of the chemical energy stored in the cathode is released:



The gas in Eq. (8) includes CO_2 and other oxidation products of the electrolyte. The reaction can take place whether or not the cell can pass the overcharge test. The difference between them is the reaction rate and the rate of heat dissipation. For an LIPB that can pass the overcharge test, its chemical energy stored in the cathode must be released at a sufficiently slow speed and dissipated at a rather high speed by which the internal temperature of the cell is below some critical value. In this process, the energy stored in the anode is remained.

For a cell that cannot pass the overcharge test, however, its cathode releases its chemical energy at a rather high speed in comparison to the heat dissipation rate. In this way, the temperature of the cell rises sharply and reaches some critical value, inducing reactions in the anode. Then the anode further releases much of its chemical energy, triggering thermal runaway. It is known that metallic lithium melts at $180^\circ C$ and becomes very active at and above this temperature. Therefore, it seems that $170^\circ C$ is the highest temperature that the cell can tolerate without catching fire during the overcharge test. With this, it is proposed that the critical temperature for the thermal runaway is ca. $180^\circ C$.

In order to show the importance of the temperature control or the rate of heat generation/dissipation for the safety of the

overcharged cell, further experiments were done based on Eq. (8). The main results are summarized as follows:

- (i) Although the cell with normal package cannot pass the 3 C/12 V overcharge test, the 650 mAh LIPB can pass this test if its seven bi-cells were separated and put in seven pockets, which enlarges the heat dissipation surface of the battery by about seven times. In this way, the heat dissipation becomes much faster. Similar to this, in comparison with large lithium-ion polymer cells, smaller ones have larger specific surface areas for heat dissipation. Therefore the overcharge performance of small LIPB is better than that of the large ones.
- (ii) By filling the same 650 mAh LIPB with 2/3 of its normal amount of electrolyte, less heat was generated during overcharge according to Eq. (8). This cell passed the 3 C/12 V overcharge test. Similar to this, a pinhole was made on the pocket to make some initial leakage before the overcharge test. In this way, the pocket did not swell and the heat dissipation became better. The cell also passed the 3 C/12 V overcharge test.

Based on the above experiments and analysis to the overcharge process, solutions against overcharge should be considered from the cathode materials and electrolyte according to Eq. (8). If x can always be controlled above 0.16 or the reaction between $x = 0.16$ and 0 can be slowed down so as to keep the battery temperature below 180 °C, the cells with LiCoO₂ cathode materials can pass the overcharge tests.

4. Conclusions

The overcharge performances of Bellcore lithium polymer batteries have been studied with various overcharge modes. By

correlating the battery temperature and maximum voltage with the lithium concentration in the cathode, it is found that $x = 0.16$ is a critical point for the overcharge safety of the batteries. Li _{x} CoO₂ will have an exothermic chemical reaction with the electrolyte after $x = 0.16$. If x can be kept above 0.16 or the reaction can be slowed down between $x = 0.16$ and 0, the battery temperature will be below 180 °C during overcharge and the batteries can pass the overcharge tests. Batteries with different capacities, geometries and cathode materials may have different critical x values. Controlling the lithium concentration in the active material or slowing down the chemical reaction after some critical lithium concentration should be important measures to take to ensure overcharge safety of the batteries.

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